CHEM 100: CHEMISTRY AND SOCIETY



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CHEM 100: Chemistry and Society
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Glossary

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Licensing

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CHAPTER OVERVIEW

1: Chemistry, Matter, and Measurement

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

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

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1.1: Prelude to Chemistry, Matter, and Measurement

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

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

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1.2: What is Chemistry?

Learning Objectives

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

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

Chemistry is one branch of science. Science is the process by which we learn about the natural universe by observing, testing, and then generating models that explain our observations. Because the physical universe is so vast, there are many different branches of science (Figure **1.2.1**). Thus, chemistry is the study of matter, biology is the study of living things, and geology is the study of rocks and the earth. Mathematics is the language of science, and we will use it to communicate some of the ideas of chemistry.

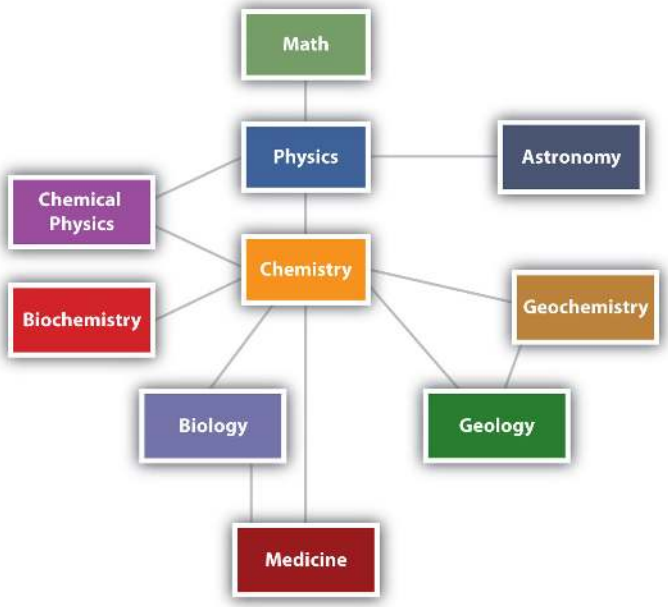


Figure **1.2.1**: The Relationships between Some of the Major Branches of Science. Chemistry lies more or less in the middle, which emphasizes its importance to many branches of science.

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

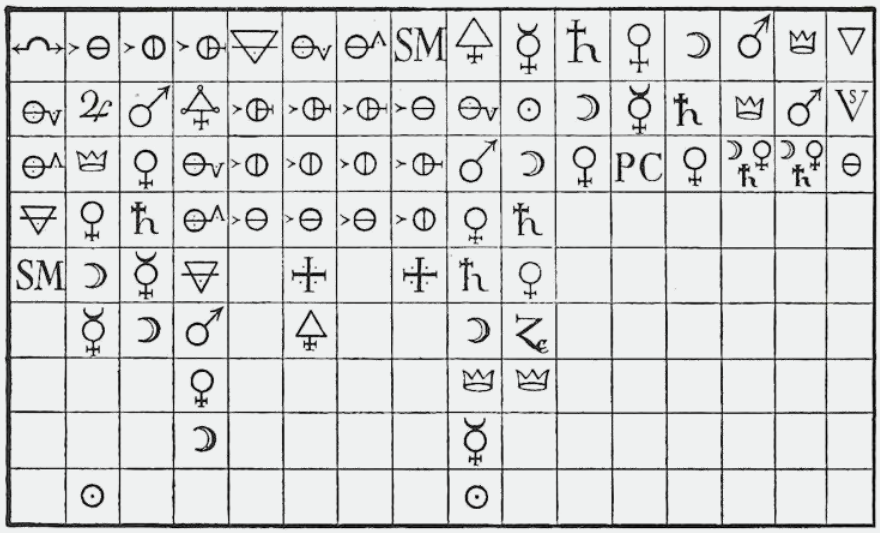
> *There are many other fields of science in addition to the ones listed here.*

Alchemy

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

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

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



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

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

Exercise 1.2.1

Which fields of study are branches of science? Explain.

a. sculpture
b. astronomy

Answer a

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

Answer b

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

Exercise 1.2.2

Which fields of study are branches of science?

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

Answer

a, b and c only

How do scientists work? Generally, they follow a process called the scientific method. The scientific method is an organized procedure for learning answers to questions and making explanations for observations. To find the answer to a question (for example, “Why do birds fly toward Earth’s equator during the cold months?”), a scientist goes through the following steps, which are also illustrated in Figure **1.2.2**:

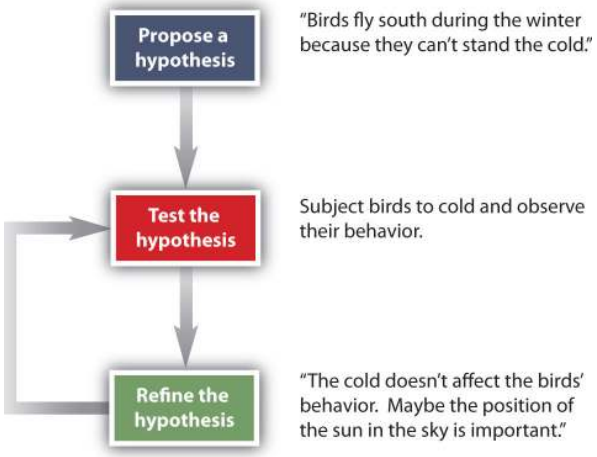


Figure **1.2.2**: The General Steps of the Scientific Method. After an observation is made or a question is identified, a hypothesis is made and experiments are designed to test the hypothesis.

The steps may not be as clear-cut in real life as described here, but most scientific work follows this general outline.

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

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

1.2.3 Exercise

Define science and chemistry.

Answer

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

1.2.4 Exercise

Name the steps of the scientific method.

Answer

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

Key Takeaways

- Chemistry is the study of matter and how it behaves.
- The scientific method is the general process by which we learn about the natural universe.

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

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

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

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

3. Which of the following are examples of matter?

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

4. Which of the following are examples of matter?

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

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

Answers

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

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

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

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

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

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1.3: The Classification of Matter

Learning Objectives

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

Part of understanding matter is being able to describe it. One way chemists describe matter is to assign different kinds of properties to different categories.

Physical and Chemical Properties

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



Figure **1.3.1**: (left) Ice Melting is a physical change. When liquid water (H_2O) freezes into a solid state (ice), it appears changed; However, this change is only physical as the the composition of the constituent molecules is the same: 11.19% hydrogen and 88.81% oxygen by mass. (right) Burning of wax to generate water and carbon dioxide is a chemical reaction. (CC-SA-BY-3.0; Andrikkos)

Elements and Compounds

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

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

The smallest part of an element that maintains the identity of that element is called an **atom**. Atoms are extremely tiny; to make a line of iron atoms that is 1 inch long, you would need approximately 217 million iron atoms. The smallest part of a compound that maintains the identity of that compound is called a **molecule**. Molecules are composed of two or more atoms that are attached

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

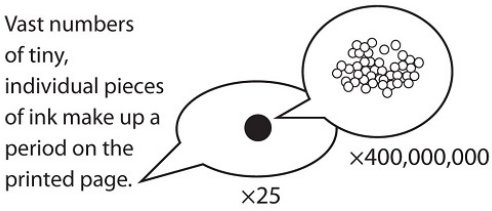


Figure **1.3.2**: How Many Particles Are Needed for a Period in a Sentence? Although we do not notice it from a macroscopic perspective, matter is composed of microscopic particles so tiny that billions of them are needed to make a speck we can see with the naked eye. The ×25 and ×400,000,000 indicate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

Mixtures

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

✔ Example 1.3.1

How would a chemist categorize each example of matter?

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

Answer a

Saltwater acts as if it were a single substance even though it contains two substances—salt and water. Saltwater is a *homogeneous mixture*, or a solution.

Answer b

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

Answer c

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

Answer d

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

? Exercise 1.3.2

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.

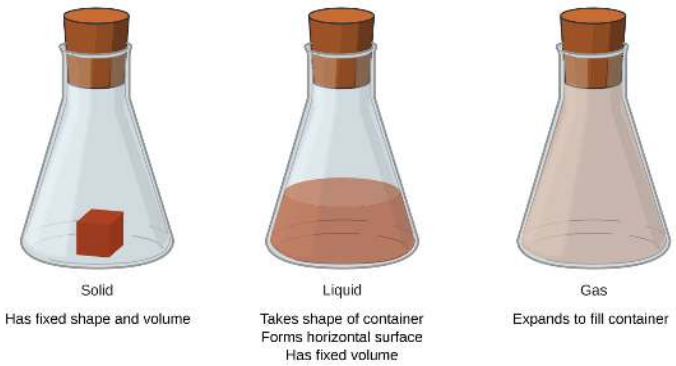


Figure 1.3.3: The three most common states or phases of matter are solid, liquid, and gas. (CC BY-4.0; OpenStax)

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 1.3.2).



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

We know from our experience with water that substances can change from one phase to another if the conditions are right. Typically, varying the temperature of a substance (and, less commonly, the pressure exerted on it) can cause a **phase change**, a physical process in which a substance changes from one phase to another (Figure 1.3.5). Phase changes are identified by particular names depending on what phases are involved, as summarized in Table 1.3.1.

Table 1.3.1: Phase Changes

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

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

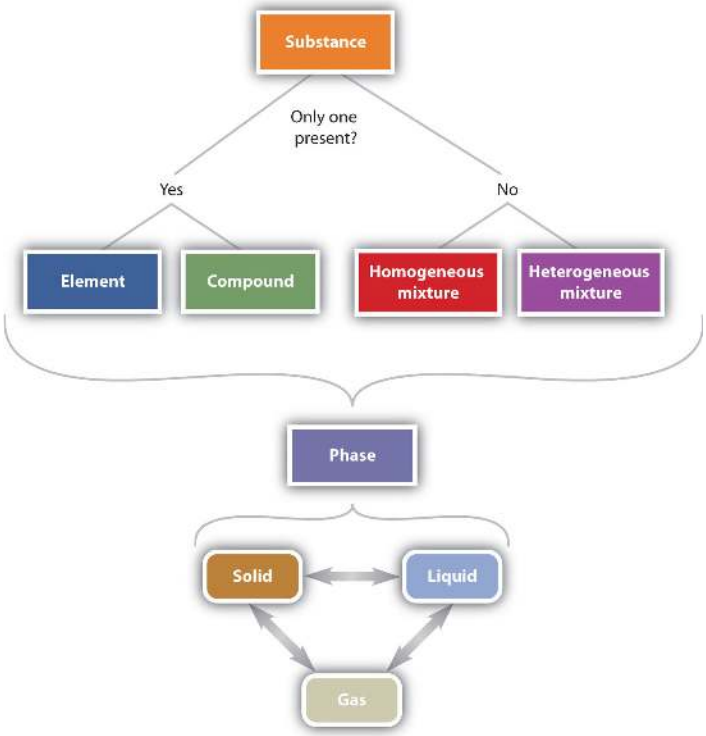


Figure **1.3.6**: The Classification of Matter. Matter can be classified in a variety of ways, depending on its properties.
This table starts with a substance. If there is only one present, it can either be an element or a compound. If there is more than one present, it can either be a homogeneous mixture 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 1.3.3

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 1.3.4

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 1.3.5

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 1.3.6

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 1.3.7

Give two examples of a heterogeneous mixture.

Answer

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

Exercise 1.3.8

Give two examples of a homogeneous mixture.

Answer

vinegar and rubbing alcohol (answers will vary)

Exercise 1.3.9

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 1.3.10

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 1.3.11

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 1.3.12

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 1.3.13

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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1.4: Measurements

Learning Objectives

- Express quantities properly using a number and a unit.

A coffee maker's instructions tell you to fill the coffeepot with 4 cups of water and use 3 scoops of coffee. When you follow these instructions, you are measuring. When you visit a doctor's office, a nurse checks your temperature, height, weight, and perhaps blood pressure (Figure **1.4.1**); the nurse is also measuring.



Figure **1.4.1**: Measuring Blood Pressure. A nurse or a doctor measuring a patient's blood pressure is taking a measurement. (GNU Free Documentation License; Pia von Lützau via Wikipedia).

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

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

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

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

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

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

Exercise 1.4.1

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

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

Answer a

The number is one, and the unit is dozen.

Answer b

The number is 2.54, and the unit is centimeter.

Answer c

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

Answer d

The number is 88, and the unit is meters per second. Note that in this case the unit is actually a combination of two units: meters and seconds.

? Exercise 1.4.2

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

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

Answer a

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

Answer b

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

Answer c

The number 32, and the unit is fluid ounces

Answer d

The number is 98.6, and the unit is degrees Fahrenheit

? Exercise 1.4.2

What are the two necessary parts of a quantity?

Answer

The two necessary parts are the number and the unit.

Key Takeaway

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

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1.5: 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 **1.5.1**, 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:

$$K = °C + 273 \tag{1.5.1}$$

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 **1.5.1**: 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 **1.5.1**). 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 **1.5.2**. (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 **1.5.2**: 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 **1.5.1**: 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.

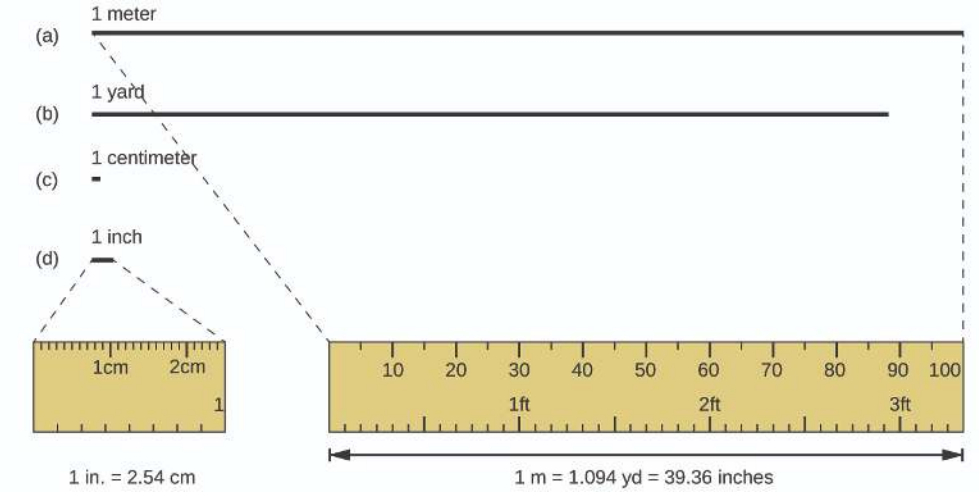


Figure 1.5.2: The relative lengths of 1 m, 1 yd, 1 cm, and 1 in. are shown (not actual size), as well as comparisons of 2.54 cm and 1 in., and of 1 m and 1.094 yd. (CC BY 4.0; OpenStax)

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 1.5.3, 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.

$$1\ mL = 1\ cm^3 \tag{1.5.2}$$

Example 1.5.1

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 1.5.1

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)

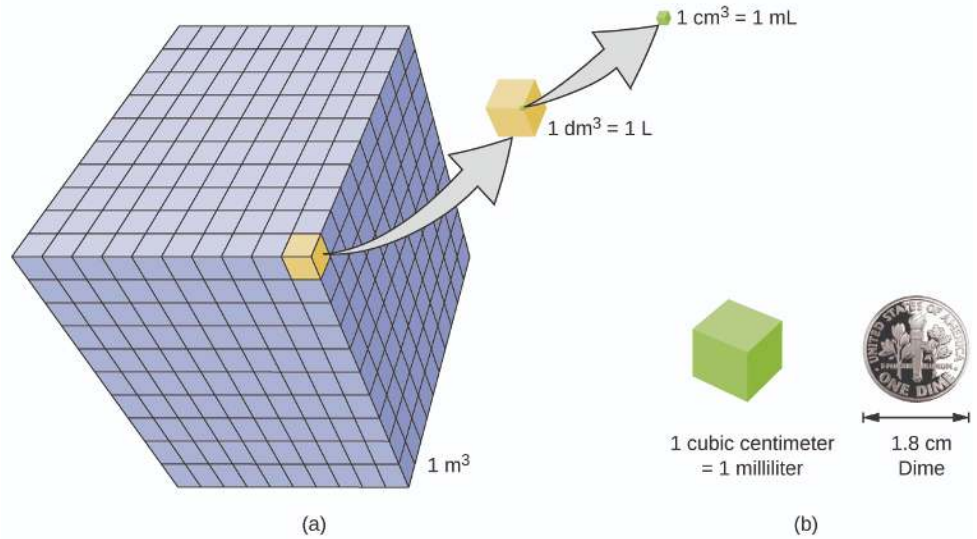


Figure **1.5.3**: Units of Volume. (a) The relative volumes are shown for cubes of 1 m^3, 1 dm^3 (1 L), and 1 cm^3 (1 mL) (not to scale). A liter (L) is defined as a cube 1 dm (1/10th of a meter) on a side. A milliliter (mL), 1/1,000th of a liter, is equal to 1 cubic centimeter. (b) The diameter of a 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.

$$\text{density} = \frac{\text{mass}}{\text{volume}} \tag{1.5.3}$$

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 **1.5.2**: 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 1.5.2: 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 1.5.2: Density of Oxygen

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

Answer

1.45 g/L

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

Concept Review Exercises

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

Answers

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

Key Takeaways

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

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1.6: 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: Expressing Numbers - Significant Figures

Learning Objectives

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

Scientists have established certain conventions for communicating the degree of **precision** of a measurement, which is dependent on the measuring device used. Imagine, for example, that you are using a meterstick to measure the width of a table. The centimeters (cm) marked on the meterstick, tell you how many *centimeters* wide the table is. Many metersticks also have markings for millimeters (mm), so we can measure the table to the nearest *millimeter*. Most metersticks do not have any smaller (or more precise) markings indicated, so you cannot report the measured width of the table any more precise than to the nearest millimeter. However, you can *estimate* one past the smallest marking, in this case the millimeter, to the next decimal place in the measurement (Figure 1.7.1).

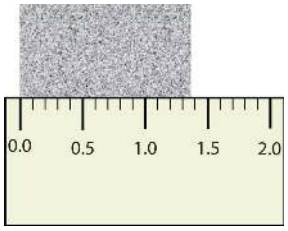


Figure 1.7.1: Measuring an Object to the Correct Number of Digits. How many digits should be reported for the length of this object?

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

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

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

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

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

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

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

Example 1.7.1

How many significant figures does each number have?

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

Answer a

four (by rules 1 and 4)

Answer b

seven (by rules 1 and 2)

Answer c

nine (by rules 1, 2, and 4)

Answer d

four (by rules 1 and 3)

Exercise 1.7.1

How many significant figures does each number have?

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

Answer a

five

Answer b

four

Answer c

four

Answer d

one

Answer e

one

Rounding off numbers

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

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

Table 1.5.1: Rounding examples

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

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

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

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

Combining Numbers

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

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

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

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

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

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

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

Example 1.7.2

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

a. 23.096 × 90.300
b. 125 × 9.000
c. 1,027 + 610.0 + 363.06

Answer a

The calculator answer is 2,085.5688, but we need to round it to five significant figures. Because the first digit to be dropped (in the hundredths place) is greater than 5, we round up to 2,085.6, which in scientific notation is 2.0856×10^3.

Answer b

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

Answer c

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

Exercise 1.7.2

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

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

Answer a

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

Answer b

$1437 = 1.437 \times 10^3$

Answer c

$156 = 1.56 \times 10^2$

Answer d

$2.14 = 2.14 \times 10^0$

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

Exercise 1.7.1

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

Answer

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

? Exercise 1.7.2

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

Answer

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

? Exercise 1.7.3

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

Answer

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

Key Takeaways

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

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1.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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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.

2.1: Prelude to Elements, Atoms, and the Periodic Table
2.2: The Elements
2.3: Atomic Theory
2.4: The Structure of Atoms
2.5: Nuclei of Atoms
2.6: Atomic Masses
2.7: Arrangements of Electrons
2.8: The Periodic Table
2.9: PhET- Build an Atom
2.E: Elements, Atoms, and the Periodic Table (Exercises)

Template:HideTOC

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

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2.1: Prelude to Elements, Atoms, and the Periodic Table

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

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

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

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2.2: The Elements

Learning Objectives

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

An element is a substance that cannot be broken down into simpler chemical substances. There are about 90 naturally occurring elements known on Earth. Using technology, scientists have been able to create nearly 30 additional elements that do not occur in nature. Today, chemistry recognizes 118 elements—some of which were created an atom at a time. Figure **2.2.1** shows some of the chemical elements.



Figure **2.2.1**: Samples of Elements. Gold is a yellowish solid, iron is a silvery solid, while mercury is a silvery liquid at room temperature. © Thinkstock

Abundance

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

Table **2.2.1**: Elemental Composition of Earth

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

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

On the planet Earth, however, the situation is rather different. Oxygen makes up 46.1% of the mass of Earth's crust (the relatively thin layer of rock forming Earth's surface), mostly in combination with other elements, while silicon makes up 28.2%. Hydrogen, the most abundant element in the universe, makes up only 0.14% of Earth's crust. Table **2.2.1** lists the relative abundances of elements on Earth as a whole and in Earth's crust. Table **2.2.2** lists the relative abundances of elements in the human body. If you compare Table **2.2.1** and Table **2.2.2**, you will find disparities between the percentage of each element in the human body and on Earth. Oxygen has the highest percentage in both cases, but carbon, the element with the second highest percentage in the body, is relatively rare on Earth and does not even appear as a separate entry in Table **2.2.1**; carbon is part of the 0.174% representing "other" elements. How does the human body concentrate so many apparently rare elements?

Table **2.2.2**: Elemental Composition of a Human Body

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

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

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

LOOKING CLOSER: PHOSPHOROUS, THE CHEMICAL BOTTLENECK

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

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

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

Names and Symbols

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

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

The names of the elements can be cumbersome to write in full, especially when combined to form the names of compounds. Therefore, each element name is abbreviated as a one- or two-letter chemical symbol. By convention, the first letter of a chemical symbol is a capital letter, while the second letter (if there is one) is a lowercase letter. The first letter of the symbol is usually the first letter of the element's name, while the second letter is some other letter from the name. Some elements have symbols that derive from earlier, mostly Latin names, so the symbols may not contain any letters from the English name. Table **2.2.3** lists the names and symbols of some of the most familiar elements.

Table **2.2.3**: Element Names and Symbols

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

*The symbol comes from the Latin name of element.

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

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

Example 2.2.1

Write the chemical symbol for each element without consulting Table **2.2.3** "Element Names and Symbols".

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

Answer a

Br

Answer b

B

Answer c

C

Answer d

Ca

Answer e

Au

Exercise 2.2.1

Write the chemical symbol for each element without consulting Table 2.2.3.

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

Answer a

Mn

Answer b

Mg

Answer c

Ne

Answer d

N

Answer e

Ag

Example 2.2.2

What element is represented by each chemical symbol?

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

Answer a

sodium

Answer b

mercury

Answer c

phosphorus

Answer d

potassium

Answer e

iodine

? Exercise 2.2.2

What element is represented by each chemical symbol?

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

Answer a

lead

Answer b

tin

Answer c

uranium

Answer d

oxygen

Answer e

fluorine

Concept Review Exercises

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

Answers

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

Key Takeaways

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

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2.3: Atomic Theory

Learning Objectives

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

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

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

The modern atomic theory, proposed about 1803 by the English chemist John Dalton (Figure **2.3.1**), is a fundamental concept that states that all elements are composed of atoms. Previously, we defined an atom as the smallest part of an element that maintains the identity of that element. Individual atoms are extremely small; even the largest atom has an approximate diameter of only 5.4×10^{-10} m. With that size, it takes over 18 million of these atoms, lined up side by side, to equal the width of your little finger (about 1 cm).

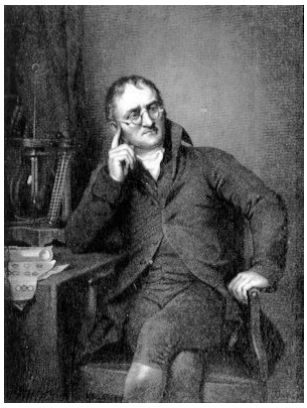


Figure **2.3.1** John Dalton was an English scientist who enunciated the modern atomic theory.

Most elements in their pure form exist as **individual atoms**. For example, a macroscopic chunk of iron (Fe) metal is composed, microscopically, of individual atoms. Some elements, however, exist as groups of atoms called molecules. Several important elements exist as two-atom combinations and are called **diatomic molecules**. In representing a diatomic molecule, we use the symbol of the element and include the ***subscript*** "2" to indicate that two atoms of that element are joined together. The elements that exist as diatomic molecules are hydrogen (H_2), nitrogen (N_2), fluorine (F_2), oxygen (O_2), iodine (I_2), chlorine (Cl_2) and bromine (Br_2). A few other elements can exist as 3-atom molecules like ozone (O_3) and 4-atom molecules like phosphorus (P_4). The most common form of the element sulfur is composed of molecules that consist of eight atoms of sulfur; its molecular formula is S_8 (Figure **2.3.2**).

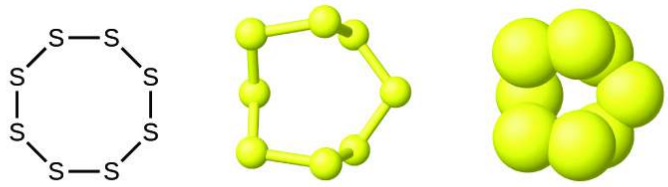


Figure **2.3.2**: A molecule of sulfur is composed of eight sulfur atoms and is therefore written as S_8. It can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. Sulfur atoms are represented by yellow spheres.

Figure A shows eight sulfur atoms, symbolized with the letter S, that are bonded to each other to form an octagon. Figure B shows a 3-D, ball-and-stick model of the arrangement of the sulfur atoms. The shape is clearly not octagonal as it is represented in the structural formula. Figure C is a space-filling model that shows each sulfur atom is partially embedded into the sulfur atom it bonds with.

It is important to note that a subscript following a symbol and a number in front of a symbol do not represent the same thing; for example, H_2 and 2H represent distinctly different species. H_2 is a molecular formula; it represents a diatomic molecule of hydrogen, consisting of two atoms of the element that are chemically bonded together. The expression 2H, on the other hand, indicates two separate hydrogen atoms that are **not** combined as a unit. The expression $2H_2$ represents two molecules of diatomic hydrogen (Figure **2.3.3**).

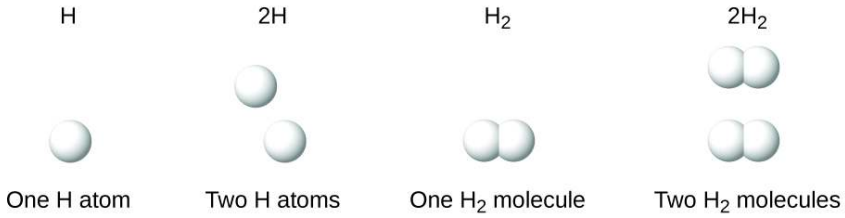


Figure **2.3.3**: The symbols H, 2H, H_2, and $2H_2$ represent very different entities.

This figure shows four diagrams. The diagram for H shows a single, white sphere and is labeled one H atom. The diagram for 2 H shows two white spheres that are not bonded together. It is labeled 2 H atoms. The diagram for H subscript 2 shows two white spheres bonded together. It is labeled one H subscript 2 molecule. The diagram for 2 H subscript 2 shows two sets of bonded, white spheres. It is labeled 2 H subscript 2 molecules.

✔ Example 2.3.1

Write the chemical formula of the following elements:

a. oxygen
b. carbon
c. potassium

Solution

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

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

2.3.1 Exercise

Write the chemical formula of the following elements:

a. hydrogen
b. nitrogen
c. neon

Answer a

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

Answer b

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

Answer c

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

Looking Closer: Atomic Theory

Dalton's ideas are called the *modern* atomic theory because the concept of atoms is very old. The Greek philosophers Leucippus and Democritus originally introduced atomic concepts in the fifth century BC. (The word *atom* comes from the Greek word *atomos*, which means "indivisible" or "uncuttable.") Dalton had something that the ancient Greek philosophers didn't have, however; he had experimental evidence, such as the formulas of simple chemicals and the behavior of gases. In the 150 years or so before Dalton, natural philosophy had been maturing into modern science, and the scientific method was being used to study nature. So when Dalton announced a modern atomic theory, he was proposing a fundamental theory to describe many previous observations of the natural world; he was not just participating in a philosophical discussion.

Concept Review Exercises

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

Answers

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

Key Takeaways

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

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2.4: The Structure of Atoms

Learning Objectives

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

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

Subatomic Particles

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

Finally, additional experiments pointed to the existence of a third particle. Evidence produced in 1932 established the existence of the neutron, a particle with about the same mass as a proton but with no electrical charge, it is *neutral*. We understand now that all atoms can be broken down into subatomic particles: protons, neutrons, and electrons. Table **2.4.1** lists some of their important characteristics and the symbols used to represent each particle.

Table **2.4.1**: Properties of the Subatomic Particles

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

The Nucleus

How are these subatomic particles arranged? Between 1909 and 1911, Ernest Rutherford, a Cambridge physicist, and his associates Hans Geiger and Ernest Marsden performed experiments that provided strong evidence concerning the internal structure of an atom. They took a very thin metal foil, such as gold or platinum, and aimed a beam of positively charged particles (called alpha particles, which are combinations of two protons and two neutrons) from a radioactive source toward the foil. Surrounding the foil was a detector—either a scintillator (a material that glows when hit by such particles) or some unexposed film (which is exposed where the particles hit it). The detector allowed the scientists to determine the distribution of the alpha particles after they interacted with the foil. Figure **2.4.1** shows a diagram of the experimental setup.

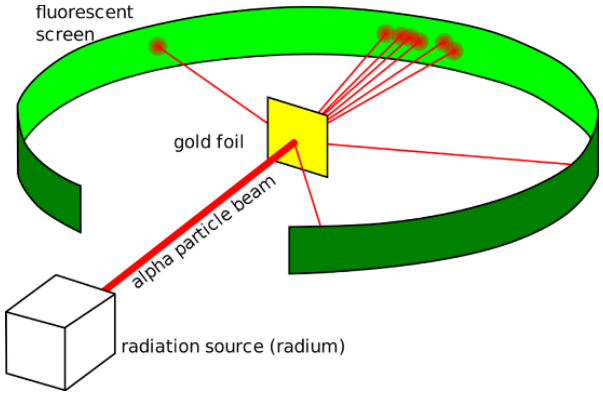


Figure **2.4.1**: The Geiger-Marsden Experimental Setup. Experiments using this setup were used to investigate the structure of atoms. In this experiment, most of the particles traveled straight through the foil, but some alpha particles were deflected off to one side. Some were even deflected back toward the source. This was unexpected. Rutherford once said, "It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you." (CC SA-BY 3.0; Kurzon).

Rutherford proposed the following model to explain these experimental results. Protons and neutrons are concentrated in a central region he called the nucleus (plural, *nuclei*) of the atom. Electrons are outside the nucleus and orbit about it because they are attracted to the positive charge in the nucleus. Most of the mass of an atom is in the nucleus, while the orbiting electrons account for an atom's size. As a result, an atom consists largely of empty space. Rutherford called his description the "planetary model" of the atom. Figure **2.4.2** shows how this model explains the experimental results.

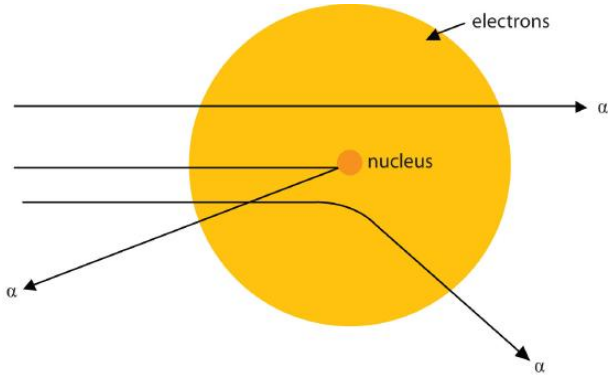


Figure **2.4.2**: Rutherford's Metal Foil Experiments. Rutherford explained the results of the metal foil experiments by proposing that most of the mass and the positive charge of an atom are located in its nucleus, while the relatively low-mass electrons orbit about the nucleus. Most alpha particles go straight through the empty space, a few particles are deflected, and fewer still ricochet back toward the source. The nucleus is much smaller proportionately than depicted here.

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

Rutherford's model is essentially the same model that we use today to describe atoms but with one important modification. The planetary model suggests that electrons occupy certain specific, circular orbits about the nucleus. We know now that this model is overly simplistic. A better description is that electrons form fuzzy clouds around nuclei. Figure **2.4.3** shows a more modern version of our understanding of atomic structure.

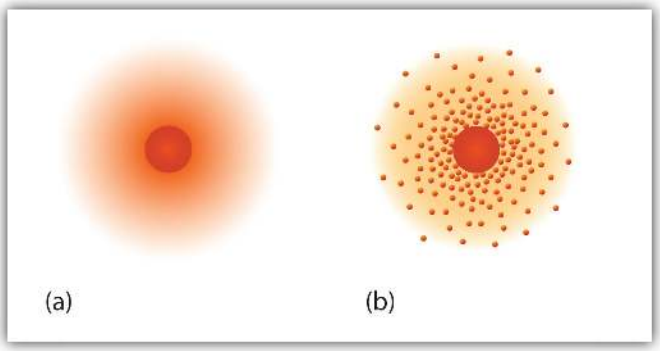


Figure **2.4.3**: A Modern Depiction of Atomic Structure. A more modern understanding of atoms, reflected in these representations of the electron in a hydrogen atom, is that electrons occupy regions of space about the nucleus; they are not in discrete orbits like planets around the sun. (a) The darker the color, the higher the probability that an electron will be at that point. (b) In a two-dimensional cross section of the electron in a hydrogen atom, the more crowded the dots, the higher the probability that an electron will be at that point. In both (a) and (b), the nucleus is in the center of the diagram.

Concept Review Exercises

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

Answers

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

Key Takeaways

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

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2.5: Nuclei of Atoms

Learning Objectives

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

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

Atomic Number

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

For example, hydrogen has the atomic number 1; all hydrogen atoms have 1 proton in their nuclei. Helium has the atomic number 2; all helium atoms have 2 protons in their nuclei. There is no such thing as a hydrogen atom with 2 protons in its nucleus; a nucleus with 2 protons would be a helium atom. The atomic number *defines* an element. Table **2.5.1** lists some common elements and their atomic numbers. Based on its **atomic number**, you can determine the **number of protons in the nucleus** of an atom. The largest atoms have over 100 protons in their nuclei.

Example 2.5.1

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

a. aluminum
b. iron
c. carbon

Answer a

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

Answer b

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

Answer c

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

Exercise 2.5.1

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

a. sodium
b. oxygen
c. chlorine

Answer a

Sodium has 11 protons in its nucleus.

Answer b

Oxygen has 8 protons in its nucleus.

Answer c

Chlorine has 17 protons in its nucleus

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

Example 2.5.2

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

a. sulfur
b. tungsten
c. argon

Answer a

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

Answer b

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

Answer c

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

Exercise 2.5.2

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

a. magnesium
b. potassium
c. iodine

Answer a

Mg has 12 electrons.

Answer b

K has 19 electrons.

Answer c

I has 53 electrons.

Table **2.5.1**: Some Common Elements and Their Atomic Numbers

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

Isotopes

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

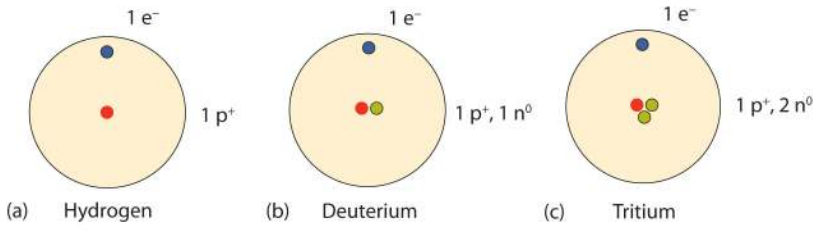


Figure **2.5.1**: Isotopes of Hydrogen. Most hydrogen atoms have only a proton in the nucleus (a). A small amount of hydrogen exists as the isotope deuterium, which has one proton and one neutron in its nucleus (b). A tiny amount of the hydrogen isotope tritium, with one proton and two neutrons in its nucleus, also exists on Earth (c). The nuclei and electrons are proportionately much smaller than depicted here.

An important series of isotopes is found with hydrogen atoms. Most hydrogen atoms have a nucleus with only a single proton. About 1 in 10,000 hydrogen nuclei, however, also has a neutron; this particular isotope is called *deuterium*. An extremely rare hydrogen isotope, *tritium*, has 1 proton and 2 neutrons in its nucleus. Figure **2.5.1** compares the three isotopes of hydrogen.

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

Most elements exist as mixtures of isotopes. In fact, there are currently over 3,500 isotopes known for all the elements. When scientists discuss individual isotopes, they need an efficient way to specify the number of neutrons in any particular nucleus. The *mass number* (A) of an atom is the sum of the numbers of protons and neutrons in the nucleus. Given the mass number for a nucleus (and knowing the atomic number of that particular atom), you can determine the number of neutrons by subtracting the atomic number from the mass number.

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

$$\begin{matrix}\text{mass number}\longrightarrow 56\\ \text{atomic number}\longrightarrow 26\end{matrix}\mathrm{Fe} \tag{2.5.1}$$

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

✔ Example 2.5.3

How many protons and neutrons are in each atom?

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

Answer a

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

Answer b

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

? Exercise 2.5.3

How many protons and neutrons are in each atom?

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

Answer a

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

Answer b

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

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

Summary

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

Almost all of the mass of an atom is from the total protons and neutrons contained within a tiny (and therefore very dense) nucleus. The majority of the volume of an atom is the surrounding space in which the electrons reside. A representation of a carbon-12 atom is shown below in Figure **2.5.2**.

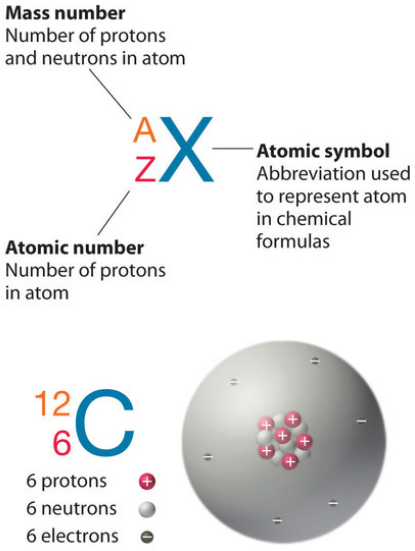


Figure **2.5.2**: Formalism used for identifying specific nuclide (any particular kind of nucleus)

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

Concept Review Exercises

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

Answers

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

Key Takeaways

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

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2.6: Atomic Masses

Learning Objectives

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

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

Atomic Mass Unit

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

$$1\ \text{u} = \frac{1}{12}\ \text{the mass of}\ ^{12}\text{C atom} \tag{2.6.1}$$

It is equal to 1.661×10^{-24} g.

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

Atomic Mass is the Weighted Average Mass of Isotopes

As stated above, most elements occur naturally as a mixture of two or more isotopes. Listed below (Table **2.6.1**) are the naturally occurring isotopes of selected elements along with the percent natural abundance of each.

Table **2.6.1**: Atomic Masses and Percent Abundances of Some Natural Isotopes

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

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

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

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

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

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

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

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

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

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

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

Example 2.6.1

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

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

Solution

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

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

2.6.1 Exercise

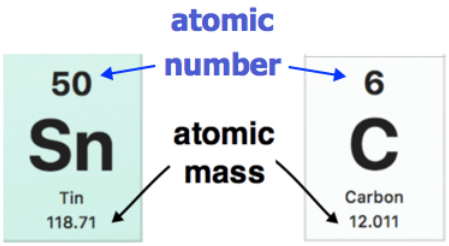
Calculate the atomic mass of copper. Copper exists as a mixture of 2 isotopes. Their respective masses and natural abundance are shown below.

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

Answer

63.546 u

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



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

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

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

Example 2.6.2: Mass of Carbon

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

Solution

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

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

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

Exercise 2.6.2: Mass of Tin

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

Answer

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

Concept Review Exercises

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

Answers

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

Key Takeaway

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

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2.7: Arrangements of Electrons

Learning Objectives

- Describe how electrons are grouped within atoms.

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

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

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

Table **2.7.1**: Shells and Subshells

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

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

Table **2.7.2**: Number of Electrons

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

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

We use numbers to indicate which shell an electron is in. As shown in Table **2.7.1**, the first shell, closest to the nucleus and with the lowest-energy electrons, is shell 1. This first shell has only one subshell, which is labeled 1*s* and can hold a maximum of 2 electrons. We combine the shell and subshell labels when referring to the organization of electrons about a nucleus and use a superscript to indicate how many electrons are in a subshell. Thus, because a hydrogen atom has its single electron in the *s* subshell of the first shell, we use $\mathbf{1}s^{\mathbf{1}}$ to describe the electronic structure of hydrogen. This structure is called an electron configuration. Electron configurations are shorthand descriptions of the arrangements of electrons in atoms. The electron configuration of a hydrogen atom is spoken out loud as “one-ess-one.”

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

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

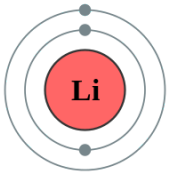


Figure **2.7.1**: Shell diagram of lithium (Li) atom.

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

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

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

Electron filling always starts with **1*s***, the subshell closest to the nucleus. Next is **2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5s, 4d, 5p, 6s,** etc., shown in the electron shell filling order diagram in Figure **2.7.2**. Follow each arrow in order **from top to bottom**. The subshells you reach along each arrow give the ordering of filling of subshells in larger atoms.

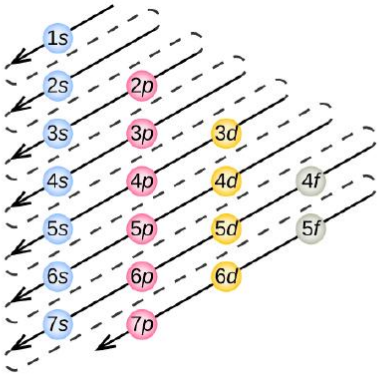


Figure **2.7.2**: The order of electron filling in an atom.

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 $1s^2 2s^2 2p^6 3s^2 3p^5$.

Since the arrangement of the periodic table is based on the electron configurations, Figure **2.7.3** provides an alternative method for determining the electron configuration. The filling order simply **begins at the top left,** with hydrogen (Z=1) and includes each subshell as you proceed in increasing atomic number (*Z*) order.

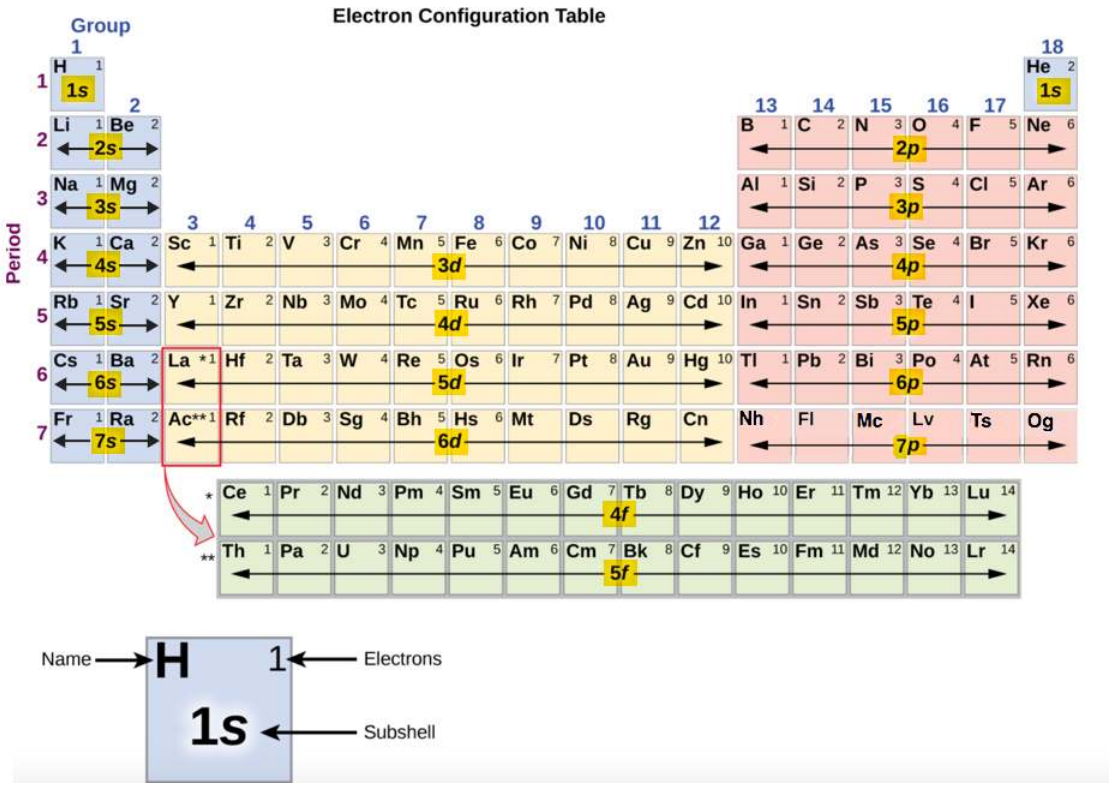


Figure **2.7.3**: This periodic table shows the electron configuration for each subshell. By “building up” from hydrogen, this table can be used to determine the electron configuration for any atom on the periodic table.

For example, the first row (Period 1) contains H and He only, because only two electrons are required to fill the 1s subshell. The second row s-block, contains only two elements, Li and Be, to fill the 2s subshell. This is followed by the second row p-block, containing 6 elements (B through Ne) since six electrons are required to fill the 2p subshell. The third row is similar to the second row elements. Two electrons are needed (Na and Mg) to fill the 3s subshell and six electrons are required (Al through Ar) to complete the 3p subshell. After filling the 3*p* block up to Ar, we see the next subshell will be 4s (K, Ca), followed by the 3*d* subshell, which are filled by ten electrons (Sc through Zn). The 4p subshell is filled next by six electrons (Ga through Kr). As you can see, the periodic table shown in Figure **2.7.3** provides a simple way to remember the order of filling the subshells in determining the electron configuration. The order of filling subshells is the same: **1s, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5s, 4d, 5p, 6s,** etc.

✔ Example 2.7.2: Aluminum

Using Figure **2.7.3** as your guide, write the electron configuration of neutral aluminum atom. The atomic number of Al is 13.

Solution

Aluminum has 13 electrons.

Start at Period 1 of the periodic table, Figure **2.7.3**. Place two electrons in the 1s subshell (**$1s^2$**).

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

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

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

2.7.2 Exercise

Using Figure **2.7.3** as your guide, write the electron configuration of the atom that has 20 electrons

Answer

Start at Period 1 of Figure **2.7.3**. Place two electrons in the 1s subshell (**$1s^2$**).

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

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

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

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

Valence Electrons

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

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

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

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

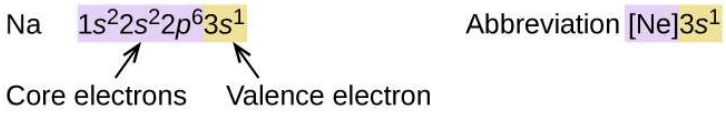


Figure **2.7.4**: A core-abbreviated electron configuration (right) replaces the core electrons with the noble gas symbol whose configuration matches the core electron configuration of the other element.

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

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

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

Example 2.7.3

Examine the electron configuration of neutral phosphorus atoms in Example **2.7.1**, $1s^2 2s^2 2p^6 3s^2 3p^3$ and write the abbreviated notation.

Solution

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

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

The 10 inner shell (core) electrons, $1s^2 2s^2 2p^6$ can be replaced by [Ne] (see Figure **2.7.3**). Abbreviated notation is : [Ne]$3s^2 3p^3$

Exercise 2.7.3

Examine the electron configuration of neutral calcium atom (Exercise **2.7.2**), $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$, and write the abbreviated notation.

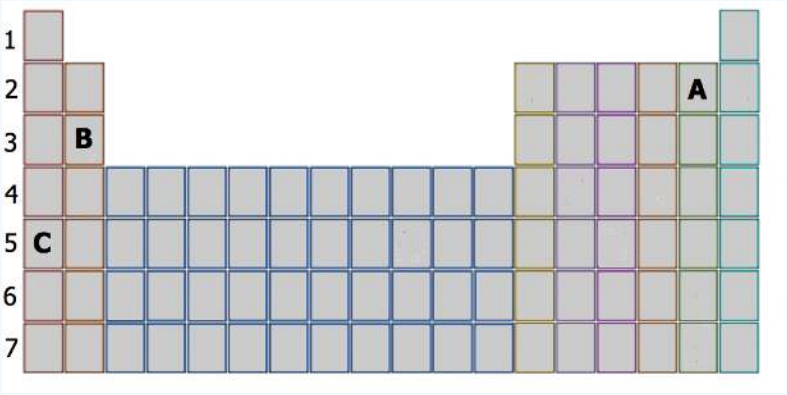
Answer

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

The 18 inner-shell (core) electrons, $1s^2 2s^2 2p^6 3s^2 3p^6$, can be replaced by [Ar], see Figure **2.7.3**. The abbreviated notation is: [Ar]$4s^2$

Example 2.7.4

Based on their respective locations in the periodic table (use Figure **2.7.3**), determine the number of valence electrons and the valence shell configuration of elements A, B and C.



Solution

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

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

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

2.7.4 Exercise

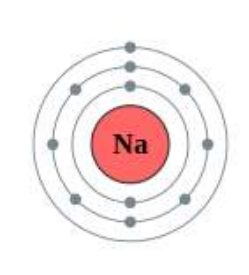
Using the location of Na is the periodic table (Figure **2.7.3**), draw the shell diagram of sodium atom.

Answer

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

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

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



Concept Review Exercises

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

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

Answers

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

Key Takeaway

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

Exercises

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2.8: The Periodic Table

Learning Objectives

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

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

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

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

The periodic table is one of the cornerstones of chemistry because it organizes all the known elements on the basis of their chemical properties. A modern version is shown in Figure **2.8.1**. Most periodic tables provide additional data (such as atomic mass) in a box that contains each element's symbol. The elements are listed in order of atomic number.

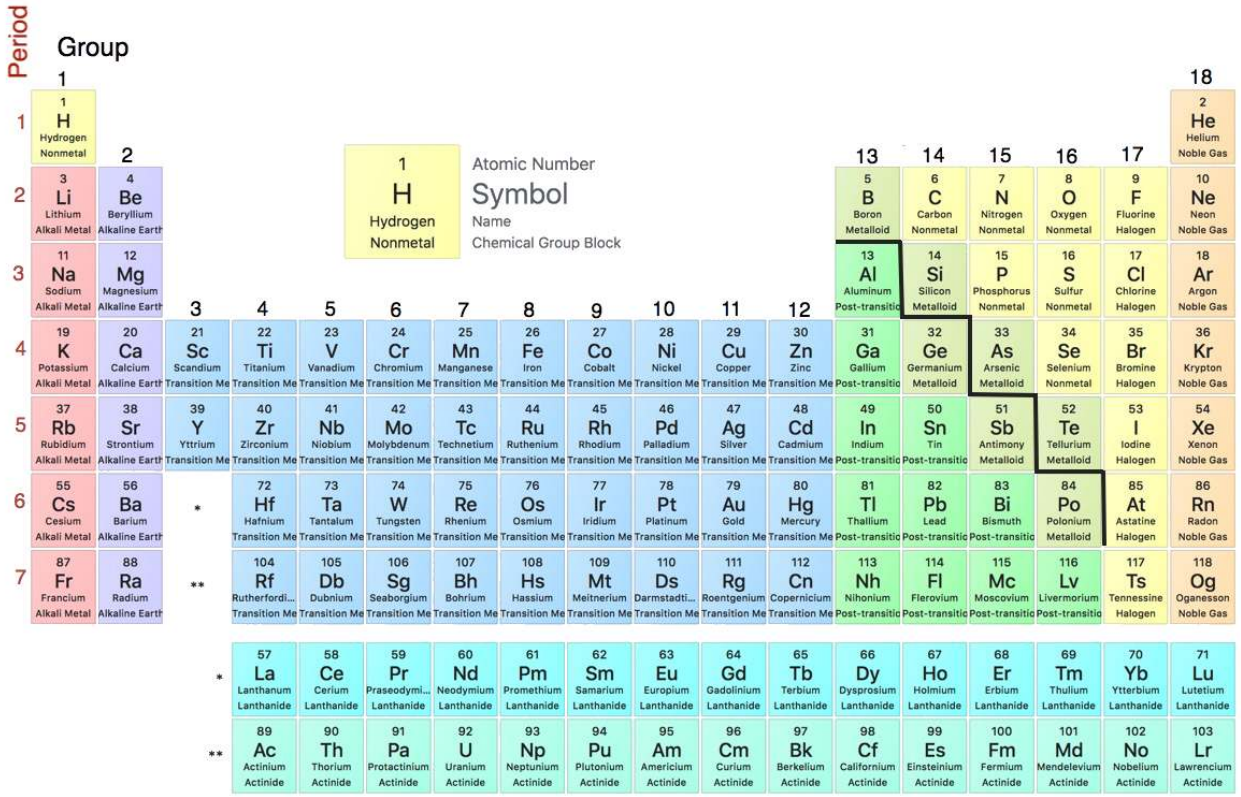


Figure **2.8.1**: Modern Periodic Table. (Public Domain; PubChem modified Leticia Colmenares).

Features of the Periodic Table

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

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

Metals, Nonmetals and Metalloids

Certain elemental properties become apparent in a survey of the periodic table as a whole. Every element can be classified as either a metal, a nonmetal, or a semimetal, as shown in Figure **2.8.2**. A metal is a substance that is shiny, typically (but not always) silvery in color, and an excellent conductor of electricity and heat. Metals are also malleable (they can be beaten into thin sheets) and ductile (they can be drawn into thin wires). A nonmetal is typically dull and a poor conductor of electricity and heat. Solid nonmetals are also very brittle. As shown in Figure **2.8.2**, **metals** occupy the left three-fourths of the periodic table, while **nonmetals** (except for hydrogen) are clustered in the upper right-hand corner of the periodic table. The elements with properties intermediate between those of metals and nonmetals are called **semimetals** (or **metalloids**). Elements adjacent to the **bold zigzag** line in the right-hand portion of the periodic table have semimetal properties.

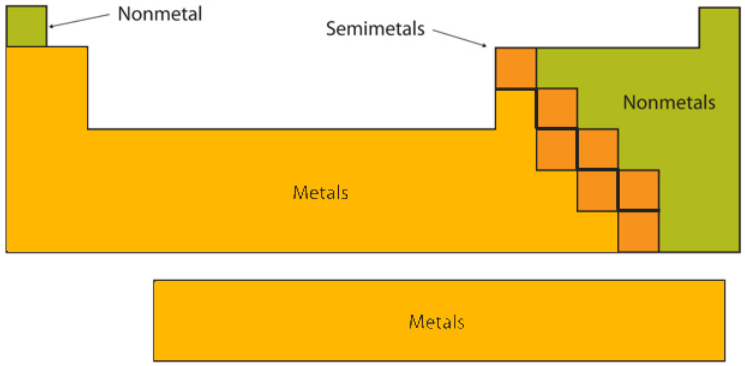


Figure **2.8.2**: Types of Elements. Elements are either metals, nonmetals, or semimetals. Each group is located in a different part of the periodic table.

Example 2.8.1

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

Solution

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

2.8.1 Exercise

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

Answer

metal

Representative, Transition and Inner-transition

Another way to categorize the elements of the periodic table is shown in Figure **2.8.3**. The first two columns on the left and the last six columns on the right are called the **main group** or **representative** elements. The ten-column block between these columns contains the **transition metals**. The two rows beneath the main body of the periodic table contain the inner transition metals. The elements in these two rows are also referred to as, respectively, the **lanthanide metals** and the **actinide metals**.

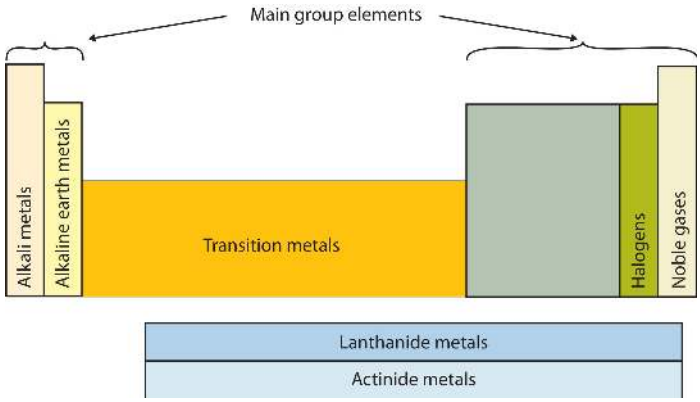


Figure **2.8.3**: Special Names for Sections of the Periodic Table. Some sections of the periodic table have special names. The elements lithium, sodium, potassium, rubidium, cesium, and francium are collectively known as alkali metals.

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

To Your Health: Transition Metals in the Body

Most of the elemental composition of the human body consists of main group elements. The first element appearing on the list that is not a main group element is iron, at 0.006 percentage by mass. Because iron has relatively massive atoms, it would appear even lower on a list organized in terms of percent by *atoms* rather than percent by mass.

Iron is a transition metal. Transition metals have interesting chemical properties, partially because some of their electrons are in *d* subshells. The chemistry of iron makes it a key component in the proper functioning of red blood cells.

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

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

Other transition metals have important functions in the body, despite being present in low amounts. Zinc is needed for the body's immune system to function properly, as well as for protein synthesis and tissue and cell growth. Copper is also needed for several proteins to function properly in the body. Manganese is needed for the body to metabolize oxygen properly. Cobalt is a necessary component of vitamin B-12, a vital nutrient. These last three metals are not listed explicitly in Table 2.1.2, so they are present in the body in very small quantities. However, even these small quantities are required for the body to function properly.

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

Group 1: The Alkali Metals

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

Group 2: The Alkaline Earth Metals

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

Group 17: The Halogens

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

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

Group 18: The Noble Gases

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

To Your Health: Radon

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

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

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

Why do elements in a given group have similar properties?

The periodic table is organized on the basis of similarities in elemental properties, but what explains these similarities? It turns out that the shape of the periodic table reflects the filling of subshells with electrons, as shown in Figure **2.8.4**. Starting with the first

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

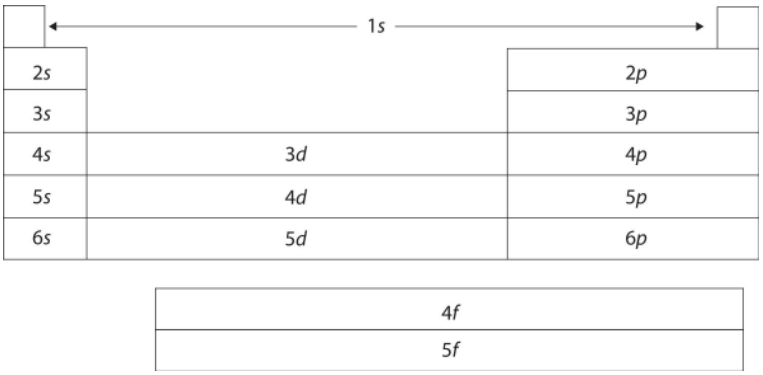


Figure **2.8.4** The Shape of the Periodic Table. The shape of the periodic table reflects the order in which electron shells and subshells fill with electrons.

Example 2.8.1

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

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

Answer a

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

Answer b

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

Exercise 2.8.1

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

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

Answer a

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

Answer b

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

Valence Electrons and Group Number

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

Table **2.8.1**. The Group number and the number of valence electrons.

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

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

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

Atomic Radius

The periodic table is useful for understanding atomic properties that show periodic trends. One such property is the atomic radius (Figure **2.8.5**). The atomic radius is defined as one-half the distance between the nuclei of identical atoms that are bonded together. The units for atomic radii are picometers, equal to 10^{-12} meters. As an example, the internuclear distance between the two hydrogen atoms in an $\mathbf{H_2}$ molecule is measured to be $\mathbf{74\ pm}$. Therefore, the atomic radius of a hydrogen atom is $\frac{74}{2} = \mathbf{37\ pm}$.

As mentioned earlier, the higher the shell number, the farther from the nucleus the electrons in that shell are likely to be. In other words, the size of an atom is generally determined by the number of the valence electron shell. Therefore, as we go down a column on the periodic table, the atomic radius increases. As we go *across* a period on the periodic table, however, electrons are being added to the *same* valence shell; meanwhile, more protons are being added to the nucleus, so the positive charge of the nucleus is increasing. The increasing positive charge attracts the electrons more strongly, pulling them closer to the nucleus. Consequently, as we go across a period, from left to right, the atomic radius decreases. These trends are seen clearly in Figure **2.8.5**

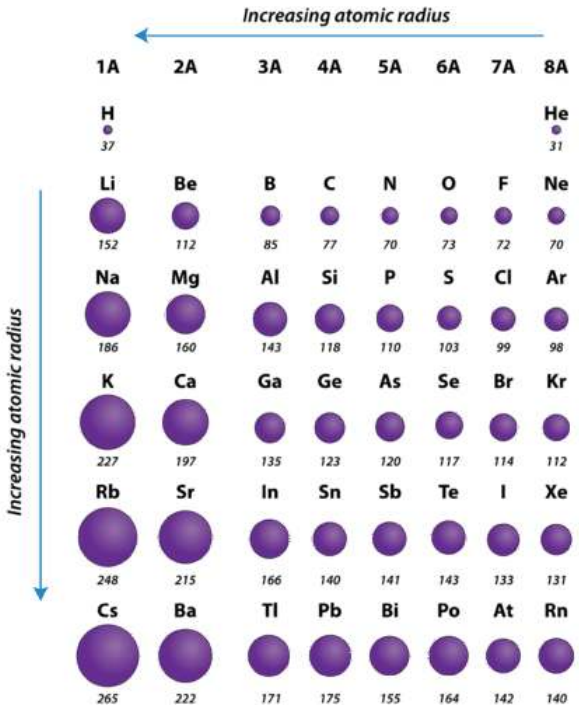


Figure **2.8.5** Trends on the Periodic Table. Atomic radii of the representative elements measured in picometers. The relative sizes of the atoms show several trends with regard to the structure of the periodic table. Atoms become larger going down a group and going from right to left across a period.

✔ Example 2.8.2

Using the periodic table (rather than Figure **2.8.5**), which atom is larger?

a. N or Bi
b. Mg or Cl

Answer a

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

Answer b

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

? Exercise 2.8.2

Using the periodic table (rather than Figure **2.8.5**), which atom is larger?

a. Li or F
b. Na or K

Answer a

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

Answer b

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

Career Focus: Clinical Chemist

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

Concept Review Exercises

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

Answers

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

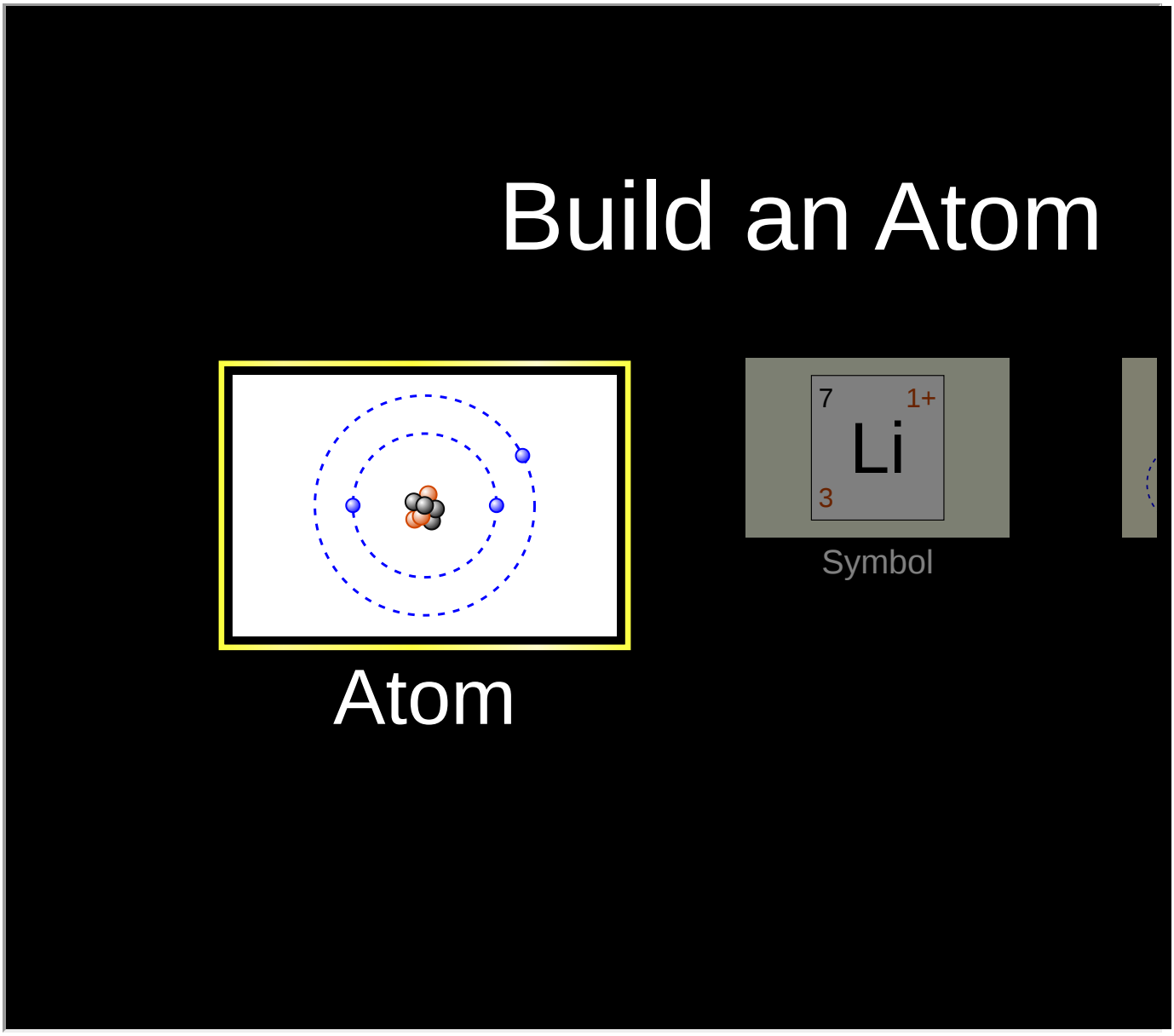
Key Takeaways

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

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2.9: PhET- Build an Atom



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

02.E: Exercises II

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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.

3.1: Prelude to Ionic Bonding and Simple Ionic Compounds
3.2: Two Types of Bonding
3.3: Ions
3.4: Formulas for Ionic Compounds
3.5: Ionic Nomenclature
3.6: Formula Mass
3.7: Characteristics of Ionic Compounds
3.E: Ionic Bonding and Simple Ionic Compounds (Exercises)

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3.1: Prelude to Ionic Bonding and Simple Ionic Compounds

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

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

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

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3.2: Two Types of Bonding

Learning Objectives

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

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

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

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

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

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

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

Example 3.2.1

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

Solution

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

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 3.2.1

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

Answer

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

Key Takeaways

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

Exercises

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.

Answers

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.

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3.3: Ions

Learning Objectives

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

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

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

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

Electron Transfer

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

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

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.

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

Figure **3.3.1** is a graphical depiction of this process.

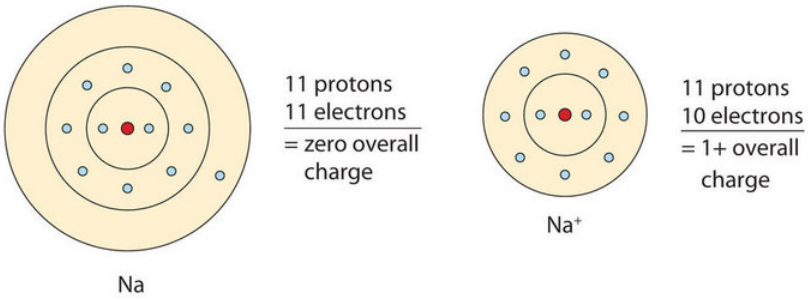


Figure **3.3.1**: The Formation of a Sodium Ion. On the left, a sodium atom has 11 electrons. On the right, the sodium ion only has 10 electrons and a 1+ charge.

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

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 **3.3.2** is a graphical depiction of this process.

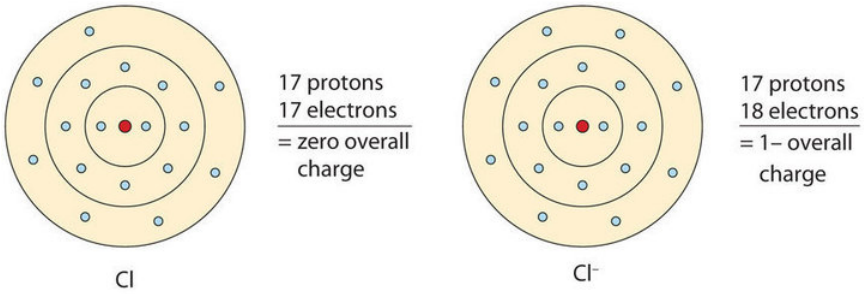


Figure **3.3.2**: The Formation of a Chlorine Ion. On the left, the chlorine atom has 17 electrons. On the right, the chloride ion has 18 electrons and has a 1− charge.

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 3.3.1

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

Solution

The electron configuration of Al atom is $1s^2 2s^2 2p^6 3s^2 3p^1$. 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, $1s^2 2s^2 2p^6$.

3.3.1 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 **3.3.3** shows how the charge on many ions can be predicted by the location of an element on the periodic table. Note the convention of first writing the number and then the sign on a multiply charged ion. The barium cation is written Ba^{2+}, not Ba^{+2}.

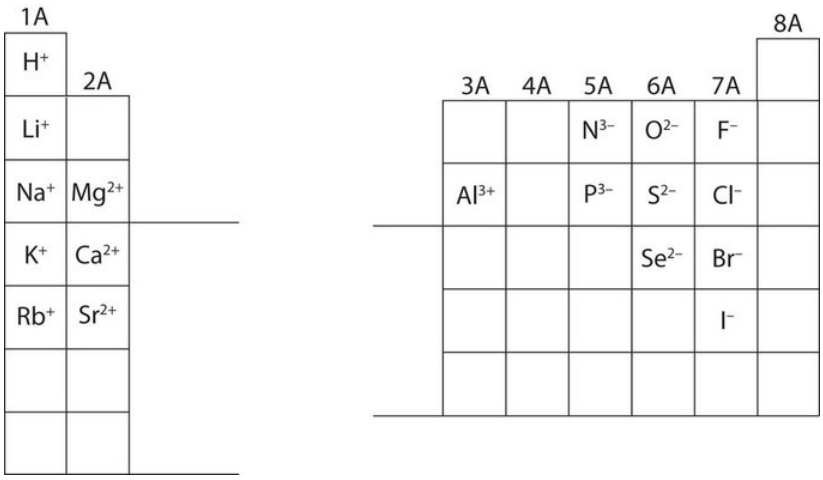


Figure **3.3.3**: Predicting Ionic Charges. The charge that an atom acquires when it becomes an ion is related to the structure of the periodic table. Within a group (family) of elements, atoms form ions of a certain charge.

Example 3.3.2

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

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

Solution

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

3.3.2 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:

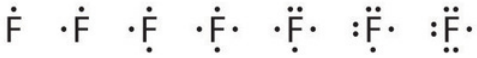
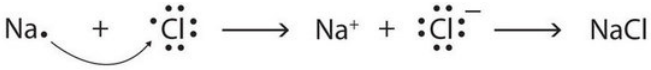


Figure **3.3.4** shows the electron configurations and Lewis diagrams of the elements lithium through neon, which is the entire second period of the periodic table. For the **main group** elements, the **number of valence electrons** is the **same as the group number** listed at the top of the periodic table.



Figure **3.3.4**: Lewis Electron Dot Diagrams of the Elements Lithium through Neon

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



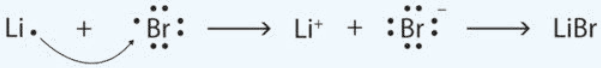
In representing the final formula, the dots are omitted.

Example 3.3.3

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

Solution

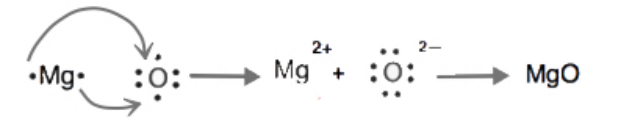
From the periodic table, we see that lithium is in the same column as sodium, so it will have the same valence shell electron configuration. That means that the neutral lithium atom will have the same Lewis diagram that the sodium atom has. Similarly, bromine is in the same column as chlorine, so it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



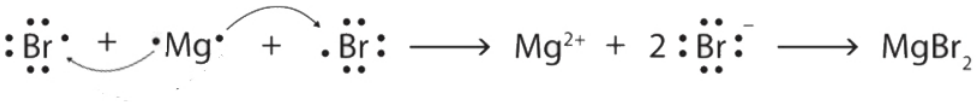
Exercise 3.3.3

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

Answer



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



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

Most of the elements that make ionic compounds form an ion that has a characteristic charge. For example, sodium makes ionic compounds in which the sodium ion always has a 1+ charge. Chlorine makes ionic compounds in which the chloride ion always has a 1− charge. Some elements, especially transition metals, can form ions of multiple charges. Figure **3.3.5** shows the characteristic charges for some of these ions. As we saw in Figure **3.3.1**, there is a pattern to the charges on many of the main group ions, but there is no simple pattern for transition metal ions (or for the larger main group elements).

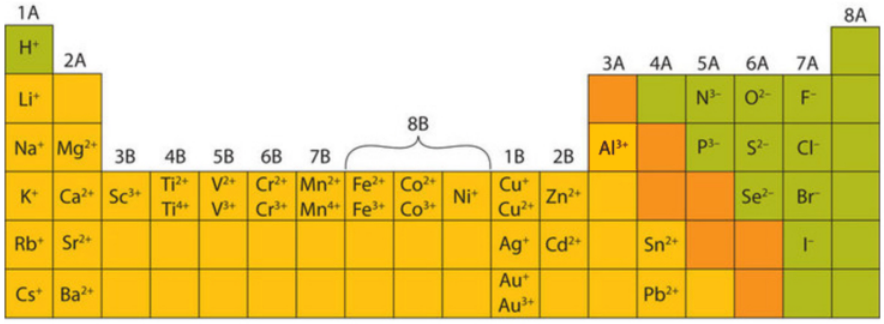


Figure **3.3.5**: Charges of the Monatomic Ions. Note that some atoms commonly form ions of variable charges.

Key Takeaways

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

Exercises

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?

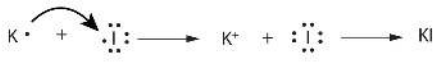
15. What characteristic charge do atoms in the second column of the periodic table have when they become ions?

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?

Answers

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. $Li\bullet$, Li^+

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

c. $:\ddot{F}:$, $:\ddot{F}:^-$

d. $:\ddot{S}:$, $:\ddot{S}:^{2-}$

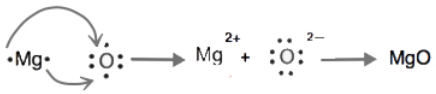
$Na\bullet$, Na^+

$\bullet Be\bullet$, Be^{2+}

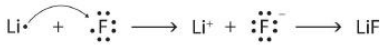
$:\ddot{Cl}:$, $:\ddot{Cl}:^-$

$:\ddot{O}:$, $:\ddot{O}:^{2-}$

9.

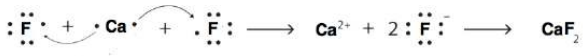


10.



11.

12.



13.



14. 1+

15. 2+

16. 2−

17. 1−

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3.4: Formulas for Ionic Compounds

Learning Objectives

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

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

Ionic compounds exist as alternating positive and negative ions in regular, three-dimensional arrays called crystals (Figure 3.4.1). As you can see, there are no individual NaCl "particles" in the array; instead, there is a continuous lattice of alternating sodium and chloride ions. However, we can use the ratio of sodium ions to chloride ions, expressed in the lowest possible whole numbers, as a way of describing the compound. In the case of sodium chloride, the ratio of sodium ions to chloride ions, expressed in lowest whole numbers, is 1:1, so we use NaCl (one Na symbol and one Cl symbol) to represent the compound. Thus, NaCl is the chemical formula for sodium chloride, which is a concise way of describing the relative number of different ions in the compound. A macroscopic sample is composed of myriads of NaCl pairs; each individual pair called a **formula unit**. Although it is convenient to think that NaCl crystals are composed of individual NaCl units, Figure 3.4.1 shows that no single ion is exclusively associated with any other single ion. Each ion is surrounded by ions of opposite charge.

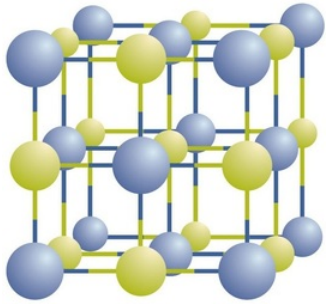


Figure 3.4.1: A Sodium Chloride Crystal. A crystal contains a three-dimensional array of alternating positive and negative ions. The precise pattern depends on the compound. A crystal of sodium chloride, shown here, is a collection of alternating sodium and chlorine ions.

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

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

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

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

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

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

$$Mg^{2+}Cl^{-}$$

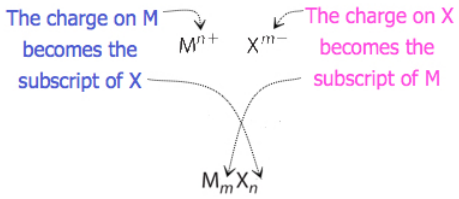
Combining one ion of each does not completely balance the positive and negative charges. The easiest way to balance these charges is to assume the presence of *two* chloride ions for each magnesium ion:

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

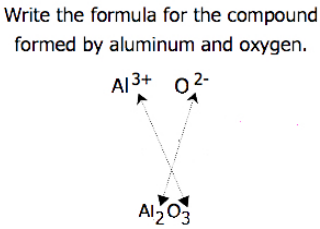
Now the positive and negative charges are balanced. We could write the chemical formula for this ionic compound as **MgClCl**, but the convention is to use a numerical subscript when there is more than one ion of a given type—**$MgCl_2$**. This chemical formula says that there are one magnesium ion and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

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

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



The image shows M with a charge of n+ and X with a charge of m-. The charge on the M becomes the subscript of X, and the charge on X becomes the subscript of M, making the final product M subscript m X subscript n.



The image asks to write the formula for the compound formed by aluminum and oxygen. It shows Al with a charge of 3+ and O with a charge of 2-. By crossing charges, the final result is Al subscript 2 O subscript 3.

Figure **3.4.2**: Crossing charges. One method for obtaining subscripts in the empirical formula is by crossing charges.

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

✔ Example 3.4.1

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

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

Solution

a. To obtain a valence shell octet, sodium forms an ion with a 1+ charge, while the sulfur ion has a 2− charge. Two sodium 1+ ions are needed to balance the 2− charge on the sulfur ion. Rather than writing the formula as $\mathbf{NaNaS}$, we shorten it by convention to $\mathbf{Na_2S}$.

b. The aluminum ion has a 3+ charge, while the fluoride ion formed by fluorine has a 1− charge. Three fluorine 1− ions are needed to balance the 3+ charge on the aluminum ion. This combination is written as $\mathbf{AlF_3}$.

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

? Exercise 3.4.1

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

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

Answer a:

CaO

Answer b:

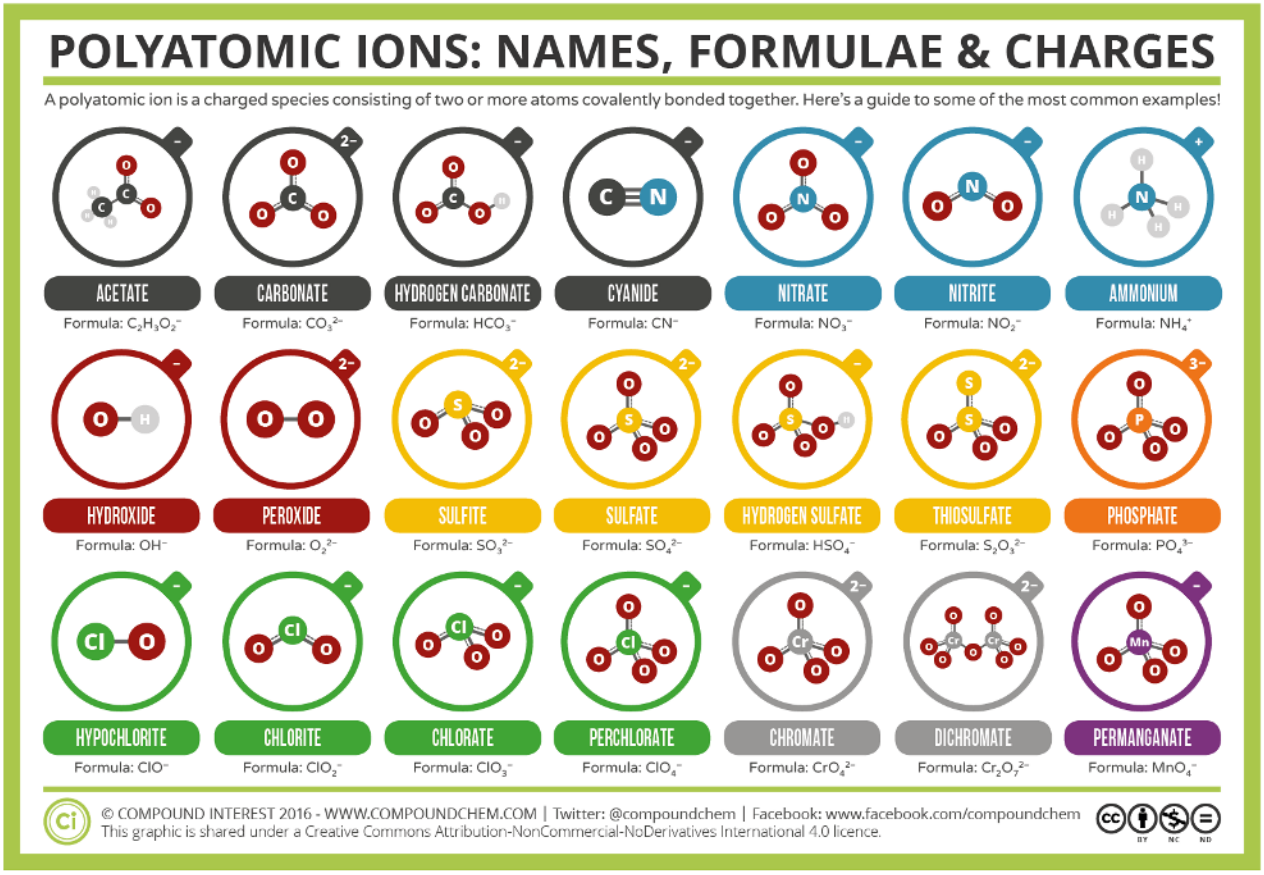
CuS

Answer c:

Cu_2S

Polyatomic Ions

Some ions consist of groups of atoms ***covalently*** bonded together and have an **overall electric charge**. Because these ions contain more than one atom, they are called polyatomic ions. The Lewis structures, names and formulas of some polyatomic ions are found in Table 3.3.1.



Some Polyatomic Ions

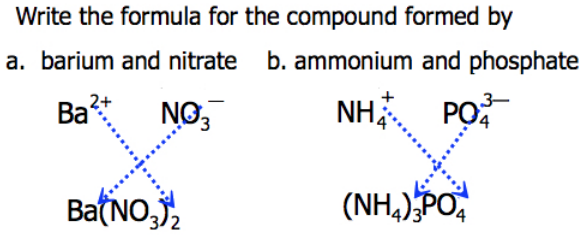
Polyatomic ions have defined formulas, names, and charges that cannot be modified in any way. Table **3.4.2** lists the ion names and ion formulas of the most common polyatomic ions. For example, $\mathbf{NO_3^-}$ is the nitrate ion; it has one nitrogen atom and three oxygen atoms and an overall 1− charge. Figure **3.4.2** lists the most common polyatomic ions.

Table **3.4.2**: Ion Names and Ion Formulas of Common Polyatomic Ions

Ion Name	Ion Formula
ammonium ion	NH_4^{+1}
hydroxide ion	OH^{-1}
cyanide ion	CN^{-1}
carbonate ion	CO_3^{-2}
bicarbonate or hydrogen carbonate	HCO_3^{-}
acetate ion	$C_2H_3O_2^{-1}$ **or** $CH_3CO_2^{-1}$
nitrate ion	NO_3^{-1}
nitrite ion	NO_2^{-1}
sulfate ion	SO_4^{-2}
sulfite ion	SO_3^{-2}
phosphate ion	PO_4^{-3}
phosphite ion	PO_3^{-3}

Note that only one polyatomic ion in this Table, the ammonium ion ($NH_4^{+1)}$, is a cation. This polyatomic ion contains one nitrogen and four hydrogens that collectively bear a +1 charge. The remaining polyatomic ions are all negatively-charged and, therefore, are classified as anions. However, only two of these, the hydroxide ion and the cyanide ion, are named using the "-ide" suffix that is typically indicative of negatively-charged particles. The remaining polyatomic anions, which all contain oxygen, in combination with another non-metal, exist as part of a series in which the number of oxygens within the polyatomic unit can vary. As has been repeatedly emphasized in several sections of this text, no two chemical formulas should share a common chemical name. A single suffix, "-ide," is insufficient for distinguishing the names of the anions in a related polyatomic series. Therefore, "-ate" and "-ite" suffixes are employed, in order to denote that the corresponding polyatomic ions are part of a series. Additionally, these suffixes also indicate the relative number of oxygens that are contained within the polyatomic ions. Note that all of the polyatomic ions whose names end in "-ate" contain one more oxygen than those polyatomic anions whose names end in "-ite." Unfortunately, much like the common system for naming transition metals, these suffixes only indicate the *relative* number of oxygens that are contained within the polyatomic ions. For example, the nitrate ion, which is symbolized as NO_3^{-1}, has one more oxygen than the nitrite ion, which is symbolized as NO_2^{-1}. However, the sulfate ion is symbolized as SO_4^{-2}. While both the nitrate ion and the sulfate ion share an "-ate" suffix, the former contains three oxygens, but the latter contains four. Additionally, both the nitrate ion and the sulfite ion contain three oxygens, but these polyatomic ions do not share a common suffix. Unfortunately, the relative nature of these suffixes mandates that the ion formula/ion name combinations of the polyatomic ions must simply be memorized.

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



The image asks a two-part question: Write the formula for the compound formed by (a) barium and nitrate, and (b) ammonium and phosphate. For (a), Ba has a charge of 2+ and NO_3 has a charge of -1. By crossing charges, the formula is $Ba(NO_3)_2$. For (b), NH_4 has a charge of +1 and PO_4 has a charge of 3-, so by crossing charges the formula is $(NH_4)_3PO_4$.

Example 3.4.2

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

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

Solution

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

Exercise 3.4.2

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

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

Answer a:

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

Answer b:

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

Recognizing Ionic Compounds

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

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

Example 3.4.3

Identify each compound as ionic or not ionic.

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

Solution

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

Exercise 3.4.3

Identify each compound as ionic or not ionic.

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

Answer a:

not ionic

Answer b:

ionic

Answer c:

ionic

Answer d:

not ionic

Looking Closer: Blood and Seawater

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

Table showing a comparison of the amounts of ions in blood and seawater.

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

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

Key Takeaways

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

EXERCISES

1. What information is contained in the formula of an ionic compound?

- Why do the chemical formulas for some ionic compounds contain subscripts, while others do not?

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

   a. Mg^{2+} and I^-
   b. Na^+ and O^{2-}

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

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

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

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

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

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

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

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

c. Li^{+} and P^{3-}

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

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

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

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

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

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

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

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

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

a. Ba and S
b. Cs and I

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

a. K and S
b. Sc and Br

14. Which compounds would you predict to be ionic?

a. Li_2O
b. $(NH_4)_2O$
c. CO_2
d. $FeSO_3$
e. C_6H_6
f. C_2H_6O

15. Which compounds would you predict to be ionic?

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

Answers

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

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

3.
    a. MgI_2
    b. Na_2O

4.
    a. NaBr
    b. $MgBr_2$
    c. MgS

5.
    a. KCl
    b. $MgCl_2$
    c. MgSe

6.
    a. Na_3N
    b. Mg_3N_2
    c. Al_2S_3

7.
    a. Li_3N
    b. Mg_3P_2
    c. Li_3P

8.
    a. $FeBr_3$
    b. $FeBr_2$
    c. Au_2S_3
    d. Au_2S

9.
    a. Cr_2O_3
    b. CrO
    c. $PbCl_2$
    d. $PbCl_4$

10.
    a. $Cr(NO_3)_3$
    b. $Fe_3(PO_4)_2$
    c. $CaCrO_4$
    d. $Al(OH)_3$

11.
    a. NH_4NO_3
    b. $H_2Cr_2O_7$
    c. Cu_2CO_3
    d. $NaHCO_3$

12.

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

13.

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

14.

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

15.

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

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3.5: Ionic Nomenclature

Learning Objectives

- To use the rules for naming ionic compounds

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

Naming Ions

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

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

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

Table **3.5.1**: The Common System of Cation Names

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

The second system, called the **common system**, is not conventional but is still prevalent and used in the health sciences. This system recognizes that many metals have two common cations. The common system uses two suffixes (*-ic* and *-ous*) that are appended to the stem of the element name. The *-ic* suffix represents the greater of the two cation charges, and the *-ous* suffix represents the lower one. In many cases, the stem of the element name comes from the Latin name of the element. Table **3.5.1** lists the elements that use the common system, along with their respective cation names.

The name of a monatomic anion consists of the stem of the element name, the suffix *-ide*, and then the word *ion*. Thus, as we have already seen, Cl^- is "chlor-" + "-ide ion," or the chloride ion. Similarly, O^{2-} is the oxide ion, Se^{2-} is the selenide ion, and so forth. Table **3.5.2** lists the names of some common monatomic ions.

Table **3.5.2**: Some Monatomic Anions

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

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

✔ Example 3.5.1

Name each ion.

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

Answer a

the calcium ion

Answer b

the sulfide ion (from Table **3.5.2**)

Answer c

the sulfite ion

Answer d

the ammonium ion

Answer e

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

? Exercise 3.5.1

Name each ion.

a. Fe^{2+}
b. Fe^{3+}
c. SO_4^{2-}

d. Ba^{2+}
e. HCO_3^-

Answer a

the iron (II) or ferrous ion

Answer b

the iron (III) or ferric ion

Answer c

the sulfate ion

Answer d

the barium ion

Answer e

the bicarbonate ion or hydrogen carbonate ion

Example 3.5.2

Write the formula for each ion.

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

Answer a

Br^-

Answer b

PO_4^{3-}

Answer c

Cu^{2+}

Answer d

Mg^{2+}

Exercise 3.5.2

Write the formula for each ion.

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

Answer a

F^-

Answer b

CO_3^{2-}

Answer c

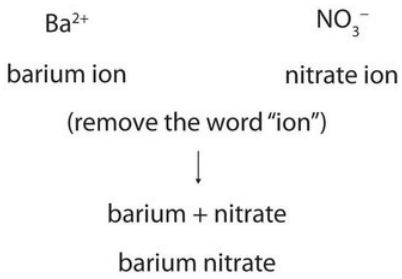
Fe^{2+}

Answer d

K^+

Naming Compounds

Now that we know how to name ions, we are ready to name ionic compounds. We do so by placing the name of the cation first, followed by the name of the anion, and dropping the word *ion* from both parts. For example, what is the name of the compound whose formula is $\mathbf{Ba(NO_3)_2}$?



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

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

✔ Example 3.5.3

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

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

Answer a

calcium phosphate

Answer b

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

Answer c

potassium chloride

Answer d

copper(I) chloride or cuprous chloride

Answer e

tin(II) fluoride or stannous fluoride

? Exercise 3.5.3

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

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

Answer a

zinc bromide

Answer b

iron (III) nitrate or ferric nitrate

Answer c

aluminum oxide

Answer d

copper (II) fluoride or cupric fluoride

Answer e

silver fluoride

Figure 3.5.1 is a synopsis of how to name simple ionic compounds.

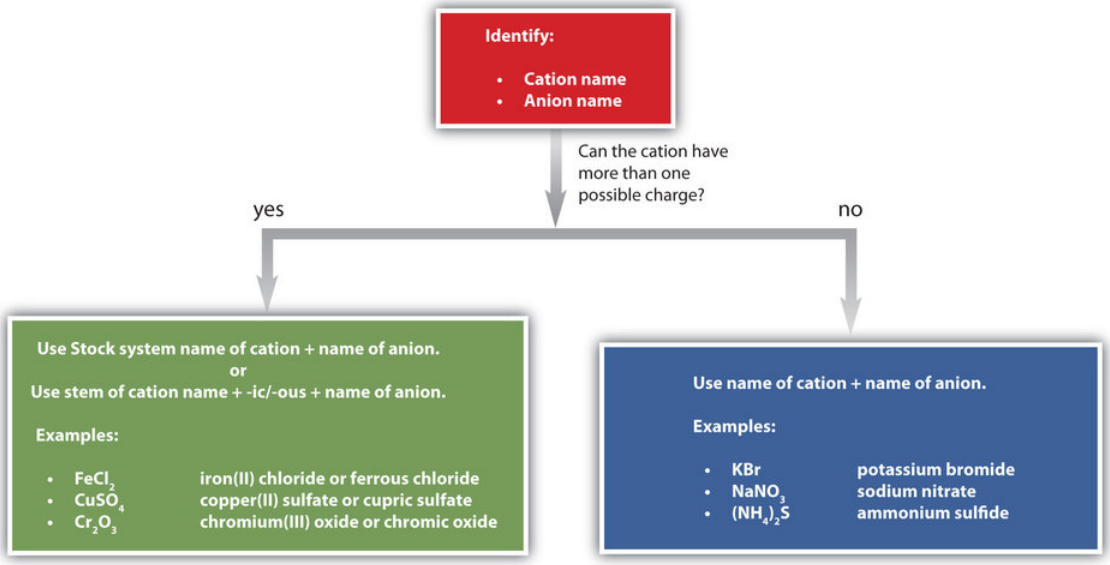


Figure 3.5.1: A Guide to Naming Simple Ionic Compounds. Follow these steps to name a simple ionic compound.

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 $FeCl_2$, which is iron(II) chloride of ferrous chloride, $CuSO_4$, which is copper(II) sulfate or cupric sulfate, and Cr_2O_3, 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, $NaNO_3$, which is sodium nitrate, and $(NH_4)_2S$, which is ammonium sulfide.

KEY TAKEAWAY

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

EXERCISES

1. Briefly describe the process for naming an ionic compound.

- In what order do the names of ions appear in the names of ionic compounds?

3. Which ionic compounds can be named using two different systems? Give an example.

4. Name each ion.

   a. Ra^{2+}
   b. P^{3-}
   c. $H_2PO_4^-$
   d. Sn^{4+}

5. Name each ion.

   a. Cs^+
   b. As^{3-}
   c. HSO_4^-
   d. Sn^{2+}

6. Name the ionic compound formed by each pair of ions.

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

7. Name the ionic compound formed by each pair of ions.

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

8. Name 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-}

9. Name 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-}

10. Name the ionic compound formed by each pair of ions. Use both the Stock and common systems, where appropriate.

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

11. Name the ionic compound formed by each pair of ions. Use both the Stock and common systems, where appropriate.

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

12. Name the ionic compound formed by each pair of ions. Use both the Stock and common systems, where appropriate.

    a. Cr^{3+} and NO_3^-

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

13. Name the ionic compound formed by each pair of ions. Use both the Stock and common systems, where appropriate.

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

14. Give two names for each compound.

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

15. Give two names for each compound.

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

AnswerS

1. Name the cation and then the anion but don't use numerical prefixes.
2. the cation name followed by the anion name
3. Ionic compounds in which the cation can have more than one possible charge have two naming systems. $FeCl_3$ is either iron(III) chloride or ferric chloride (answers will vary).

4.

a. the radium ion
b. the phosphide ion
c. the dihydrogen phosphate ion
d. the tin(IV) ion or the stannic ion

5.

a. the cesium ion
b. the arsenide ion
c. the hydrogen sulfate ion
d. the tin(II) ion or the stannous ion

6.

a. sodium bromide
b. magnesium bromide
c. magnesium sulfide

7.

a. potassium chloride
b. magnesium chloride
c. magnesium selenide

8.

a. sodium nitride
b. magnesium nitride
c. aluminum sulfide

9.

a. lithium nitride
b. magnesium phosphide
c. lithium phosphide

10.

a. iron(III) bromide or ferric bromide
b. iron(II) bromide or ferrous bromide
c. gold(III) sulfide or auric sulfide
d. gold(I) sulfide or aurous sulfide

11.

a. chromium(III) oxide or chromic oxide
b. chromium(II) oxide or chromous oxide
c. lead(II) chloride or plumbous chloride
d. lead(IV) chloride or plumbic chloride

12.

a. chromium(III) nitrate or chromic nitrate
b. iron(II) phosphate or ferrous phosphate
c. calcium chromate
d. aluminum hydroxide

13.

a. ammonium nitrate
b. potassium dichromate
c. copper(I) carbonate or cuprous carbonate
d. sodium hydrogen carbonate or sodium bicarbonate

14.

a. aluminum hydrogen sulfate or aluminum bisulfate
b. magnesium hydrogen sulfate or magnesium bisulfate

15.

a. cobalt hydrogen carbonate or cobalt bicarbonate
b. lithium hydrogen carbonate or lithium bicarbonate

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3.6: Formula Mass

Learning Objectives

- To determine the formula mass of an ionic compound.

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

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

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

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

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

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

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

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

The formula mass of CaF_2 is 78.08 amu.

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

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

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

The formula mass of KNO_3 is 101.11 amu.

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

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

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

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

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

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

Example 3.6.1

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

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

Solution

a.

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

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

The formula mass of $FeCl_3$ is 162.19 amu.

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

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

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

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

Exercise 3.6.1

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

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

d. $Fe_3(PO_4)_2$

Answer a:

47.87 + 2 (16.00) = 79.87 amu

Answer b:

107.87 + 79.90 = 187.77 amu

Answer c:

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

Answer d:

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

To Your Health: Hydrates

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

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



Magnesium sulfate heptahydrate. (Public Domain; Chemicalinterest).

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

Table **3.6.1**: Names and Formulas of Some Widely Used Hydrates

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

KEY TAKEAWAY

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

EXERCISES

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

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

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

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

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

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

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

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

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

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

7. What is the formula mass for each compound?

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

8. What is the formula mass for each compound?

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

9. What is the formula mass for each compound?

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

10. What is the formula mass for each compound?

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

11. What is the formula mass for each compound?

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

12. What is the formula mass for each compound?

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

Answers

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

3.

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

4.

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

5.

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

6.

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

7.

    a. 295.55 amu
    b. 215.65 amu
    c. 490.15 amu
    d. 426.01 amu

8.

    a. 152.00 amu
    b. 68.00 amu
    c. 278.10 amu
    d. 349.00 amu

9.

    a. 238.03 amu
    b. 357.49 amu
    c. 156.08 amu
    d. 78.01 amu

10.

    a. 80.06 amu

b. 294.20 amu
c. 187.11 amu
d. 84.01 amu

11.

a. 318.22 amu
b. 218.47 amu

12.

a. 180.97 amu
b. 67.96 amu

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3.7: Characteristics of Ionic Compounds

Learning Objectives

- To describe the physical properties of ionic compounds.

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

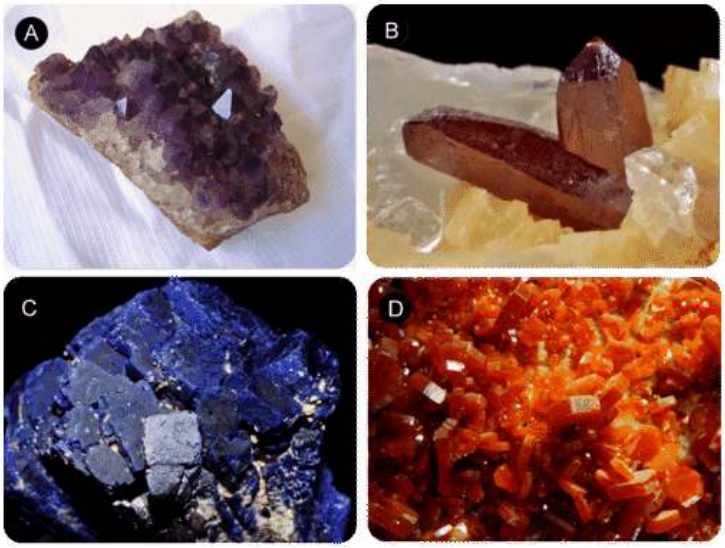


Figure 3.6.1: *In nature, the ordered arrangement of ionic solids gives rise to beautiful crystals. (A) Amethyst - a form of quartz, SiO_2, whose purple color comes from iron ions. (B) Cinnabar - the primary ore of mercury is mercury (II) sulfide, HgS (C) Azurite - a copper mineral, $Cu_3(CO_3)_2(OH)_2$.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

Physical Properties of Ionic Compounds

Melting Points

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

Shattering

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

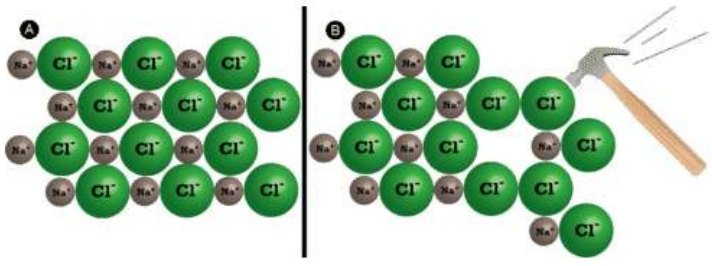


Figure 3.6.2: *(A) The sodium chloride crystal is shown in two dimensions. (B) When struck by a hammer, the negatively-charged chloride ions are forced near each other and the repulsive force causes the crystal to shatter.*

Conductivity

Another characteristic property of ionic compounds is their **electrical conductivity**. The figure below shows three experiments in which two electrodes that are connected to a light bulb are placed in beakers containing three different substances.

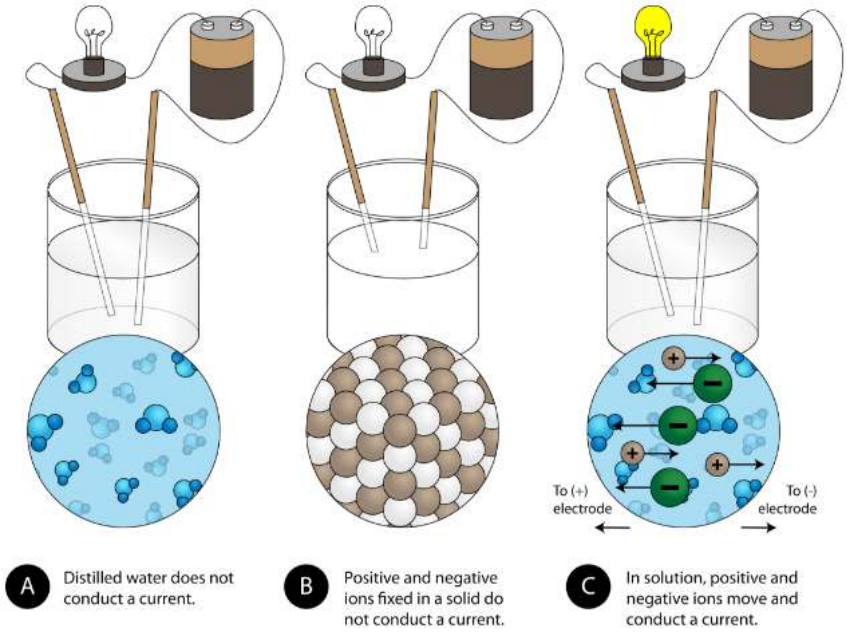


Figure 3.6.3: *(A) Distilled water does not conduct electricity. (B) A solid ionic compound also does not conduct. (C) A water solution of an ionic compound conducts electricity well.*

In the first beaker, distilled water does not conduct a current because water is a molecular compound. In the second beaker, solid sodium chloride also does not conduct a current. Despite being ionic and thus composed of charged particles, the solid crystal lattice does not allow the ions to move between the electrodes. Mobile charged particles are required for the circuit to be complete and the light bulb to light up. In the third beaker, the NaCl has been dissolved into the distilled water. Now the crystal lattice has been broken apart and the individual positive and negative ions can move. Cations move to one electrode, while anions move to the other, allowing electricity to flow (see figure below). Melting an ionic compound also frees the ions to conduct a current. Ionic compounds conduct an electric current when melted or dissolved in water. The dissolution of ionic compounds in water will be discussed in Section 9.3.

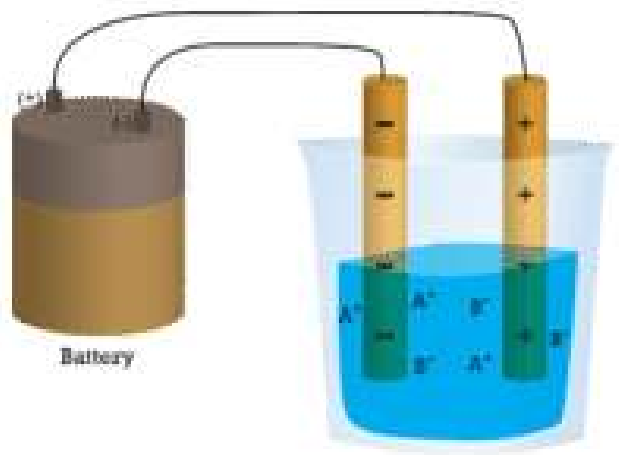


Figure 3.6.4: *In an ionic solution, the A^+ ions migrate toward the negative electrode, while the B^- ions migrate toward the positive electrode.*

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Example 3.7.1

Write the dissociation equation of solid NaCl in water.

Solution

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

3.7.1 Exercise

Write the dissociation equation of solid NH_4NO_3 in water.

Answer

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

Key Takeaways

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

Contributors and Attributions

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

Exercises

1. Explain how the bonding in an ionic solid explains some of the properties of these solids.

2. Which type(s) of solid conduct(s) electricity in their liquid state but not in their solid state?

3. Based on chemical formula, identify which of the following is an ionic solid?

    a. Hg

    b. PH_3

    c. $Ba(NO_3)_2$

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

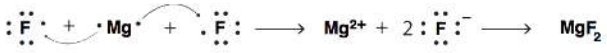
Additional Exercises

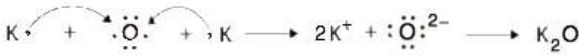
1. What number shell is the valence electron shell of a sodium atom? What number shell is the valence shell of a sodium ion? Explain the difference.
2. What number shell is the valence electron shell of a bromine atom? What number shell is the valence shell of a bromide ion? Explain the difference between 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. 9.701×10^{-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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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.

4.1: Prelude to Covalent Bonding and Simple Molecular Compounds
4.2: Covalent Bonds
4.3: Covalent Compounds - Formulas and Names
4.4: Drawing Lewis Structures
4.5: Characteristics of Covalent Bonds
4.6: Characteristics of Molecules
4.7: PhET- Molecule Shapes
4.E: Covalent Bonding and Simple Molecular Compounds (Exercises)

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4.1: Prelude to Covalent Bonding and Simple Molecular Compounds

Cholesterol ($C_{27}H_{46}O$), a compound that is sometimes in the news, is a white, waxy solid produced in the liver of every animal, including humans. It is important for building cell membranes and in producing certain hormones (chemicals that regulate cellular activity in the body). As such, it is necessary for life, but why is cholesterol the object of attention?

Besides producing cholesterol, we also ingest some whenever we eat meat or other animal-based food products. People who eat such products in large quantities, or whose metabolisms are unable to handle excess amounts, may experience an unhealthy buildup of cholesterol in their blood. Deposits of cholesterol, called plaque, may form on blood vessel walls, eventually blocking the arteries and preventing the delivery of oxygen to body tissues. Heart attacks, strokes, and other circulatory problems can result.

Most medical professionals recommend diets that minimize the amount of ingested cholesterol as a way of preventing heart attacks and strokes. Tests are available to measure cholesterol in the blood, and there are several drugs capable of lowering cholesterol levels.

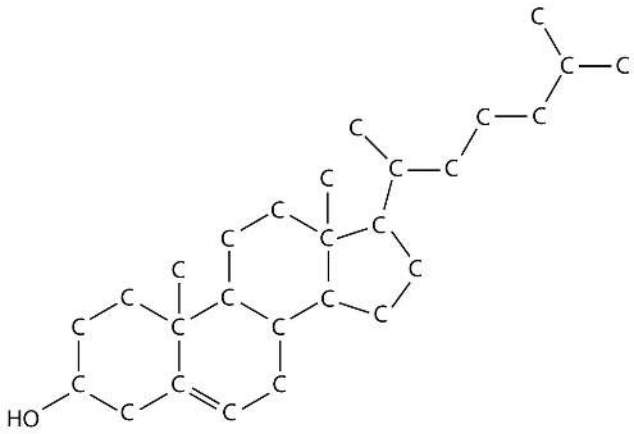


Figure 4.1.1: A Molecular Model of Cholesterol

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4.2: Covalent Bonds

Learning Objectives

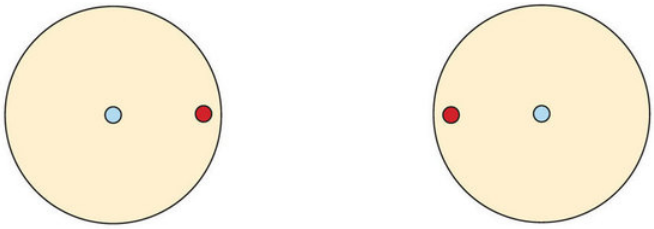
- To describe how a covalent bond forms.
- To apply the octet rule to covalent compounds

You have already seen examples of substances that contain covalent bonds. One substance mentioned previously was water (H_2O). You can tell from its formula that it is not an ionic compound; it is not composed of a metal and a nonmetal. Consequently, its properties are different from those of ionic compounds.

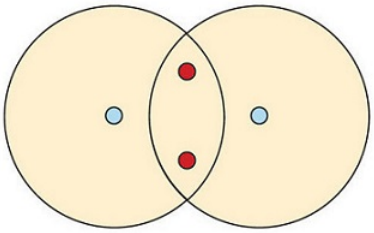
Electron Sharing

Previously, we discussed ionic bonding where electrons can be transferred from one atom to another so that both atoms have an energy-stable outer electron shell. Because most filled electron shells have eight electrons in them, chemists called this tendency the octet rule. However, there is another way an atom can achieve a full valence shell: atoms can *share* electrons.

This concept can be illustrated by using two hydrogen atoms, each of which has a single electron in its valence shell. (For small atoms such as hydrogen atoms, the valence shell will be the first shell, which holds only two electrons.) We can represent the two individual hydrogen atoms as follows:



In contrast, when two hydrogen atoms get close enough together to share their electrons, they can be represented as follows:



By sharing their valence electrons, both hydrogen atoms now have two electrons in their respective valence shells. Because each valence shell is now filled, this arrangement is more stable than when the two atoms are separate. The sharing of electrons between atoms is called a covalent bond, and the two electrons that join atoms in a covalent bond are called a bonding pair of electrons. A discrete group of atoms connected by covalent bonds is called a molecule—the smallest part of a compound that retains the chemical identity of that compound.

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



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



This depiction of molecules is simplified further by using a dash to represent a covalent bond. The hydrogen molecule is then represented as follows:



Remember that the dash, also referred to as a single bond, represents a *pair* of electrons.

The bond in a hydrogen molecule, measured as the distance between the two nuclei, is about 7.4×10^{-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:

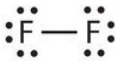


Each fluorine atom contributes one valence electron, making a single bond and giving each atom a complete valence shell, which fulfills the **octet** rule:



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.

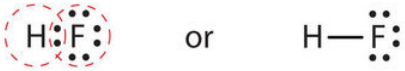
Each fluorine atom has six electrons, or three pairs of electrons, that are not participating in the covalent bond. Rather than being shared, they are considered to belong to a single atom. These are called nonbonding pairs (or lone pairs) of electrons.

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 4.2.1

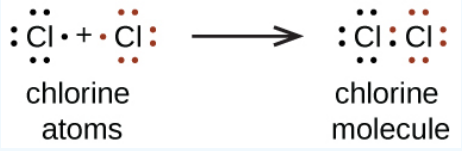
Use Lewis diagrams to indicate the formation of the following:

a. Cl_2
b. HBr

Solution

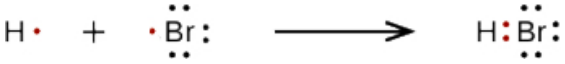
a. When two chlorine atoms form a chlorine molecule, they share one pair of electrons. In Cl_2 molecule, each chlorine atom is surrounded by an **octet** number of electrons.

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



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 4.2.1

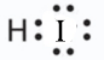
Draw the Lewis diagram for each compound.

a. a molecule composed of one chlorine atom and one fluorine atom
b. a molecule composed of one hydrogen atom and one iodine atom

Answer a:

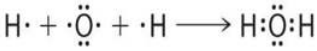


Answer b:



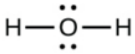
Covalent Bonds in Larger Molecules

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



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.

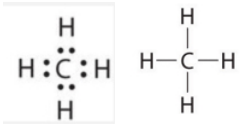
The structure on the right is the *Lewis electron structure*, or *Lewis structure*, for H_2O. With two bonding pairs and two lone pairs, the oxygen atom has now completed its **octet**. Moreover, by sharing a bonding pair with oxygen, each hydrogen atom now has a full valence shell of two electrons.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



Water

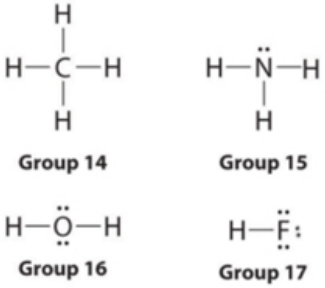
Other large molecules are constructed in a similar fashion, with some atoms participating in more than one covalent bond. For example, methane (CH_4), the central carbon atom bonded to four hydrogen atoms, can be represented using either of the Lewis

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 **4.2.1** shows the number of covalent bonds various atoms typically form.

The transition elements and inner transition elements also do not follow the octet rule since they have d and f electrons involved in their valence shells.

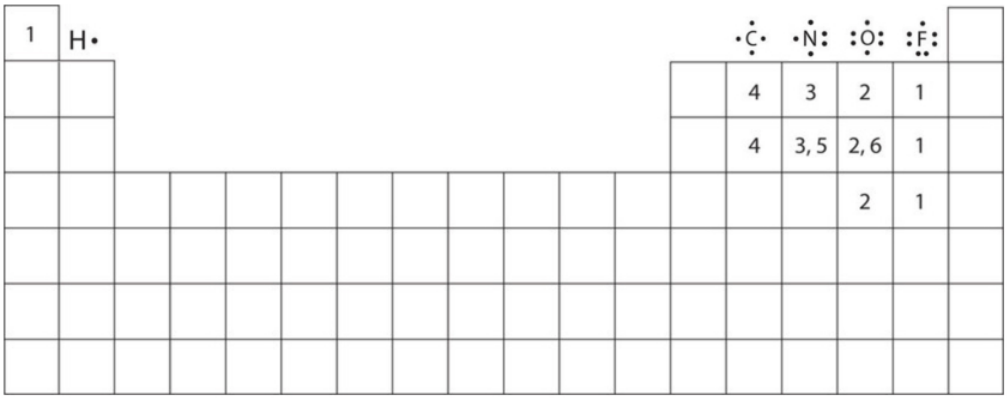
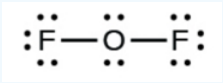


Figure **4.2.1**: How Many Covalent Bonds Are Formed? In molecules, there is a pattern to the number of covalent bonds that different atoms can form. Each block with a number indicates the number of covalent bonds formed by that atom in neutral compounds.

Example 4.2.2

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



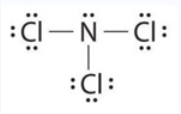
F surrounded by 6 dots, connected to O with a long dash. O surrounded by 4 dots and connects to another F with a long dash. F surrounded by 6 dots.

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.

4.2.2Exercise

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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4.3: Covalent Compounds - Formulas and Names

Learning Objectives

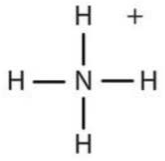
- Identify covalent and ionic compounds.
- Determine the chemical formula of a simple covalent compound from its name.
- Determine the name of a simple covalent compound from its chemical formula.

COVALENT AND IONIC COMPOUNDS

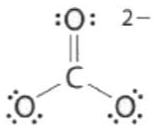
What elements make covalent bonds? Covalent bonds form when two or more nonmetals combine. For example, both hydrogen and oxygen are nonmetals, and when they combine to make water, they do so by forming covalent bonds. Compounds that are composed of only non-metals or semi-metals with non-metals will display covalent bonding and will be classified as molecular compounds.

As a general rule of thumb, compounds that involve a metal binding with either a non-metal or a semi-metal will display ionic bonding. Thus, the compound formed from sodium and chlorine will be ionic (a metal and a non-metal). Nitrogen monoxide (NO) will be a covalently bound molecule (two non-metals), silicon dioxide (SiO_2) will be a covalently bound molecule (a semi-metal and a non-metal) and $MgCl_2$ will be ionic (a metal and a non-metal).

A polyatomic ion is an ion composed of two or more atoms that have a charge as a group (poly = many). The ammonium ion (see figure below) consists of one nitrogen atom and four hydrogen atoms. Together, they comprise a single ion with a 1+ charge and a formula of NH_4^+. The carbonate ion (see figure below) consists of one carbon atom and three oxygen atoms and carries an overall charge of 2−. The formula of the carbonate ion is CO_3^{2-}.



ammonium ion



carbonate ion

The atoms of a polyatomic ion are tightly bonded together and so the entire ion behaves as a single unit. Several examples are found in Table 3.3.1. Nonmetal atoms in polyatomic ions are joined by covalent bonds, but the ion as a whole participates in ionic bonding. For example, ammonium chloride (NH_4Cl) has ionic bonding between a polyatomic ion, $\mathbf{NH_4^+}$, and $\mathbf{Cl^-}$ ions, but within the ammonium ion (NH_4^+), the nitrogen and hydrogen atoms are connected by covalent bonds (shown above).

Both ionic and covalent bonding are also found in calcium carbonate. Calcium carbonate ($CaCO_3$) has ionic bonding between calcium ion $\mathbf{Ca^{2+}}$ and a polyatomic ion, $\mathbf{CO_3^{2-}}$, but within the carbonate ion (CO_3^{2-}), the carbon and oxygen atoms are connected by covalent bonds (shown above).

Characteristics of Covalent (Molecular) Compounds

Compounds that contain covalent bonds (also called molecular compounds) exhibit different physical properties than ionic compounds. Because the attraction between molecules, which are electrically neutral, is weaker than that between electrically charged ions, covalent compounds generally have much lower melting and boiling points than ionic compounds (discussed in Section 3.6). For example, water (molecular compound) boils at 100 °C while sodium chloride (ionic compound) boils at 1413 °C. In fact, many covalent compounds are liquids or gases at room temperature, and, in their solid states, they are typically much softer than ionic solids. Furthermore, whereas ionic compounds are good conductors of electricity when dissolved in water, most covalent compounds, being electrically neutral, are poor conductors of electricity in any state. The attraction between molecules (called intermolecular forces) will be discussed in more detail in Section 8.1

Example 4.3.1

Is each compound formed from ionic bonds, covalent bonds, or both?

a. Na_2O
b. Na_3PO_4
c. N_2O_4

Answer a

The elements in Na_2O are a metal and a nonmetal, which form ionic bonds.

Answer b

Because sodium is a metal and we recognize the formula for the phosphate ion, we know that this compound is ionic. However, within the polyatomic phosphate ion, the atoms are held together by covalent bonds, so this compound contains both ionic and covalent bonds.

Answer c

The elements in N_2O_4| are both nonmetals, rather than a metal and a nonmetal. Therefore, the atoms form covalent bonds.

Exercise 4.3.1

Is each compound are formed from ionic bonds, covalent bonds, or both?

a. $Ba(OH)_2$
b. F_2
c. PCl_3

Answer a:

both

Answer b:

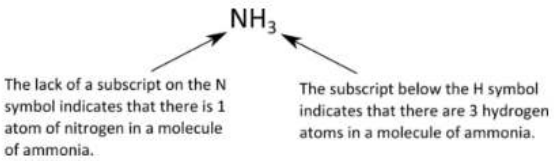
covalent

Answer c:

covalent

MOLECULAR FORMULAS

The chemical formulas for covalent compounds are referred to as **molecular formulas** because these compounds exist as separate, discrete molecules. Typically, a molecular formula begins with the nonmetal that is closest to the lower left corner of the periodic table, except that hydrogen is almost never written first (H_2O is the prominent exception). Then the other nonmetal symbols are listed. Numerical subscripts are used if there is more than one of a particular atom. For example, we have already seen CH_4, the molecular formula for methane. Below is the molecular formula of ammonia, NH_3.



NH_3. An arrow points to the N and says, "The lack of a subscript on the N symbol indicates that there is 1 atom of nitrogen in a molecule of ammonia". An arrow points to H and says, "The subscript below the H symbol indicates that there are 3 hydrogen atoms in a molecule of ammonia".

NAMING COVALENT COMPOUNDS

Naming *binary* (two-element) covalent compounds is similar to naming simple ionic compounds. The first element in the formula is simply listed using the name of the element. The second element is named by taking the stem of the element name and adding

the suffix *-ide*. A system of numerical prefixes is used to specify the number of atoms in a molecule. Table **4.3.1** lists these numerical prefixes. Normally, no prefix is added to the first element's name if there is only one atom of the first element in a molecule. If the second element is oxygen, the trailing vowel is usually omitted from the end of a polysyllabic prefix but not a monosyllabic one (that is, we would say "monoxide" rather than "monooxide" and "trioxide" rather than "troxide").

Table **4.3.1**: Numerical Prefixes for Naming Binary Covalent Compounds

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

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

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

✔ Example 4.3.2

Write the molecular formula for each compound.

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

Solution

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

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

? Exercise 4.3.2

Write the molecular formula for each compound.

a. nitrogen dioxide
b. dioxygen difluoride
c. sulfur hexafluoride

d. selenium monoxide

Answer a:

a. NO_2

Answer b:

O_2F_2

Answer c:

SF_6

Answer d:

SeO

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

Example 4.3.3

Write the name for each compound.

a. BrF_5
b. S_2F_2
c. CO

Solution

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

Exercise 4.3.3

Write the name for each compound.

a. CF_4
b. $SeCl_2$
c. SO_3

Answer a:

carbon tetrafluoride

Answer b:

selenium dichloride

Answer c:

sulfur trioxide

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

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

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

Key Takeaways

- The chemical formula of a simple covalent compound can be determined from its name.
- The name of a simple covalent compound can be determined from its chemical formula.

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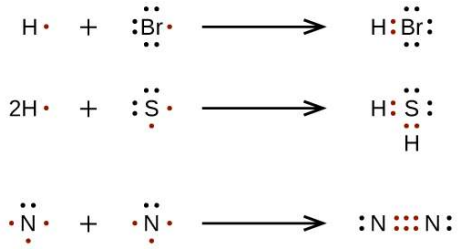
4.4: Drawing Lewis Structures

Learning Objectives

- To draw Lewis structures.
- To recognize molecules that are likely to have multiple covalent bonds.

DRAWING LEWIS STRUCTURES

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



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

1. Determine the total number of valence (outer shell) electrons among all the atoms. For cations, subtract one electron for each positive charge. For anions, add one electron for each negative charge.
2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom. (Generally, the least electronegative element should be placed in the center.) Connect each atom to the central atom with a single bond (one electron pair).
3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen), completing an octet around each atom.
4. Place all remaining electrons on the central atom.
5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

Let us determine the Lewis structures of OF_2 and HCN as examples in following this procedure:

1. Determine the total number of valence (outer shell) electrons in the molecule or ion. For a molecule, we add the number of valence electrons (use the main group number) on each atom in the molecule. This is the total number of electrons that must be used in the Lewis structure.

$$O + 2\,(F) = OF_2$$

$$6e^- + (2 \times 7e^-) = 20e^-$$

$$H + C + N = HCN$$

$$1e^- + 4e^- + 5e^- = 10e^-$$

2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom and connecting each atom to the central atom with a single (one electron pair) bond. Note that H and F can only form one bond, and are always on the periphery rather than the central atom.

F—O—F H—C—N

3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen) to complete their valence shells with an octet of electrons.

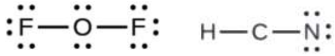
- In OF_2, six electrons are placed on each F.

- In HCN, six electrons placed on N



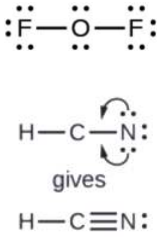
4. Place all remaining electrons on the central atom.

- In OF_2, 4 electrons are placed on O.
- In HCN: no electrons remain (the total valence of $10e^-$ is reached) so nothing changes.



5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

- In OF_2, each atom has an octet as drawn, so nothing changes.
- In HCN, form two more C–N bonds

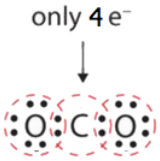


H dash C dash N with 6 dots around the N. 4 of the dots are pointing to the dash connecting the C and the N. This turns the formula into H dash C and three lines connecting the C and N together, with two dots on the outside of the N.

Finally, check to see if the total number of valence electrons are present in the Lewis structure. And then, inspect if the H atom has 2 electrons surrounding it and if each of the main group atoms is surrounded by 8 electrons.

MULTIPLE BONDS

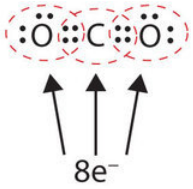
In many molecules, the octet rule would not be satisfied if each pair of bonded atoms shares only two electrons. Review HCN in Step 5 above. Another example is carbon dioxide (CO_2). CO_2 has a total valence of $4e^- + (2 \times 6e^-) = 16e^-$. Following steps 1 to 4, we draw the following:



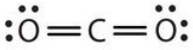
This does not give the carbon atom a complete octet; only four electrons are in its valence shell. This arrangement of shared electrons is far from satisfactory.



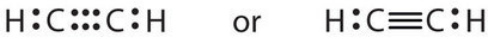
In this case, more than one pair of electrons must be shared between two atoms for both atoms to have an octet. A second electron pair from each oxygen atom must be shared with the central carbon atom shown by the arrows above. A lone pair from each O must be converted into a bonding pair of electrons.



In this arrangement, the carbon atom shares four electrons (two pairs) with the oxygen atom on the left and four electrons with the oxygen atom on the right. There are now eight electrons around each atom. Two pairs of electrons shared between two atoms make a double bond between the atoms, which is represented by a double dash:



Some molecules contain triple bonds (like HCN, shown above). Triple bonds are covalent bonds in which *three* pairs of electrons are shared by two atoms. Another compound that has a triple bond is acetylene (C_2H_2), whose Lewis diagram is as follows:



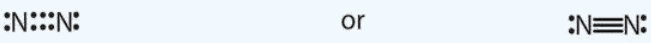
Example 4.4.1

Draw the Lewis diagram for each molecule.

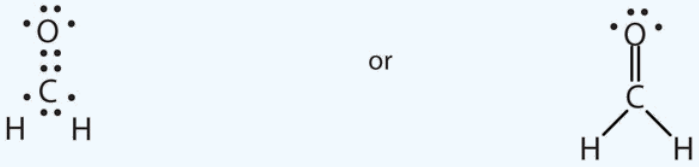
1. $\mathbf{N_2}$
2. $\mathbf{CH_2O}$ (The carbon atom is the central atom.) One application of CH_2O, also called formaldehyde, is the preservation of biological specimens. Aqueous solutions of CH_2O are called formalin and have a sharp, characteristic (pungent) odor.

Solution

1. The total number of electrons is 2 x 5 = 10 electrons. The bond between the two nitrogen atoms is a triple bond. The Lewis diagram for $N_2$is as follows:



2. The total number of electrons is 4 x 2(1) + 6 = 12 electrons. In CH_2O, the central atom is surrounded by two different types of atoms. The Lewis diagram that fills each atom's valence electron shell is as follows:

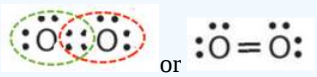


Exercise 4.4.1

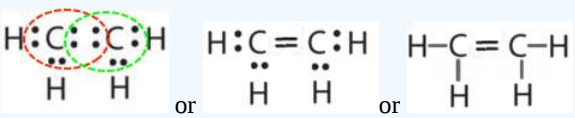
Draw the Lewis diagram for each molecule.

a. $\mathbf{O_2}$
b. $\mathbf{C_2H_4}$

Answer a:

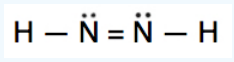


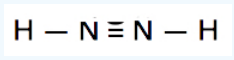
Answer b:

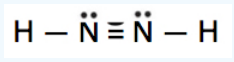


Example 4.4.2

Which is the correct Lewis structure for N_2H_2?

A. 

B. 

C. 

Solution

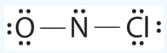
Lewis structure A is the correct answer. It has a total of (2 x $5e^-$) + (2 x $1e^-$) = $12e^-$. Each of the N atoms satisfy the octet requirement and the H atoms follow the duet rule.

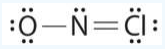
Structure B is electron deficient. It has only $10e^-$ instead of 12.

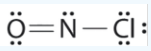
Structure C has 14 (2 extra) electrons. The N atoms do not satisfy the octet.

4.4.2 Exercise

Which is the correct Lewis structure for NOCl?

A. 

B. 

C. 

Answer

Structure A violates the octet rule; N is surrounded by only $6e^-$.

Structure B violates the octet rule; Cl has $10e^-$ around it. Furthermore, there are a total of $20e^-$ instead of $18e^-$.

Structure C is the correct structure. It has a total of $6e^-$ + $5e^-$ + $7e^-$ = $18e^-$. Each atom is surrounded by 8 electrons (octet rule).

Key Takeaways

- A Lewis structure shows the bonding and nonbonding electrons around individual atoms in a molecule.
- Some molecules must have multiple covalent bonds between atoms to satisfy the octet rule.
- A double bond contains four electrons and a triple bond contains six electrons.

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4.5: Characteristics of Covalent Bonds

Learning Objectives

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

Bond Length

We previously stated that the covalent bond in the hydrogen molecule (H_2) has a certain length (about 7.4×10^{-11} m). Other covalent bonds also have known bond lengths, which are dependent on both the identities of the atoms in the bond and whether the bonds are single, double, or triple bonds. Table **4.5.1** lists the approximate bond lengths for some single covalent bonds. The exact bond length may vary depending on the identity of the molecule but will be close to the value given in the table.

Table **4.5.1**: Approximate Bond Lengths of Some Single Bonds

Bond	Length ($\times 10^{-12}\ m$)
H–H	74
H–C	110
H–N	100
H–O	97
H–I	161
C–C	154
C–N	147
C–O	143
N–N	145
O–O	145

Table **4.5.2** compares the lengths of single covalent bonds with those of double and triple bonds between the same atoms. Without exception, as the number of covalent bonds between two atoms increases, the bond length decreases. With more electrons between the two nuclei, the nuclei can get closer together before the internuclear repulsion is strong enough to balance the attraction.

Table **4.5.2**: Comparison of Bond Lengths for Single and Multiple Bonds

Bond	Length ($\times 10^{-12}\,m$)
C–C	154
C=C	134
C≡C	120
C–N	147
C=N	128
C≡N	116
C–O	143
C=O	120
C≡O	113
N–N	145
N=N	123
N≡N	110
O–O	145
O=O	121

Electronegativity and Bond Polarity

Although we defined covalent bonding as electron sharing, the electrons in a covalent bond are not always shared equally by the two bonded atoms. Unless the bond connects two atoms of the same element, as in H_2, there will always be one atom that attracts the electrons in the bond more strongly than the other atom does, as in HCl, shown in Figure **4.5.1**. A covalent bond that has an equal sharing of electrons (Figure **4.5.1***a*) is called a **nonpolar covalent bond**. A covalent bond that has an unequal sharing of electrons, as in Figure **4.5.1***b*, is called a **polar covalent bond**.

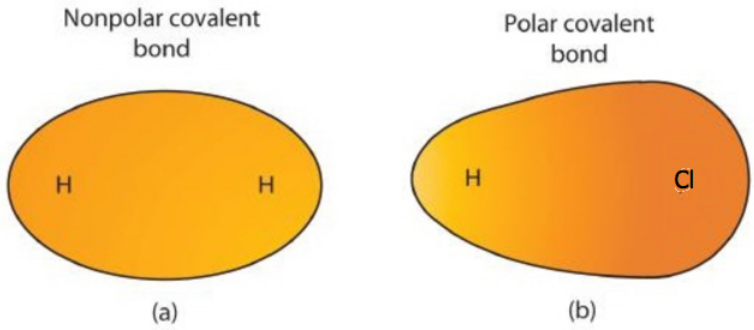


Figure **4.5.1** Polar versus Nonpolar Covalent Bonds. (a) The electrons in the covalent bond are equally shared by both hydrogen atoms. This is a nonpolar covalent bond. (b) The chlorine atom attracts the electrons in the bond more than the hydrogen atom does, leading to an imbalance in the electron distribution. This is a polar covalent bond.

The distribution of electron density in a polar bond is uneven. It is greater around the atom that attracts the electrons more than the other. For example, the electrons in the H–Cl bond of a hydrogen chloride molecule spend more time near the chlorine atom than near the hydrogen atom. Note that the shaded area around Cl in Figure **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). This is seen in Figure **4.5.2***a*. The separation of charge in a polar covalent bond results in an electric dipole (two poles), represented by the arrow in Figure **4.5.2***b*. The direction of the arrow is pointed toward the δ− end while the + tail of the arrow indicates the δ+ end of the bond.

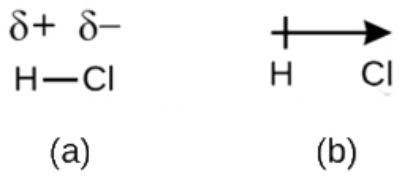


Figure **4.5.2**: (a) Unequal sharing of the bonding pair of electrons between H and Cl leads to partial positive charge on the H atom and partial negative charge on the Cl. Symbols δ+ and δ– indicate the polarity of the H–Cl bond. (b) The dipole is represented by an arrow with a cross at the tail. The cross is near the δ+ end and the arrowhead coincides with the δ–.

Any covalent bond between atoms of different elements is a polar bond, but the degree of polarity varies widely. Some bonds between different elements are only minimally polar, while others are strongly polar. Ionic bonds can be considered the ultimate in polarity, with electrons being transferred rather than shared. To judge the relative polarity of a covalent bond, chemists use **electronegativity**, which is a relative measure of how strongly an atom attracts electrons when it forms a covalent bond. There are various numerical scales for rating electronegativity. Figure **4.5.3** shows one of the most popular—the Pauling scale.

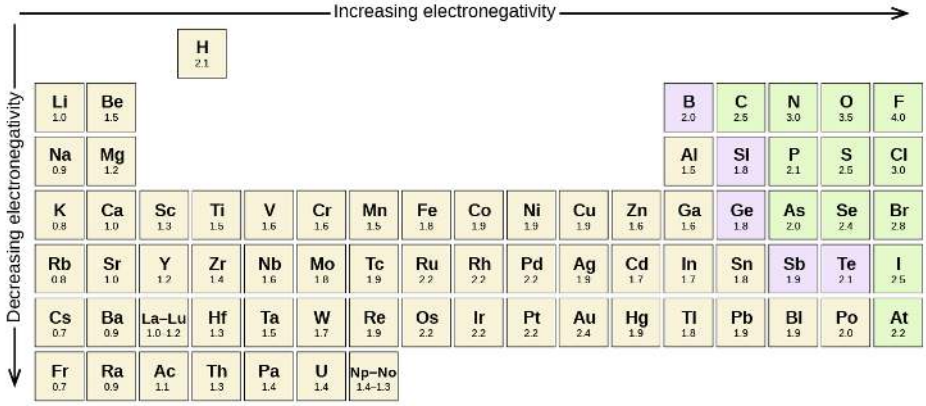
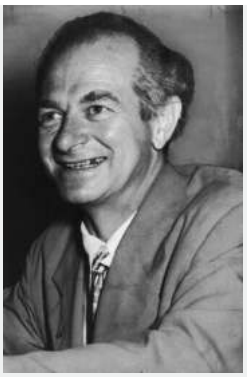


Figure **4.5.3** The electronegativity values derived by Pauling follow predictable periodic trends with the higher electronegativities toward the upper right of the periodic table. Fluorine has the highest value (4.0).

Looking Closer: Linus Pauling

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

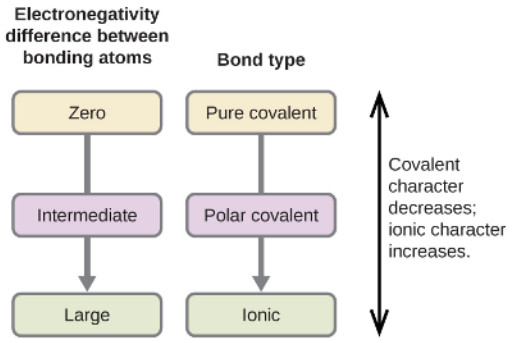
By 1935, Pauling's interest turned to biological molecules, and he was awarded the 1954 Nobel Prize in Chemistry for his work on protein structure. (He was very close to discovering the double helix structure of DNA when James Watson and James Crick announced their own discovery of its structure in 1953.)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



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

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

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



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

Figure **4.5.4**: 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.

Bond Polarity and Molecular Polarity

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

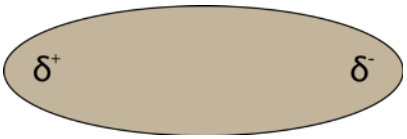


Figure 4.5.5: A molecular dipole results from the unequal distribution of electron density throughout a molecule.

When placed between oppositely charged plates, polar molecules orient themselves so that their positive ends are closer to the negative plate and their negative ends are closer to the positive plate (see Figure 4.4.6 below).

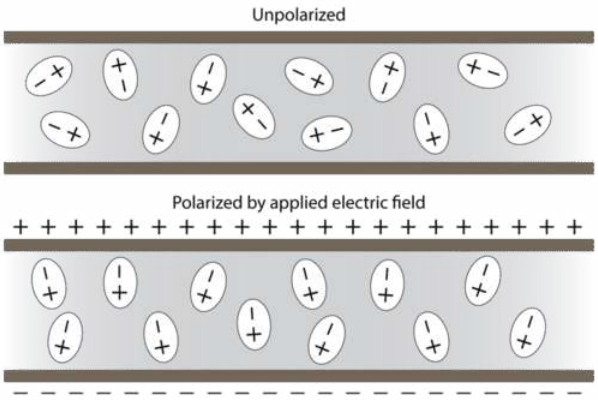


Figure 4.5.6: Polar molecules are randomly oriented in the absence of an applied electric field (top). In an electric field, the molecules orient themselves to maximize the attraction between opposite charges (bottom).

Experimental techniques involving electric fields can be used to determine if a certain substance is composed of polar molecules and to measure the degree of polarity.

For molecules with more than two atoms, the **molecular geometry** must also be taken into account when determining if the molecule is polar or nonpolar. (Figure **4.5.7**) is a comparison between carbon dioxide and water. Carbon dioxide (CO_2) is a **linear** molecule. The oxygen atoms are more electronegative than the carbon atom, so there are two individual dipoles pointing outward from the C atom to each O atom. However, since the dipoles are of equal strength and are oriented directly opposite each other, they cancel each other out, and the overall molecular polarity of CO_2 is zero. CO_2 is a **nonpolar** molecule. In H_2O, the orientation of the two O–H bonds is **bent**: one end of the molecule has a partial positive charge, and the other end has a partial negative charge. In short, the molecule itself is **polar**. The polarity of water has an enormous impact on its physical and chemical properties. For example, the boiling point of water (100°C) is high for such a small molecule due to the fact that polar molecules attract each other strongly. On the other hand, the nonpolar carbon dioxide becomes a gas at −77°C, almost 200° lower than the temperature at which water boils. More details will be presented in the next section.



Figure **4.5.7** Physical Properties and Polarity. The physical properties of water and carbon dioxide are affected by their polarities.

Key Takeaways

- Covalent bonds between different atoms have different bond lengths.
- Covalent bonds can be polar or nonpolar, depending on the electronegativity difference between the atoms involved.

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4.6: Characteristics of Molecules

Learning Objectives

- Determine the molecular mass of a molecule.
- Predict the general shape of a simple covalent molecule.
- Predict the polarity of the molecule.
- Compare the properties of ionic and molecular compounds.

Unlike the ions in ionic compounds, which are arranged in lattices called crystals, molecules of covalent compounds exist as discrete units with a characteristic mass and a certain three-dimensional shape.

Molecular Mass

The mass of a molecule—the molecular mass (sometimes called the molecular weight)—is simply the sum of the masses of its atoms. As with formula masses, it is important that you keep track of the number of atoms of each element in the molecular formula to obtain the correct molecular mass.

Example 4.6.1

What is the molecular mass of each covalent compound?

a. H_2O
b. C_6H_6
c. NO_2
d. N_2O_5

Solution

Use the atomic masses from the Periodic Table in Section 2.7.

The molecular formula H_2O indicates that there are two hydrogen atoms and one oxygen atom in each molecule. Summing the masses of these atoms,

This table finds the mass of atoms.

2 H:	2 × 1.01 =	2.02 amu
1 O:		+ 16.00 amu
Total:		18.02 amu

The molecular mass of H_2O is **18.02** amu.

This table finds the mass of atoms.

6 C:	6 × 12.01 =	72.06 amu
6 H:	6 × 1.01 =	+ 6.06 amu
Total:		78.12 amu

The molecular mass of C_6H_6 is **78.12** amu.

This table finds the mass of atoms.

1 N:		14.01 amu
2 O:	2 × 16.00 =	+ 32.00 amu
Total:		46.01 amu

The molecular mass of NO_2 is **46.01** amu.

This table finds the mass of atoms.

2 N:	2 × 14.01 =	28.02 amu
5 O:	5 × 16.00 =	+ 80.00 amu
Total:		108.02 amu

The molecular mass of N_2O_5 is **108.02** amu.

Note that the two different nitrogen and oxygen compounds in these examples have different molecular masses.

? Exercise 4.6.1

What is the molecular mass of each covalent compound?

a. C_2H_2
b. CO
c. CO_2
d. BF_3

Answer a:

26.04 amu

Answer b:

28.01 amu

Answer c:

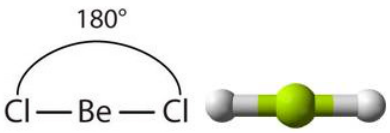
44.01 amu

Answer d:

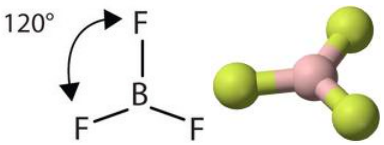
67.81 amu

Molecular Shape: VSEPR Theory

Unlike ionic compounds, with their extended crystal lattices, covalent molecules are discrete units with specific three-dimensional shapes. The shape of a molecule is determined by the fact that covalent bonds, which are composed of negatively charged electrons, tend to repel one another. This concept is called the **valence shell electron pair repulsion (VSEPR) theory**. For example, the two covalent bonds in $BeCl_2$ **stay as far from each other** as possible, ending up 180° apart from each other. The result is a ***linear*** molecule:



The three covalent bonds in BF_3 repel each other to form 120° angles in a plane, in a shape called ***trigonal planar***:



The molecules $BeCl_2$ and BF_3 actually violate the octet rule; however, such exceptions are rare and will not be discussed in this text.

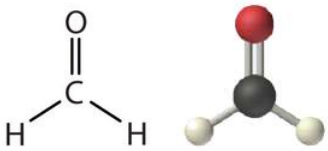
> Try sticking three toothpicks into a marshmallow or a gumdrop and see if you can find different positions where your "bonds" are farther apart than the planar 120° orientation.

The four covalent bonds in CCl_4 arrange themselves three dimensionally, pointing toward the corner of a tetrahedron and making bond angles of 109.5°. CCl_4 is said to have a ***tetrahedral*** shape:

Table describes how to use the number of atoms around the central atom to determine the geometry of a molecule, as well as examples.

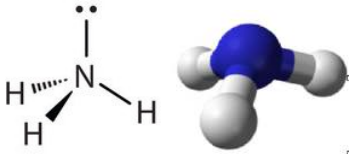
Atoms Around Central Atom	Geometry	Example
2 $\mathbf{AB_2}$	Linear	$\mathbf{BeCl_2}$
3 $\mathbf{AB_3}$	Trigonal Planar	$\mathbf{BF_3}$
4 $\mathbf{AB_4}$	Tetrahedral	$\mathbf{CCl_4}$

In determining the shapes of molecules, it is useful to first determine the Lewis diagram for a molecule. The shapes of molecules with multiple bonds are determined by treating the multiple bonds as one bond. Thus, formaldehyde (CH_2O) has a shape similar to that of BF_3. It is ***trigonal planar***.

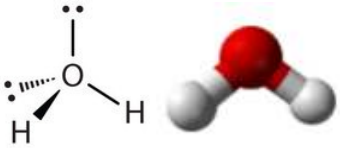


Molecules With Lone Pairs Around Central Atom

Molecules with lone electron pairs around the central atom have a shape based on the position of the atoms, not the electron pairs. For example, NH_3 has **one lone electron pair** and **three bonded electron pairs**. These four electron pairs repel each other and adopt a tetrahedral arrangement. However, the shape of the molecule is described in terms of the positions of the atoms, not the lone electron pairs. Thus, NH_3 is said to have a ***trigonal pyramidal*** shape, not a tetrahedral one.



Similarly, H_2O has **two lone pairs** of electrons around the central oxygen atom and **two bonded electron pairs**. Although the four electron pairs adopt a tetrahedral arrangement, the shape of the molecule is described by the positions of the atoms only. The shape of H_2O is ***bent*** with an approximate 109.5° angle.

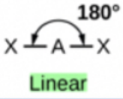
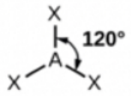
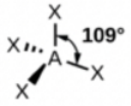


In summary, to determine the molecular geometry:

Step 1: Draw the Lewis structure.

Step 2: Count the number of bonds (a double/triple bond counts as one) and lone pairs around the **central atom**.

Step 3: Use Table 4.5.1 to determine the molecular geometry.

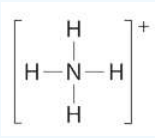
Number of bonds and lone pairs	Number of bonds 0 lone pair	1 lone pair	2 lone pairs
2	 Linear		
3	 Trigonal planar	 Bent or angular	Lone Pair
4	 Tetrahedral	 Trigonal pyramid	 Bent or angular

If a molecule has 2 bonds and 0 lone pairs, it is linear. If a molecule has 3 bonds and 0 lone pairs, it is trigonal planar. If a molecule has 3 bonds and 1 lone pair, it is bent or angular. If a molecule has 4 bonds and 0 lone pairs, it is tetrahedral. If a molecule has 4 bonds and 1 lone pair, it is trigonal pyramid. If a molecule has 4 bonds and 2 lone pairs, it is bent or angular.

Table 4.5.1: *The molecular geometry depends on the number of bonds and lone pairs around the* **central atom, A.**

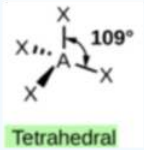
Example 4.6.1

What is the geometry of the ammonium ion, NH_4^+? Its Lewis structure is shown below. How is this different from ammonia, NH_3?

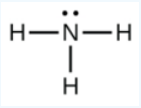


Solution

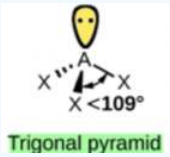
In ammonium ion, the central atom N has 4 bonds and no lone pair. It is equivalent to the below in Table 4.5.1. Hence, this is *tetrahedral*.



In ammonia (NH_3), shown below, N has 3 bonds and one lone pair.



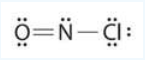
It is equivalent to the below in Table 4.5.1. Hence, the shape of this molecule is *trigonal pyramid*.



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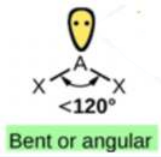
4.6.1 Exercise

What is the molecular shape of nitrosyl chloride, a highly corrosive, reddish-orange gas? Its Lewis structure is shown below.



Answer

Focus on the central atom, N. It has a double bond to O, count this as one bond. It also has a single bond to Cl. Thus, N has 2 bonds and one lone pair. These 3 electron pairs will spread out 120 degrees from each other. But, since the shape is defined by the arrangement of the atoms only, the shape is bent or angular. If you consult Table 4.5.1, this molecule is equivalent to the below. Hence, two bonds and one lone pair has a *bent or angular* shape.



Molecular Polarity

In general, a molecule is nonpolar if all its bonds are nonpolar. Examples are I_2, O_2, H_2, CH_4, C_2H_6 and C_3H_8.

In general, a molecule is polar if it contains polar bonds EXCEPT when the bond polarities cancel each other. As mentioned in Section 4.4, the shape of the CO_2 molecule (linear) orients the two C=O polar bonds **directly opposite** each other, thus **cancelling** each other's effect. **Carbon dioxide** (CO_2) is a ***nonpolar*** molecule.

On the other hand, water (as discussed above) is a bent molecule because of the two lone pairs on the central oxygen atom. Because of the bent shape, the dipoles do not cancel each other out and the water molecule is ***polar***. In the figure below, the individual H-O polar bonds represented by the two red arrows are not directly opposite each other. These two dipoles don't cancel each other out. In fact, the net dipole (blue arrow) points upward. There is a resultant partial positive charge at one end (between the two H atoms) and a partial negative charge on the other end (where O is located). The uneven distribution of charge or the overall dipole is shown by the blue arrow below (Figure 4.5.1). Hence, **water is *polar*** (has + and - poles) while **carbon dioxide is *nonpolar***.

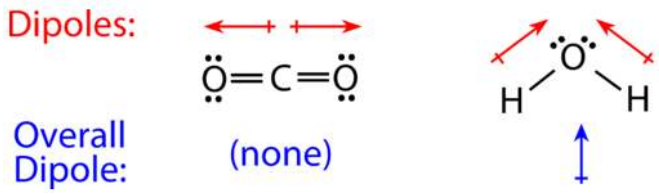


Figure 4.5.1: The molecular geometry of a molecule (linear vs. bent) affects its polarity.

Similarly, in BF_3 (trigonal planar), the effect of a B-F bond is cancelled by the sum of the other two B-F bonds (see video). Hence, a trigonal planar molecule (BF_3) is nonpolar because the bond polarities cancel each other, but a trigonal pyramidal molecule (NH_3) is polar.

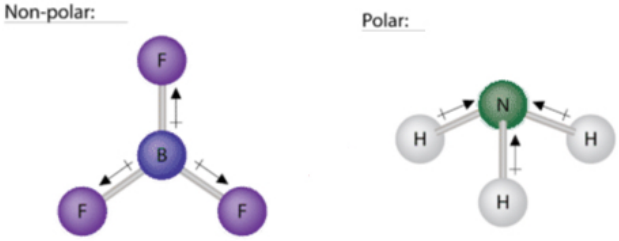


Figure 4.5.2: The molecular geometry of a molecule (trigonal planar vs. trigonal pyramid) affects its polarity.

Some other molecules are shown in the figure below. Notice that a tetrahedral molecule such as CCl_4 is ***nonpolar***. However, if the peripheral atoms are not of the same electronegativity, the bond polarities don't cancel and the molecule becomes ***polar***, as in CH_3Cl.

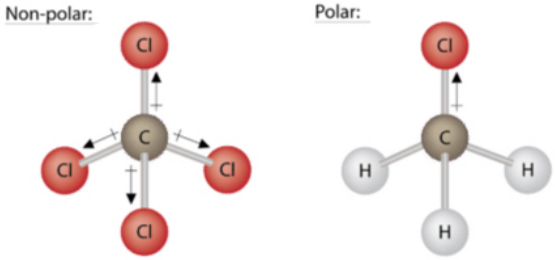


Figure 4.5.3: *The same molecular geometry but peripheral bonds are of different electronegativity. CCl_4 is nonpolar but CH_3Cl is polar.*

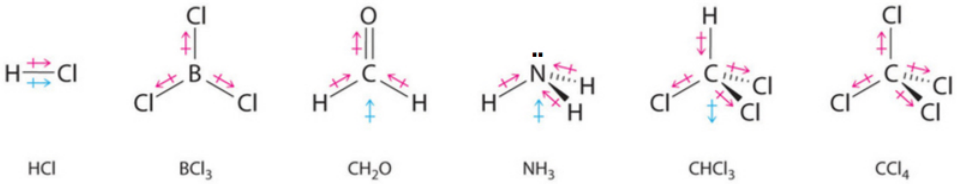


Figure **4.6.4**: Molecules with Polar Bonds. Individual bond dipole moments are indicated in red. Due to their different three-dimensional geometry, some molecules with polar bonds have a net dipole moment (HCl, CH_2O, NH_3, and $CHCl_3$), indicated in blue, whereas others do not because the bond dipoles cancel due to symmetry (BCl_3 and CCl_4).

Physical Properties of Molecular Compounds

The physical state and properties of a particular compound depend in large part on the type of chemical bonding it displays. **Molecular compounds**, sometimes called covalent compounds, display a wide range of physical properties due to the different types of intermolecular attractions such as different kinds of polar interactions. The melting and boiling points of molecular compounds are generally quite low compared to those of **ionic compounds**. This is because the energy required to disrupt the **intermolecular forces** (discussed in Section 8.1) between molecules is far less than the energy required to break the ionic bonds in a crystalline ionic compound. Since molecular compounds are composed of neutral molecules, their electrical conductivity is generally quite poor, whether in the solid or liquid state. Ionic compounds do not conduct electricity in the solid state because of their rigid structure, but conduct well when either molten or dissolved into a solution. The water solubility of molecular compounds is variable and depends primarily on the type of intermolecular forces involved. Substances that exhibit hydrogen bonding or dipole-dipole forces are generally water soluble, whereas those that exhibit only London dispersion forces are generally insoluble. Most, but not all, ionic compounds are quite soluble in water. The table below summarizes some of the differences between ionic and molecular compounds.

Table 4.5.2: Comparison of Ionic and Molecular Compounds

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

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

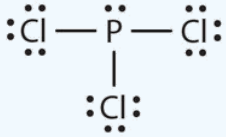
Example 4.6.2

Describe the shape of each molecule. Is it polar or nonpolar?

a. PCl_3
b. CO_2

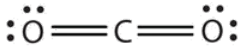
Solution

a. The Lewis diagram for PCl_3 is as follows:



Focus on the central atom, P that has 3 bonds and one lone pair. The four electron pairs arrange themselves tetrahedrally, but the lone electron pair is not considered in describing the molecular shape. Like NH_3, this molecule is *pyramidal*. The 3 P-Cl bonds don't cancel each other. This is *polar.*

- The Lewis diagram for CO_2 is as follows:



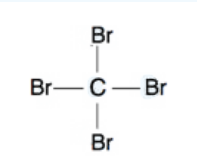
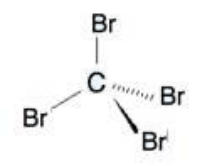
Focus on the central atom, C. The multiple bonds are treated as one group, hence C has 2 bonds and zero lone pair. CO_2 has only two groups of electrons that repel each other. They will direct themselves 180° apart from each other, so CO_2 molecules are *linear*. This is highly symmetrical, with the two opposite dipoles cancelling each other. The CO_2 molecule is *nonpolar*.

Exercise 4.6.2

Describe the shape of each molecule. Is it polar or nonpolar?

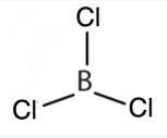
a. CBr_4
b. BCl_3

Answer a:


or


The Lewis structure shows 4 groups attached to the central atom, hence *tetrahedral*. All the 4 groups are identical and the shape is symmetrical. Hence, it is *nonpolar.*

Answer b:



The Lewis diagram shows 3 groups attached to the central atom, hence *trigonal planar*. All the 3 groups are identical and shape is symmetrical, hence, it is *nonpolar.*

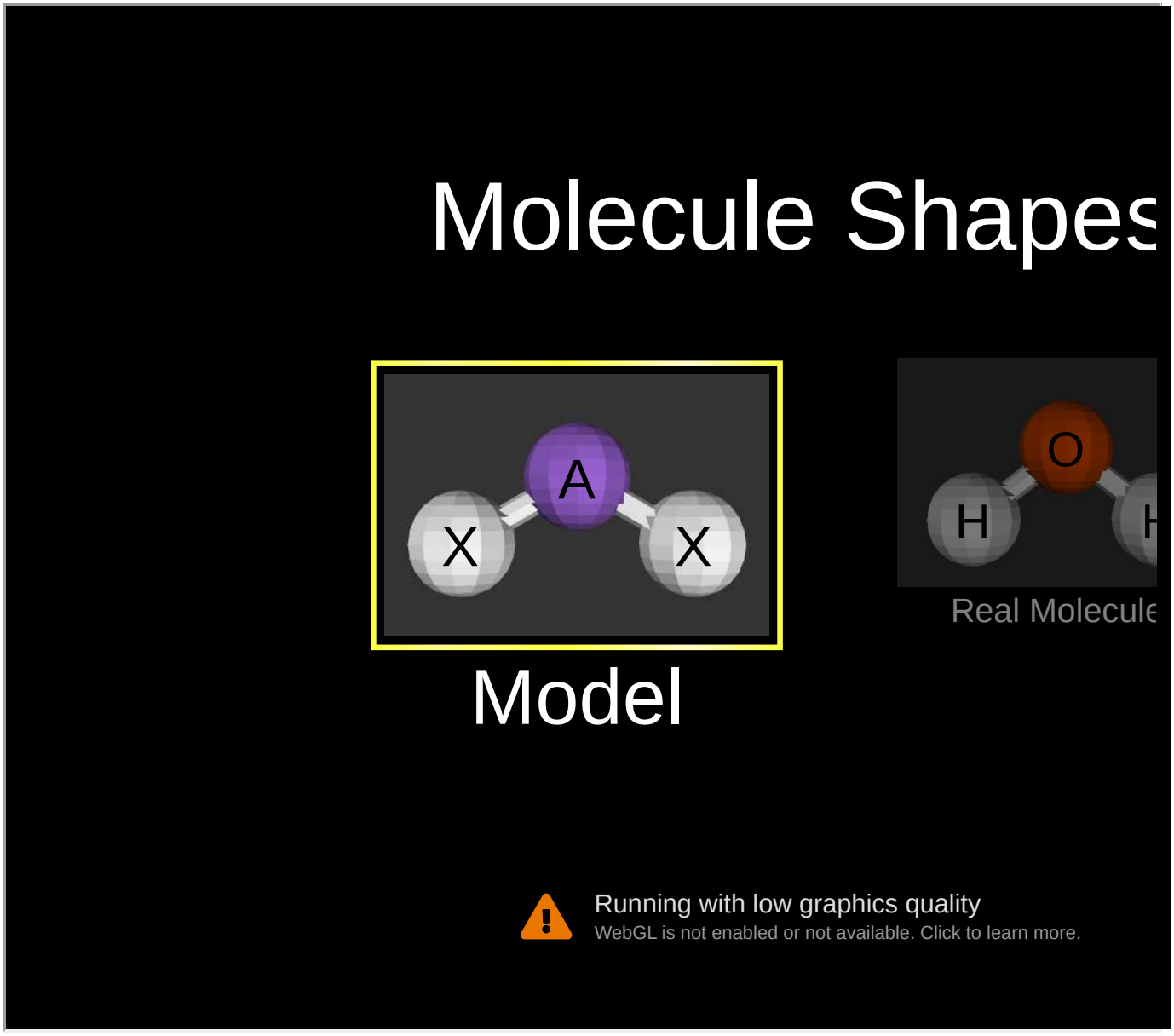
Key Takeaways

- A molecule has a certain mass, called the molecular mass.
- Simple molecules have geometries that can be determined from VSEPR theory.
- Polar molecules result from differences in electronegativity of the atoms in the molecule.
- Dipoles that are directly opposite one another cancel each other out.

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4.7: PhET- Molecule Shapes



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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?

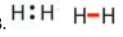
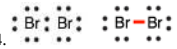
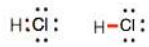
Answers

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.

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.

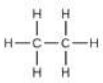


b.



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c.



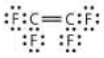
d.



3. a.



b.



c.

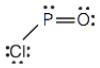


4. a. $\ddot{N} \equiv \ddot{N}$

b. $:C \equiv O:$

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

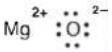
d.



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

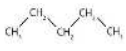
Concept Review Exercises

1. What is organic chemistry?
2. What is a functional group? Give at least two examples of functional groups.

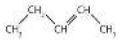
Answers

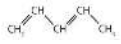
1. Organic chemistry is the study of the chemistry of carbon compounds.
2. A functional group is a specific structural arrangement of atoms or bonds that imparts a characteristic chemical reactivity to the molecule; alcohol group and carboxylic group (answers will vary).

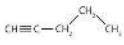
Exercises

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.

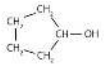
a. 

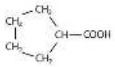
b. 

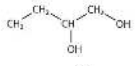
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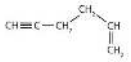
d. 

5. Identify the functional group(s) in each molecule.

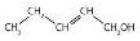
a. 

b. 

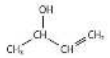
c. 

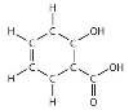
d. 

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:

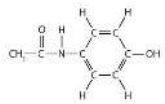


This molecule can lose a hydrogen ion (H^+) and the resulting anion can combine with other cations, such as Na^+:



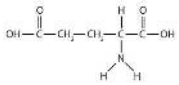
Name this ionic compound.

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

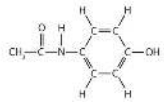
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5. Acetic acid has the following structure:



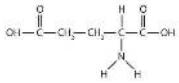
   This molecule can lose a hydrogen ion (H^+) and the resulting anion can combine with other cations, such as Na^+:



   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)?
12. What is the greatest possible electronegativity difference between any two atoms? Use Figure 4.4 to find the answer.
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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CHAPTER OVERVIEW

5: 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.

5.1: Prelude to Solids, Liquids, and Gases

5.2: Intermolecular Interactions

5.3: Solids and Liquids

5.4: Gases and Pressure

5.5: PhET- States of Matter

5.E: Solids, Liquids, and Gases (Exercises)

Template:HideTOC

Thumbnail: A water drop. (CC BY 2.0; José Manuel Suárez via Wikipedia).

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5.1: Prelude to Solids, Liquids, and Gases

We normally experience carbon dioxide (CO_2) as a gas, but if it were cooled down to about −78°C, it would become a solid. The everyday term for solid carbon dioxide is dry ice.

Why “dry” ice? Solid carbon dioxide is called dry ice because it converts from a solid to a gas directly, without going through the liquid phase, in a process called sublimation. Thus, there is no messy liquid phase to worry about. Although it is a novelty, dry ice has some potential dangers. Because it is so cold, it can freeze living tissues very quickly, so people handling dry ice should wear special protective gloves. The cold carbon dioxide gas is also heavier than air (because it is cold and more dense), so people in the presence of dry ice should be in a well-ventilated area.



Figure **5.1.1**: Dry ice. (CC BY SA 3.0 unported; ProjectManhattan).

Dry ice has several common uses. Because it is so cold, it is used as a refrigerant to keep other things cold or frozen (e.g., meats or ice cream). In the medical field, dry ice is used to preserve medical specimens, blood products, and drugs. It also has dermatological applications (e.g., freezing off warts). Organs for transplant are kept cool with dry ice until the recipient of the new organ is ready for surgery. In this respect, carbon dioxide is much like water—more than one phase of the same substance has significant uses in the real world.

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5.2: Intermolecular Interactions

Learning Objectives

- Define *phase*.
- Identify the types of interactions between molecules.

A phase is a certain form of matter that includes a specific set of physical properties. That is, the atoms, the molecules, or the ions that make up the phase do so in a consistent manner throughout the phase. Science recognizes three stable phases: the ***solid*** *phase*, in which individual particles can be thought of as in contact and held in place; the ***liquid*** *phase*, in which individual particles are in contact but moving with respect to each other; and the ***gas*** *phase*, in which individual particles are separated from each other by relatively large distances (see Figure 8.1.1). Not all substances will readily exhibit all phases. For example, carbon dioxide does not exhibit a liquid phase unless the pressure is greater than about six times normal atmospheric pressure. Other substances, especially complex organic molecules, may decompose at higher temperatures, rather than becoming a liquid or a gas.

> *For many substances, there are different arrangements the particles can take in the solid phase, depending on temperature and pressure.*

Which phase a substance adopts depends on the pressure and the temperature it experiences. Of these two conditions, temperature variations are more obviously related to the phase of a substance. When it is very cold, H_2O exists in the solid form as ice. When it is warmer, the liquid phase of H_2O is present. At even higher temperatures, H_2O boils and becomes steam.

Pressure changes can also affect the presence of a particular phase (as we indicated for carbon dioxide), but its effects are less obvious most of the time. We will mostly focus on the temperature effects on phases, mentioning pressure effects only when they are important. Most chemical substances follow the same pattern of phases when going from a low temperature to a high temperature: the solid phase, then the liquid phase, and then the gas phase. However, the temperatures at which these phases are present differ for all substances and can be rather extreme. Table **5.2.1** shows the temperature ranges for solid, liquid, and gas phases for three substances. As you can see, there is extreme variability in the temperature ranges.

Table **5.2.1**: Temperature Ranges for the Three Phases of Various Substances

Substance	Solid Phase Below	Liquid Phase Above	Gas Phase Above
hydrogen (H_2)	−259°C	−259°C	−253°C
water (H_2O)	0°C	0°C	100°C
sodium chloride (NaCl)	801°C	801°C	1413°C

> *The melting point of a substance is the temperature that separates a solid and a liquid. The boiling point of a substance is the temperature that separates a liquid and a gas.*

What accounts for this variability? Why do some substances become liquids at very low temperatures, while others require very high temperatures before they become liquids? It all depends on the strength of the **intermolecular forces (IMF)** between the **particles** of substances and the **kinetic energies** (KE) of its molecules. (Although ionic compounds are not composed of discrete molecules, we will still use the term *intermolecular* to include interactions between the ions in such compounds.) Substances that experience **strong intermolecular interactions** require **higher temperatures to become liquids and, finally, gases.** Substances that experience **weak intermolecular interactions** do not need much energy (as measured by temperature) to become liquids and gases and will exhibit these phases at **lower temperatures.**

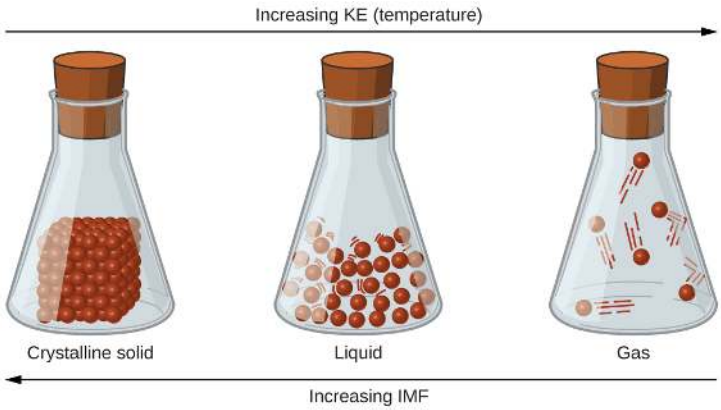


Figure 5.2.1: Transitions between solid, liquid, and gaseous states of a substance occur when conditions of temperature or pressure favor the associated changes in intermolecular forces. (Note: The space between particles in the gas phase is much greater than shown.) (CC BY 4.0; OpenStax)

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 5.2.2). Diamond is composed entirely of carbon atoms, each bonded to four other carbon atoms in a tetrahedral geometry. Melting a covalent network solid is not accomplished by overcoming the relatively weak intermolecular forces. Rather, all of the covalent bonds must be broken, a process that requires extremely high temperatures. Diamond, in fact, does not melt at all. Instead, it vaporizes to a gas at temperatures above 3,500°C. Diamond is extremely hard and is one of the few materials that can cut glass.

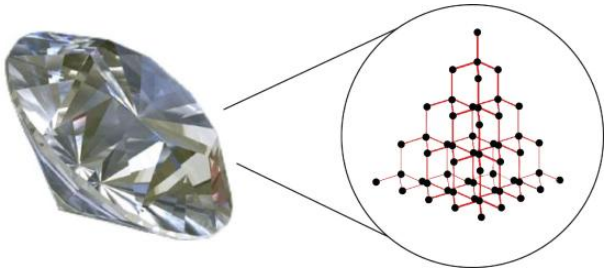


Figure 5.2.2: Diamond. Diamond, a form of pure carbon, has covalent network bonding. It takes a very high temperature—over 3,500°C—for diamond to leave the solid state. Source: Photo © Thinkstock

Ionic Compounds

The strongest force between any two particles is the ionic bond, in which two ions of opposing charge are attracted to each other. Thus, ionic interactions between particles are another type of intermolecular interaction. Substances that contain ionic interactions are relatively strongly held together, so these substances typically have high melting and boiling points. Sodium chloride (Figure 5.2.3) is an example of a substance whose particles experience ionic interactions (Table 5.2.1). These attractive forces are sometimes referred to as ion-ion interactions.

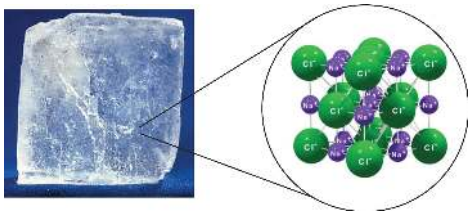


Figure 5.2.3: Sodium Chloride. Solid NaCl is held together by ionic interactions. Source: Photo © Thinkstock

Covalent Molecular Compounds

There are two different covalent structures: molecular and network. Covalent network compounds like SiO_2 (quartz) have structures of atoms in a network like diamond described earlier. In this section, we are dealing with the molecular type that contains individual molecules. The bonding between atoms in the individual molecule is covalent but the attractive forces between the molecules are called ***intermolecular forces (IMF)***.

In contrast to *intramolecular* forces (see Figure 8.1.4), such as the covalent bonds that hold atoms together in molecules and polyatomic ions, intermolecular forces hold molecules together in a **liquid or solid**. Intermolecular forces are generally much weaker than covalent bonds. For example, it requires 927 kJ to overcome the intramolecular forces and break both O–H bonds in 1 mol of water, but it takes only about 41 kJ to overcome the intermolecular attractions and convert 1 mol of liquid water to water vapor at 100°C. (Despite this seemingly low value, the intermolecular forces in liquid water are among the strongest such forces known!) Given the large difference in the strengths of intra- and intermolecular forces, changes between the solid, liquid, and gaseous states almost invariably occur for molecular substances ***without breaking covalent bonds.***

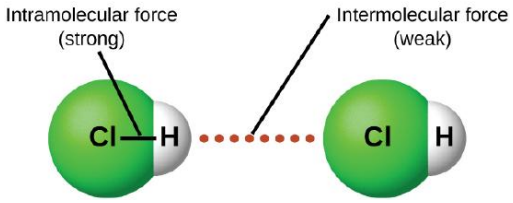


Figure **5.2.4**: **Intramolecular** forces keep a molecule intact. **Intermolecular** forces hold multiple molecules together and determine many of a substance's properties. (CC BY 4.0; OpenStax)

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 **5.2.5**: 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 **5.2.6**).

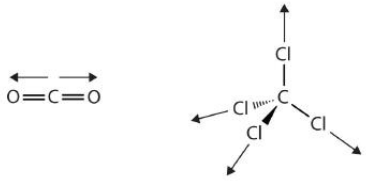


Figure **5.2.6**: Nonpolar Molecules. Although the individual bonds in both CO_2 and CCl_4 are polar, their effects cancel out because of the spatial orientation of the bonds in each molecule. As a result, such molecules experience little or no dipole-dipole interaction.

Recall from the Sections 4.4 and 4.5, on chemical bonding and molecular geometry that *polar* molecules have a partial positive charge on one side and a partial negative charge on the other side of the molecule—a separation of charge called a ***dipole.*** Consider a polar molecule such as hydrogen chloride, HCl. In the HCl molecule, the more electronegative Cl atom bears the partial negative charge, whereas the less electronegative H atom bears the partial positive charge. An attractive force between HCl molecules results from the attraction between the positive end of one HCl molecule and the negative end of another. This attractive force is called a dipole-dipole attraction—the electrostatic force between the partially positive end of one polar molecule and the partially negative end of another, as illustrated in Figure **5.2.7**.

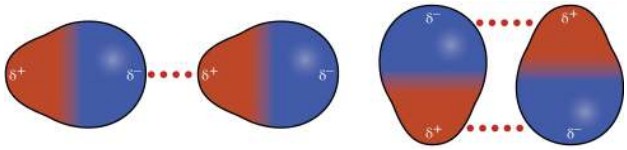


Figure **5.2.7**: This image shows two arrangements of polar molecules, such as HCl, that allow an attraction between the partial negative end of one molecule and the partial positive end of another.

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 5.2.1

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.

5.2.1 Exercise

Predict which will have the higher boiling point: **ICl** or $\mathbf{Br_2}$. 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

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covalently bonded, its positively charged nucleus is almost completely exposed, allowing strong attractions to other nearby lone pairs of electrons.

Examples of hydrogen bonds include HF···HF, H_2O···HOH, and H_3N···HNH_2, in which the **hydrogen bonds** are denoted by **dots**. Figure **5.2.8** illustrates hydrogen bonding between water molecules. The physical properties of water, which has two O–H bonds, are strongly affected by the presence of hydrogen bonding between water molecules. Most molecular compounds that have a mass similar to water are gases at room temperature. However, because of the strong hydrogen bonds, water molecules are able to stay condensed in the liquid state.

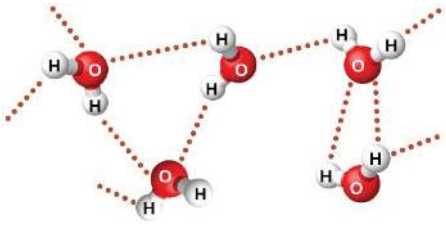


Figure **5.2.8**: Water molecules participate in multiple hydrogen-bonding interactions with nearby water molecules.
Five water molecules are shown near one another, but not touching. A dotted line lies between many of the hydrogen atoms on one molecule and the oxygen atom on another molecule.

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 **5.2.9** shows how methanol (CH_3OH) molecules experience hydrogen bonding. Methanol contains both a hydrogen atom attached to O; methanol can thus form hydrogen bonds by acting as either a hydrogen bond donor or a hydrogen bond acceptor (lone pair). The hydrogen-bonded structure of methanol is as follows:

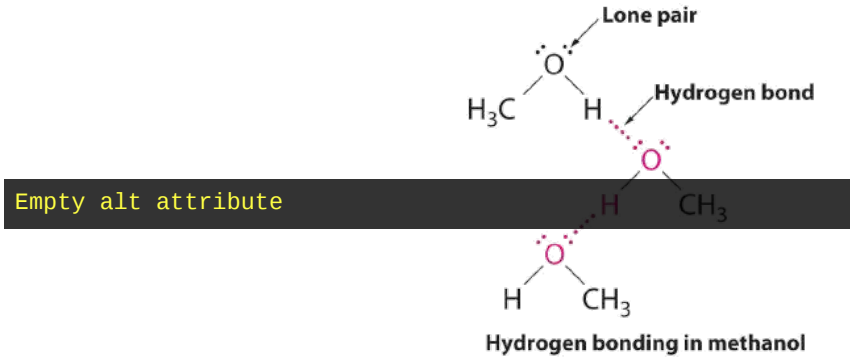


Figure **5.2.9**: Methanol molecules participate in multiple hydrogen-bonding interactions with nearby water molecules.

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 5.2.2

Ethane (CH_3CH_3) has a melting point of −183 °C and a boiling point of −89 °C. Predict the melting and boiling points for methylamine (CH_3NH_2). Explain your reasoning.

Answer

The melting point and boiling point for methylamine are predicted to be significantly greater than those of ethane. CH_3CH_3 and CH_3NH_2 are similar in size and mass, but methylamine possesses an −NH group and therefore may exhibit hydrogen bonding. This greatly increases its IMFs, and therefore its melting and boiling points. It is difficult to predict values, but the known values are a melting point of −93 °C and a boiling point of −6 °C.

Hydrogen Bonding and DNA

Deoxyribonucleic acid (DNA) is found in every living organism and contains the genetic information that determines the organism's characteristics, provides the blueprint for making the proteins necessary for life, and serves as a template to pass this information on to the organism's offspring. A DNA molecule consists of two (anti-)parallel chains of repeating nucleotides, which form its well-known double helical structure, as shown in Figure 5.2.10.

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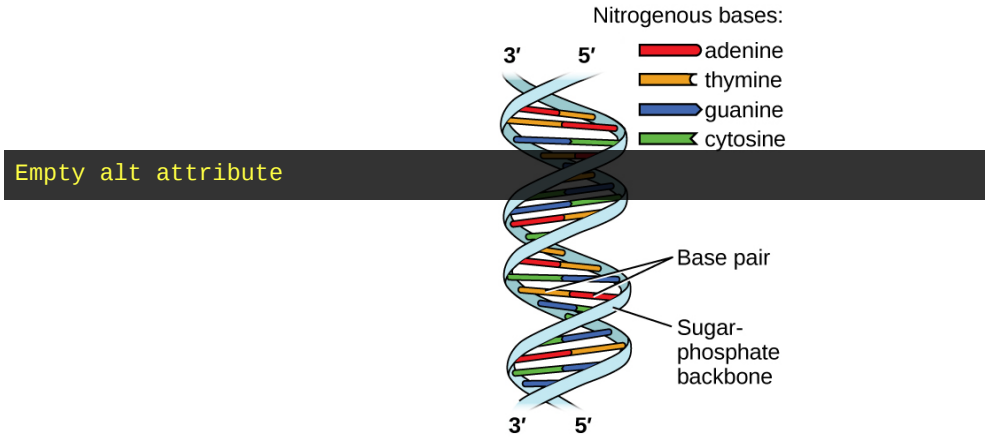


Figure 5.2.10: Two separate DNA molecules form a double-stranded helix in which the molecules are held together via hydrogen bonding. (credit: modification of work by Jerome Walker, Dennis Myts)

Each nucleotide contains a (deoxyribose) sugar bound to a phosphate group on one side, and one of four nitrogenous bases on the other. Two of the bases, cytosine (C) and thymine (T), are single-ringed structures known as pyrimidines. The other two, adenine (A) and guanine (G), are double-ringed structures called purines. These bases form complementary base pairs consisting of one purine and one pyrimidine, with adenine pairing with thymine, and cytosine with guanine. Each base pair is held together by hydrogen bonding. A and T share two hydrogen bonds, C and G share three, and both pairings have a similar shape and structure Figure 5.2.11

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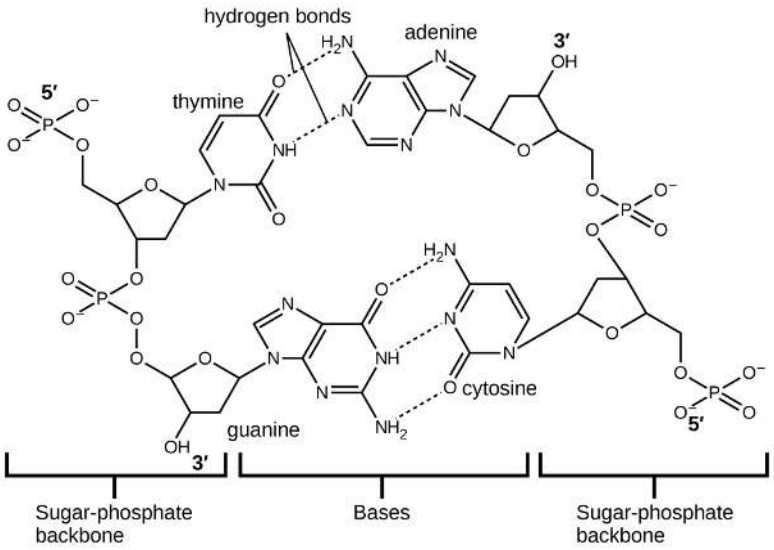


Figure 5.2.11: The geometries of the base molecules result in maximum hydrogen bonding between adenine and thymine (AT) and between guanine and cytosine (GC), so-called "complementary base pairs."

The cumulative effect of millions of hydrogen bonds effectively holds the two strands of DNA together. Importantly, the two strands of DNA can relatively easily "unzip" down the middle since hydrogen bonds are relatively weak compared to the covalent bonds that hold the atoms of the individual DNA molecules together. This allows both strands to function as a template for replication.

London Dispersion Forces

Finally, there are forces between all molecules that are caused by electrons being in different places in a molecule at any one time, which sets up a temporary separation of charge that disappears almost as soon as it appears. These are very weak intermolecular interactions and are called **dispersion forces (or London forces)**. (An alternate name is London dispersion forces.) Molecules that experience no other type of intermolecular interaction will at least experience dispersion forces. Substances that experience only dispersion forces are typically soft in the solid phase and have relatively low melting points. Examples include *waxes*, which are long hydrocarbon chains that are solids at room temperature because the molecules have so many electrons. The resulting dispersion forces between these molecules make them assume the solid phase at normal temperatures.

Dispersion forces that develop between atoms in different molecules can attract the two molecules to each other. The forces are relatively weak, however, and become significant only when the molecules are very close. **Larger and heavier atoms and molecules** exhibit **stronger dispersion forces** than do smaller and lighter atoms and molecules. F_2 and Cl_2 are gases at room temperature (reflecting weaker attractive forces); Br_2 is a liquid, and I_2 is a solid (reflecting stronger attractive forces). Trends in observed melting and boiling points for the halogens clearly demonstrate this effect, as seen in Table 8.1.2.

Table 5.2.2: **Melting and Boiling Points of the Halogens**

Halogen	Molar Mass	Atomic Radius	Melting Point	Boiling Point
fluorine, F_2	38 g/mol	72 pm	53 K	85 K
chlorine, Cl_2	71 g/mol	99 pm	172 K	238 K
bromine, Br_2	160 g/mol	114 pm	266 K	332 K
iodine, I_2	254 g/mol	133 pm	387 K	457 K
astatine, At_2	420 g/mol	150 pm	575 K	610 K

The increase in melting and boiling points with increasing atomic/molecular size may be rationalized by considering how the strength of dispersion forces is affected by the electronic structure of the atoms or molecules in the substance. In a larger atom, the valence electrons are, on average, farther from the nuclei than in a smaller atom. Thus, they are less tightly held and can more easily form the temporary dipoles that produce the attraction. The measure of how easy or difficult it is for another electrostatic charge (for example, a nearby ion or polar molecule) to distort a molecule's charge distribution (its electron cloud) is known as **polarizability**. A molecule

that has a charge cloud that is easily distorted is said to be very polarizable and will have large dispersion forces; one with a charge cloud that is difficult to distort is not very polarizable and will have small dispersion forces.

Example 5.2.3

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.

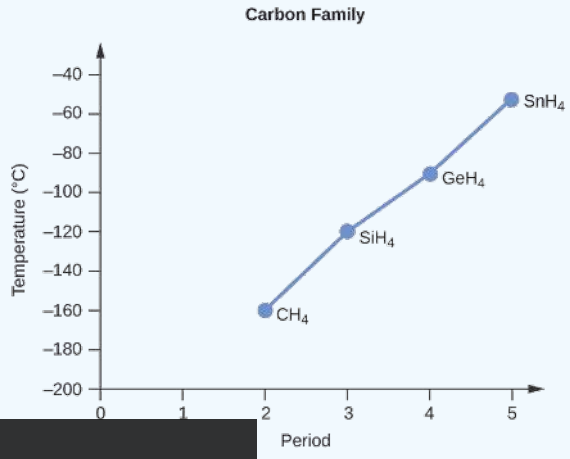
Solution

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As mentioned 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.”

5.2.3 Exercise

Order the following hydrocarbons from lowest to highest boiling point: C_2H_6, C_3H_8, and C_4H_{10}.

Answer

All of these compounds are nonpolar and only have London dispersion forces: the larger the molecule, the larger the dispersion forces and the higher the boiling point. The ordering from lowest to highest boiling point is therefore

$$C_2H_6 < C_3H_8 < C_4H_{10}.$$

Applications: Geckos and Intermolecular Forces

Geckos have an amazing ability to adhere to most surfaces. They can quickly run up smooth walls and across ceilings that have no toe-holds, and they do this without having suction cups or a sticky substance on their toes. And while a gecko can lift its feet easily as it walks along a surface, if you attempt to pick it up, it sticks to the surface. How are geckos (as well as spiders and some

other insects) able to do this? Although this phenomenon has been investigated for hundreds of years, scientists only recently uncovered the details of the process that allows geckos' feet to behave this way.

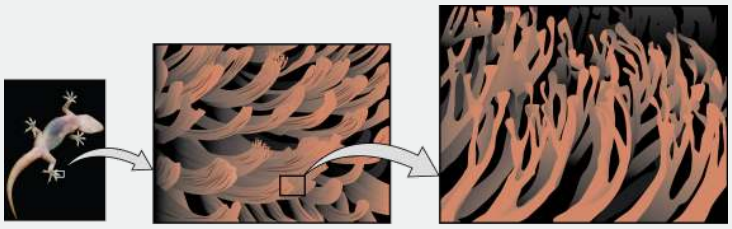


Figure **5.2.12**: *Geckos' toes contain large numbers of tiny hairs (setae), which branch into many triangular tips (spatulae). Geckos adhere to surfaces because of van der Waals attractions between the surface and a gecko's millions of spatulae. By changing how the spatulae contact the surface, geckos can turn their stickiness "on" and "off." (credit photo: modification of work by "JC*+A!"/Flickr)*

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 **5.2.3**: 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 5.2.4: Intermolecular Forces

What intermolecular forces besides dispersion forces, if any, exist in each substance? Are any of these substances solids at room temperature?

a. potassium chloride (KCl)
b. ethanol (C_2H_5OH)
c. bromine (Br_2)

Solution

a. Potassium chloride is composed of ions, so the intermolecular interaction in potassium chloride is ionic forces. Because ionic interactions are strong, it might be expected that potassium chloride is a solid at room temperature.
b. Ethanol has a hydrogen atom attached to an oxygen atom, so it would experience hydrogen bonding. If the hydrogen bonding is strong enough, ethanol might be a solid at room temperature, but it is difficult to know for certain. (Ethanol is actually a liquid at room temperature.)
c. Elemental bromine has two bromine atoms covalently bonded to each other. Because the atoms on either side of the covalent bond are the same, the electrons in the covalent bond are shared equally, and the bond is a nonpolar covalent bond. Thus, diatomic bromine does not have any intermolecular forces other than dispersion forces. It is unlikely to be a solid at room temperature unless the dispersion forces are strong enough. Bromine is a liquid at room temperature.

Exercise 5.2.4

What intermolecular forces besides dispersion forces, if any, exist in each substance? Are any of these substances solids at room temperature?

a. methylamine (CH_3NH_2)
b. calcium sulfate ($CaSO_4$)
c. carbon monoxide (CO)

Answer

a. dipole-dipole, hydrogen bonding
b. ionic forces (solid at room temperature)
c. dipole-dipole

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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5.3: Solids and Liquids

Learning Objectives

- To describe the solid and liquid phases.

Solids and liquids are collectively called *condensed phases* because their particles are in virtual contact. The two states share little else, however.

Solids

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



Figure 5.3.1: Crystalline Arrangement of Quartz crystal cluster. Some large crystals look the way they do because of the regular arrangement of atoms (ions) in their crystal structure. from Wikipedia.

Solids usually have their constituent particles arranged in a regular, three-dimensional array of alternating positive and negative ions called a crystal. The effect of this regular arrangement of particles is sometimes visible macroscopically, as shown in Figure 5.3.1. Some solids, especially those composed of large molecules, cannot easily organize their particles in such regular crystals and exist as amorphous (literally, “without form”) solids. Glass is one example of an amorphous solid.

Liquids

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



Figure 5.3.2: The formation of a spherical droplet of liquid water minimizes the surface area, which is the natural result of surface tension in liquids. from Wikipedia.

Gases

If the particles of a substance have enough energy to completely overcome intermolecular interactions, then the particles can separate from each other and move about randomly in space. Like liquids, gases have no definite shape, but unlike solids and liquids, gases have no definite volume either.

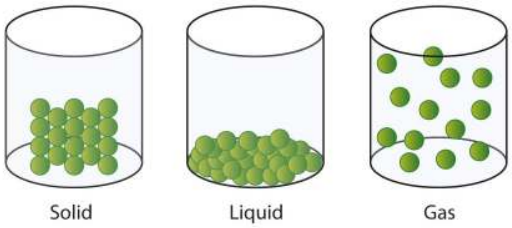


Figure 5.3.3: A Representation of the Solid, Liquid, and Gas States. A solid has definite volume and shape, a liquid has a definite volume but no definite shape, and a gas has neither a definite volume nor shape.

The change from solid to liquid usually does not significantly change the volume of a substance. However, the change from a liquid to a gas significantly increases the volume of a substance, by a factor of 1,000 or more. Figure 5.3.3 shows the differences among solids, liquids, and gases at the molecular level, while Table 5.3.1 lists the different characteristics of these states.

Table 5.3.1: Characteristics of the Three States of Matter

Characteristic	Solid	Liquid	Gas
shape	definite	indefinite	indefinite
volume	definite	definite	indefinite
relative intermolecular interaction strength	strong	moderate	weak
relative particle positions	in contact and fixed in place	in contact but not fixed	not in contact, random positions

✔ Example 5.3.1

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

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

Solution

a. This statement describes either the liquid state or the solid state.
b. This statement describes either the liquid state or the gas state.
c. This statement describes the liquid state.

? Exercise 5.3.1

What state or states of matter does each statement describe?

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

Answer

a. solid
b. gas
c. solid

Looking Closer: Water, the Most Important Liquid

Earth is the only known body in our solar system that has liquid water existing freely on its surface. That is a good thing because life on Earth would not be possible without the presence of liquid water.

Water has several properties that make it a unique substance among substances. It is an excellent solvent; it dissolves many other substances and allows those substances to react when in solution. In fact, water is sometimes called the *universal solvent* because of this ability. Water has unusually high melting and boiling points (0°C and 100°C, respectively) for such a small molecule. The boiling points for similar-sized molecules, such as methane (BP = −162°C) and ammonia (BP = −33°C), are more than 100° lower. Though a liquid at normal temperatures, water molecules experience a relatively strong intermolecular interaction that allows them to maintain the liquid phase at higher temperatures than expected.

Unlike most substances, the solid form of water is less dense than its liquid form, which allows ice to float on water. The most energetically favorable configuration of H_2O molecules is one in which each molecule is hydrogen-bonded to four neighboring molecules. Owing to the thermal motions, this ideal is never achieved in the liquid, but when water freezes to ice, the molecules settle into exactly this kind of an arrangement in the ice crystal. This arrangement requires that the molecules be somewhat farther apart than would otherwise be the case; as a consequence, ice, in which hydrogen bonding is at its maximum, has a more open structure, and thus a lower density than water.

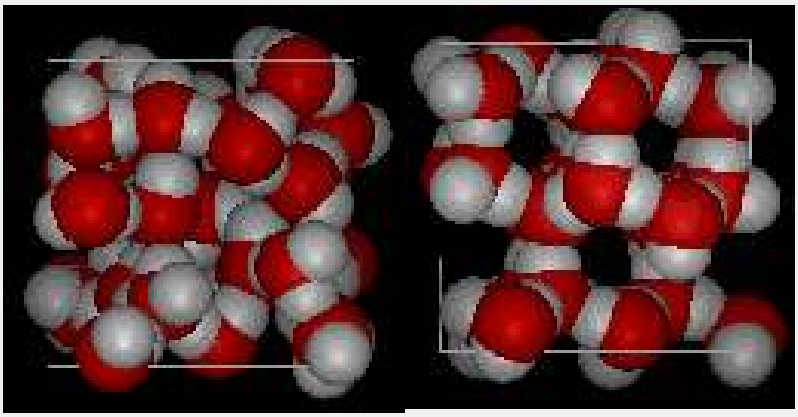


Figure **5.3.4**: Three-dimensional views of a typical local structure of liquid water (left) and ice (right).

Here are three-dimensional views of a typical local structure of water (left) and ice (right.) Notice the greater openness of the ice structure which is necessary to ensure the strongest degree of hydrogen bonding in a uniform, extended crystal lattice. The structure of liquid water is very similar, but in the liquid, the hydrogen bonds are continually broken and formed because of rapid molecular motion. Because ice is less dense than liquid water, rivers, lakes, and oceans freeze from the top down. In fact, the ice forms a protective surface layer that insulates the rest of the water, allowing fish and other organisms to survive in the lower levels of a frozen lake or sea. If ice were denser than the liquid, the ice formed at the surface in cold weather would sink as fast as it formed. Bodies of water would freeze from the bottom up, which would be lethal for most aquatic creatures. The expansion of water when freezing also explains why automobile or boat engines must be protected by “antifreeze” and why unprotected pipes in houses break if they are allowed to freeze.

Water also requires an unusually large amount of energy to change temperature. While 100 J of energy will change the temperature of 1 g of Fe by 230°C, this same amount of energy will change the temperature of 1 g of H_2O by only 100°C. Thus, water changes its temperature slowly as heat is added or removed. This has a major impact on weather, as storm systems like hurricanes can be impacted by the amount of heat that ocean water can store.

Water’s influence on the world around us is affected by these properties. Isn’t it fascinating that such a small molecule can have such a big impact?

Key Takeaway

- Solids and liquids are phases that have their own unique properties.

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5.4: 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 **5.4.1**). 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.

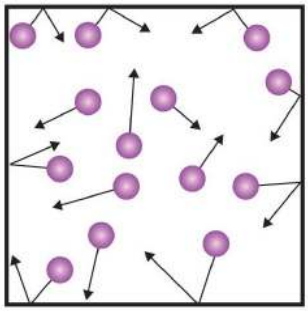


Figure **5.4.1**: Gas Pressure. Pressure is what results when gas particles rebound off the walls of their container.

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 5.4.1: 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 5.4.1: 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.

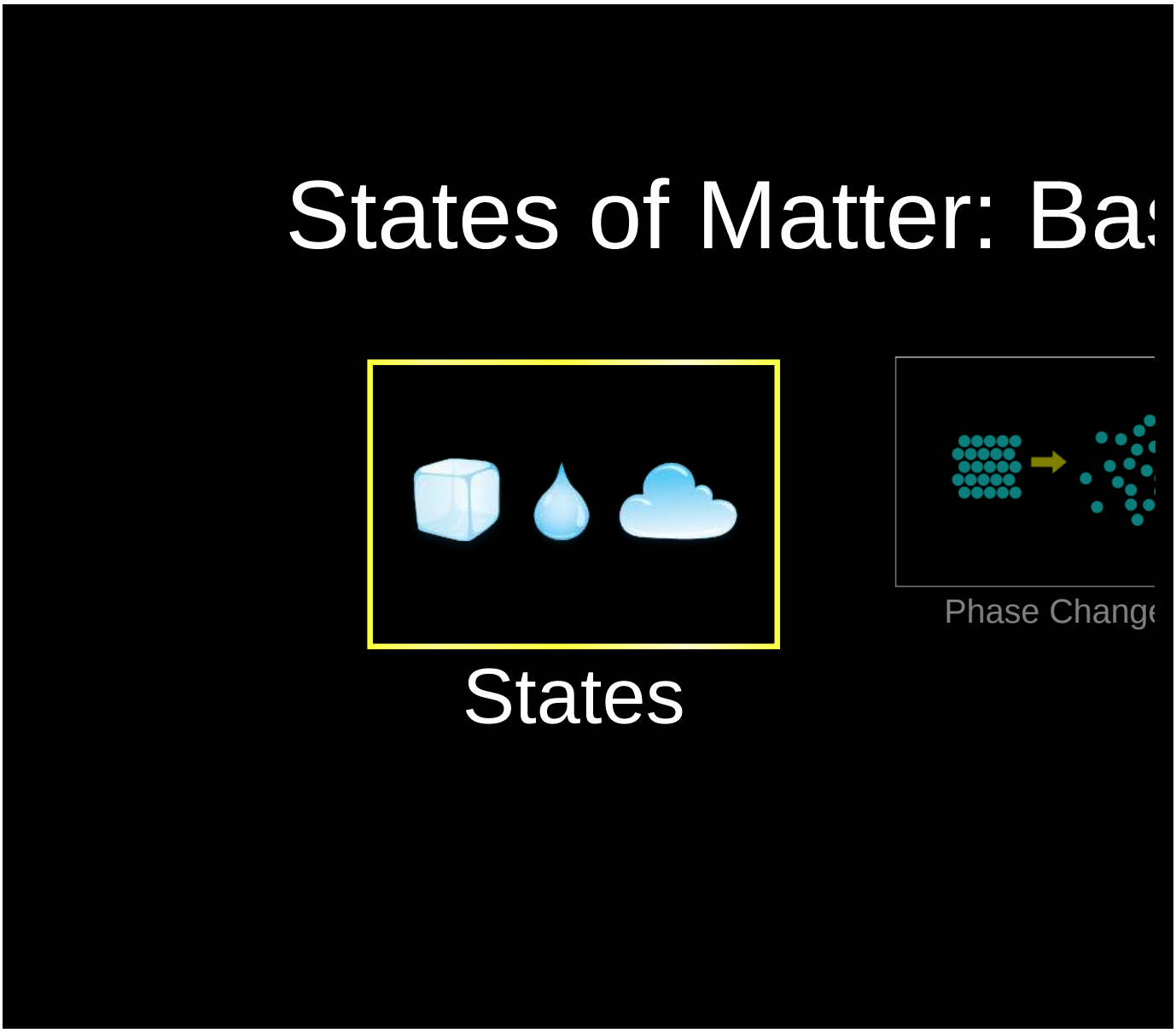
Key Takeaway

- The gas phase has certain general properties characteristic of that phase.

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5.5: PhET- States of Matter



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5.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?

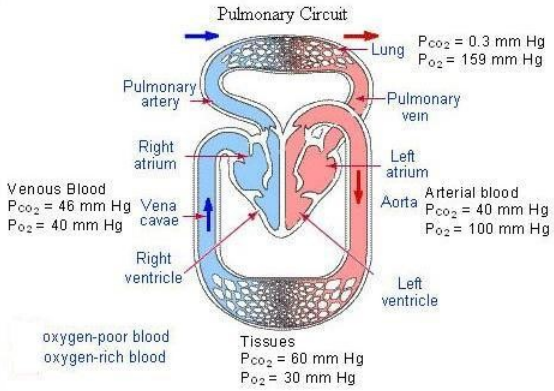
22. What is the pressure of 1.00 mol of Ar gas that has a volume of 843.0 mL and a temperature of −86.0°C?

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:

$$C_3H_{8(g)} + 5O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(\ell)} \tag{5.E.1}$$

   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:

$$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)} \tag{5.E.2}$$

   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:

$$\frac{\mathrm{P_i}}{\mathrm{T_i}} = \frac{\mathrm{P_f}}{\mathrm{T_f}}$$

    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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CHAPTER OVERVIEW

6: 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.

6.1: Prelude to Solutions
6.2: Solutions
6.3: Concentration
6.4: The Dissolution Process
6.5: Properties of Solutions
6.E: Solutions (Exercises)

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6.1: Prelude to Solutions

If you watch any of the medical dramas on television, you may have heard a doctor (actually an actor) call for an intravenous solution of “Ringer’s lactate” (or “lactated Ringer’s” or "Ri-Lac"). So what is Ringer’s lactate?

Intravenous (IV) solutions are administered for two main reasons:

1. to introduce necessary substances into the bloodstream, such as ions for proper body function, sugar and other food substances for energy, or drugs to treat a medical condition, and
2. to increase the volume of the bloodstream.

Many people with acute or long-term medical conditions have received some type of an IV solution.

One basic IV solution, called a *normal saline solution*, is simply a dilute solution of NaCl dissolved in water. Normal saline is 9.0 g of NaCl dissolved in each liter of solution. *Ringer’s lactate* is a normal saline solution that also has small amounts of potassium and calcium ions mixed in. In addition, it contains about 2.5 g of lactate ions ($C_3H_5O_3^-$) per liter of solution. The liver metabolizes lactate ions into bicarbonate (HCO_3^-) ions, which help maintain the acid-base balance of blood. Many medical problems, such as heart attacks and shock, affect the acid-base balance of blood, and the presence of lactate in the IV solution eases problems caused by this imbalance.

Physicians can select from a range of premade IV solutions, in accordance with a patient’s particular needs. Ringer’s lactate is commonly used when a patient’s blood volume must be increased quickly. Another frequently used IV solution, called D5W, is a 5% solution of dextrose (a form of sugar) in water.

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6.2: Solutions

Learning Objectives

- To understand what causes solutions to form.

A solution is another name for a homogeneous mixture. A *mixture* as a material composed of two or more substances. In a solution, the combination is so intimate that the different substances cannot be differentiated by sight, even with a microscope. Compare, for example, a mixture of salt and pepper and another mixture consisting of salt and water. In the first mixture, we can readily see individual grains of salt and the flecks of pepper. A mixture of salt and pepper is not a solution. However, in the second mixture, no matter how carefully we look, we cannot see two different substances. Salt dissolved in water is a solution.

The major component of a solution, called the **solvent**, is typically the same phase as the solution itself. Each minor component of a solution (and there may be more than one) is called the **solute**. In most of the solutions we will describe in this textbook, there will be no ambiguity about whether a component is the solvent or the solute. For example, in a solution of salt in water, the solute is salt, and solvent is water.

Solutions come in all phases, and the solvent and the solute do not have to be in the same phase to form a solution (such as salt and water). For example, air is a gaseous solution of about 80% nitrogen and about 20% oxygen, with some other gases present in much smaller amounts. An alloy is a solid solution consisting of a metal (like iron) with some other metals or nonmetals dissolved in it. Steel, an alloy of iron and carbon and small amounts of other metals, is an example of a solid solution. Table **6.2.1** lists some common types of solutions, with examples of each.

Table **6.2.1**: Types of Solutions

Solvent Phase	Solute Phase	Example
gas	gas	air
liquid	gas	carbonated beverages
liquid	liquid	ethanol (C_2H_5OH) in H_2O (alcoholic beverages)
liquid	solid	saltwater
solid	gas	H_2 gas absorbed by Pd metal
solid	liquid	Hg(ℓ) in dental fillings
solid	solid	steel alloys

What causes a solution to form? The simple answer is that the solvent and the solute must have similar intermolecular interactions. When this is the case, the individual particles of solvent and solute can easily mix so intimately that each particle of solute is surrounded by particles of solvent, forming a solution. However, if two substances have very different intermolecular interactions, large amounts of energy are required to force their individual particles to mix intimately, so a solution does not form. Thus two alkanes like *n*-heptane, C_7H_{16}, and *n*-hexane, C_6H_{14}, are completely miscible in all proportions. The C_7H_{16} and C_6H_{14} molecules are so similar (recall Section 4.6) that there are only negligible differences in intermolecular forces.

For a similar reason, methanol, CH_3OH, is completely miscible with water. In this case both molecules are polar and can form hydrogen bonds among themselves, and so there are strong intermolecular attractions within each liquid. However, CH_3OH dipoles can align with H_2O dipoles, and CH_3OH molecules can hydrogen bond to H_2O molecules, and so the attractions among unlike molecules in the solution are similar to those among like molecules in each pure liquid.

This process leads to a simple rule of thumb: *like dissolves like*. Solvents that are very polar will dissolve solutes that are very polar or even ionic. Solvents that are nonpolar will dissolve nonpolar solutes. Thus water, being polar, is a good solvent for ionic

compounds and polar solutes like ethanol (C_2H_5OH). However, water does not dissolve nonpolar solutes, such as many oils and greases (Figure **6.2.1**).



Figure **6.2.1**: A beaker holds water with blue food dye (upper liquid layer) and a much more dense perfluoroheptane (a fluorocarbon) lower liquid layer. The two fluids cannot mix and the dye cannot dissolve in fluorocarbon. A goldfish and a crab have been introduced into the water. The goldfish cannot penetrate the dense fluorocarbon. The crab floats at the liquid boundary with only parts of his legs penetrating the fluorocarbon fluid, unable to sink to the bottom of the beaker. Quarter coins rest on the bottom of the beaker. Animals were rescued from their predicament after the photo was taken. Figure used with permission from Wikipedia (Sbharris (Steven B. Harris)).

We use the word soluble to describe a solute that dissolves in a particular solvent, and the word insoluble for a solute that does not dissolve in a solvent. Thus, we say that sodium chloride is soluble in water but insoluble in hexane (C_6H_{14}). If the solute and the solvent are both liquids and soluble in any proportion, we use the word miscible, and the word immiscible if they are not.

✔ Example 6.2.1

Water is considered a polar solvent. Which substances should dissolve in water?

1. methanol (CH_3OH)
2. sodium sulfate (Na_2SO_4)
3. octane (C_8H_{18})

Solution

Because water is polar, substances that are polar or ionic will dissolve in it.

1. Because of the OH group in methanol, we expect its molecules to be polar. Thus, we expect it to be soluble in water. As both water and methanol are liquids, the word *miscible* can be used in place of *soluble*.
2. Sodium sulfate is an ionic compound, so we expect it to be soluble in water.
3. Like other hydrocarbons, octane is nonpolar, so we expect that it would not be soluble in water.

? Exercise 6.2.1

Toluene ($C_6H_5CH_3$) is widely used in industry as a nonpolar solvent. Which substances should dissolve in toluene?

a. water (H_2O)
b. sodium sulfate (Na_2SO_4)
c. octane (C_8H_{18})

Answer

Octane only.

Example 6.2.2

Predict which of the following compounds will be most soluble in water:

a. $\underset{\text{Ethanol}}{CH_3CH_2OH}$

b. $\underset{\text{Hexanol}}{CH_3CH_2CH_2CH_2CH_2CH_2OH}$

Solution

Since ethanol contains an **OH** group, it can hydrogen bond to water. Although the same is true of hexanol, the OH group is found only at one end of a fairly large molecule. The rest of the molecule can be expected to behave much as though it were a nonpolar alkane. This substance should thus be much less soluble than the first. Experimentally we find that ethanol is completely miscible with water, while only 0.6 g hexanol dissolves in 100 g water.

6.2.2 Exercise

Would I_2 be more soluble in CCl_4 or H_2O?

Answer

I_2 is nonpolar. Of the two solvents, CCl_4 is nonpolar and H_2O is polar, so I_2 would be expected to be more soluble in CCl_4.

Key Takeaway

- Solutions form because a solute and a solvent experience similar intermolecular interactions.

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6.3: 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 **6.3.1** lists the solubilities of various solutes in water. Solubilities vary with temperature, so Table **6.3.1** includes the temperature at which the solubility was determined.

Table **6.3.1**: 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 **6.3.1**. If a solution contains less solute than the solubility limit, it is **unsaturated**. Under special circumstances, more solute can be dissolved even after the normal solubility limit is reached; such solutions are called ***supersaturated*** and are not stable. If the solute is solid, excess solute can easily recrystallize. If the solute is a gas, it can bubble out of solution uncontrollably, like what happens when you shake a soda can and then immediately open it.

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* 6.3.1*: Watered-down sodium acetate trihydrate. Needle crystal is truly wonderful structures

Most solutions we encounter are unsaturated, so knowing the solubility of the solute does not accurately express the amount of solute in these solutions. There are several common ways of specifying the concentration of a solution.

Percent Composition

There are several ways of expressing the concentration of a solution by using a percentage. The **mass/mass percent** (% m/m) is defined as the mass of a solute divided by the mass of a solution times 100:

$$\%\,\mathrm{m/m} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

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 6.3.1

A saline solution with a mass of 355 g has 36.5 g of NaCl dissolved in it. What is the mass/mass percent concentration of the solution?

Solution

We can substitute the quantities given in the equation for mass/mass percent:

$$\%\,\mathrm{m/m} = \frac{36.5\ \mathrm{g}}{355\ \mathrm{g}} \times 100\% = 10.3\%$$

Exercise 6.3.1

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 6.3.1). 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 6.3.1: Mass/Volume Percent.The 0.9% NaCl concentration on this IV bag is mass/volume percent (left). Such solution is used for other purposes and available in bottles (right). Figures used with permission from Wikipedia

Using Percent Composition in Calculations

The **percent concentration** can be used to produce a **conversion factor** between the **amount of solute** and the **amount of solution**. As such, concentrations can be useful in a variety of stoichiometry problems as discussed in Chapter 6. In many cases, it is best to use the original definition of the concentration unit; it is that definition that provides the conversion factor.

As an example, if the given concentration is **5% v/v solution of alcohol**, this means that there are 5 mL of alcohol dissolved in every 100 mL solution.

5 mL alcohol = 100 mL solution

The two possible conversion factors are written as follows:

$$\frac{\text{5 mL alcohol}}{\text{100 mL solution}} \text{ or } \frac{\text{100 mL solution}}{\text{5 mL alcohol}}$$

Use the first conversion factor to convert from a given amount of solution to amount of solute. The second conversion factor is used to convert from a given amount of solute to amount of solution. Given any two quantities in any percent composition, the third quantity can be calculated, as the following example illustrates.

Example 6.3.2

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:

$$45.0\%\ \text{v/v} \rightarrow \frac{\text{45 mL } C_2H_5OH}{\text{100 mL solution}}$$

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 6.3.2

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 6.3.3

A normal saline IV solution contains 9.0 g of NaCl in every liter of solution. What is the mass/volume percent of normal saline?

Solution

We can use the definition of mass/volume percent, but first we have to express the volume in milliliter units:

1 L = 1,000 mL

Because this is an exact relationship, it does not affect the significant figures of our result.

$$\%\ \text{m/v} = \frac{9.0\ \text{g NaCl}}{1,000\ \text{mL solution}} \times 100\% = 0.90\%\ \text{m/v}$$

? Exercise 6.3.3

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 6.3.4

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 6.3.4

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:

$$\text{molarity} = \frac{\text{number of moles of solute}}{\text{number of liters of solution}}$$

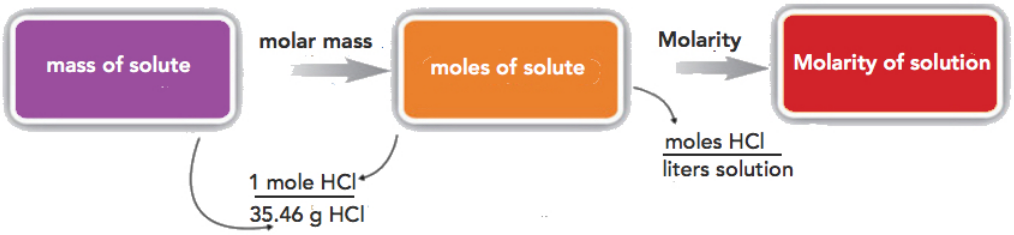
Molarity is abbreviated M (often referred to as "molar"), and the units are often abbreviated as mol/L. It is important to remember that "mol" in this expression refers to moles of solute and that "L" refers to liters of solution. For example, if you have 1.5 mol of NaCl dissolved in 0.500 L of solution, 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:

$$M = \frac{0.614\ mol\ HCl}{1.56 L\ solution} = 0.394\ M HCl$$

Example 6.3.5

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 6.3.5

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**.

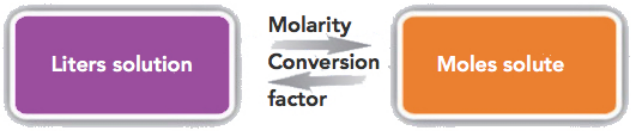
Molarity is defined as moles solute per liter solution. There is an understood 1 in the denominator of the conversion factor. For example, a **3.0 M solution of sucrose** means that there are three moles of sucrose dissolved in every **liter of solution**. Mathematically, this is stated as follows:

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 6.3.6

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.

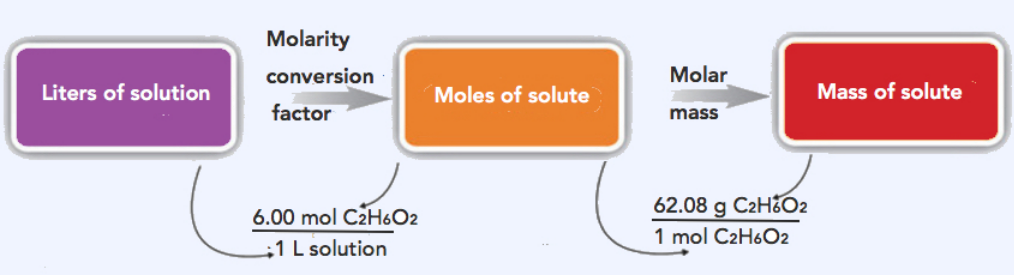
Step 1: Convert the given volume (5.00 L) to moles ethylene glycol.

$$5.00\ \text{L solution} \times \frac{6.00\ \text{mol}\ C_2H_6O_2}{1\ \text{L solution}} = 30.0\ \text{mol}\ C_2H_6O_2$$

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:



$$5.00\ \text{L solution} \times \frac{6.00\ \text{mol}\ C_2H_6O_2}{1\ \text{L solution}} \times \frac{62.08\ \text{g}\ C_2H_6O_2}{1\ \text{mol}\ C_2H_6O_2} = 1,860\ \text{g}\ C_2H_6O_2$$

https://chem.libretexts.org/@go/page/303863

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 6.3.6A

1. What volume of a 0.0753 M solution of dimethylamine [$(CH_3)_2NH$] is needed to obtain 0.450 mol of the compound?
2. Ethylene glycol ($C_2H_6O_2$) is mixed with water to make auto engine coolants. How many grams of $C_2H_6O_2$ are in 5.00 L of a 6.00 M aqueous solution?

Solution

This is an alternative method in case you don't want to use the conversion factor for molarity. In both parts, we will use the definition of molarity to solve for the desired quantity.

1. $$0.0753\ \text{M} = \frac{0.450\ \text{mol}\ (CH_3)_2NH}{\text{volume of solution}}$$

   To solve for the volume of solution, we multiply both sides by volume of solution and divide both sides by the molarity value to isolate the volume of solution on one side of the equation:

   $$\text{volume of solution} = \frac{0.450\ \text{mol}\ (CH_3)_2NH}{0.0753\ \text{M}} = 5.98\ \text{L}$$

   Note that because the definition of molarity is mol/L, the division of mol by M yields L, a unit of volume.

2. The molar mass of $C_2H_6O_2$ is 62.08 g/mol., so

   $$6.00\ \text{M} = \frac{\text{moles of solute}}{5.00\ \text{L}}$$

   To solve for the number of moles of solute, we multiply both sides by the volume:

   $$\text{moles of solute} = (6.00\ \text{M})(5.00\ \text{L}) = 30.0\ \text{mol}$$

   Note that because the definition of molarity is mol/L, the product M × L gives mol, a unit of amount. Now, using the molar mass of $C_3H_8O_3$, we convert mol to g:

   $$30.0\ \text{mol} \times \frac{62.08\ \text{g}}{\text{mol}} = 1,860\ \text{g}$$

   Thus, there are 1,860 g of $C_2H_6O_2$ in the specified amount of engine coolant.

Exercise 6.3.6

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:

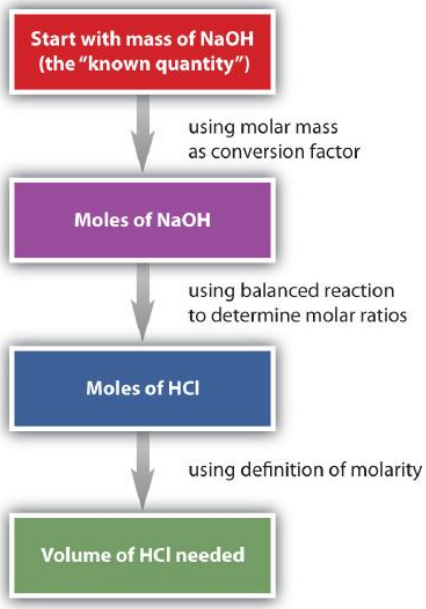


***Figure* 6.3.2**: *Typical approach to solving Molarity problems*

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 6.3.7

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:

$$\mathrm{HCl(aq) + NaOH(s) \rightarrow H_2O(\ell) + NaCl(aq)}$$

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:

$$\mathrm{185\ g\ NaOH \times \frac{1\ mol\ NaOH}{40.00\ g\ NaOH} = 4.63\ mol\ NaOH}$$

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:

$$\mathrm{4.63\ mol\ NaOH \times \frac{1\ mol\ HCl}{1\ mol\ NaOH} = 4.63\ mol\ HCl}$$

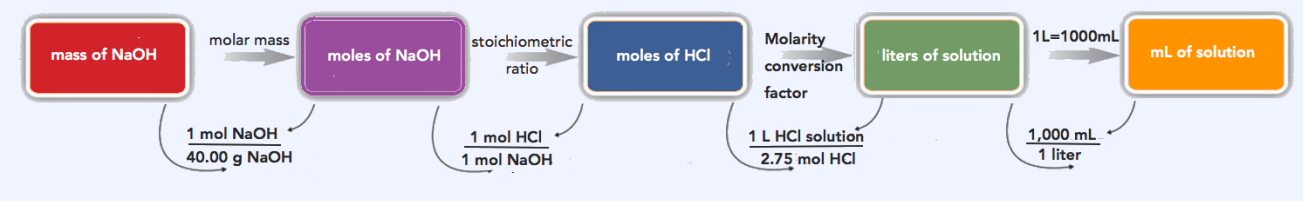
Finally, we use the definition of molarity to determine the volume of 2.75 M HCl needed:

$$\mathrm{2.75\ M\ HCl = \frac{4.63\ mol\ HCl}{volume\ of\ HCl\ solution}}$$

$$\mathrm{volume\ of\ HCl = \frac{4.63\ mol\ HCl}{2.75\ M\ HCl} = 1.68\ L \times \frac{1,000\ mL}{1\ L} = 1,680\ mL}$$

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 6.3.7

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 **6.3.3**. You may want to consult this figure when working with solutions in chemical reactions. The double arrows in Figure **6.3.3** 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.

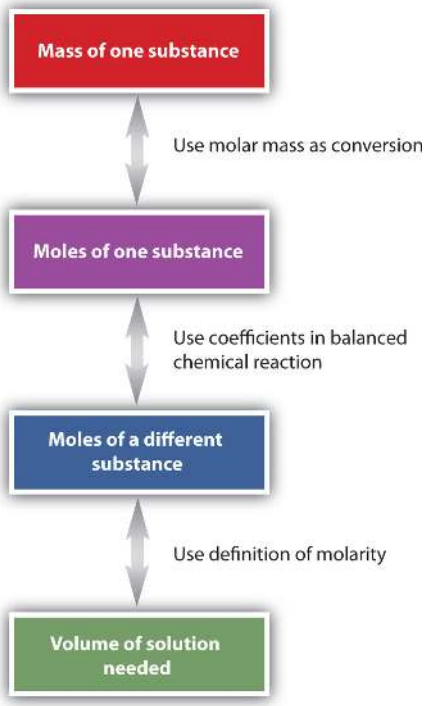


Figure **6.3.3**: Diagram of Steps for Using Molarity in Stoichiometry Calculations. When using molarity in stoichiometry calculations, a specific sequence of steps usually leads you to the correct answer.

Many of the fluids found in our bodies are solutions. The solutes range from simple ionic compounds to complex proteins. Table **6.3.2** lists the typical concentrations of some of these solutes.

Table **6.3.2**: 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.

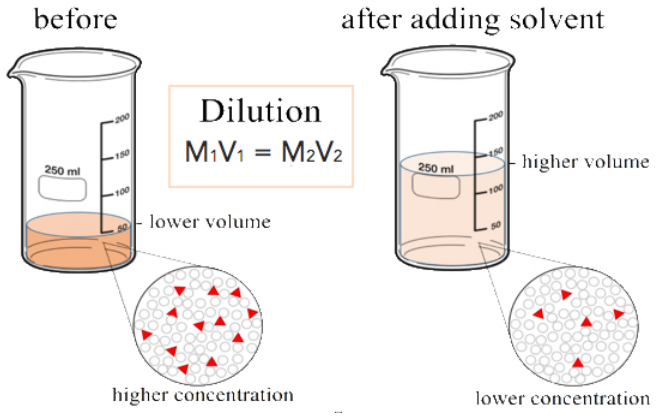


Figure 6.3.1: Figure 6.3.4: Diluting a solution by adding more solvent. Through the dilution process, the volume increases and the concentrations of the solutes decrease. As a consequence, there is more solution in the beaker after dilution, and the color of the solution becomes fainter. The inset shows that at the particular level (picometer to nanometer scale), there are less solute particles (red triangles) per volume. The content in the central box shows the dilution law, i.e. that the product of concentration and volume stays constant upon dilution. CC BY-SA 4.0.

Dilution Equations

Any units of concentration and volume can be used, as long as both concentrations and both volumes have the same unit. For example, if we are using M (molarity), then we can express the equation as follows:

$$\text{Molarity}_{\text{initial}} \times \text{volume}_{\text{initial}} = \text{Molarity}_{\text{final}} \times \text{volume}_{\text{final}} \text{ or}$$

$$M_1V_1 = M_2V_2$$

If we are using percent, the dilution equation is as follows:

$$\%_{\text{initial}} \times \text{volume}_{\text{initial}} = \%_{\text{final}} \times \text{volume}_{\text{final}} \text{ or}$$

$$\%_1V_1 = \%_2V_2$$

Example 6.3.8

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 $(\text{concentration} \times \text{volume})_{\text{initial}} = (\text{concentration} \times \text{volume})_{\text{final}}$:

$$(0.900\ \text{M} \times 125\ \text{mL}) = (\text{concentration} \times 1{,}125\ \text{mL})$$

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 6.3.8

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 6.3.5:*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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6.4: 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 **6.4.1**. When the solvent is water, the word **hydration**, rather than solvation, is used.

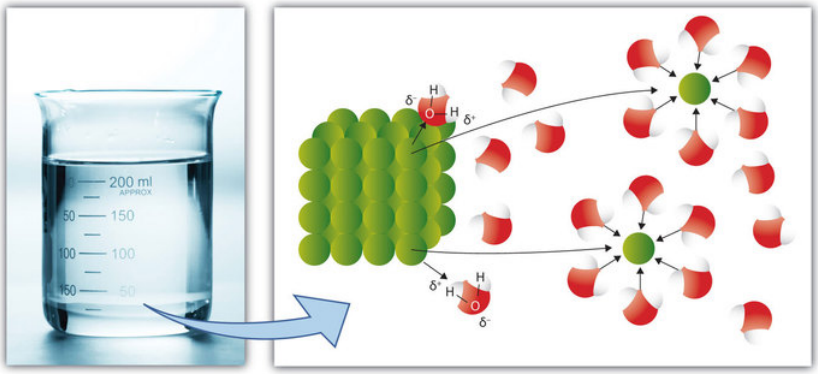


Figure **6.4.1**: Solvation. When a solute dissolves, the individual particles of solute become surrounded by solvent particles. Eventually the particle detaches from the remaining solute, surrounded by solvent molecules in solution. Source: Photo © Thinkstock

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 **6.4.1**).

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 6.4.1

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 6.4.1

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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6.5: 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 **6.5.1**.

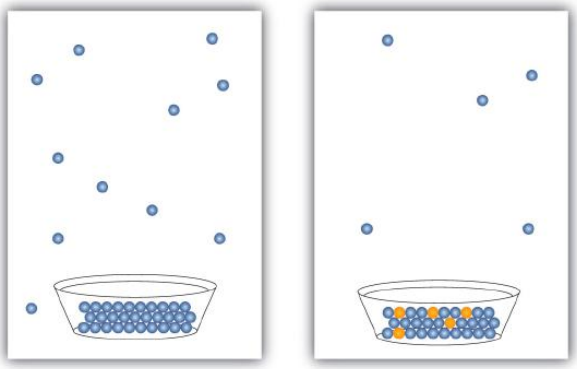


Figure **6.5.1**: Vapor Pressure Depression. The presence of solute particles blocks some of the ability for liquid particles to evaporate. Thus, solutions of solid solutes typically have a lower vapor pressure than the pure solvent.

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.**

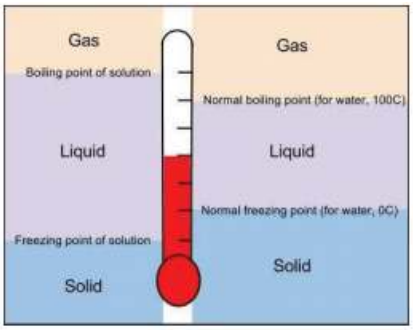


Figure **6.5.2**: Comparison of boiling and freezing points of a pure liquid (right side) with a solution (left side).

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 **6.5.2**). 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 **6.5.2**: 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 6.5.1

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 6.5.1

Which solution's boiling point deviates more from that of pure water—a 1 M solution of $\mathbf{CaCl_2}$ or a 1 M solution of $MgSO_4$?

Answer

$\mathbf{CaCl_2}$

✔ Example 6.5.2

Estimate the boiling point of 0.2 M $\mathbf{CaCl_2}$ 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 $\mathbf{CaCl_2}$ solution contains 0.2 moles of $\mathbf{CaCl_2}$ solution formula units per liter of solution. Each $\mathbf{CaCl_2}$ unit separates into three ions.

$$0.2 \text{ mol } \mathbf{CaCl_2} \times \frac{3 \text{ mol ions}}{1 \text{ mol } \mathbf{CaCl_2}} \times \frac{0.5 \text{ deg C}}{1 \text{ mol ion}} = 0.3 \text{ deg C}$$

The normal boiling point of water is 100^0C, so the boiling point of the solution is raised to 100.3^0C.

6.5.2Exercise

Estimate the freezing point of 0.3 M $\mathbf{CaCl_2}$ 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):

$$osmol = M \times i \tag{6.5.1}$$

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 6.5.3

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 6.5.3

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 $\mathbf{Al(NO_3)_3}$ 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 **6.5.3**: 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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6.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 **6.*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 **6.*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.

https://chem.libretexts.org/@go/page/303866

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. $2O_3\ (g) \rightleftharpoons 3O_2\ (g)$

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. $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$ $K = 4.6 \times 10^4$

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:

$$Ca(NO_3)_{2(aq)} + Na_2CO_{3(aq)} \rightarrow CaCO_{3(s)} + NaNO_{3(aq)} \tag{6.E.1}$$

   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:

$$HCl_{(aq)} + Na_2CO_{3(aq)} \rightarrow H_2O_{(\ell)} + CO_{2(g)} + NaCl_{(aq)} \tag{6.E.2}$$

   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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CHAPTER OVERVIEW

7: Chemical Reactions

Chemistry is largely about chemical changes. Indeed, if there were no chemical changes, chemistry as such would not exist! Chemical changes are a fundamental part of chemistry. Because chemical changes are so central, it may be no surprise that chemistry has developed some special ways of presenting them.

7.1: Prelude to Chemical Reactions
7.2: The Chemical Equation
7.3: The Mole
7.4: The Mole in Chemical Reactions
7.5: Composition, Decomposition, and Combustion Reactions
7.6: Single and Double Replacement Reactions
7.7: Ionic Equations - A Closer Look
7.8: Neutralization Reactions
7.9: Energy and Chemical Reactions
7.10: Reaction Rates
7.11: PhET- Balancing Chemical Equations
7.E: Chemical Reactions and Equations (Exercises)

Thumbnail: Reaction of sodium and water breaks the glass vessel. (CC SA-BY-3.0; Tony Mach).

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7.1: Prelude to Chemical Reactions

The space shuttle—and any other rocket-based system—uses chemical reactions to propel itself into space and maneuver itself when it gets into orbit. The rockets that lift the orbiter are of two different types. The three main engines are powered by reacting liquid hydrogen with liquid oxygen to generate water. Then there are the two solid rocket boosters, which use a solid fuel mixture that contains mainly ammonium perchlorate and powdered aluminum. The chemical reaction between these substances produces aluminum oxide, water, nitrogen gas, and hydrogen chloride. Although the solid rocket boosters each have a significantly lower mass than the liquid oxygen and liquid hydrogen tanks, they provide over 80% of the lift needed to put the shuttle into orbit—all because of chemical reactions.



Figure **7.1.1** The Space Shuttle. (Public Domain; NASA).

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7.2: The Chemical Equation

Learning Objectives

- Define *chemical equation*.
- Identify the parts of a chemical equation.

A chemical reaction expresses a chemical change. For example, one chemical property of hydrogen is that it will react with oxygen to make water. We can write that as follows:

$$\textbf{hydrogen reacts with oxygen to make water}$$

We can represent this chemical change more succinctly as:

$$\textbf{hydrogen} + \textbf{oxygen} \rightarrow \textbf{water}$$

where the + sign means that the two substances interact chemically with each other and the → symbol implies that a chemical reaction takes place. But substances can also be represented by chemical formulas. Remembering that hydrogen and oxygen both exist as diatomic molecules, we can rewrite our chemical change as:

$$\mathrm{H_2 + O_2 \longrightarrow H_2O}$$

This is an example of a chemical equation, which is a concise way of representing a **chemical reaction**. The initial substances are called **reactants** and the final substances are called **products**.

Unfortunately, it is also an *incomplete* chemical equation. The law of conservation of matter says that matter cannot be created or destroyed. In chemical equations, the number of atoms of each element in the reactants must be the same as the number of atoms of each element in the products. If we count the number of hydrogen atoms in the reactants and products, we find two hydrogen atoms. But if we count the number of oxygen atoms in the reactants and products, we find that there are two oxygen atoms in the reactants, but only one oxygen atom in the products.

What can we do? Can we change the subscripts in the formula for water so that it has two oxygen atoms in it? No—you *cannot* change the formulas of individual substances, because the chemical formula for a given substance is characteristic of that substance. What you *can* do, however, is to change the number of molecules that react or are produced. We do this one element at a time, going from one side of the reaction to the other, changing the number of molecules of a substance until all elements have the same number of atoms on each side.

To accommodate the two oxygen atoms as reactants, let us assume that we have two water molecules as products:

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

The 2 in front of the formula for water is called a **coefficient**. Now there are the same number of oxygen atoms in the reactants as there are in the product. But in satisfying the need for the same number of oxygen atoms on both sides of the reaction, we have also changed the number of hydrogen atoms on the product side, so the number of hydrogen atoms is no longer equal. No problem, simply go back to the reactant side of the equation, and add a coefficient in front of the H_2. The coefficient that works is 2:

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

There are now four hydrogen atoms in the reactants and also four atoms of hydrogen in the product. There are two oxygen atoms in the reactants and two atoms of oxygen in the product. The law of conservation of matter has been satisfied. When the reactants and products of a chemical equation have the same number of atoms of all elements present, we say that an equation is **balanced**. All proper chemical equations are balanced. If a substance does not have a coefficient written in front of it, it is assumed to be 1. Also, the convention is to use all whole numbers when balancing chemical equations. This sometimes makes us do a bit more "back and forth" work when balancing a chemical equation.

Example 7.2.1

Write and balance the chemical equation for each given chemical reaction.

1. Hydrogen and chlorine react to make HCl
2. Ethane, $\mathrm{C_2H_6}$, reacts with oxygen to make carbon dioxide and water.

Solution

1. Let us start by simply writing a chemical equation in terms of the formulas of the substances, remembering that both elemental hydrogen and chlorine are diatomic:

$$\mathrm{H_2 + Cl_2 \longrightarrow HCl}$$

There are two hydrogen atoms and two chlorine atoms in the reactants and one of each atom in the product. We can fix this by including the coefficient 2 on the product side:

$$\mathrm{H_2 + Cl_2 \longrightarrow 2\,HCl}$$

Now there are two hydrogen atoms and two chlorine atoms on both sides of the chemical equation, so it is balanced.

2. Start by writing the chemical equation in terms of the substances involved:

$$\mathrm{C_2H_6 + O_2 \longrightarrow CO_2 + H_2O}$$

We have two carbon atoms on the left, so we need two carbon dioxide molecules on the product side, so that each side has two carbon atoms; that element is balanced. We have six hydrogen atoms in the reactants, so we need six hydrogen atoms in the products. We can get this by having three water molecules:

$$\mathrm{C_2H_6 + O_2 \longrightarrow 2\,CO_2 + 3\,H_2O}$$

Now we have seven oxygen atoms in the products (four from the CO_2 and three from the H_2O). This means we need seven oxygen atoms in the reactants. However, because oxygen is a diatomic molecule, we can only get an even number of oxygen atoms at a time. We can achieve this by multiplying the other coefficients by 2:

$$\mathrm{2\,C_2H_6 + O_2 \longrightarrow 4\,CO_2 + 6\,H_2O}$$

By multiplying everything else by 2, we do not unbalance the other elements, and we now get an even number of oxygen atoms in the product—14. We can get 14 oxygen atoms on the reactant side by having 7 oxygen molecules:

$$\mathrm{2\,C_2H_6 + 7\,O_2 \longrightarrow 4\,CO_2 + 6\,H_2O}$$

As a check, recount everything to determine that each side has the same number of atoms of each element. This chemical equation is now balanced.

Exercise 7.2.1

Write and balance the chemical equation that represents nitrogen and hydrogen reacting to produce ammonia, NH_3.

Answer

\[\ce{N2 + 3H2 → 2NH3 \nonumber \nonumber \]

Many chemical equations also include phase labels for the substances: (s) for solid, (ℓ) for liquid, (g) for gas, and (aq) for aqueous (i.e., dissolved in water). Special conditions, such as temperature, may also be listed above the arrow. For example,

$$\mathrm{2\,NaHCO_3\,(s) \overset{200^\circ C}{\rightarrow} Na_2CO_3\,(s) + CO_2\,(g) + H_2O\,(l)}$$

Key Takeaways

- A chemical equation is a concise description of a chemical reaction.
- Proper chemical equations are balanced.

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7.3: The Mole

Learning Objectives

- Describe the unit *mole*.
- Relate the mole quantity of substance to its mass.

So far, we have been talking about chemical substances in terms of individual atoms and molecules. Yet we do not typically deal with substances an atom or a 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. A **mole** (mol) is a number of things equal to the number of atoms in exactly 12 g of carbon-12. Experimental measurements have determined that this number is very large:

$$1 \text{ mol} = 6.02214179 \times 10^{23} \text{ things}$$

Understand that a mole means a specific number of things, just like a dozen means a certain number of things—twelve, in the case of a dozen. But a mole is a much larger number of things. These things can be atoms, or molecules, or eggs; however, in chemistry, we usually use the mole to refer to the amounts of atoms or molecules. Although the number of things in a mole is known to eight decimal places, it is usually fine to use only two or three decimal places in calculations. The numerical value of things in a mole is often called *Avogadro's number* (N_A). *Avogadro's number* is also known as the *Avogadro constant*, after Amadeo Avogadro, an Italian chemist who first proposed its importance.

Example 7.3.1

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 7.3.1

How many molecules are present in 4.61×10^{-2} mol of O_2?

Answer

2.78×10^{22} molecules

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. A mole is a lot of things—but atoms and molecules are very tiny. One mole of carbon atoms would make a cube that is 1.74 cm on a side, small enough to carry in your pocket.

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:

$$1.50 \times 10^{25} \cancel{\text{atoms C}} \times \frac{12.0000\,g\,C}{6.022 \times 10^{23} \cancel{\text{atoms C}}} = 299\,g\,C$$

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.)

Here are some examples. The mass of a 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 + 1.0079 = 2.0158 u, while 1 mol H_2 has a mass of 2.0158 g. A 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 7.3.2: 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.

Solutions to Example 5.3.2

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 7.3.2

What is the molar mass of $AgNO_3$?

Answer

169.87 g/mol

Knowing the molar mass of a substance, we can calculate the number of moles in a certain mass of a substance and vice versa, as these examples illustrate. The molar mass is used as the conversion factor.

Example 7.3.3

What is the mass of 3.56 mol of $HgCl_2$? The molar mass of $HgCl_2$ is 271.49 g/mol.

Solution

Use the molar mass as a conversion factor between moles and grams. Because we want to cancel the mole unit and introduce the gram unit, we can use the molar mass as given:

$$3.56 \cancel{mol\ HgCl_2} \times \frac{271.49\ g\ HgCl_2}{\cancel{mol\ HgCl_2}} = 967\ g\ HgCl_2$$

Exercise 7.3.3

What is the mass of 33.7 mol of $\mathbf{H_2O}$?

Answer

607 g

Example 7.3.4

How many moles of H_2O are present in 240.0 g of water (about the mass of a cup of water)?

Solution

Use the molar mass of H_2O as a conversion factor from mass to moles. The molar mass of water is

$$(1.0079 + 1.0079 + 15.999) = 18.015\ g/mol.$$

However, because we want to cancel the gram unit and introduce moles, we need to take the reciprocal of this quantity, or 1 mol/18.015 g:

$$240.0\ \cancel{g\ H_2O} \times \frac{1\ mol\ H_2O}{18.015\ \cancel{g\ H_2O}} = 13.32\ mol\ H_2O$$

Exercise 7.3.4

How many moles are present in 35.6 g of H_2SO_4 (molar mass = 98.08 g/mol)?

Answer

0.363 mol

Other conversion factors can be combined with the definition of mole—density, for example.

Example 7.3.5

The density of ethanol is 0.789 g/mL. How many moles are in 100.0 mL of ethanol? The molar mass of ethanol is 46.08 g/mol.

Solution

Here, we use density to convert from volume to mass and then use the molar mass to determine the number of moles.

$$100\ \cancel{ml}\ ethanol \times \frac{0.789\ g}{\cancel{ml}} \times \frac{1\ mol}{46.08\ \cancel{g}} = 1.71\ mol\ ethanol$$

Exercise 7.3.5

If the density of benzene, C_6H_6, is 0.879 g/mL, how many moles are present in 17.9 mL of benzene?

Answer

0.201 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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7.4: The Mole in Chemical Reactions

Learning Objectives

- Balance a chemical equation in terms of moles.
- Use the balanced equation to construct conversion factors in terms of moles.
- Calculate moles of one substance from moles of another substance using a balanced chemical equation.

Consider this balanced chemical equation:

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

We interpret this as "two molecules of hydrogen react with one molecule of oxygen to make two molecules of water." The chemical equation is balanced as long as the coefficients are in the ratio 2:1:2. For instance, this chemical equation is also balanced:

$$100\,H_2 + 50\,O_2 \longrightarrow 100\,H_2O$$

This equation is not conventional—because convention says that we use the lowest ratio of coefficients—but it is balanced. So is this chemical equation:

$$5{,}000\,H_2 + 2{,}500\,O_2 \longrightarrow 5{,}000\,H_2O$$

Again, this is not conventional, but it is still balanced. Suppose we use a much larger number:

$$12.044 \times 10^{23} H_2 + 6.022 \times 10^{23} O_2 \rightarrow 12.044 \times 10^{23} H_2O$$

These coefficients are also in the ratio of 2:1:2. But these numbers are related to the number of things in a mole: the first and last numbers are two times Avogadro's number, while the second number is Avogadro's number. That means that the first and last numbers represent 2 mol, while the middle number is just 1 mol. Well, why not just use the number of moles in balancing the chemical equation?

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

is the same balanced chemical equation we started with! What this means is that chemical equations are not just balanced in terms of molecules; *they are also balanced in terms of moles*. We can just as easily read this chemical equation as "two moles of hydrogen react with one mole of oxygen to make two moles of water." All balanced chemical reactions are balanced in terms of moles.

Example 7.4.1

Interpret this balanced chemical equation in terms of moles.

$$P_4 + 5\,O_2 \longrightarrow P_4O_{10}$$

Solution

The coefficients represent the number of moles that react, not just molecules. We would speak of this equation as "one mole of molecular phosphorus reacts with five moles of elemental oxygen to make one mole of tetraphosphorus decoxide."

Exercise 7.4.1

Interpret this balanced chemical equation in terms of moles.

$$N_2 + 3\,H_2 \longrightarrow 2\,NH_3$$

Answer

One mole of elemental nitrogen reacts with three moles of elemental hydrogen to produce two moles of ammonia.

In Section 4.1, we stated that a chemical equation is simply a recipe for a chemical reaction. As such, chemical equations also give us equivalents—equivalents between the reactants and the products. However, now we understand that *these equivalents are expressed in terms of moles*. Consider the chemical equation

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

This chemical reaction gives us the following equivalents:

$$2 \text{ mol } H_2 \Leftrightarrow 1 \text{ mol } O_2 \Leftrightarrow 2 \text{ mol } H_2O$$

Any two of these quantities can be used to construct a conversion factor that lets us relate the number of moles of one substance to an equivalent number of moles of another substance. If, for example, we want to know how many moles of oxygen will react with 17.6 mol of hydrogen, we construct a conversion factor between 2 mol of H_2 and 1 mol of O_2 and use it to convert from moles of one substance to moles of another:

$$17.6\,\cancel{mol\,H_2} \times \frac{1\,mol\,O_2}{2\,\cancel{mol\,H_2}} = 8.80\,mol\,O_2$$

Note how the mol H_2 unit cancels, and mol O_2 is the new unit introduced. This is an example of a **mole-mole calculation,** when you start with moles of one substance and convert to moles of another substance by using the balanced chemical equation. The example may seem simple because the numbers are small, but numbers won't always be so simple!

Example 7.4.2

For the balanced chemical equation

$$2\,C_4H_{10}\,(g) + 13\,O_2 \longrightarrow 8\,CO_2\,(g) + 10\,H_2O(\ell)$$

if 154 mol of O_2 are reacted, how many moles of CO_2 are produced?

Solution

We are relating an amount of oxygen to an amount of carbon dioxide, so we need the equivalence between these two substances. According to the balanced chemical equation, the equivalence is

$$13 \text{ mol } O_2 \Leftrightarrow 8 \text{ mol } CO_2$$

We can use this equivalence to construct the proper conversion factor. We start with what we are given and apply the conversion factor:

$$154\,\cancel{mol\,O_2} \times \frac{8\,mol\,CO_2}{13\,\cancel{mol\,O_2}} = 94.8\,mol\,CO_2$$

The mol O_2 unit is in the denominator of the conversion factor so it cancels. Both the 8 and the 13 are exact numbers, so they do not contribute to the number of significant figures in the final answer.

Exercise 7.4.2

Using the above equation, how many moles of H_2O are produced when 154 mol of O_2 react?

Answer

118 mol

It is important to reiterate that balanced chemical equations are balanced in terms of *moles*. Not grams, kilograms, or liters—but moles. Any stoichiometry problem will likely need to work through the mole unit at some point, especially if you are working with a balanced chemical reaction.

Summary

Balanced chemical reactions are balanced in terms of moles. A balanced chemical reaction gives equivalents in moles that allow stoichiometry calculations to be performed.

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7.5: Composition, Decomposition, and Combustion Reactions

Learning Objectives

- Recognize composition, decomposition, and combustion reactions.
- Predict the products of a combustion reaction.

Three classifications of chemical reactions will be reviewed in this section. Predicting the products in some of them may be difficult, but the reactions are still easy to recognize.

A **composition reaction** (sometimes also called a *combination reaction* or a *synthesis reaction*) produces a single substance from multiple reactants. A single substance as a product is the key characteristic of the composition reaction. There may be a coefficient other than one for the substance, but if the reaction has only a single substance as a product, it can be called a composition reaction. In the reaction

$$2\,H_2\,(g) + O_2\,(g) \longrightarrow 2\,H_2O(\ell)$$

water is produced from hydrogen and oxygen. Although there are two molecules of water being produced, there is only one substance—water—as a product. So this is a composition reaction.

A **decomposition reaction** starts from a single substance and produces more than one substance; that is, it decomposes. The key characteristics of a decomposition reaction are: one substance as a reactant and more than one substance as the products. For example, in the decomposition of sodium hydrogen carbonate (also known as sodium bicarbonate):

$$2\,NaHCO_3\,(s) \longrightarrow Na_2CO_3\,(s) + CO_2\,(g) + H_2O(\ell)$$

sodium carbonate, carbon dioxide, and water are produced from the single substance sodium hydrogen carbonate.

Composition and decomposition reactions are difficult to predict; however, they should be easy to recognize.

Example 7.5.1: Identifying Reactions

Identify each equation as a composition reaction, a decomposition reaction, or neither.

a. $Fe_2O_3 + 3\,SO_3 \longrightarrow Fe_2(SO_4)_3$
b. $NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$
c. $(NH_4)_2Cr_2O_7 \longrightarrow Cr_2O_3 + 4\,H_2O + N_2$

Solution

a. In this equation, two substances combine to make a single substance. This is a composition reaction.
b. Two different substances react to make two new substances. This does not fit the definition of either a composition reaction or a decomposition reaction, so it is neither. In fact, you may recognize this as a double-replacement reaction.
c. A single substance reacts to make multiple substances. This is a decomposition reaction.

Exercise 7.5.1

Identify the equation as a composition reaction, a decomposition reaction, or neither.

$$C_3H_8 \longrightarrow C_3H_4 + 2\,H_2$$

Answer

decomposition

A **combustion reaction** occurs when a reactant combines with oxygen, many times from the atmosphere, to produce oxides of all other elements as products; any nitrogen in the reactant is converted to elemental nitrogen, N_2. Many reactants, called *fuels*,

contain mostly carbon and hydrogen atoms, reacting with oxygen to produce CO_2 and H_2O. For example, the balanced chemical equation for the combustion of methane, CH_4, is as follows:

$$\mathrm{CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O}$$

Kerosene can be approximated with the formula $\mathrm{C_{12}H_{26}}$, and its combustion equation is:

$$\mathrm{2\,C_{12}H_{26} + 37\,O_2 \longrightarrow 24\,CO\text{-}2 + 26\,H_2O}$$

Sometimes fuels contain oxygen atoms, which must be counted when balancing the chemical equation. One common fuel is ethanol, $\mathrm{C_2H_5OH}$, whose combustion equation is:

$$\mathrm{C_2H_5OH + 3\,O_2 \longrightarrow 2\,CO_2 + 3\,H_2O}$$

If nitrogen is present in the original fuel, it is converted to $\mathrm{N_2}$, not to a nitrogen-oxygen compound. Thus, for the combustion of the fuel dinitroethylene, whose formula is $\mathrm{C_2H_2N_2O_4}$, we have:

$$\mathrm{2\,C_2H_2N_2O_4 + O_2 \longrightarrow 4\,CO_2 + 2\,H_2O + 2\,N_2}$$

Example 7.5.2: Combustion Reactions

Complete and balance each combustion equation.

1. the combustion of propane ($\mathrm{C_3H_8}$)
2. the combustion of ammonia ($\mathrm{NH_3}$)

Solution

1. The products of the reaction are CO_2 and H_2O, so our unbalanced equation is

   $$\mathrm{C_3H_8 + O_2 \longrightarrow CO_2 + H_2O}$$

   Balancing (and you may have to go back and forth a few times to balance this), we get

   $$\mathrm{C_3H_8 + 5\,O_2 \longrightarrow 3\,CO_2 + 4\,H_2O}$$

2. The nitrogen atoms in ammonia will react to make N_2, while the hydrogen atoms will react with O_2 to make H_2O:

   $$\mathrm{NH_3 + O_2 \longrightarrow N_2 + H_2O}$$

   To balance this equation without fractions (which is the convention), we get

   $$\mathrm{4\,NH_3 + 3\,O_2 \longrightarrow 2\,N_2 + 6\,H_2O}$$

Exercise 7.5.2

Complete and balance the combustion equation for cyclopropanol (\ce{C3H6O}\)).

Answer

$$\mathrm{C_3H_6O + 4\,O_2 \longrightarrow 3\,CO_2 + 3\,H_2O}$$



Figure **7.5.1** A 20 lb (9.1 kg) steel propane cylinder.

Key Takeaways

- A composition reaction produces a single substance from multiple reactants.
- A decomposition reaction produces multiple products from a single reactant.
- Combustion reactions are the combination of some compound with oxygen to make oxides of the other elements as products (although nitrogen atoms react to make N_2).

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7.6: Single and Double Replacement Reactions

Learning Objectives

- Recognize chemical reactions as single-replacement reactions and double-replacement reactions.
- Use the periodic table, an activity series, or solubility rules to predict whether single-replacement reactions or double-replacement reactions will occur.

Up until now, we have presented chemical reactions as a topic, but we have not discussed how the products of a chemical reaction can be predicted. Here we will begin our study of certain types of chemical reactions that allow us to predict what the products of the reaction will be.

A **single-replacement reaction** is a chemical reaction in which one element is substituted for another element in a compound, generating a new element and a new compound as products. Presented below:

$$2\,HCl\,(aq) + Zn\,(s) \longrightarrow ZnCl_2\,(aq) + H_2\,(g)$$

is an example of a single-replacement reaction. The hydrogen atoms in **HCl** are replaced by **Zn** atoms, and in the process a new element—hydrogen—is formed. Another example of a single-replacement reaction is

$$2\,NaCl\,(aq) + F_2\,(g) \longrightarrow 2\,NaF\,(s) + Cl_2\,(g)$$

Here the negatively charged ion changes from chloride to fluoride. A typical characteristic of a single-replacement reaction is that there is one element as a reactant and another element as a product.

Not all proposed single-replacement reactions will occur between two given reactants. This is most easily demonstrated with fluorine, chlorine, bromine, and iodine. Collectively, these elements are called the *halogens* and are in the next-to-last column on the periodic table (Figure **7.6.1**). The elements on top of the column will replace the elements below them on the periodic table, but not the other way around. Thus, the reaction represented by

$$CaI_2\,(s) + Cl_2\,(g) \longrightarrow CaCl_2\,(s) + I_2\,(s)$$

will occur; but the reaction

$$CaF_2\,(s) + Br_2(\ell) \longrightarrow CaBr_2\,(s) + F_2\,(g)$$

will not, because bromine is below fluorine on the periodic table. This is just one of many ways the periodic table helps us to understand chemistry.

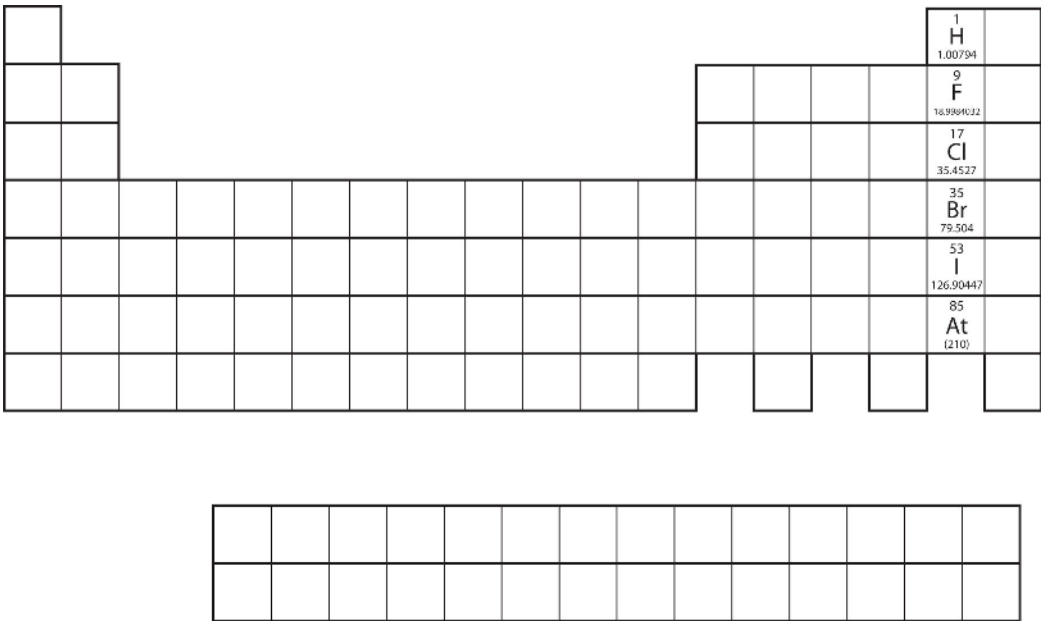


Figure **7.6.1**: Halogens on the Periodic Table. The halogens are the elements in the next-to-last column on the periodic table.

Example 7.6.1

Will a single-replacement reaction occur? If so, identify the products.

a. $MgCl_2 + I_2 \rightarrow ?$
b. $CaBr_2 + F_2 \rightarrow ?$

Solution

a. Because iodine is below chlorine on the periodic table, a single-replacement reaction will not occur.
b. Because fluorine is above bromine on the periodic table, a single-replacement reaction will occur, and the products of the reaction will be CaF_2 and Br_2.

Exercise 7.6.1

Will a single-replacement reaction occur? If so, identify the products.

$$\mathbf{FeI_2 + Cl_2 \longrightarrow}$$

Answer

Yes; $FeCl_2$ and I_2

Chemical reactivity trends are easy to predict when replacing anions in simple ionic compounds—simply use their relative positions on the periodic table. However, when replacing the cations, the trends are not as straightforward. This is partly because there are so many elements that can form cations; an element in one column on the periodic table may replace another element nearby, or it may not. A list called the **activity series** does the same thing the periodic table does for halogens: it lists the elements that will replace elements below them in single-replacement reactions. A simple activity series is shown below.

Activity Series for Cation Replacement in Single-Replacement Reactions

- Li
- K
- Ba
- Sr
- Ca

- Na
- Mg
- Al
- Mn
- Zn
- Cr
- Fe
- Ni
- Sn
- Pb
- H_2
- Cu
- Hg
- Ag
- Pd
- Pt
- Au

Using the activity series is similar to using the positions of the halogens on the periodic table. An element on top will replace an element below it in compounds undergoing a single-replacement reaction. Elements will not replace elements above them in compounds.

Example 7.6.2

Use the activity series to predict the products, if any, of each equation.

1. $FeCl_2 + Zn \rightarrow ?$
2. $HNO_3 + Au \rightarrow ?$

Solution

1. Because zinc is above iron in the activity series, it will replace iron in the compound. The products of this single-replacement reaction are $ZnCl_2$ and Fe.
2. Gold is below hydrogen in the activity series. As such, it will not replace hydrogen in a compound with the nitrate ion. No reaction is predicted.

Exercise 7.6.2

Use the activity series to predict the products, if any, of this equation.

$$AlPO_4 + Mg \longrightarrow$$

Answer

$Mg_3(PO_4)_2$ and Al

A **double-replacement reaction** occurs when parts of two ionic compounds are exchanged, making two new compounds. A characteristic of a double-replacement equation is that there are two compounds as reactants and two different compounds as products. An example is

$$CuCl_2\,(aq) + 2\,AgNO_3\,(aq) \longrightarrow Cu(NO_3)_2\,(aq) + 2\,AgCl\,(s)$$

There are two equivalent ways of considering a double-replacement equation: either the cations are swapped, or the anions are swapped. (You cannot swap both; you would end up with the same substances you started with.) Either perspective should allow you to predict the proper products, as long as you pair a cation with an anion, and not a cation with a cation or an anion with an anion.

Example 7.6.3

Predict the products of this double-replacement equation:

$$\mathrm{BaCl_2 + Na_2SO_4 \longrightarrow}$$

Solution

Thinking about the reaction as either switching the cations or switching the anions, we would expect the products to be $BaSO_4$ and NaCl.

Exercise 7.6.3

Predict the products of this double-replacement equation:

$$\mathrm{KBr + AgNO_3 \longrightarrow}$$

Answer

KNO_3 and AgBr

Predicting whether a double-replacement reaction occurs is somewhat more difficult than predicting a single-replacement reaction. However, there is one type of double-replacement reaction that we can predict: the precipitation reaction. A **precipitation reaction** occurs when two ionic compounds are dissolved in water and form a new ionic compound that does not dissolve; this new compound falls out of solution as a solid **precipitate.** The formation of a solid precipitate is the driving force that makes the reaction proceed.

To judge whether double-replacement reactions will occur, we need to know what kinds of ionic compounds form precipitates. For this, we use **solubility rules**, which are general statements that predict which ionic compounds dissolve (are soluble) and which do not (are not soluble, or insoluble). Table **7.6.1** lists some general solubility rules. We need to consider each ionic compound (both the reactants and the possible products) in light of the solubility rules. If a compound is soluble, we use the (aq) label with it, indicating that it dissolves. If a compound is not soluble, we use the (s) label with it and assume that it will precipitate out of solution. If everything is soluble, then no reaction will be expected.

Table **7.6.1**: Some Useful Solubility Rules (soluble)

These compounds generally dissolve in water (are soluble):	Exceptions:
All compounds of Li^+, Na^+, K^+, Rb^+, Cs^+, and NH_4^+	None
All compounds of NO_3^- and $C_2H_3O_2^-$	None
Compounds of Cl^-, Br^-, I^-	Ag^+, Hg_2^{2+}, Pb^{2+}
Compounds of SO_4^{2}	Hg_2^{2+}, Pb^{2+}, Sr^{2+}, Ba^{2+}

Table **7.6.2**: Some Useful Solubility Rules (insoluble)

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

For example, consider the possible double-replacement reaction between Na_2SO_4 and $SrCl_2$. The solubility rules say that all ionic sodium compounds are soluble and all ionic chloride compounds are soluble, except for Ag^+, Hg_2^{2+}, and Pb^{2+}, which are not being considered here. Therefore, Na_2SO_4 and $SrCl_2$ are both soluble. The possible double-replacement reaction products are NaCl and $SrSO_4$. Are these soluble? NaCl is (by the same rule we just quoted), but what about $SrSO_4$? Compounds of the sulfate

ion are generally soluble, but Sr^{2+} is an exception: we expect it to be insoluble—a precipitate. Therefore, we expect a reaction to occur, and the balanced chemical equation would be:

$$\mathrm{Na_2SO_4\,(aq) + SrCl_2\,(aq) \longrightarrow 2\,NaCl\,(aq) + SrSO_4\,(s)}$$

You would expect to see a visual change corresponding to $SrSO_4$ precipitating out of solution (Figure **7.6.2**).



Figure **7.6.2**: Double-Replacement Reactions. Some double-replacement reactions are obvious because you can see a solid precipitate coming out of solution. Source: Photo courtesy of Choij, http://commons.wikimedia.org/wiki/File:Copper_solution.jpg(opens in new window).

Example 7.6.4

Will a double-replacement reaction occur? If so, identify the products.

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

Solution

1. According to the solubility rules, both $Ca(NO_3)_2$ and KBr are soluble. Now we consider what the double-replacement products would be by switching the cations (or the anions)—namely, $CaBr_2$ and KNO_3. However, the solubility rules predict that these two substances would also be soluble, so no precipitate would form. Thus, we predict no reaction in this case.
2. According to the solubility rules, both NaOH and $FeCl_2$ are expected to be soluble. If we assume that a double-replacement reaction may occur, we need to consider the possible products, which would be NaCl and $Fe(OH)_2$. NaCl is soluble, but, according to the solubility rules, $Fe(OH)_2$ is not. Therefore, a reaction would occur, and $Fe(OH)_2$(s) would precipitate out of solution. The balanced chemical equation is

$$\mathrm{2\,NaOH\,(aq) + FeCl_2\,(aq) \longrightarrow 2\,NaCl\,(aq) + Fe(OH)_2\,(s)}$$

Exercise 7.6.4

$$\mathrm{Sr(NO_3)_2 + KCl \longrightarrow}$$

Answer

No reaction; all possible products are soluble.

Key Takeaways

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

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7.7: Ionic Equations - A Closer Look

Learning Objectives

- Write ionic equations for chemical reactions between ionic compounds.
- Write net ionic equations for chemical reactions between ionic compounds.

For single-replacement and double-replacement reactions, many of the reactions included ionic compounds—compounds between metals and nonmetals, or compounds that contained recognizable polyatomic ions. Now, we take a closer look at reactions that include ionic compounds.

One important aspect about ionic compounds that differs from molecular compounds has to do with dissolution in a liquid, such as water. When molecular compounds, such as sugar, dissolve in water, the individual molecules drift apart from each other. When ionic compounds dissolve, *the ions physically separate from each other*. We can use a chemical equation to represent this process—for example, with NaCl:

$$\mathrm{NaCl\,(s)} \xrightarrow{\mathrm{H_2O}} \mathrm{Na^+\,(aq) + Cl^-\,(aq)}$$

When NaCl dissolves in water, the ions separate and go their own way in solution; the ions are now written with their respective charges, and the (aq) phase label emphasizes that they are dissolved (Figure **7.7.1**). This process is called **dissociation;** we say that the ions *dissociate*.

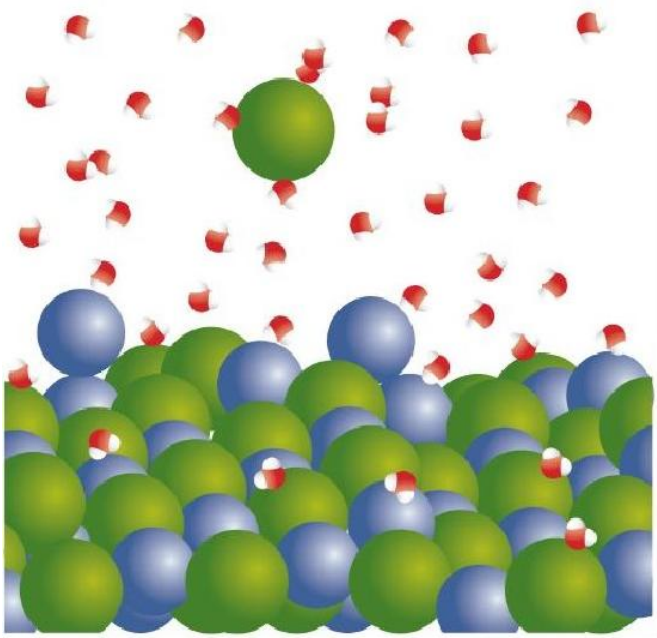


Figure **7.7.1** Ionic Solutions. When an ionic compound dissociates in water, water molecules surround each ion and separate it from the rest of the solid. Each ion goes its own way in solution.

All ionic compounds that dissolve behave this way. This behavior was first suggested by the Swedish chemist Svante August Arrhenius [1859–1927] as part of his PhD dissertation in 1884. Interestingly, his PhD examination team had a hard time believing that ionic compounds would behave like this, so they gave Arrhenius a barely passing grade. Later, this work was cited when Arrhenius was awarded the Nobel Prize in Chemistry. Keep in mind that when the ions separate, *all* the ions separate. Thus, when $CaCl_2$ dissolves, the one Ca^{2+} ion and the two Cl^- ions separate from one another:

$$\mathrm{CaCl_2(s) \xrightarrow{H_2O} Ca^{2+}(aq) + Cl^-(aq) + Cl^-(aq)}$$

$$\mathrm{CaCl_2(s) \xrightarrow{H_2O} Ca^{2+}(aq) + 2Cl^-(aq)}$$

That is, the two chloride ions go off on their own. They do not remain as Cl_2 (that would be elemental chlorine; these are chloride ions), and they do not stick together to make Cl_2^- or Cl_2^{2-}. They become dissociated ions in their own right. Polyatomic ions also retain their overall identity when they are dissolved.

Example 7.7.1

Write the chemical equation that represents the dissociation of each ionic compound.

1. KBr
2. Na_2SO_4

Solution

1. $KBr(s) \rightarrow K^+(aq) + Br^-(aq)$
2. Not only do the two sodium ions go their own way, but the sulfate ion stays together as the sulfate ion. The dissolving equation is $Na_2SO_4(s) \rightarrow 2Na^+(aq) + SO_4^{2-}(aq)$

Exercise 7.7.1

Write the chemical equation that represents the dissociation of $(NH_4)_2S$.

Answer

$(NH_4)_2S(s) \rightarrow 2NH_4^+(aq) + S^{2-}(aq)$

When chemicals in solution react, the proper way of writing the chemical formulas of the dissolved ionic compounds is in terms of the dissociated ions, not the complete ionic formula. A **complete ionic equation** is a chemical equation in which the dissolved ionic compounds are written as separated ions. Solubility rules are very useful in determining which ionic compounds are dissolved and which are not. For example, when NaCl(aq) reacts with $AgNO_3$(aq) in a double-replacement reaction to precipitate AgCl(s) and form $NaNO_3$(aq), the complete ionic equation includes NaCl, $AgNO_3$, and $NaNO_3$ written as separate ions:

$$\mathrm{Na^+(aq) + Cl^-(aq) + Ag^+(aq) + NO_3^-(aq) \longrightarrow AgCl(s) + Na^+(aq) + NO_3^-(aq)}$$

This is more representative of what is occurring in the solution.

Example 7.7.1

Write the complete ionic equation for each chemical reaction.

1. $KBr(aq) + AgC_2H_3O_2(aq) \rightarrow KC_2H_3O_2(aq) + AgBr(s)$
2. $MgSO_4(aq) + Ba(NO_3)_2(aq) \rightarrow Mg(NO_3)_2(aq) + BaSO_4(s)$

Solution

For any ionic compound that is aqueous, we will write the compound as separated ions.

1. The complete ionic equation is $K^+(aq) + Br^-(aq) + Ag^+(aq) + C_2H_3O_2^-(aq) \rightarrow K^+(aq) + C_2H_3O_2^-(aq) + AgBr(s)$
2. The complete ionic equation is $Mg^{2+}(aq) + SO_4^{2-}(aq) + Ba^{2+}(aq) + 2NO_3^-(aq) \rightarrow Mg^{2+}(aq) + 2NO_3^-(aq) + BaSO_4(s)$

Exercise 7.7.1

Write the complete ionic equation for

$$\mathrm{CaCl_2(aq) + Pb(NO_3)_2(aq) \longrightarrow Ca(NO_3)_2(aq) + PbCl_2(s)}$$

Answer

$Ca^{2+}(aq) + 2Cl^-(aq) + Pb^{2+}(aq) + 2NO_3^-(aq) \rightarrow Ca^{2+}(aq) + 2NO_3^-(aq) + PbCl_2(s)$

You may notice that in a complete ionic equation, some ions do not change their chemical form; they stay exactly the same on the reactant and product sides of the equation. For example, in

$Na^+(aq) + Cl^-(aq) + Ag^+(aq) + NO_3^-(aq) \rightarrow AgCl(s) + Na^+(aq) + NO_3^-(aq)$

the $Ag^+(aq)$ and $Cl^-(aq)$ ions become $AgCl(s)$, but the $Na^+(aq)$ ions and the $NO_3^-(aq)$ ions stay as $Na^+(aq)$ ions and $NO_3^-(aq)$ ions. These two ions are examples of spectator ions—ions that do nothing in the overall course of a chemical reaction. They are present, but they do not participate in the overall chemistry. It is common to cancel spectator ions (something also done with algebraic quantities) on the opposite sides of a chemical equation:

$$\cancel{Na^+(aq)} + Cl^-(aq) + Ag^+(aq) + \cancel{NO_3^-(aq)} \rightarrow AgCl(s) + \cancel{Na^+(aq)} + \cancel{NO_3^-(aq)}$$

What remains when the spectator ions are removed is called the **net ionic equation**, which represents the actual chemical change occurring between the ionic compounds:

$Cl^-(aq) + Ag^+(aq) \rightarrow AgCl(s)$

It is important to reiterate that the spectator ions are still present in solution, but they do not experience any net chemical change, so they are not written in a net ionic equation.

Example 7.7.1

Write the net ionic equation for each chemical reaction.

1. $K^+(aq) + Br^-(aq) + Ag^+(aq) + C_2H_3O_2^-(aq) \rightarrow K^+(aq) + C_2H_3O_2^-(aq) + AgBr(s)$
2. $Mg^{2+}(aq) + SO_4^{2-}(aq) + Ba^{2+}(aq) + 2NO_3^-(aq) \rightarrow Mg^{2+}(aq) + 2NO_3^-(aq) + BaSO_4(s)$

Solution

1. In the first equation, the $K^+(aq)$ and $C_2H_3O_2^-(aq)$ ions are spectator ions, so they are canceled:

$$\cancel{K^+(aq)} + Br^-(aq) + Ag^+(aq) + \cancel{C_2H_3O_2^-(aq)} \rightarrow K^+(aq) + \cancel{C_2H_3O_2^-(aq)} + AgBr(s)$$

The net ionic equation is

$$Br^-(aq) + Ag^+(aq) \rightarrow AgBr(s)$$

2. In the second equation, the $Mg^{2+}(aq)$ and $NO_3^-(aq)$ ions are spectator ions, so they are canceled:

$$\cancel{Mg^{2+}(aq)} + SO_4^{2-}(aq) + Ba^{2+}(aq) + \cancel{2NO_3^-(aq)} \rightarrow Mg^{2+}(aq) + \cancel{2NO_3^-(aq)} + BaSo_4(s)$$

The net ionic equation is

$SO_4^{2-}(aq) + Ba^{2+}(aq) \rightarrow BaSO_4(s)$

Exercise 7.7.1

Write the net ionic equation for

$CaCl_2(aq) + Pb(NO_3)_2(aq) \rightarrow Ca(NO_3)_2(aq) + PbCl_2(s)$

Answer

$Pb^{2+}(aq) + 2Cl^-(aq) \rightarrow PbCl_2(s)$

Chemistry is Everywhere: Soluble and Insoluble Ionic Compounds

The concept of solubility versus insolubility in ionic compounds is a matter of degree. Some ionic compounds are very soluble, some are only moderately soluble, and some are soluble so little that they are considered insoluble. For most ionic compounds, there is also a limit to the amount of compound that can be dissolved in a sample of water. For example, you can dissolve a

maximum of 36.0 g of NaCl in 100 g of water at room temperature, but you can dissolve only 0.00019 g of AgCl in 100 g of water. We consider **NaCl** soluble but **AgCl** insoluble.

One place where solubility is important is in the tank-type water heater found in many homes in the United States. Domestic water frequently contains small amounts of dissolved ionic compounds, including calcium carbonate ($CaCO_3$). However, $CaCO_3$ has the relatively unusual property of being less soluble in hot water than in cold water. So as the water heater operates by heating water, $CaCO_3$ can precipitate if there is enough of it in the water. This precipitate, called *limescale*, can also contain magnesium compounds, hydrogen carbonate compounds, and phosphate compounds. The problem is that too much limescale can impede the function of a water heater, requiring more energy to heat water to a specific temperature or even blocking water pipes into or out of the water heater, causing dysfunction.



Figure **7.7.2** Tank water heater © Thinkstock. Most homes in the United States have a tank-type water heater like this one.

Another place where solubility versus insolubility is an issue is the Grand Canyon. We usually think of rock as insoluble. But it is actually ever so slightly soluble. This means that over a period of about two billion years, the Colorado River carved rock from the surface by slowly dissolving it, eventually generating a spectacular series of gorges and canyons. And all because of solubility!



Figure **7.7.3**: The Grand Canyon was formed by water running through rock for billions of years, very slowly dissolving it. Note the Colorado River is still present in the lower part of the photo. (Sonaal Bangera via unsplash)

Key Takeaways

- Ionic compounds that dissolve separate into individual ions.
- Complete ionic equations show dissolved ionic solids as separated ions.
- Net ionic equations show only the ions and other substances that change in a chemical reaction.

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7.8: Neutralization Reactions

Learning Objectives

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

In Chapter 3, we defined an acid as an ionic compound that contains H^+ as the cation. This is slightly incorrect, but until additional concepts were developed, a better definition needed to wait. Now we can redefine an acid: an **acid** is any compound that increases the amount of hydrogen ion (H^+) in an aqueous solution. The chemical opposite of an acid is a base. The equivalent definition of a base is that a **base** is a compound that increases the amount of hydroxide ion (OH^-) in an aqueous solution. These original definitions were proposed by Arrhenius (the same person who proposed ion dissociation) in 1884, so they are referred to as the **Arrhenius definition** of an acid and a base, respectively.

You may recognize that, based on the description of a hydrogen atom, an H^+ ion is a hydrogen atom that has lost its lone electron; that is, H^+ is simply a proton. Do we really have bare protons moving about in aqueous solution? No. What is more likely is that the H^+ ion has attached itself to one (or more) water molecule(s). To represent this chemically, we define the **hydronium ion** as H_3O^+, which represents an additional proton attached to a water molecule. We use the hydronium ion as the more logical way that a hydrogen ion appears in an aqueous solution, although in many chemical reactions H^+ and H_3O^+ are treated equivalently.

The reaction of an acid and a base is called a **neutralization reaction**. Although acids and bases have their own unique chemistries, the acid and base cancel each other's chemistry to produce a rather innocuous substance—water. In fact, the general reaction between an acid and a base is:

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

where the term **salt** is generally used to define any ionic compound (soluble or insoluble) that is formed from a reaction between an acid and a base. (In chemistry, the word *salt* refers to more than just table salt.) For example, the balanced chemical equation for the reaction between HCl(aq) and KOH(aq) is

$$\mathrm{HCl\,(aq) + KOH\,(aq) \longrightarrow H_2O(\ell) + KCl\,(aq)}$$

where the salt is KCl. By counting the number of atoms of each element, we find that only one water molecule is formed as a product. However, in the reaction between HCl(aq) and $Mg(OH)_2$(aq), additional molecules of HCl and H_2O are required to balance the chemical equation:

$$\mathrm{2\,HCl\,(aq) + Mg(OH)_2\,(aq) \longrightarrow 2\,H_2O(\ell) + MgCl_2\,(aq)}$$

Here, the salt is $MgCl_2$. (This is one of several reactions that take place when a type of antacid—a base—is used to treat stomach acid.)

Example 7.8.1

Write the neutralization reactions between each acid and base.

a. HNO_3(aq) and $Ba(OH)_2$(aq)
b. H_3PO_4(aq) and $Ca(OH)_2$(aq)

Solution

First, we will write the chemical equation with the formulas of the reactants and the expected products; then we will balance the equation.

a. The expected products are water and barium nitrate, so the initial chemical reaction is

$$\mathrm{HNO_3\,(aq) + Ba(OH)_2\,(aq) \longrightarrow H_2O(\ell) + Ba(NO_3)_2\,(aq)}$$

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

$$2\,HNO_3\,(aq) + Ba(OH)_2\,(aq) \longrightarrow 2\,H_2O(\ell) + Ba(NO_3)_2\,(aq)$$

This chemical equation is now balanced.

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

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

According to the solubility rules, $Ca_3(PO_4)_2$ is insoluble, so it has an (s) phase label. To balance this equation, we need two phosphate ions and three calcium ions. We end up with six water molecules to balance the equation:

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

This chemical equation is now balanced.

? Exercise 7.8.1

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

Answer

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

Neutralization reactions are one type of chemical reaction that proceeds even if one reactant is not in the aqueous phase. For example, the chemical reaction between HCl(aq) and $Fe(OH)_3$(s) still proceeds according to the equation:

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

even though $Fe(OH)_3$ is not soluble. When one realizes that $Fe(OH)_3$(s) is a component of rust, this explains why some cleaning solutions for rust stains contain acids—the neutralization reaction produces products that are soluble and wash away. (Washing with acids like HCl is one way to remove rust and rust stains, but HCl must be used with caution!)

Complete and net ionic reactions for neutralization reactions will depend on whether the reactants and products are soluble, even if the acid and base react. For example, in the reaction of HCl(aq) and NaOH(aq),

$$HCl\,(aq) + NaOH\,(aq) \longrightarrow H_2O(\ell) + NaCl\,(aq)$$

the complete ionic reaction is

$$H^+\,(aq) + Cl^-\,(aq) + Na^+\,(aq) + OH^-\,(aq) \longrightarrow H_2O(\ell) + Na^+\,(aq) + Cl^-\,(aq)$$

The Na^+(aq) and Cl^-(aq) ions are spectator ions, so we can remove them to have

$$H^+\,(aq) + OH^-\,(aq) \longrightarrow H_2O(\ell)$$

as the net ionic equation. If we wanted to write this in terms of the hydronium ion, H_3O^+(aq), we would write it as

$$H_3O^+\,(aq) + OH^-\,(aq) \longrightarrow 2\,H_2O(\ell)$$

With the exception of the introduction of an extra water molecule, these two net ionic equations are equivalent.

However, for the reaction between HCl(aq) and $Cr(OH)_2$(s), because chromium(II) hydroxide is insoluble, we cannot separate it into ions for the complete ionic equation:

$$2\,H^+\,(aq) + 2\,Cl^-\,(aq) + Cr(OH)_2\,(s) \longrightarrow 2\,H_2O(\ell) + Cr^{2+}\,(aq) + 2\,Cl^-\,(aq)$$

The chloride ions are the only spectator ions here, so the net ionic equation is

$$2\,H^+\,(aq) + Cr(OH)_2\,(s) \longrightarrow 2\,H_2O(\ell) + Cr^{2+}\,(aq)$$

✔ Example 7.8.2

Oxalic acid, $H_2C_2O_4$(s), and $Ca(OH)_2$(s) react very slowly. What is the net ionic equation between these two substances if the salt formed is insoluble? (The anion in oxalic acid is the oxalate ion, $C_2O_4^{2-}$.)

Solution

The products of the neutralization reaction will be water and calcium oxalate:

$H_2C_2O_4(s) + Ca(OH)_2(s) \rightarrow 2H_2O(\ell) + CaC_2O_4(s)$

Because nothing is dissolved, there are no substances to separate into ions, so the net ionic equation is the equation of the three solids and one liquid.

? Exercise 7.8.2

What is the net ionic equation between $HNO_3(aq)$ and $Ti(OH)_4(s)$?

Answer

$4H^+(aq) + Ti(OH)_4(s) \rightarrow 4H_2O(\ell) + Ti^{4+}(aq)$

Key Takeaways

- The Arrhenius definition of an acid is a substance that increases the amount of H^+ in an aqueous solution.
- The Arrhenius definition of a base is a substance that increases the amount of OH^- in an aqueous solution.
- Neutralization is the reaction of an acid and a base, which forms water and a salt.
- Net ionic equations for neutralization reactions may include solid acids, solid bases, solid salts, and water.

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7.9: Energy and Chemical Reactions

Learning Objectives

- Define endothermic and exothermic reactions.
- Determine whether a reaction is endothermic or exothermic through observations, temperature changes, or an energy diagram.
- Describe the calculation of heat of reaction using bond energies.

When physical or chemical changes occur, they are generally accompanied by a transfer of energy. The **law of conservation of energy** states that in any physical or chemical process, energy is neither created nor destroyed. In other words, the entire energy in the universe is conserved. In order to better understand the energy changes taking place during a reaction, we need to define two parts of the universe, called the system and the surroundings. The **system** is the specific portion of matter in a given space that is being studied during an experiment or an observation. The **surroundings** is everything in the universe that is not part of the system. In practical terms for a laboratory chemist, the system is the particular chemicals being reacted, while the surroundings is the immediate vicinity within the room. During most processes, energy is exchanged between the system and the surroundings.

In the course of an **endothermic** process, the system gains heat from the surroundings and so the **temperature of the surroundings decreases.** A chemical reaction or physical change 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** (Figure **7.9.1**)**.** Exothermic and endothermic reactions can be thought of as having energy as either a product of the reaction or a reactant. **Exothermic** reactions give off energy, so energy is a product. **Endothermic** reactions require energy, so energy is a reactant.

Phase changes, discussed in the previous section 7.3, are also classified in a similar way. The change from gas to liquid (condensation) and liquid to solid (freezing) are **exothermic**. The change from solid to liquid (melting), and liquid to gas (evaporation and boiling) are **endothermic**. The **exothermic processes release heat** to the surroundings while the **endothermic processes absorb heat** from the surroundings.

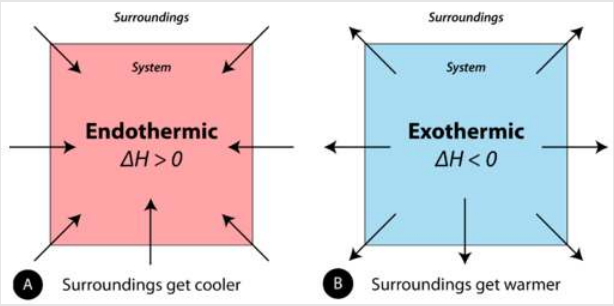


Figure **7.9.1**. (A) Endothermic reaction. (B) Exothermic reaction.

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.

$$\text{CH}_4\,(g) + 2\text{O}_2\,(g) \rightarrow \text{CO}_2\,(g) + 2\text{H}_2\text{O}\,(l) + 890.4\,\text{kJ}$$

The process in the above thermochemical equation can be shown visually in the figure below.

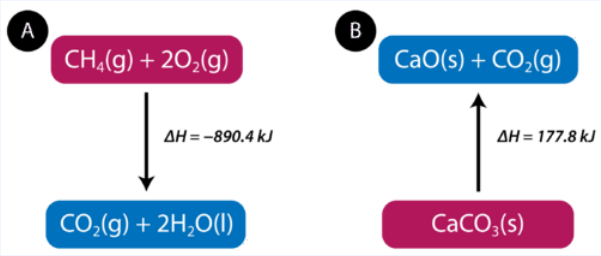


Figure 7.9.2 (A) As reactants are converted to products in an exothermic reaction, enthalpy is released into the surroundings. The enthalpy change of the reaction is negative. (B) As reactants are converted to products in an endothermic reaction, enthalpy is absorbed from the surroundings. The enthalpy change of the reaction is positive. (CC BY-NC; CK-12)

In the combustion of methane example, the enthalpy change is negative because heat is being released by the system. Therefore, the overall enthalpy of the system decreases. The **heat of reaction** is the enthalpy change for a chemical reaction. In the case above, the heat of reaction is $-890.4\ \text{kJ}$. The thermochemical reaction can also be written in this way:

$$\text{CH}_4\,(g) + 2\text{O}_2\,(g) \rightarrow \text{CO}_2\,(g) + 2\text{H}_2\text{O}\,(l) \quad \Delta H = -890.4\ \text{kJ}$$

Endothermic reactions absorb energy from the surroundings as the reaction occurs. When $1\ \text{mol}$ of calcium carbonate decomposes into $1\ \text{mol}$ of calcium oxide and $1\ \text{mol}$ of carbon dioxide, $177.8\ \text{kJ}$ of heat is absorbed. The process is shown visually in the figure above (B). The thermochemical reaction is shown below.

$$\text{CaCO}_3\,(s) + 177.8\ \text{kJ} \rightarrow \text{CaO}\,(s) + \text{CO}_2\,(g)$$

Because the heat is absorbed by the system, the $177.8\ \text{kJ}$ is written as a reactant. The heat of reaction is positive for an endothermic reaction.

✔ Example 7.9.1

-

Label each of the following processes as endothermic or exothermic.

a. water boiling
b. gasoline burning
c. ice forming on a pond

Solution

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

? Exercise 7.9.1

Label each of the following processes as endothermic or exothermic.

a. water vapor condensing
b. gold melting

Answer (a)

exothermic

Answer (b)

endothermic

Example 7.9.2

Is each chemical reaction exothermic or endothermic?

a. $2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell) + 135$ kcal
b. $N_2(g) + O_2(g) + 45$ kcal $\rightarrow 2NO(g)$

Solution

a. Because energy is a product, energy is given off by the reaction. Therefore, this reaction is exothermic.
b. Because energy is a reactant, energy is absorbed by the reaction. Therefore, this reaction is endothermic.

Exercise 7.9.2

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

Bond Energy

Atoms bond together to form compounds because in doing so they attain lower energies than they possess as individual atoms. A quantity of energy, equal to the difference between the energies of the bonded atoms and the energies of the separated atoms, is released, usually as heat. That is, the bonded atoms have a lower energy than the individual atoms do. *When atoms combine to make a compound, energy is always given off, and the compound has a lower overall energy.*

When a chemical reaction occurs, molecular bonds are broken and other bonds are formed to make different molecules. For example, the bonds of two water molecules are broken to form hydrogen and oxygen.

$$2H_2O \rightarrow 2H_2 + O_2$$

Energy is always required to break a bond, which is known as bond energy. While the concept may seem simple, bond energy serves a very important purpose in describing the structure and characteristics of a molecule.

> *Energy is always required to break a bond. Energy is released when a bond is made.*

Table **7.9.1** Approximate Bond Energies

Bond	Bond Energy (kJ/mol)
C–H	413
C–O	358
C=O*	745
C–N	305
C–C	347
C=C	614
C≡C	839
N–H	391
O—H	467
H–H	432
H—Cl	427
H—I	295
*C = O(CO_2) = 799	

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 **7.9.1**.

In this process, one adds energy to the reaction to break bonds, and extracts energy for the bonds that are formed.

$$\textbf{enthalpy change} = \sum(\textbf{bonds broken}) - \sum(\textbf{bonds formed})$$

Example 7.9.3: Generation of Hydrogen Iodide

What is the enthalpy change for this reaction and is it endothermic or exothermic?

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

Solution

First look at the equation and identify which bonds exist on in the reactants.

- one H-H bond and
- one I-I bond

Now do the same for the products

- two H-I bonds

Then identify the bond energies of these bonds from the table above:

- H-H bonds: 436 kJ/mol
- I-I bonds: 151 kJ/mol

The sum of enthalpies on the reaction side is:

436 kJ/mole + 151 kJ/mole = 587 kJ/mol.

This is how much energy is needed to break the bonds on the reactant side. Then we look at the bond formation which is on the product side:

- 2 mol H-I bonds: 297 kJ/mol

The sum of enthalpies on the product side is:

$$2 \text{ x } 297 \text{ kJ/mol} = 594 \text{ kJ/mol}$$

This is how much energy is released when the bonds on the product side are formed. The net change of the reaction is therefore

$$587 \text{ kJ/mol} - 594 \text{ kJ/mol} = -7 \text{ kJ/mol}.$$

Since this is negative, the reaction is *exothermic*.

Exercise 7.9.3: Decomposition of Water

Using the bond energies given in the chart above, find the enthalpy change for the thermal decomposition of water:

$$2H_2O(g) \rightarrow 2H_2 + O_2(g)$$

Is the reaction written above exothermic or endothermic? Explain.

Solution

The enthalpy change deals with breaking two mole of O-H bonds and the formation of 1 mole of O-O bonds and two moles of H-H bonds (Table **7.9.1**).

- The sum of the energies required to break the bonds on the reactants side is 4 x 460 kJ/mol = 1840 kJ/mol.
- The sum of the energies released to form the bonds on the products side is
  - 2 moles of H-H bonds = 2 x 436.4 kJ/mol = 872.8 kJ/mol
  - 1 moles of O=O bond = 1 x 498.7 kJ/mil = 498.7 kJ/mol

which is an output (released) energy = 872.8 kJ/mol + 498.7 kJ/mol = 1371.5 kJ/mol.

Total energy difference is 1840 kJ/mol – 1371.5 kJ/mol = 469 kJ/mol, which indicates that the reaction is *endothermic* and that 469 kJ of heat is needed to be supplied to carry out this reaction.

This reaction is endothermic since it requires energy in order to create bonds.

Summary

- Chemical processes are labeled as exothermic or endothermic based on whether they give off or absorb energy, respectively.
- Atoms are held together by a certain amount of energy called bond energy.
- Energy is released to generate bonds, which is why the enthalpy change for breaking bonds is positive. Energy is required to break bonds. Atoms are much happier when they are "married" and release energy because it is easier and more stable to be in a relationship (e.g., to generate *octet electronic configurations*). The enthalpy change is negative because the system is releasing energy when forming bond.

Contributors and Attributions

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7.10: Reaction Rates

Learning Objectives

- Define chemical reaction rate.
- Describe the effects of temperature, concentration, surface area, and catalysis on reaction rates.

The lizard in the photograph is not simply enjoying the sunshine or working on its tan. The heat from the sun's rays is critical to the lizard's survival. A warm lizard can move faster than a cold one because the chemical reactions that allow its muscles to move occur more rapidly at higher temperatures. In the absence of warmth, the lizard is an easy meal for predators.



Figure 7.10.1 An agama lizard basks in the sun. As its body warms, the chemical reactions of its metabolism speed up.

From baking a cake to determining the useful lifespan of a bridge, rates of chemical reactions play important roles in our understanding of processes that involve chemical changes.

A **rate** is a measure of how some property varies with time. Speed is a familiar rate that expresses the distance traveled by an object in a given amount of time. Wage is a rate that represents the amount of money earned by a person working for a given amount of time. Likewise, the rate of a chemical reaction is a measure of how much reactant is consumed, or how much product is produced, by the reaction in a given amount of time.

The rate of reaction is the change in the amount of a reactant or product per unit time. Reaction rates are therefore determined by measuring the time dependence of some property that can be related to reactant or product amounts. Rates of reactions that consume or produce gaseous substances, for example, are conveniently determined by measuring changes in volume or pressure. For reactions involving one or more colored substances, rates may be monitored via measurements of light absorption. For reactions involving aqueous electrolytes, rates may be measured via changes in a solution's conductivity.

For reactants and products in solution, their relative amounts (concentrations) are conveniently used for purposes of expressing reaction rates. If we measure the concentration of hydrogen peroxide, H_2O_2, in an aqueous solution, we find that it changes slowly over time as the H_2O_2 decomposes, according to the equation:

$$2\,H_2O_2(aq) \longrightarrow 2\,H_2O(l) + O_2(g)$$

The rate at which the hydrogen peroxide decomposes can be expressed in terms of the rate of change of its concentration, as shown here:

$$\text{rate of decomposition of } H_2O_2 = -\frac{\text{change in concentration of reactant}}{\text{time interval}}$$

Factors Affecting Reaction Rates

By their nature, some reactions occur very quickly, while others are very slow. However, certain changes in the reacting conditions can have an effect on the rate of a given chemical reaction.

Concentration

The rates of many reactions depend on the concentrations of the reactants. Rates usually increase when the concentration of one or more of the reactants increases. In a polluted atmosphere where the concentration of sulfur dioxide is high, calcium carbonate deteriorates more rapidly than in less polluted air. Similarly, phosphorus burns much more rapidly in an atmosphere of pure oxygen than in air, which is only about 20% oxygen.

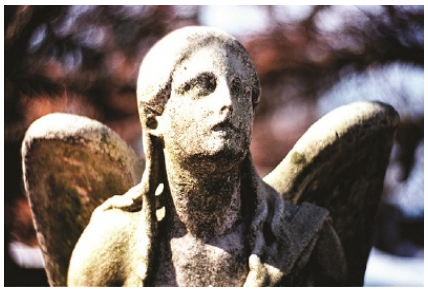


Figure **7.10.2** Pollutants like sulfur dioxide can accelerate weathering of statues made from carbonate compounds such as limestone and marble (credit: James P Fisher III).

Phosphorus Burning



***Video* 7.10.1** *Phosphorous burns rapidly in air, but it will burn even more rapidly if the concentration of oxygen in is higher.*

Surface Area

A large log placed in a fire will burn relatively slowly. If the same mass of wood were added to the fire in the form of small twigs, they would burn much more quickly. This is because the twigs provide a greater surface area than the log does. An increase in the surface area of a reactant increases the rate of a reaction. Surface area is larger when a given amount of a solid is present as smaller particles. A powdered reactant has a greater surface area than the same reactant as a solid chunk. In order to increase the surface area of a substance, it may be ground into smaller particles or dissolved into a liquid. In solution, the dissolved particles are separated from each other and will react more quickly with other reactants.

Temperature

Chemical reactions typically occur faster at higher temperatures. Food can spoil quickly when left on the kitchen counter. However, the lower temperature inside of a refrigerator slows that process so that the same food remains fresh for days. We use a burner or a hot plate in the laboratory to increase the speed of reactions that proceed slowly at ordinary temperatures. In many cases, an increase in temperature of only 10 °C will approximately double the rate of a reaction in a homogeneous system.

The Presence of a Catalyst

Hydrogen peroxide solutions foam when poured onto an open wound because substances in the exposed tissues act as catalysts, increasing the rate of hydrogen peroxide’s decomposition. However, in the absence of these catalysts (for example, in the bottle in the medicine cabinet) complete decomposition can take months. A catalyst is a substance that increases the rate of a chemical reaction by providing an alternative pathway or mechanism for the reaction to follow.

Summary

- The reaction rate indicates how fast the reaction proceeds.
- Factors affecting reaction rate are:
  - Concentration of reactants

- Surface area
- Temperature
- Presence of catalysts

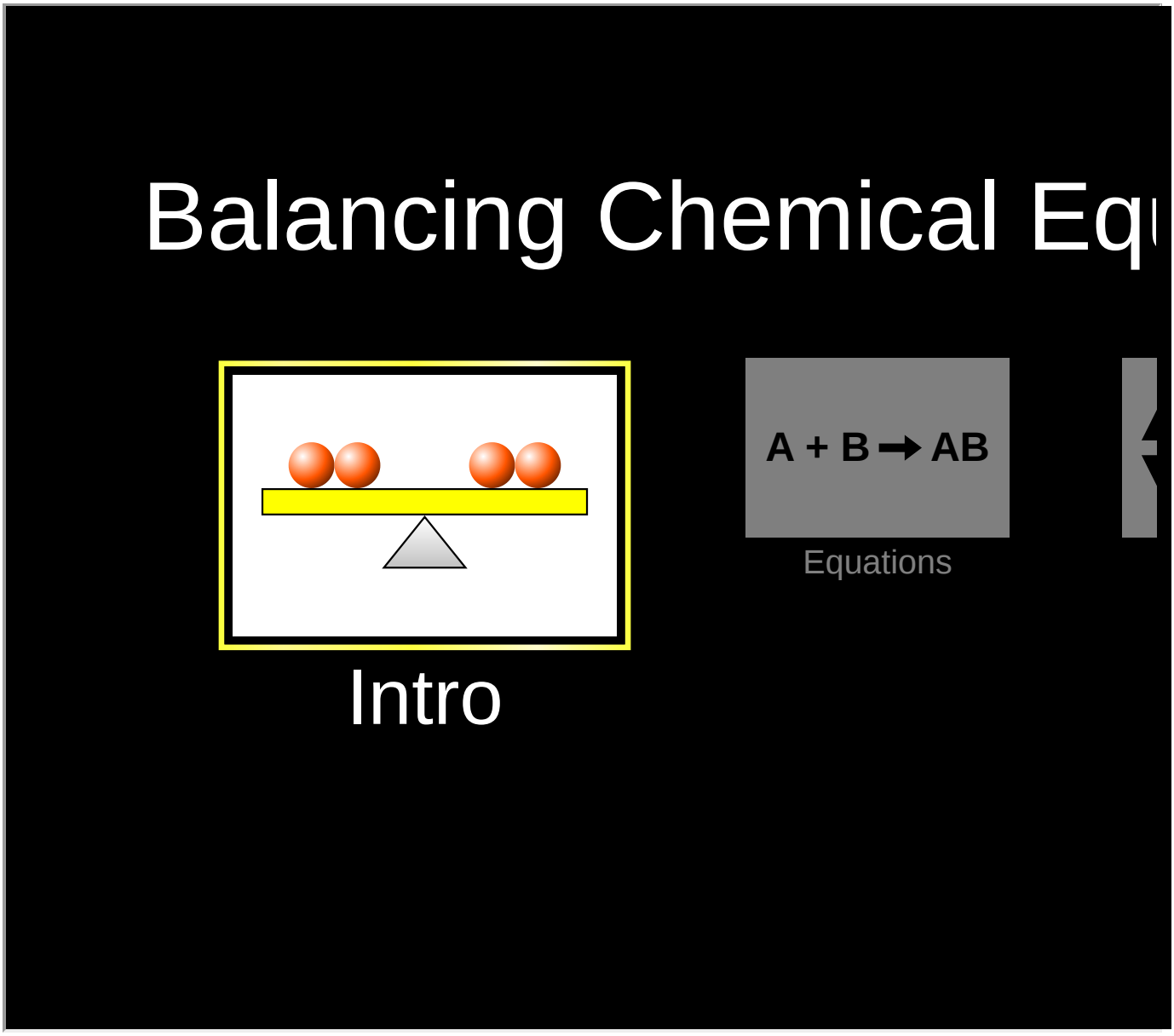
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7.11: PhET- Balancing Chemical Equations



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7.E: Chemical Reactions and Equations (Exercises)

Exercises (The Chemical Equation)

1. From the statement “nitrogen and hydrogen react to produce ammonia,” identify the reactants and the products.
2. From the statement “sodium metal reacts with water to produce sodium hydroxide and hydrogen,” identify the reactants and the products.
3. From the statement “magnesium hydroxide reacts with nitric acid to produce magnesium nitrate and water,” identify the reactants and the products.
4. From the statement “propane reacts with oxygen to produce carbon dioxide and water,” identify the reactants and the products.
5. Write and balance the chemical equation described by Exercise 1.
6. Write and balance the chemical equation described by Exercise 2.
7. Write and balance the chemical equation described by Exercise 3.
8. Write and balance the chemical equation described by Exercise 4. The formula for propane is C_3H_8.
9. Balance: ___$NaClO_3$ → ___NaCl + ___O_2
10. Balance: ___N_2 + ___H_2 → ___N_2H_4
11. Balance: ___Al + ___O_2 → ___Al_2O_3
12. Balance: ___C_2H_4 + ___O_2 → ___CO_2 + ___H_2O
13. How would you write the balanced chemical equation in Exercise 10 if all substances were gases?
14. How would you write the balanced chemical equation in Exercise 12 if all the substances except water were gases and water itself were a liquid?

Answers

1. reactants: nitrogen and hydrogen; product: ammonia

3. reactants: magnesium hydroxide and nitric acid; products: magnesium nitrate and water

5. $N_2 + 3H_2 \rightarrow 2NH_3$

7. $Mg(OH)_2 + 2HNO_3 \rightarrow Mg(NO_3)_2 + 2H_2O$

9. $2NaClO_3 \rightarrow 2NaCl + 3O_2$

11. $4Al + 3O_2 \rightarrow 2Al_2O_3$

13. $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

Exercises (Types of Chemical Reactions - Single and Double Displacement Reactions)

1. What are the general characteristics that help you recognize single-replacement reactions?

2. What are the general characteristics that help you recognize double-replacement reactions?

3. Assuming that each single-replacement reaction occurs, predict the products and write each balanced chemical equation.
   a. $Zn + Fe(NO_3)_2 \rightarrow$?
   b. $F_2 + FeI_3 \rightarrow$?

4. Assuming that each single-replacement reaction occurs, predict the products and write each balanced chemical equation.
   a. $Li + MgSO_4 \rightarrow$?

b. $NaBr + Cl_2 \rightarrow ?$

5. Assuming that each single-replacement reaction occurs, predict the products and write each balanced chemical equation.
   a. $Sn + H_2SO_4 \rightarrow ?$
   b. $Al + NiBr_2 \rightarrow ?$

6. Assuming that each single-replacement reaction occurs, predict the products and write each balanced chemical equation.
   a. $Mg + HCl \rightarrow ?$
   b. $HI + Br_2 \rightarrow ?$

7. Use the periodic table or the activity series to predict if each single-replacement reaction will occur and, if so, write a balanced chemical equation.
   a. $FeCl_2 + Br_2 \rightarrow ?$
   b. $Fe(NO_3)_3 + Al \rightarrow ?$

8. Use the periodic table or the activity series to predict if each single-replacement reaction will occur and, if so, write a balanced chemical equation.
   a. $Zn + Fe_3(PO_4)_2 \rightarrow ?$
   b. $Ag + HNO_3 \rightarrow ?$

9. Use the periodic table or the activity series to predict if each single-replacement reaction will occur and, if so, write a balanced chemical equation.
   a. $NaI + Cl_2 \rightarrow ?$
   b. $AgCl + Au \rightarrow ?$

10. Use the periodic table or the activity series to predict if each single-replacement reaction will occur and, if so, write a balanced chemical equation.
    a. $Pt + H_3PO_4 \rightarrow ?$
    b. $Li + H_2O \rightarrow ?$ (Hint: treat H_2O as if it were composed of H^+ and OH^- ions.)

11. Assuming that each double-replacement reaction occurs, predict the products and write each balanced chemical equation.
    a. $Zn(NO_3)_2 + NaOH \rightarrow ?$
    b. $HCl + Na_2S \rightarrow ?$

12. Assuming that each double-replacement reaction occurs, predict the products and write each balanced chemical equation.
    a. $Ca(C_2H_3O_2)_2 + HNO_3 \rightarrow ?$
    b. $Na_2CO_3 + Sr(NO_2)_2 \rightarrow ?$

13. Assuming that each double-replacement reaction occurs, predict the products and write each balanced chemical equation.
    a. $Pb(NO_3)_2 + KBr \rightarrow ?$
    b. $K_2O + MgCO_3 \rightarrow ?$

14. Assuming that each double-replacement reaction occurs, predict the products and write each balanced chemical equation.
    a. $Sn(OH)_2 + FeBr_3 \rightarrow ?$
    b. $CsNO_3 + KCl \rightarrow ?$

15. Use the solubility rules to predict if each double-replacement reaction will occur and, if so, write a balanced chemical equation.

a. $Pb(NO_3)_2 + KBr \rightarrow ?$
b. $K_2O + Na_2CO_3 \rightarrow ?$

16. Use the solubility rules to predict if each double-replacement reaction will occur and, if so, write a balanced chemical equation.

a. $Na_2CO_3 + Sr(NO_2)_2 \rightarrow ?$
b. $(NH_4)_2SO_4 + Ba(NO_3)_2 \rightarrow ?$

17. Use the solubility rules to predict if each double-replacement reaction will occur and, if so, write a balanced chemical equation.

a. $K_3PO_4 + SrCl_2 \rightarrow ?$
b. $NaOH + MgCl_2 \rightarrow ?$

18. Use the solubility rules to predict if each double-replacement reaction will occur and, if so, write a balanced chemical equation.

a. $KC_2H_3O_2 + Li_2CO_3 \rightarrow ?$
b. $KOH + AgNO_3 \rightarrow ?$

Answers

1. One element replaces another element in a compound.

3.

a. $Zn + Fe(NO_3)_2 \rightarrow Zn(NO_3)_2 + Fe$
b. $3F_2 + 2FeI_3 \rightarrow 3I_2 + 2FeF_3$

5.

a. $Sn + H_2SO_4 \rightarrow SnSO_4 + H_2$
b. $2Al + 3NiBr_2 \rightarrow 2AlBr_3 + 3Ni$

7.

a. No reaction occurs.
b. $Fe(NO_3)_3 + Al \rightarrow Al(NO_3)_3 + Fe$

9.

a. $2NaI + Cl_2 \rightarrow 2NaCl + I_2$
b. No reaction occurs.

11.

1. $Zn(NO_3)_2 + 2NaOH \rightarrow Zn(OH)_2 + 2NaNO_3$
2. $2HCl + Na_2S \rightarrow 2NaCl + H_2S$

13.

a. $Pb(NO_3)_2 + 2KBr \rightarrow PbBr_2 + 2KNO_3$
b. $K_2O + MgCO_3 \rightarrow K_2CO_3 + MgO$

15.

a. $Pb(NO_3)_2 + 2KBr \rightarrow PbBr_2(s) + 2KNO_3$
b. No reaction occurs.

17.

a. $2K_3PO_4 + 3SrCl_2 \rightarrow Sr_3(PO_4)_2(s) + 6KCl$
b. $2NaOH + MgCl_2 \rightarrow 2NaCl + Mg(OH)_2(s)$

Exercises (Ionic Equations - A Closer Look)

1. Write a chemical equation that represents NaBr(s) dissociating in water.
2. Write a chemical equation that represents $SrCl_2$(s) dissociating in water.
3. Write a chemical equation that represents $(NH_4)_3PO_4$(s) dissociating in water.
4. Write a chemical equation that represents $Fe(C_2H_3O_2)_3$(s) dissociating in water.
5. Write the complete ionic equation for the reaction of $FeCl_2$(aq) and $AgNO_3$(aq). You may have to consult the solubility rules.
6. Write the complete ionic equation for the reaction of $BaCl_2$(aq) and Na_2SO_4(aq). You may have to consult the solubility rules.
7. Write the complete ionic equation for the reaction of KCl(aq) and $NaC_2H_3O_2$(aq). You may have to consult the solubility rules.
8. Write the complete ionic equation for the reaction of $Fe_2(SO_4)_3$(aq) and $Sr(NO_3)_2$(aq). You may have to consult the solubility rules.
9. Write the net ionic equation for the reaction of $FeCl_2$(aq) and $AgNO_3$(aq). You may have to consult the solubility rules.
10. Write the net ionic equation for the reaction of $BaCl_2$(aq) and Na_2SO_4(aq). You may have to consult the solubility rules.
11. Write the net ionic equation for the reaction of KCl(aq) and $NaC_2H_3O_2$(aq). You may have to consult the solubility rules.
12. Write the net ionic equation for the reaction of $Fe_2(SO_4)_3$(aq) and $Sr(NO_3)_2$(aq). You may have to consult the solubility rules.
13. Identify the spectator ions in Exercises 9 and 10.
14. Identify the spectator ions in Exercises 11 and 12.

Answers

1. $\mathrm{NaBr(s) \xrightarrow{H_2O} Na^+(aq) + Br^-(aq)}$
3. $\mathrm{(NH_4)_3\,PO_4(\,s) \xrightarrow{H_2O} 3NH_4^+(aq) + PO_4^{3-}(aq)}$
5. $\mathrm{Fe^{2+}(aq) + 2Cl^-(aq) + 2Ag^+(aq) + 2NO_3^-(aq) \rightarrow Fe^{2+}(aq) + 2NO_3^-(aq) + 2AgCl(s)}$
7. $\mathrm{K^+(aq) + Cl^-(aq) + Na^+(aq) + C_2H_3O_2^-(aq) \rightarrow Na^+(aq) + Cl^-(aq) + K^+(aq) + C_2H_3O_2^-(aq)}$
9. $\mathrm{2Cl^-(aq) + 2Ag^+(aq) \rightarrow 2AgCl(s)}$
11. There is no overall reaction.
13. In Exercise 9, $\mathrm{Fe^{2+}(aq)}$ and $\mathrm{NO_3^-(aq)}$ are spectator ions; in Exercise 10, $\mathrm{Na^+(aq)}$ and $\mathrm{Cl^-(aq)}$ are spectator ions.

Exercises (Composition, Decomposition, and Combustion Reactions)

1. Which is a composition reaction and which is not?
   a. $NaCl + AgNO_3 \rightarrow AgCl + NaNO_3$
   b. $CaO + CO_2 \rightarrow CaCO_3$

2. Which is a composition reaction and which is not?
   a. $H_2 + Cl_2 \rightarrow 2HCl$
   b. $2HBr + Cl_2 \rightarrow 2HCl + Br_2$

3. Which is a composition reaction and which is not?
   a. $2SO_2 + O_2 \rightarrow 2SO_3$
   b. $6C + 3H_2 \rightarrow C_6H_6$

4. Which is a composition reaction and which is not?
   a. $4Na + 2C + 3O_2 \rightarrow 2Na_2CO_3$

b. $Na_2CO_3 \rightarrow Na_2O + CO_2$

5. Which is a decomposition reaction and which is not?
   a. $HCl + NaOH \rightarrow NaCl + H_2O$
   b. $CaCO_3 \rightarrow CaO + CO_2$

6. Which is a decomposition reaction and which is not?
   a. $3O_2 \rightarrow 2O_3$
   b. $2KClO_3 \rightarrow 2KCl + 3O_2$

7. Which is a decomposition reaction and which is not?
   a. $Na_2O + CO_2 \rightarrow Na_2CO_3$
   b. $H_2SO_3 \rightarrow H_2O + SO_2$

8. Which is a decomposition reaction and which is not?
   a. $2C_7H_5N_3O_6 \rightarrow 3N_2 + 5H_2O + 7CO + 7C$
   b. $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

9. Which is a combustion reaction and which is not?
   a. $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$
   b. $2Fe_2S_3 + 9O_2 \rightarrow 2Fe_2O_3 + 6SO_2$

10. Which is a combustion reaction and which is not?
    a. $CH_4 + 2F_2 \rightarrow CF_4 + 2H_2$
    b. $2H_2 + O_2 \rightarrow 2H_2O$

11. Which is a combustion reaction and which is not?
    a. $P_4 + 5O_2 \rightarrow 2P_2O_5$
    b. $2Al_2S_3 + 9O_2 \rightarrow 2Al_2O_3 + 6SO_2$

12. Which is a combustion reaction and which is not?
    a. $C_2H_4 + O_2 \rightarrow C_2H_4O_2$
    b. $C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$

13. Is it possible for a composition reaction to also be a combustion reaction? Give an example to support your case.

14. Is it possible for a decomposition reaction to also be a combustion reaction? Give an example to support your case.

15. Complete and balance each combustion equation.
    a. $C_4H_9OH + O_2 \rightarrow ?$
    b. $CH_3NO_2 + O_2 \rightarrow ?$

16. Complete and balance each combustion equation.
    a. $B_2H_6 + O_2 \rightarrow ?$ (The oxide of boron formed is B_2O_3.)
    b. $Al_2S_3 + O_2 \rightarrow ?$ (The oxide of sulfur formed is SO_2.)
    c. $Al_2S_3 + O_2 \rightarrow ?$ (The oxide of sulfur formed is SO_3.)

Answers

1.

a. not composition
b. composition

3.

a. composition
b. composition

5.

a. not decomposition
b. decomposition

7.

a. not decomposition
b. decomposition

9.

a. combustion
b. combustion

11.

a. combustion
b. combustion

13. Yes; $2H_2 + O_2 \rightarrow 2H_2O$ (answers will vary)

15.

a. $C_4H_9OH + 6O_2 \rightarrow 4CO_2 + 5H_2O$
b. $4CH_3NO_2 + 3O_2 \rightarrow 4CO_2 + 6H_2O + 2N_2$

Exercises (Neutralization Reactions)

1. What is the Arrhenius definition of an acid?

2. What is the Arrhenius definition of a base?

3. Predict the products of each acid-base combination listed. Assume that a neutralization reaction occurs.
   a. HCl and KOH
   b. H_2SO_4 and KOH
   c. H_3PO_4 and $Ni(OH)_2$

4. Predict the products of each acid-base combination listed. Assume that a neutralization reaction occurs.
   a. HBr and $Fe(OH)_3$
   b. HNO_2 and $Al(OH)_3$
   c. $HClO_3$ and $Mg(OH)_2$

5. Write a balanced chemical equation for each neutralization reaction in Exercise 3.

6. Write a balanced chemical equation for each neutralization reaction in Exercise 4.

7. Write a balanced chemical equation for the neutralization reaction between each given acid and base. Include the proper phase labels.
   a. $HI(aq) + KOH(aq) \rightarrow ?$
   b. $H_2SO_4(aq) + Ba(OH)_2(aq) \rightarrow ?$

8. Write a balanced chemical equation for the neutralization reaction between each given acid and base. Include the proper phase labels.
   a. $HNO_3(aq) + Fe(OH)_3(s) \rightarrow ?$
   b. $H_3PO_4(aq) + CsOH(aq) \rightarrow ?$

9. Write the net ionic equation for each neutralization reaction in Exercise 7.

10. Write the net ionic equation for each neutralization reaction in Exercise 8.

11. Write the complete and net ionic equations for the neutralization reaction between $HClO_3(aq)$ and $Zn(OH)_2(s)$. Assume the salt is soluble.

12. Write the complete and net ionic equations for the neutralization reaction between $H_2C_2O_4(s)$ and $Sr(OH)_2(aq)$. Assume the salt is insoluble.

13. Explain why the net ionic equation for the neutralization reaction between HCl(aq) and KOH(aq) is the same as the net ionic equation for the neutralization reaction between $HNO_3(aq)$ and RbOH.

14. Explain why the net ionic equation for the neutralization reaction between HCl(aq) and KOH(aq) is different from the net ionic equation for the neutralization reaction between HCl(aq) and AgOH.

15. Write the complete and net ionic equations for the neutralization reaction between HCl(aq) and KOH(aq) using the hydronium ion in place of H^+. What difference does it make when using the hydronium ion?

16. Write the complete and net ionic equations for the neutralization reaction between $HClO_3(aq)$ and $Zn(OH)_2(s)$ using the hydronium ion in place of H^+. Assume the salt is soluble. What difference does it make when using the hydronium ion?

Answers

1. An Arrhenius acid increases the amount of H^+ ions in an aqueous solution.

3.
   a. KCl and H_2O
   b. K_2SO_4 and H_2O
   c. $Ni_3(PO_4)_2$ and H_2O

5.
   a. $HCl + KOH \rightarrow KCl + H_2O$
   b. $H_2SO_4 + 2KOH \rightarrow K_2SO_4 + 2H_2O$
   c. $2H_3PO_4 + 3Ni(OH)_2 \rightarrow Ni_3(PO_4)_2 + 6H_2O$

7.
   a. $HI(aq) + KOH(aq) \rightarrow KI(aq) + H_2O(\ell)$
   b. $H_2SO_4(aq) + Ba(OH)_2(aq) \rightarrow BaSO_4(s) + 2H_2O(\ell)$

9.

a. $H^+(aq) + OH^-(aq) \rightarrow H_2O(\ell)$
b. $2H^+(aq) + SO_4^{2-}(aq) + Ba^{2+}(aq) + 2OH^-(aq) \rightarrow BaSO_4(s) + 2H_2O(\ell)$

11. Complete ionic equation:

$2H^+(aq) + 2ClO_3^-(aq) + Zn^{2+}(aq) + 2OH^-(aq) \rightarrow Zn^{2+}(aq) + 2ClO_3^-(aq) + 2H_2O(\ell)$

Net ionic equation:

$2H^+(aq) + 2OH^-(aq) \rightarrow 2H_2O(\ell)$

13. Because the salts are soluble in both cases, the net ionic reaction is just $H^+(aq) + OH^-(aq) \rightarrow H_2O(\ell)$.

15. Complete ionic equation:

$H_3O^+(aq) + Cl^-(aq) + K^+(aq) + OH^-(aq) \rightarrow 2H_2O(\ell) + K^+(aq) + Cl^-(aq)$

Net ionic equation:

$H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O(\ell)$

17. The difference is simply the presence of an extra water molecule as a product.

Exercises (Oxidation-Reduction Reactions)

1. Is the reaction

$2K(s) + Br_2(\ell) \rightarrow 2KBr(s)$

an oxidation-reduction reaction? Explain your answer.

2. Is the reaction

$NaCl(aq) + AgNO_3(aq) \rightarrow NaNO_3(aq) + AgCl(s)$

an oxidation-reduction reaction? Explain your answer.

3. In the reaction

$2Ca(s) + O_2(g) \rightarrow 2CaO$

indicate what has lost electrons and what has gained electrons.

4. In the reaction

$16Fe(s) + 3S_8(s) \rightarrow 8Fe_2S_3(s)$

indicate what has lost electrons and what has gained electrons.

5. In the reaction

$2Li(s) + O_2(g) \rightarrow Li_2O_2(s)$

indicate what has been oxidized and what has been reduced.

6. In the reaction

$2Ni(s) + 3I_2(s) \rightarrow 2NiI_3(s)$

indicate what has been oxidized and what has been reduced.

7. What are two different definitions of oxidation?

8. What are two different definitions of reduction?

9. Assign oxidation numbers to each atom in each substance.
   a. P_4
   b. SO_2
   c. SO_2^{2-}
   d. $Ca(NO_3)_2$

10. Assign oxidation numbers to each atom in each substance.
   a. PF_5
   b. $(NH_4)_2S$
   c. Hg
   d. Li_2O_2 (lithium peroxide)

11. Assign oxidation numbers to each atom in each substance.
   a. CO
   b. CO_2
   c. $NiCl_2$
   d. $NiCl_3$

12. Assign oxidation numbers to each atom in each substance.
   a. NaH (sodium hydride)
   b. NO_2
   c. NO_2^-
   d. $AgNO_3$

13. Assign oxidation numbers to each atom in each substance.
   a. CH_2O
   b. NH_3
   c. Rb_2SO_4
   d. $Zn(C_2H_3O_2)_2$

14. Assign oxidation numbers to each atom in each substance.
   a. C_6H_6
   b. $B(OH)_3$
   c. Li_2S
   d. Au

15. Identify what is being oxidized and reduced in this redox equation by assigning oxidation numbers to the atoms.

   $2NO + Cl_2 \rightarrow 2NOCl$

16. Identify what is being oxidized and reduced in this redox equation by assigning oxidation numbers to the atoms.

   $Fe + SO_3 \rightarrow FeSO_3$

17. Identify what is being oxidized and reduced in this redox equation by assigning oxidation numbers to the atoms.

   $2KrF_2 + 2H_2O \rightarrow 2Kr + 4HF + O_2$

18. Identify what is being oxidized and reduced in this redox equation by assigning oxidation numbers to the atoms.

$SO_3 + SCl_2 \rightarrow SOCl_2 + SO_2$

19. Identify what is being oxidized and reduced in this redox equation by assigning oxidation numbers to the atoms.

$2K + MgCl_2 \rightarrow 2KCl + Mg$

20. Identify what is being oxidized and reduced in this redox equation by assigning oxidation numbers to the atoms.

$C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O$

Answers

1. Yes; both K and Br are changing oxidation numbers.

3. Ca has lost electrons, and O has gained electrons.

5. Li has been oxidized, and O has been reduced.

7. loss of electrons; increase in oxidation number

9.

a. P: 0
b. S: +4; O: −2
c. S: +2; O: −2
d. Ca: 2+; N: +5; O: −2

11.

a. C: +2; O: −2
b. C: +4; O: −2
c. Ni: +2; Cl: −1
d. Ni: +3; Cl: −1

13.

a. C: 0; H: +1; O: −2
b. N: −3; H: +1
c. Rb: +1; S: +6; O: −2
d. Zn: +2; C: 0; H: +1; O: −2

15. N is being oxidized, and Cl is being reduced.

17. O is being oxidized, and Kr is being reduced.

19.K is being oxidized, and Mg is being reduced.

Additional Exercises

1. Chemical equations can also be used to represent physical processes. Write a chemical reaction for the boiling of water, including the proper phase labels.

2. Chemical equations can also be used to represent physical processes. Write a chemical reaction for the freezing of water, including the proper phase labels.

3. Explain why

$4Na(s) + 2Cl_2(g) \rightarrow 4NaCl(s)$

should not be considered a proper chemical equation.

4. Explain why

$H_2(g) + 1/2O_2(g) \rightarrow H_2O(\ell)$

should not be considered a proper chemical equation.

5. Does the chemical reaction represented by

$3Zn(s) + 2Al(NO_3)_3(aq) \rightarrow 3Zn(NO_3)_2(aq) + 2Al(s)$

proceed as written? Why or why not?

6. Does the chemical reaction represented by

$2Au(s) + 2HNO_3(aq) \rightarrow 2AuNO_3(aq) + H_2(g)$

proceed as written? Gold is a relatively useful metal for certain applications, such as jewelry and electronics. Does your answer suggest why this is so?

7. Explain what is wrong with this double-replacement reaction.

$NaCl(aq) + KBr(aq) \rightarrow NaK(aq) + ClBr(aq)$

8. Predict the products of and balance this double-replacement reaction.

$Ag_2SO_4(aq) + SrCl_2(aq) \rightarrow ?$

9. Write the complete and net ionic equations for this double-replacement reaction.

$BaCl_2(aq) + Ag_2SO_4(aq) \rightarrow ?$

10. Write the complete and net ionic equations for this double-replacement reaction.

$Ag_2SO_4(aq) + SrCl_2(aq) \rightarrow ?$

11. Identify the spectator ions in this reaction. What is the net ionic equation?

$NaCl(aq) + KBr(aq) \rightarrow NaBr(aq) + KCl(aq)$

12. Complete this reaction and identify the spectator ions. What is the net ionic equation?

$3H_2SO_4(aq) + 2Al(OH)_3(s) \rightarrow ?$

13. Can a reaction be a composition reaction and a redox reaction at the same time? Give an example to support your answer.

14. Can a reaction be a combustion reaction and a redox reaction at the same time? Give an example to support your answer.

15. Can a reaction be a decomposition reaction and a redox reaction at the same time? Give an example to support your answer.

16. Can a reaction be a combustion reaction and a double-replacement reaction at the same time? Give an example to support your answer.

17. Why is CH_4 not normally considered an acid?

18. Methyl alcohol has the formula CH_3OH. Why would methyl alcohol not normally be considered a base?

19. What are the oxidation numbers of the nitrogen atoms in these substances?

a. N_2
b. NH_3
c. NO
d. N_2O
e. NO_2
f. N_2O_4
g. N_2O_5
h. $NaNO_3$

20. What are the oxidation numbers of the sulfur atoms in these substances?

a. SF_6
b. Na_2SO_4
c. K_2SO_3
d. SO_3

e. SO_2
f. S_8
g. Na_2S

21. Disproportion is a type of redox reaction in which the same substance is both oxidized and reduced. Identify the element that is disproportionating and indicate the initial and final oxidation numbers of that element.

$$2CuCl(aq) \rightarrow CuCl_2(aq) + Cu(s)$$

22. Disproportion is a type of redox reaction in which the same substance is both oxidized and reduced. Identify the element that is disproportionating and indicate the initial and final oxidation numbers of that element.

$$3Cl_2(g) + 6OH^-(aq) \rightarrow 5Cl^-(aq) + ClO_3^-(aq) + 3H_2O(\ell)$$

Answers

1. $H_2O(\ell) \rightarrow H_2O(g)$

3. The coefficients are not in their lowest whole-number ratio.

5. No; zinc is lower in the activity series than aluminum.

7. In the products, the cation is pairing with the cation, and the anion is pairing with the anion.

9. Complete ionic equation: $Ba^{2+}(aq) + 2Cl^-(aq) + 2Ag^+(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s) + 2AgCl(s)$

Net ionic equation: The net ionic equation is the same as the complete ionic equation.

11. Each ion is a spectator ion; there is no overall net ionic equation.

13. Yes; $H_2 + Cl_2 \rightarrow 2HCl$ (answers will vary)

15, Yes; $2HCl \rightarrow H_2 + Cl_2$ (answers will vary)

17. It does not increase the H^+ ion concentration; it is not a compound of H^+.

19.

a. 0
b. −3
c. +2
d. +1
e. +4
f. +4
g. +5
h. +5

21. Copper is disproportionating. Initially, its oxidation number is +1; in the products, its oxidation numbers are +2 and 0, respectively.

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CHAPTER OVERVIEW

8: Acids and Bases

Acids and bases are important classes of chemical compounds. They are part of the foods and beverages we ingest, they are present in medicines and other consumer products, and they are prevalent in the world around us. In this chapter, we will focus on acids and bases and their chemistry.

8.1: Introduction
8.2: Arrhenius Acids and Bases
8.3: Brønsted-Lowry Acids and Bases
8.4: Acid-Base Titrations
8.5: Strong and Weak Acids and Bases and their Salts
8.6: Autoionization of Water
8.7: The pH Scale
8.8: Buffers
8.9: PhET- pH Scale
8.E: Acids and Bases (Exercises)

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8.1: Introduction

Formerly there were rather campy science-fiction television shows in which the hero was always being threatened with death by being plunged into a vat of boiling acid: "Mwa ha ha, Buck Rogers [or whatever the hero's name was], prepare to meet your doom by being dropped into a vat of boiling acid!" (The hero always escapes, of course.) This may have been interesting drama, but not very good chemistry. If the villain knew his/her/its science, the hero would have been dropped into a vat of boiling base.

Recall that the active component of a classic acid is the H^+ ion, while the active part of a classic base is the OH^- ion. Both ions are related to water in that all H^+ ion needs to become a water molecule is an OH^- ion, while all an OH^- ion needs to become water is an H^+ ion. Consider the relative masses involved: an ion of mass 1 needs an ion of mass 17 to make water, while an ion of mass 17 needs an ion of mass 1 to make water. Which process do you think will be easier?

In fact, bases are more potentially dangerous than acids because it is much easier for an OH^- ion to rip off an H^+ ion from surrounding matter than it is for an H^+ ion to rip off an OH^- ion. Certain household chemicals, such as some brands of cleaner, can be very concentrated bases, which makes them among the most potentially hazardous substances found around the home. If spilled on the skin, these strong caustic compounds can immediately remove H^+ ions from the flesh, resulting in chemical burns. Compare this to the fact that we occasionally purposefully ingest substances such as citrus fruits, vinegar, and wine—all of which contain acids. (Of course, some parts of the body, such as the eyes, are extremely sensitive to acids as well as bases.) It seems that our bodies are more capable of dealing with acids than with bases.



Figure **8.1.1** Household chemicals © Thinkstock. On the left is a common acid, and on the right is a common base. Which one is more potentially hazardous?

A note to all of the villains out there...get your chemistry right if you want to be successful!

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8.2: Arrhenius Acids and Bases

Learning Objective

- Identify an Arrhenius acid and an Arrhenius base.
- Write the chemical reaction between an Arrhenius acid and an Arrhenius base.

Historically, the first chemical definition of an acid and a base was put forward by Svante Arrhenius, a Swedish chemist, in 1884. An **Arrhenius acid** is a compound that increases the H^+ ion concentration in an aqueous solution. The H^+ ion is just a bare proton, and it is rather clear that bare protons are not floating around in an aqueous solution. Instead, chemistry has defined the **hydronium ion** (H_3O^+) as the actual chemical species that represents an H^+ ion. H^+ ions and H_3O^+ ions are often considered interchangeable when writing chemical equations (although a properly balanced chemical equation should also include the additional H_2O). Classic Arrhenius acids can be considered ionic compounds in which H^+ is the cation. Table **8.2.1** lists some Arrhenius acids and their names.

Table **8.2.1** Some Arrhenius Acids

Formula	Name
$HC_2H_3O_2$ (also written CH_3COOH)	acetic acid
$HClO_3$	chloric acid
HCl	hydrochloric acid
HBr	hydrobromic acid
HI	hydriodic acid
HF	hydrofluoric acid
HNO_3	nitric acid
$H_2C_2O_4$	oxalic acid
$HClO_4$	perchloric acid
H_3PO_4	phosphoric acid
H_2SO_4	sulfuric acid
H_2SO_3	sulfurous acid

An **Arrhenius base** is a compound that increases the OH^- ion concentration in aqueous solution. Ionic compounds of the OH^- ion are classic Arrhenius bases.

Example 8.2.1

Identify each compound as an Arrhenius acid, an Arrhenius base, or neither.

a. HNO_3
b. CH_3OH
c. $Mg(OH)_2$

Solution

a. This compound is an ionic compound between H^+ ions and NO_3^- ions, so it is an Arrhenius acid.
b. Although this formula has an OH in it, we do not recognize the remaining part of the molecule as a cation. It is neither an acid nor a base. (In fact, it is the formula for methanol, an organic compound.)
c. This formula also has an OH in it, but this time we recognize that the magnesium is present as Mg^{2+} cations. As such, this is an ionic compound of the OH^- ion and is an Arrhenius base.

Exercise 8.2.1

Identify each compound as an Arrhenius acid, an Arrhenius base, or neither.

1. KOH
2. H_2SO_4
3. C_2H_6

Answer

1. Arrhenius base
2. Arrhenius acid
3. neither

Acids have some properties in common. They turn litmus, a plant extract, red. They react with some metals to give off H_2 gas. They react with carbonate and hydrogen carbonate salts to give off CO_2 gas. Acids that are ingested typically have a sour, sharp taste. (The name *acid* comes from the Latin word *acidus*, meaning "sour.") Bases also have some properties in common. They are slippery to the touch, turn litmus blue, and have a bitter flavor if ingested.

Acids and bases have another property: they react with each other to make water and an ionic compound called a salt. A **salt**, in chemistry, is any ionic compound made by combining an acid with a base. A reaction between an acid and a base is called a **neutralization reaction** and can be represented as:

$$\text{acid} + \text{base} \rightarrow H_2O + \text{salt}$$

The stoichiometry of the balanced chemical equation depends on the number of H^+ ions in the acid and the number of OH^- ions in the base.

Example 8.2.2

Write the balanced chemical equation for the neutralization reaction between H_2SO_4 and KOH. What is the name of the salt that is formed?

Solution

The general reaction is as follows:

$$H_2SO_4 + KOH \rightarrow H_2O + \text{salt}$$

Because the acid has two H^+ ions in its formula, we need two OH^- ions to react with it, making two H_2O molecules as product. The remaining ions, K^+ and SO_4^{2-}, make the salt potassium sulfate (K_2SO_4). The balanced chemical reaction is as follows:

$$H_2SO_4 + 2KOH \rightarrow 2H_2O + K_2SO_4$$

Exercise 8.2.2

Write the balanced chemical equation for the neutralization reaction between HCl and $Mg(OH)_2$. What is the name of the salt that is formed?

Answer

$2HCl + Mg(OH)_2 \rightarrow 2H_2O + MgCl_2$; magnesium chloride

Key Takeaways

- An Arrhenius acid is a compound that increases the H^+ ion concentration in aqueous solution.
- An Arrhenius base is a compound that increases the OH^- ion concentration in aqueous solution.
- The reaction between an Arrhenius acid and an Arrhenius base is called neutralization and results in the formation of water and a salt.

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8.3: Brønsted-Lowry Acids and Bases

Learning Objectives

- Identify a Brønsted-Lowry acid and a Brønsted-Lowry base.
- Identify conjugate acid-base pairs in an acid-base reaction.

The Arrhenius definition of acid and base is limited to aqueous (that is, water) solutions. Although this is useful because water is a common solvent, it is limited to the relationship between the H^+ ion and the OH^- ion. What would be useful is a general definition more applicable to other chemical reactions and, importantly, independent of H_2O.

In 1923, Danish chemist Johannes Brønsted and English chemist Thomas Lowry independently proposed new definitions for acids and bases, ones that focus on proton transfer. A **Brønsted-Lowry acid** is any species that can donate a proton (H^+) to another molecule. A **Brønsted-Lowry base** is any species that can accept a proton from another molecule. In short, a Brønsted-Lowry acid is a proton donor (PD), while a Brønsted-Lowry base is a proton acceptor (PA).

It is easy to see that the Brønsted-Lowry definition covers the Arrhenius definition of acids and bases. Consider the prototypical Arrhenius acid-base reaction:

$$\underset{acid}{H^+(aq)} + \underset{base}{OH^-(aq)} \rightarrow H_2O\,(l)$$

Acid species and base species are marked. The proton, however, is (by definition) a proton donor (labeled PD), while the OH^- ion is acting as the proton acceptor (labeled PA):

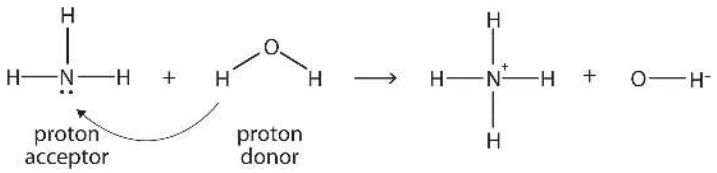
$$\underset{PD}{H^+(aq)} + \underset{PA}{OH^-(aq)} \rightarrow H_2O\,(l)$$

The proton donor is a Brønsted-Lowry acid, and the proton acceptor is the Brønsted-Lowry base:

$$\underset{BL\ acid}{H^+(aq)} + \underset{BL\ base}{OH^-(aq)} \rightarrow H_2O\,(l)$$

Thus H^+ is an acid by both definitions, and OH^- is a base by both definitions.

Ammonia (NH_3) is a base even though it does not contain OH^- ions in its formula. Instead, it generates OH^- ions as the product of a proton-transfer reaction with H_2O molecules; NH_3 acts like a Brønsted-Lowry base, and H_2O acts like a Brønsted-Lowry acid:



A reaction with water is called **hydrolysis**; we say that NH_3 hydrolyzes to make NH_4^+ ions and OH^- ions.

Even the dissolving of an Arrhenius acid in water can be considered a Brønsted-Lowry acid-base reaction. Consider the process of dissolving HCl(g) in water to make an aqueous solution of hydrochloric acid. The process can be written as follows:

$$HCl\,(g) + H_2O(\ell) \longrightarrow H_3O^+\,(aq) + Cl^-\,(aq)$$

HCl(g) is the proton donor and therefore a Brønsted-Lowry acid, while H_2O is the proton acceptor and a Brønsted-Lowry base. These two examples show that H_2O can act as both a proton donor and a proton acceptor, depending on what other substance is in the chemical reaction. A substance that can act as a proton donor or a proton acceptor is called **amphiprotic**. Water is probably the most common amphiprotic substance we will encounter, but other substances are also amphiprotic.

Example 8.3.1

Identify the Brønsted-Lowry acid and the Brønsted-Lowry base in this chemical equation.

$$\mathbf{C_6H_5OH + NH_2^- \longrightarrow C_6H_5O^- + NH_3}$$

Solution

The C_6H_5OH molecule is losing an H^+; it is the proton donor and the Brønsted-Lowry acid. The NH_2^- ion (called the amide ion) is accepting the H^+ ion to become NH_3, so it is the Brønsted-Lowry base.

Exercise 8.3.1: Aluminum Ions in Solution

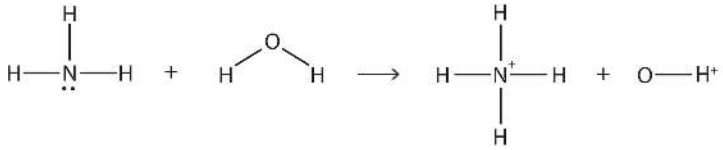
Identify the Brønsted-Lowry acid and the Brønsted-Lowry base in this chemical equation.

$$\mathbf{Al(H_2O)_6^{3+} + H_2O \longrightarrow Al(H_2O)_5(OH)^{2+} + H_3O^+}$$

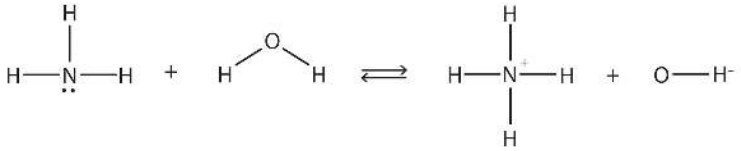
Answer

Brønsted-Lowry acid: $Al(H_2O)_6^{3+}$; Brønsted-Lowry base: H_2O

In the reaction between NH_3 and H_2O,



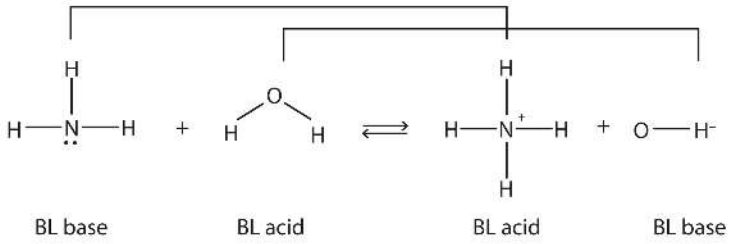
the chemical reaction does not go to completion; rather, the reverse process occurs as well, and eventually the two processes cancel out any additional change. At this point, we say the chemical reaction is at *equilibrium*. Both processes still occur, but any net change by one process is countered by the same net change of the other process; it is a *dynamic*, rather than a *static*, equilibrium. Because both reactions are occurring, it makes sense to use a double arrow instead of a single arrow:



What do you notice about the reverse reaction? The NH_4^+ ion is donating a proton to the OH^- ion, which is accepting it. This means that the NH_4^+ ion is acting as the proton donor, or Brønsted-Lowry acid, while the OH^- ion, the proton acceptor, is acting as a Brønsted-Lowry base. The reverse reaction is also a Brønsted-Lowry acid base reaction:

BL bases. NH4+ and H2O are the BL acids. lt-chem-64081" style="width: 750px; height: 173px;" width="750px" height="173px" src="/@api/deki/files/92035/3765cabac9591a0fb3dd5878f56075e2.jpg" data-quail-id="174">

This means that both reactions are acid-base reactions by the Brønsted-Lowry definition. If you consider the species in this chemical reaction, two sets of similar species exist on both sides. Within each set, the two species differ by a proton in their formulas, and one member of the set is a Brønsted-Lowry acid, while the other member is a Brønsted-Lowry base. These sets are marked here:



The two sets—NH_3/NH_4^+ and H_2O/OH^-—are called **conjugate acid-base pairs**. We say that NH_4^+ is the conjugate acid of NH_3, OH^- is the conjugate base of H_2O, and so forth. Every Brønsted-Lowry acid-base reaction can be labeled with two conjugate acid-base pairs.

✔ Example 8.3.2

Identify the conjugate acid-base pairs in this equilibrium.

$$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$$

Solution

One pair is H_2O and OH^-, where H_2O has one more H^+ and is the conjugate acid, while OH^- has one less H^+ and is the conjugate base. The other pair consists of $(CH_3)_3N$ and $(CH_3)_3NH^+$, where $(CH_3)_3NH^+$ is the conjugate acid (it has an additional proton) and $(CH_3)_3N$ is the conjugate base.

? Exercise 8.3.2

Identify the conjugate acid-base pairs in this equilibrium.

$$NH_2^- + H_2O \rightleftharpoons NH_3 + OH^-$$

Answer

H_2O (acid) and OH^- (base); NH_2^- (base) and NH_3 (acid)

✔ Chemistry is Everywhere: Household Acids and Bases

Many household products are acids or bases. For example, the owner of a swimming pool may use muriatic acid to clean the pool. Muriatic acid is another name for HCl(aq). In Section 4.6, vinegar was mentioned as a dilute solution of acetic acid [$HC_2H_3O_2$(aq)]. In a medicine chest, one may find a bottle of vitamin C tablets; the chemical name of vitamin C is ascorbic acid ($HC_6H_7O_6$).

One of the more familiar household bases is NH_3, which is found in numerous cleaning products. NH_3 is a base because it increases the OH^- ion concentration by reacting with H_2O:

$NH_3(aq) + H_2O(\ell) \rightarrow NH_4^+(aq) + OH^-(aq)$

Many soaps are also slightly basic because they contain compounds that act as Brønsted-Lowry bases, accepting protons from H_2O and forming excess OH^- ions. This is one explanation for why soap solutions are slippery.

Perhaps the most dangerous household chemical is the lye-based drain cleaner. Lye is a common name for NaOH, although it is also used as a synonym for KOH. Lye is an extremely caustic chemical that can react with grease, hair, food particles, and other substances that may build up and clog a water pipe. Unfortunately, lye can also attack body tissues and other substances in our bodies. Thus when we use lye-based drain cleaners, we must be very careful not to touch any of the solid drain cleaner or spill the water it was poured into. Safer, non-lye drain cleaners (like the one in the accompanying figure) use peroxide compounds to react on the materials in the clog and clear the drain.



Figure **8.3.1** Drain Cleaners. Drain cleaners can be made from a reactive material that is less caustic than a base. Source: Photo used by permission of Citrasolv, LLC.

Key Takeaways

- A Brønsted-Lowry acid is a proton donor; a Brønsted-Lowry base is a proton acceptor.
- Acid-base reactions include two sets of conjugate acid-base pairs.

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8.4: Acid-Base Titrations

Learning Objectives

- Describe a titration experiment.
- Explain what an indicator does.
- Perform a titration calculation correctly.

The reaction of an acid with a base to make a salt and water is a common reaction in the laboratory, partly because many compounds can act as acids or bases. Another reason that acid-base reactions are so prevalent is because they are often used to determine quantitative amounts of one or the other. Performing chemical reactions quantitatively to determine the exact amount of a reagent is called a **titration**. A titration can be performed with almost any chemical reaction for which the balanced chemical equation is known. Here, we will consider titrations that involve acid-base reactions.

In a titration, one reagent has a known concentration or amount, while the other reagent has an unknown concentration or amount. Typically, the known reagent (the **titrant**) is added to the unknown quantity and is dissolved in solution. The unknown amount of substance (the **analyte**) may or may not be dissolved in solution (but usually is). The titrant is added to the analyte using a precisely calibrated volumetric delivery tube called a burette (also spelled buret; see Figure 8.4.1). 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 8.4.1 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 8.4.1

What mass of $Ca(OH)_2$ is present in a sample if it is titrated to its equivalence point with 44.02 mL of 0.0885 M HNO_3? The balanced chemical equation is as follows:

$$2\text{HNO}_3 + \text{Ca(OH)}_2 \rightarrow \text{Ca(NO}_3\text{)}_2 + 2\text{H}_2\text{O}$$

Solution

In liters, the volume is 0.04402 L. We calculate the number of moles of titrant:

moles HNO_3 = (0.04402 L)(0.0885 M) = 0.00390 mol HNO_3

Using the balanced chemical equation, we can determine the number of moles of $Ca(OH)_2$ present in the analyte:

$$0.00390\ \cancel{mol\ HNO_3} \times \frac{1\ mol\ Ca(OH)_2}{2\ \cancel{mol\ HNO_3}} = 0.00195\ mol\ Ca(OH)_2$$

Then we convert this to a mass using the molar mass of $Ca(OH)_2$:

$$0.00195\ \cancel{mol\ Ca(OH)_2} \times \frac{74.1\ g\ Ca(OH)_2}{\cancel{mol\ Ca(OH)_2}} = 0.144\ g\ Ca(OH)_2$$

? Exercise 8.4.1

What mass of $H_2C_2O_4$ is present in a sample if it is titrated to its equivalence point with 18.09 mL of 0.2235 M NaOH? The balanced chemical reaction is as follows:

$$H_2C_2O_4 + 2\,NaOH \longrightarrow Na_2C_2O_4 + 2\,H_2O$$

Answer

0.182 g

How does one know if a reaction is at its equivalence point? Usually, the person performing the titration adds a small amount of an **indicator**, a substance that changes color depending on the acidity or basicity of the solution. Because different indicators change colors at different levels of acidity, choosing the correct one is important in performing an accurate titration.

Summary

A titration is the quantitative reaction of an acid and a base. Indicators are used to show that all of the analyte has reacted with the titrant.

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8.5: Strong and Weak Acids and Bases and their Salts

Learning Objectives

- Define a strong and a weak acid and base.
- Recognize an acid or a base as strong or weak.
- Determine if a salt produces an acidic or a basic solution.

Except for their names and formulas, so far we have treated all acids as equals, especially in a chemical reaction. However, acids can be very different in a very important way. Consider $\mathbf{HCl\,(aq)}$. When $\mathbf{HCl}$ is dissolved in $\mathbf{H_2O}$, it completely dissociates into $\mathbf{H^+\,(aq)}$ and $\mathbf{Cl^-\,(aq)}$ ions; all the $\mathbf{HCl}$ molecules become ions:

$$\mathbf{HCl \xrightarrow{100\,\%} H^+(aq) + Cl^-(aq)}$$

Any acid that dissociates 100% into ions is called a **strong acid**. If it does not dissociate 100%, it is a **weak acid**. Acetic acid ($\mathbf{HC_2H_3O_2}$) is an example of a weak acid:

$$\mathbf{HC_2H_3O_2 \xrightarrow{\sim 5\,\%} H^+(aq) + C_2H_3O_2^-(aq)}$$

Because this reaction does not go 100% to completion, it is more appropriate to write it as a reversible reaction:

$$\mathbf{HC_2H_3O_2 \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)}$$

As it turns out, there are very few strong acids, which are given in Table 8.5.1. If an acid is not listed here, it is a weak acid. It may be 1% ionized or 99% ionized, but it is still classified as a weak acid.

Table 8.5.1: Strong Acids and Bases

Acids	Bases
HCl	LiOH
HBr	NaOH
HI	KOH
HNO_3	RbOH
H_2SO_4	CsOH
$HClO_3$	$Mg(OH)_2$
$HClO_4$	$Ca(OH)_2$
	$Sr(OH)_2$
	$Ba(OH)_2$

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 8.5.1); any base not listed is a weak base. All strong bases are OH^- compounds. So a base dependent on some other mechanism, such as NH_3 (which does not contain OH^- ions as part of its formula), will be a weak base.

Example 8.5.1

Identify each acid or base as strong or weak.

a. HCl
b. $Mg(OH)_2$
c. C_5H_5N

Solution

a. Because HCl is listed in Table 8.5.1, it is a strong acid.
b. Because $Mg(OH)_2$ is listed in Table 8.5.1, it is a strong base.
c. The nitrogen in C_5H_5N would act as a proton acceptor and therefore can be considered a base, but because it does not contain an OH compound, it cannot be considered a strong base; it is a weak base.

Exercise 8.5.1

Identify each acid or base as strong or weak.

a. RbOH
b. HNO_2

Answer a

strong base

Answer b

weak acid

Example 8.5.2

Write the balanced chemical equation for the dissociation of $Ca(OH)_2$ and indicate whether it proceeds 100% to products or not.

Solution

This is an ionic compound of Ca^{2+} ions and OH^- ions. When an ionic compound dissolves, it separates into its constituent ions:

$$Ca(OH)_2 \longrightarrow Ca^{2+}(aq) + 2\,OH^-(aq)$$

Because $Ca(OH)_2$ is listed in Table 8.5.1, this reaction proceeds 100% to products.

Exercise 8.5.2

Write the balanced chemical equation for the dissociation of hydrazoic acid (HN_3) and indicate whether it proceeds 100% to products or not.

Answer

The reaction is as follows:

$$HN_3 \longrightarrow H^+(aq) + N_3^-(aq)$$

It does not proceed 100% to products because hydrazoic acid is not a strong acid.

Certain salts will also affect the acidity or basicity of aqueous solutions because some of the ions will undergo hydrolysis, just like NH_3 does, to make a basic solution. The general rule is that salts with ions that are part of strong acids or bases will not hydrolyze, while salts with ions that are part of weak acids or bases will hydrolyze.

Consider NaCl. When it dissolves in an aqueous solution, it separates into Na^+ ions and Cl^- ions:

$$NaCl \longrightarrow Na^+(aq) + Cl^-(aq)$$

Will the $Na^+(aq)$ ion hydrolyze? If it does, it will interact with the OH^- ion to make NaOH:

$$Na^+(aq) + H_2O \longrightarrow NaOH + H^+(aq)$$

However, NaOH is a strong base, which means that it is 100% ionized in solution:

$$NaOH \longrightarrow Na^+(aq) + OH^-(aq)$$

The free $OH^-(aq)$ ion reacts with the $H^+(aq)$ ion to remake a water molecule:

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O$$

The net result? There is no change, so there is no effect on the acidity or basicity of the solution from the $Na^+(aq)$ ion. What about the Cl^- ion? Will it hydrolyze? If it does, it will take an H^+ ion from a water molecule:

$$Cl^-(aq) + H_2O \longrightarrow HCl + OH^-$$

However, HCl is a strong acid, which means that it is 100% ionized in solution:

$$HCl \longrightarrow H^+(aq) + Cl^-(aq)$$

The free $H^+(aq)$ ion reacts with the $OH^-(aq)$ ion to remake a water molecule:

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O$$

The net result? There is no change, so there is no effect on the acidity or basicity of the solution from the $Cl^-(aq)$ ion. Because neither ion in NaCl affects the acidity or basicity of the solution, NaCl is an example of a neutral salt. A neutral salt is any ionic compound that does not affect the acidity or basicity of its aqueous solution.

Things change, however, when we consider a salt like $NaC_2H_3O_2$. We already know that the Na^+ ion won't affect the acidity of the solution. What about the acetate ion? If it hydrolyzes, it will take an H^+ from a water molecule:

$$C_2H_3O_2^-(aq) + H_2O \rightleftharpoons HC_2H_3O_2 + OH^-(aq)$$

Does this happen? Yes, it does. Why? *Because $HC_2H_3O_2$ is a weak acid.* Any chance a weak acid has to form, it will (the same with a weak base). As some $C_2H_3O_2^-$ ions hydrolyze with H_2O to make the molecular weak acid, OH^- ions are produced. OH^- ions make solutions basic. Thus $NaC_2H_3O_2$ solutions are slightly basic, so such a salt is called a **basic salt**.

There are also salts whose aqueous solutions are slightly acidic. NH_4Cl is an example. When NH_4Cl is dissolved in H_2O, it separates into NH_4^+ ions and Cl^- ions. We have already seen that the Cl^- ion does not hydrolyze. However, the NH_4^+ ion will:

$$NH_4^+(aq) + H_2O \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

Recall from Section 12.2, that H_3O^+ ion is the hydronium ion, the more chemically proper way to represent the H^+ ion. This is the classic acid species in solution, so a solution of $NH_4^+(aq)$ ions is slightly acidic. NH_4Cl is an example of an **acid salt**. The molecule NH_3 is a weak base, and it will form when it can, just like a weak acid will form when it can.

So there are two general rules:

1. If an ion derives from a strong acid or base, it will not affect the acidity of the solution.
2. If an ion derives from a weak acid, it will make the solution basic; if an ion derives from a weak base, it will make the solution acidic.

✔ Example 8.5.3

Identify each salt as acidic, basic, or neutral.

a. KCl
b. KNO_2
c. NH_4Br

Solution

a. The ions from KCl derive from a strong acid (HCl) and a strong base (KOH). Therefore, neither ion will affect the acidity of the solution, so KCl is a neutral salt.
b. Although the K^+ ion derives from a strong base (KOH), the NO_2^- ion derives from a weak acid (HNO_2). Therefore the solution will be basic, and KNO_2 is a basic salt.

c. Although the Br^- ions derive from a strong acid (HBr), the NH_4^+ ion derives from a weak base (NH_3), so the solution will be acidic, and NH_4Br is an acidic salt.

? Exercise 8.5.3

Identify each salt as acidic, basic, or neutral.

A. $(C_5H_5NH)Cl$
B. Na_2SO_3

Answer a

acidic

Answer b

basic

Some salts are composed of ions that come from both weak acids and weak bases. The overall effect on an aqueous solution depends on which ion exerts more influence on the overall acidity. We will not consider such salts here.

Summary

- Strong acids and bases are 100% ionized in aqueous solution.
- Weak acids and bases are less than 100% ionized in aqueous solution.
- Salts of weak acids or bases can affect the acidity or basicity of their aqueous solutions.

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8.6: Autoionization of Water

Learning Objectives

- Describe the autoionization of water.
- Calculate the concentrations of H^+ and OH^- in solutions, knowing the other concentration.

We have already seen that H_2O can act as an acid or a base:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \text{ } (H_2O \text{ acts as an acid})$$

$$HCl + H_2O \rightarrow H_3O^+ + Cl^- \text{ } (H_2O \text{ acts as a base})$$

It may not be surprising to learn, then, that within any given sample of water, some H_2O molecules are acting as acids, and other H_2O molecules are acting as bases. The chemical equation is as follows:

$$H_2O + H_2O \rightarrow H_3O^+ + OH^-$$

This occurs only to a very small degree: only about 6 in 10^8 H_2O molecules are participating in this process, which is called the **autoionization of water**. At this level, the concentration of both $H^+(aq)$ and $OH^-(aq)$ in a sample of pure H_2O is about 1.0×10^{-7} M. If we use square brackets—[ ]—around a dissolved species to imply the molar concentration of that species, we have

$$[H^+] = [OH^-] = 1.0 \times 10^{-7} \text{ M}$$

for *any* sample of pure water because H_2O can act as both an acid and a base. The product of these two concentrations is 1.0×10^{-14}:

$$[H^+] \times [OH^-] = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

In acids, the concentration of $H^+(aq)$—$[H^+]$—is greater than 1.0×10^{-7} M, while for bases the concentration of $OH^-(aq)$—$[OH^-]$—is greater than 1.0×10^{-7} M. However, the *product* of the two concentrations—$[H^+][OH^-]$—is *always* equal to 1.0×10^{-14}, no matter whether the aqueous solution is an acid, a base, or neutral:

$$[H^+][OH^-] = 1.0 \times 10^{-14}$$

This value of the product of concentrations is so important for aqueous solutions that it is called the **autoionization constant of water** and is denoted K_W:

$$K_W = [H^+][OH^-] = 1.0 \times 10^{-14}$$

This means that if you know $[H^+]$ for a solution, you can calculate what $[OH^-]$ has to be for the product to equal 1.0×10^{-14}, or if you know $[OH^-]$, you can calculate $[H^+]$. This also implies that as one concentration goes up, the other must go down to compensate so that their product always equals the value of K_W.

Example 8.6.1

What is $[OH^-]$ of an aqueous solution if $[H^+]$ is 1.0×10^{-4} M?

Solution

Using the expression and known value for K_W,

$$K_W = [H^+][OH^-] = 1.0 \times 10^{-14} = (1.0 \times 10^{-4})[OH^-]$$

We solve by dividing both sides of the equation by 1.0×10^{-4}:

$$[OH^-] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-4}} = 1.0 \times 10^{-10} M$$

It is assumed that the concentration unit is molarity, so $[OH^-]$ is 1.0×10^{-10} M.

? Exercise 8.6.1

What is $[H^+]$ of an aqueous solution if $[OH^-]$ is 1.0×10^{-9} M?

Answer

1.0×10^{-5} M

When you have a solution of a particular acid or base, you need to look at the formula of the acid or base to determine the number of H^+ or OH^- ions in the formula unit because $[H^+]$ or $[OH^-]$ may not be the same as the concentration of the acid or base itself.

✔ Example 8.6.2

What is $[H^+]$ in a 0.0044 M solution of $Ca(OH)_2$?

Solution

We begin by determining $[OH^-]$. The concentration of the solute is 0.0044 M, but because $Ca(OH)_2$ is a strong base, there are two OH^- ions in solution for every formula unit dissolved, so the actual $[OH^-]$ is two times this, or 2×0.0044 M = 0.0088 M. Now we can use the K_W expression:

$$[H^+][OH^-] = 1.0 \times 10^{-14} = [H^+](0.0088\ M)$$

Divide both sides by 0.0088:

$$[H^+] = \frac{1.0 \times 10^{-14}}{(0.0088)} = 1.1 \times 10^{-12} M$$

$[H^+]$ has decreased significantly in this basic solution.

? Exercise 8.6.2

What is $[OH^-]$ in a 0.00032 M solution of H_2SO_4? (Hint: assume both H^+ ions ionize.)

Answer

1.6×10^{-11} M

For strong acids and bases, $[H^+]$ and $[OH^-]$ can be determined directly from the concentration of the acid or base itself because these ions are 100% ionized by definition. However, for weak acids and bases, this is not so. The degree, or percentage, of ionization would need to be known before we can determine $[H^+]$ and $[OH^-]$.

✔ Example 8.6.3

A 0.0788 M solution of $HC_2H_3O_2$ is 3.0% ionized into H^+ ions and $C_2H_3O_2^-$ ions. What are $[H^+]$ and $[OH^-]$ for this solution?

Solution

Because the acid is only 3.0% ionized, we can determine $[H^+]$ from the concentration of the acid. Recall that 3.0% is 0.030 in decimal form:

$[H^+] = 0.030 \times 0.0788 = 0.00236$ M

With this $[H^+]$, then $[OH^-]$ can be calculated as follows:

$$[OH^-] = \frac{1.0 \times 10^{-14}}{0.00236} = 4.2 \times 10^{-12} M$$

This is about 30 times higher than would be expected for a strong acid of the same concentration.

Exercise 8.6.3

A 0.0222 M solution of pyridine (C_5H_5N) is 0.44% ionized into pyridinium ions ($C_5H_5NH^+$) and OH^- ions. What are $[OH^-]$ and $[H^+]$ for this solution?

Answer

$[OH^-] = 9.77 \times 10^{-5}$ M; $[H^+] = 1.02 \times 10^{-10}$ M

Summary

In any aqueous solution, the product of [H+] and [OH−] equals $\mathbf{1.0 \times 10^{-14}}$ (at room temperature).

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8.7: The pH Scale

Learning Objectives

- Define *pH*.
- Determine the pH of acidic and basic solutions.

As we have seen, $[H^+]$ and $[OH^-]$ values can be markedly different from one aqueous solution to another. So chemists defined a new scale that succinctly indicates the concentrations of either of these two ions.

pH is commonly defined as a logarithmic function of $[H^+]$:

$$\mathbf{pH = -\log[H^+]} \tag{8.7.1}$$

pH is usually (but not always) between 0 and 14. Knowing the dependence of pH on $[H^+]$, we can summarize as follows:

- If pH < 7, then the solution is acidic.
- If pH = 7, then the solution is neutral.
- If pH > 7, then the solution is basic.

This is known as the pH scale and is the range of values from 0 to 14 that describes the acidity or basicity of a solution. You can use pH to quickly determine whether a given aqueous solution is acidic, basic, or neutral.

Example 8.7.1

Label each solution as acidic, basic, or neutral based only on the stated pH.

a. milk of magnesia, pH = 10.5
b. pure water, pH = 7
c. wine, pH = 3.0

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 8.7.1

Identify each substance as acidic, basic, or neutral based only on the stated pH.

1. human blood, pH = 7.4
2. household ammonia, pH = 11.0
3. cherries, pH = 3.6

Answers

1. basic
2. basic
3. acidic

Table **8.7.1** gives the typical pH values of some common substances. Note that several food items are on the list, and most of them are acidic.

Table **8.7.1** Typical pH Values of Various Substances*

Substance	pH
stomach acid	1.7
lemon juice	2.2
vinegar	2.9
soda	3.0
wine	3.5
coffee, black	5.0
milk	6.9
pure water	7.0
blood	7.4
seawater	8.5
milk of magnesia	10.5
ammonia solution	12.5
1.0 M NaOH	14.0
*Actual values may vary depending on conditions	

pH is a *logarithmic* scale. A solution that has a pH of 1.0 has 10 times the $[H^+]$ as a solution with a pH of 2.0, which in turn has 10 times the $[H^+]$ as a solution with a pH of 3.0 and so forth.

Using the definition of pH (Equation 8.7.1), it is also possible to calculate $[H^+]$ (and $[OH^-]$) from pH and vice versa. The general formula for determining $[H^+]$ from pH is as follows:

$$[H^+] = 10^{-pH}$$

Key Takeaways

- pH is a logarithmic function of $[H^+]$.
- $[H^+]$ can be calculated directly from pH.
- pOH is related to pH and can be easily calculated from pH.

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8.8: Buffers

Learning Objectives

- Define *buffer*.
- Correctly identify the two components of a buffer.

As indicated in Section 12.5, weak acids are relatively common, even in the foods we eat. But we occasionally encounter a strong acid or base, such as stomach acid, which has a strongly acidic pH of 1.7. By definition, strong acids and bases can produce a relatively large amount of H^+ or OH^- ions and consequently have marked chemical activities. In addition, very small amounts of strong acids and bases can change the pH of a solution very quickly. If 1 mL of stomach acid [approximated as 0.1 M HCl(aq)] were added to the bloodstream and no correcting mechanism were present, the pH of the blood would decrease from about 7.4 to about 4.7—a pH that is not conducive to continued living. Fortunately, the body has a mechanism for minimizing such dramatic pH changes.

This mechanism involves a **buffer**, a solution that resists dramatic changes in pH. Buffers do so by being composed of certain pairs of solutes: either a weak acid plus a salt derived from that weak acid, or a weak base plus a salt of that weak base. For example, a buffer can be composed of dissolved $HC_2H_3O_2$ (a weak acid) and $NaC_2H_3O_2$ (the salt derived from that weak acid). Another example of a buffer is a solution containing NH_3 (a weak base) and NH_4Cl (a salt derived from that weak base).

Let us use an $HC_2H_3O_2/NaC_2H_3O_2$ buffer to demonstrate how buffers work. If a strong base—a source of OH^-(aq) ions—is added to the buffer solution, those OH^- ions will react with the $HC_2H_3O_2$ in an acid-base reaction:

$$HC_2H_3O_2\,(aq) + OH^-\,(aq) \rightarrow H_2O(\ell) + C_2H_3O_2^-\,(aq) \tag{8.8.1}$$

Rather than changing the pH dramatically by making the solution basic, the added OH^- ions react to make H_2O, so the pH does not change much.

If a strong acid—a source of H^+ ions—is added to the buffer solution, the H^+ ions will react with the anion from the salt. Because $HC_2H_3O_2$ is a weak acid, it is not ionized much. This means that if lots of H^+ ions and $C_2H_3O_2^-$ ions are present in the same solution, they will come together to make $HC_2H_3O_2$:

$$H^+\,(aq) + C_2H_3O_2^-\,(aq) \rightarrow HC_2H_3O_2\,(aq) \tag{8.8.2}$$

Rather than changing the pH dramatically and making the solution acidic, the added H^+ ions react to make molecules of a weak acid. Figure 8.8.1 illustrates both actions of a buffer.

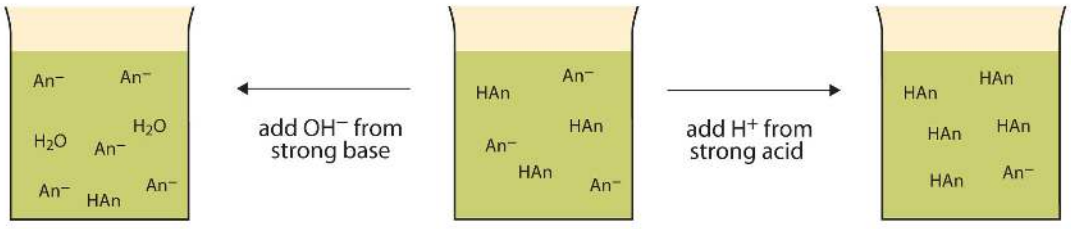


Figure 8.8.1 The Actions of Buffers. Buffers can react with both strong acids (top) and strong bases (side) to minimize large changes in pH.

Buffers made from weak bases and salts of weak bases act similarly. For example, in a buffer containing NH_3 and NH_4Cl, NH_3 molecules can react with any excess H^+ ions introduced by strong acids:

$$NH_3\,(aq) + H^+\,(aq) \rightarrow NH_4^+\,(aq) \tag{8.8.3}$$

while the **ammonium ion** (NH_4^+(aq)) can react with any hydroxide ions introduced by strong bases:

$$NH_4^+\,(aq) + OH^-\,(aq) \rightarrow NH_3\,(aq) + H_2O(\ell) \tag{8.8.4}$$

Example 8.8.1

Which combinations of compounds can make a buffer solution?

1. $HCHO_2$ and $NaCHO_2$
2. HCl and NaCl
3. CH_3NH_2 and CH_3NH_3Cl
4. NH_3 and NaOH

Solution

1. $HCHO_2$ is formic acid, a weak acid, while $NaCHO_2$ is the salt made from the anion of the weak acid (the formate ion [CHO_2^-]). The combination of these two solutes would make a buffer solution.
2. HCl is a strong acid, not a weak acid, so the combination of these two solutes would not make a buffer solution.
3. CH_3NH_2 is methylamine, which is like NH_3 with one of its H atoms substituted with a CH_3 group. Because it is not listed in Table **8.8.1**, we can assume that it is a weak base. The compound CH_3NH_3Cl is a salt made from that weak base, so the combination of these two solutes would make a buffer solution.
4. NH_3 is a weak base, but NaOH is a strong base. The combination of these two solutes would not make a buffer solution.

Exercise 8.8.1

Which combinations of compounds can make a buffer solution?

1. $NaHCO_3$ and NaCl
2. H_3PO_4 and NaH_2PO_4
3. NH_3 and $(NH_4)_3PO_4$
4. NaOH and NaCl

Answer a

Yes.

Answer b

No. Need a weak acid or base and a salt of its conjugate base or acid.

Answer c

Yes.

Answer d

No. Need a weak base or acid.

Buffers work well only for limited amounts of added strong acid or base. Once either solute is completely reacted, the solution is no longer a buffer, and rapid changes in pH may occur. We say that a buffer has a certain **capacity**. Buffers that have more initial solute dissolved within them have larger capacities, as might be expected.

Human blood has a buffering system to minimize extreme changes in pH. One buffer in blood is based on the presence of HCO_3^- and H_2CO_3 [the second compound is another way to write $CO_2(aq)$]. With this buffer present, even if some stomach acid were to find its way directly into the bloodstream, the change in the pH of blood would be minimal. Inside many of the body's cells, there is a buffering system based on phosphate ions.

Food and Drink Application: the Acid that Eases Pain

Although medicines are not exactly "food and drink," we do ingest them, so let's take a look at an acid that is probably the most common medicine: acetylsalicylic acid, also known as aspirin. Aspirin is well known as a pain reliever and antipyretic (fever reducer).

The structure of aspirin is shown in the accompanying figure. The acid part is circled; it is the H atom in that part that can be donated as aspirin acts as a Brønsted-Lowry acid. Because it is not given in Table **8.8.1**, acetylsalicylic acid is a weak acid. However, it is still an acid, and given that some people consume relatively large amounts of aspirin daily, its acidic nature can cause problems in the stomach lining, despite the stomach's defenses against its own stomach acid.

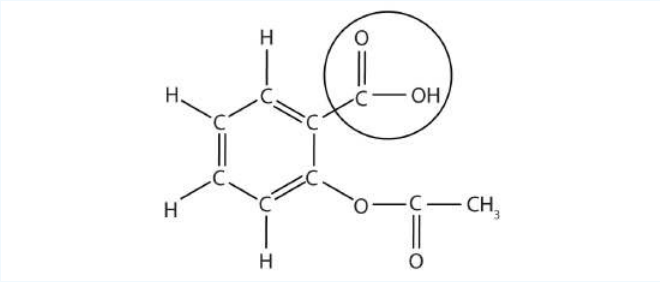


Figure **8.8.2**: The Molecular Structure of Aspirin. The circled atoms are the acid part of the molecule.

The molecule of aspartame is shown. The CO2H is circled to indicate that it is the acidic part of the molecule.

Because the acid properties of aspirin may be problematic, many aspirin brands offer a "buffered aspirin" form of the medicine. In these cases, the aspirin also contains a buffering agent—usually MgO—that regulates the acidity of the aspirin to minimize its acidic side effects.

As useful and common as aspirin is, it was formally marketed as a drug starting in 1899. The US Food and Drug Administration (FDA), the governmental agency charged with overseeing and approving drugs in the United States, wasn't formed until 1906. Some have argued that if the FDA had been formed before aspirin was introduced, aspirin may never have gotten approval due to its potential for side effects—gastrointestinal bleeding, ringing in the ears, Reye's syndrome (a liver problem), and some allergic reactions. However, recently aspirin has been touted for its effects in lessening heart attacks and strokes, so it is likely that aspirin will remain on the market.

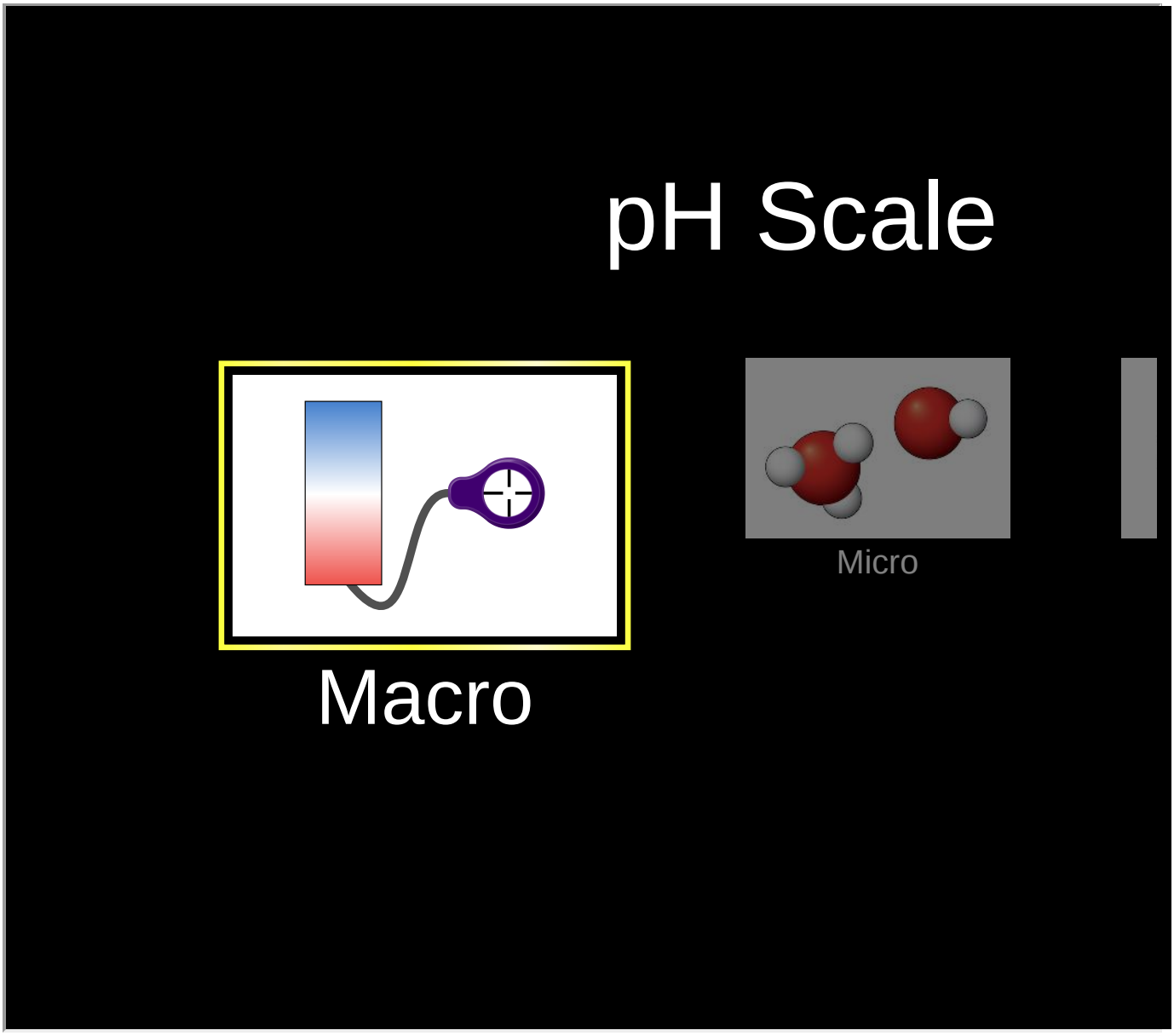
Summary

A buffer is a solution that resists sudden changes in pH.

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8.9: PhET- pH Scale



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8.E: Acids and Bases (Exercises)

Exercises (Arrhenius Acids and Bases)

1. Define *Arrhenius acid*.
2. Define *Arrhenius base*.
3. What are some general properties of Arrhenius acids?
4. What are some general properties of Arrhenius bases?
5. Identify each substance as an Arrhenius acid, an Arrhenius base, or neither.
   a. NaOH
   b. C_2H_5OH
   c. H_3PO_4
6. Identify each substance as an Arrhenius acid, an Arrhenius base, or neither.
   a. $C_6H_{12}O_6$
   b. HNO_2
   c. $Ba(OH)_2$
7. Write the balanced chemical equation for the neutralization reaction between KOH and $H_2C_2O_4$. What is the salt?
8. Write the balanced chemical equation for the neutralization reaction between $Sr(OH)_2$ and H_3PO_4. What is the salt?
9. Write the balanced chemical equation for the neutralization reaction between HCl and $Fe(OH)_3$. What is the salt?
10. Write the balanced chemical equation for the neutralization reaction between H_2SO_4 and $Cr(OH)_3$. What is the salt?
11. $CaCl_2$ would be the product of the reaction of what acid and what base?
12. $Zn(NO_3)_2$ would be product of the reaction of what acid and what base?
13. $BaSO_4$ would be product of the reaction of what acid and what base?
14. Na_3PO_4 would be product of the reaction of what acid and what base?

Answers

1. a compound that increases the H^+ concentration in water
3. sour taste, react with metals, and turn litmus red
5.
   a. Arrhenius base
   b. neither
   c. Arrhenius acid
7. $2KOH + H_2C_2O_4 \rightarrow 2H_2O + K_2C_2O_4$; $K_2C_2O_4$
9. $3HCl + Fe(OH)_3 \rightarrow 3H_2O + FeCl_3$; $FeCl_3$
11. HCl and $Ca(OH)_2$
13. H_2SO_4 and $Ba(OH)_2$

Exercises (Brønsted-Lowry Acids and Bases)

1. Define *Brønsted-Lowry acid*. How does it differ from an Arrhenius acid?
2. Define *Brønsted-Lowry base*. How does it differ from an Arrhenius base?
3. Write the dissociation of hydrogen bromide in water as a Brønsted-Lowry acid-base reaction and identify the proton donor and proton acceptor.
4. Write the dissociation of nitric acid in water as a Brønsted-Lowry acid-base reaction and identify the proton donor and proton acceptor.
5. Pyridine (C_5H_5N) acts as a Brønsted-Lowry base in water. Write the hydrolysis reaction for pyridine and identify the Brønsted-Lowry acid and Brønsted-Lowry base.
6. The methoxide ion (CH_3O^-) acts as a Brønsted-Lowry base in water. Write the hydrolysis reaction for the methoxide ion and identify the Brønsted-Lowry acid and Brønsted-Lowry base.
7. Identify the Brønsted-Lowry acid and Brønsted-Lowry base in this chemical equation.

   $H_3PO_4 + OH^- \rightarrow H_2PO_4^- + H_2O$
8. Identify the Brønsted-Lowry acid and Brønsted-Lowry base in this chemical equation.

   $H_2C_2O_4 + 2F^- \rightarrow 2HF + C_2O_4^{2-}$
9. Predict the products of this reaction, assuming it undergoes a Brønsted-Lowry acid-base reaction.

   $HC_2H_3O_2 + C_5H_5N \rightarrow ?$
10. Predict the products of this reaction, assuming it undergoes a Brønsted-Lowry acid-base reaction.

    $(C_2H_5)_3N + H_2O \rightarrow ?$
11. What is the conjugate acid of H_2O? of NH_3?
12. What is the conjugate acid of $H_2PO_4^-$? of NO_3^-?
13. What is the conjugate base of HSO_4^-? of H_2O?
14. What is the conjugate base of H_3O^+? of H_2SO_4?
15. Identify the conjugate acid-base pairs in this reaction.

    $HSO_4^- + PO_4^{3-} \rightarrow SO_4^{2-} + HPO_4^{2-}$
16. Identify the conjugate acid-base pairs in this reaction.

    $HClO_3 + (C_2H_5)_3N \rightarrow ClO_3^- + (C_2H_5)_3NH^+$
17. Identify the conjugate acid-base pairs in this reaction.

    $NH_3 + C_6H_5O^- \rightarrow C_6H_5OH + NH_2^-$
18. Identify the conjugate acid-base pairs in this reaction.

    $C_5H_5NH^+ + C_2O_4^{2-} \rightarrow C_5H_5N + HC_2O_4^-$suming it undergoes a Brønsted-Lowry acid-base reaction.

Answers

1. A Brønsted-Lowry acid is a proton donor. It does not necessarily increase the H^+ concentration in water.
3. $HBr + H_2O \rightarrow H_3O^+ + Br^-$; PD: HBr; PA: H_2O
5. $C_5H_5N + H_2O \rightarrow C_5H_5NH^+ + OH^-$; PD: H_2O; PA: C_5H_5N
7. BL acid: H_3PO_4; BL base: OH^-

9. $C_2H_3O_2^-$ and $C_5H_5NH^+$

11. H_3O^+; NH_4^+

13. SO_4^{2-}; OH^-

15. HSO_4^- and SO_4^{2-}; PO_4^{3-} and HPO_4^{2-}

17. NH_3 and NH_2^-; $C_6H_5O^-$ and C_6H_5OH

Exercises (Acid-Base Titrations)

1. Define *titration*.
2. What is the difference between the titrant and the analyte?
3. True or false: An acid is always the titrant. Explain your answer.
4. True or false: An analyte is always dissolved before reaction. Explain your answer.
5. If 55.60 mL of 0.2221 M HCl was needed to titrate a sample of NaOH to its equivalence point, what mass of NaOH was present?
6. If 16.33 mL of 0.6664 M KOH was needed to titrate a sample of $HC_2H_3O_2$ to its equivalence point, what mass of $HC_2H_3O_2$ was present?
7. It takes 45.66 mL of 0.1126 M HBr to titrate 25.00 mL of $Ca(OH)_2$ to its equivalence point. What is the original concentration of the $Ca(OH)_2$ solution?
8. It takes 9.77 mL of 0.883 M H_2SO_4 to titrate 15.00 mL of KOH to its equivalence point. What is the original concentration of the KOH solution?

Answers

1. a chemical reaction performed in a quantitative fashion

3. False; a base can be a titrant, or the reaction being performed may not even be an acid-base reaction.

5. 0.494 g

7. 0.1028 M

Exercises (Strong and Weak Acids and Bases and their Salts)

1. Differentiate between a strong acid and a weak acid.
2. Differentiate between a strong base and a weak base.
3. Identify each as a strong acid or a weak acid. Assume aqueous solutions.
   a. HF
   b. HCl
   c. HC_2O_4
4. Identify each as a strong base or a weak base. Assume aqueous solutions.
   a. NaOH
   b. $Al(OH)_3$
   c. $C_4H_9NH_2$
5. Write a chemical equation for the ionization of each acid and indicate whether it proceeds 100% to products or not.
   a. HNO_3
   b. HNO_2

c. HI_3

6. Write a chemical equation for the ionization of each base and indicate whether it proceeds 100% to products or not.
   a. NH_3
   b. $(CH_3)_3N$
   c. $Mg(OH)_2$

7. Write the balanced chemical equation for the reaction of each acid and base pair.
   a. $HCl + C_5H_5N$
   b. $H_2C_2O_4 + NH_3$
   c. $HNO_2 + C_7H_9N$

8. Write the balanced chemical equation for the reaction of each acid and base pair.
   a. $H_3C_5H_5O_7 + Mg(OH)_2$
   b. $HC_3H_3O_3 + (CH_3)_3N$
   c. $HBr + Fe(OH)_3$

9. Identify each salt as neutral, acidic, or basic.
   a. NaBr
   b. $Fe(NO_3)_2$
   c. $Fe(NO_3)_3$

10. Identify each salt as neutral, acidic, or basic.
    a. NH_4I
    b. $C_2H_5NH_3Cl$
    c. KI

11. Identify each salt as neutral, acidic, or basic.
    a. $NaNO_2$
    b. $NaNO_3$
    c. NH_4NO_3

12. Identify each salt as neutral, acidic, or basic.
    a. $KC_2H_3O_2$
    b. $KHSO_4$
    c. $KClO_3$

13. Write the hydrolysis reaction that occurs, if any, when each salt dissolves in water.
    a. K_2SO_3
    b. KI
    c. NH_4ClO_3

14. Write the hydrolysis reaction that occurs, if any, when each salt dissolves in water.
    a. $NaNO_3$
    b. CaC_2O_4
    c. C_5H_5NHCl

15. When NH_4NO_2 dissolves in H_2O, both ions hydrolyze. Write chemical equations for both reactions. Can you tell if the solution will be acidic or basic overall?

16. When pyridinium acetate ($C_5H_5NHC_2H_3O_2$) dissolves in H_2O, both ions hydrolyze. Write chemical equations for both reactions. Can you tell if the solution will be acidic or basic overall?

17. A lab technician mixes a solution of 0.015 M $Mg(OH)_2$. Is the resulting OH^- concentration greater than, equal to, or less than 0.015 M? Explain your answer.

18. A lab technician mixes a solution of 0.55 M HNO_3. Is the resulting H^+ concentration greater than, equal to, or less than 0.55 M? Explain your answer.

Answers

1. A strong acid is 100% ionized in aqueous solution, whereas a weak acid is not 100% ionized.

3.

a. weak acid
b. strong acid
c. weak acid

5.

a. $HNO_3(aq) \rightarrow H^+(aq) + NO_3^-(aq)$; proceeds 100%
b. $HNO_2(aq) \rightarrow H^+(aq) + NO_2^-(aq)$; does not proceed 100%
c. $HI_3(aq) \rightarrow H^+(aq) + I_3^-(aq)$; does not proceed 100%

7.

a. $HCl + C_5H_5N \rightarrow Cl^- + C_5H_5NH^+$
b. $H_2C_2O_4 + 2NH_3 \rightarrow C_2O_4^{2-} + 2NH_4^+$
c. $HNO_2 + C_7H_9N \rightarrow NO_2^- + C_7H_9NH^+$

9.

a. neutral
b. acidic
c. acidic

11.

a. basic
b. neutral
c. acidic

13.

a. $\mathbf{SO_3^{2-} + H_2O \rightarrow HSO_3^- + OH^-}$
b. no reaction
c. $\mathbf{NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+}$

15. $\mathbf{NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+; NO_2^- + H_2O \rightarrow HNO_2 + OH^-}$; it is not possible to determine whether the solution will be acidic or basic.

17. greater than $\mathbf{0.015 M}$ because there are two $\mathbf{OH^-}$ ions per formula unit of $\mathbf{Mg(OH)_2}$

Exercise (Autoionization of Water)

1. Does $[H^+]$ remain constant in all aqueous solutions? Why or why not?

2. Does $[OH^-]$ remain constant in all aqueous solutions? Why or why not?
3. What is the relationship between $[H^+]$ and K_W? Write a mathematical expression that relates them.
4. What is the relationship between $[OH^-]$ and K_W? Write a mathematical expression that relates them.
5. Write the chemical equation for the autoionization of water and label the conjugate acid-base pairs.
6. Write the reverse of the reaction for the autoionization of water. It is still an acid-base reaction? If so, label the acid and base.
7. For a given aqueous solution, if $[H^+] = 1.0 \times 10^{-3}$ M, what is $[OH^-]$?
8. For a given aqueous solution, if $[H^+] = 1.0 \times 10^{-9}$ M, what is $[OH^-]$?
9. For a given aqueous solution, if $[H^+] = 7.92 \times 10^{-5}$ M, what is $[OH^-]$?
10. For a given aqueous solution, if $[H^+] = 2.07 \times 10^{-11}$ M, what is $[H^+]$?
11. For a given aqueous solution, if $[OH^-] = 1.0 \times 10^{-5}$ M, what is $[H^+]$?
12. For a given aqueous solution, if $[OH^-] = 1.0 \times 10^{-12}$ M, what is $[H^+]$?
13. For a given aqueous solution, if $[OH^-] = 3.77 \times 10^{-4}$ M, what is $[H^+]$?
14. For a given aqueous solution, if $[OH^-] = 7.11 \times 10^{-10}$ M, what is $[H^+]$?
15. What are $[H^+]$ and $[OH^-]$ in a 0.344 M solution of HNO_3?
16. What are $[H^+]$ and $[OH^-]$ in a 2.86 M solution of HBr?
17. What are $[H^+]$ and $[OH^-]$ in a 0.00338 M solution of KOH?
18. What are $[H^+]$ and $[OH^-]$ in a 6.02×10^{-4} M solution of $Ca(OH)_2$?
19. If HNO_2 is dissociated only to an extent of 0.445%, what are $[H^+]$ and $[OH^-]$ in a 0.307 M solution of HNO_2?
20. If $(C_2H_5)_2NH$ is dissociated only to an extent of 0.077%, what are $[H^+]$ and $[OH^-]$ in a 0.0955 M solution of $(C_2H_5)_2NH$?

Answers

1. $[H^+]$ varies with the amount of acid or base in a solution.
3. $$[H^+] = \frac{K_W}{[OH^-]} \tag{8.E.1}$$
5. $H_2O + H_2O \rightarrow H_3O^+ + OH^-$; H_2O/H_3O^+ and H_2O/OH^-
7. 1.0×10^{-11} M
9. 1.26×10^{-10} M
11. 1.0×10^{-9} M
13. 2.65×10^{-11} M
15. $[H^+] = 0.344$ M; $[OH^-] = 2.91 \times 10^{-14}$ M
17. $[OH^-] = 0.00338$ M; $[H^+] = 2.96 \times 10^{-12}$ M
19. $[H^+] = 0.00137$ M; $[OH^-] = 7.32 \times 10^{-12}$ M

Exercises (The pH Scale)

1. Define *pH*. How is it related to pOH?
2. Define *pOH*. How is it related to pH?
3. What is the pH range for an acidic solution?
4. What is the pH range for a basic solution?

5. What is $[H^+]$ for a neutral solution?
6. What is $[OH^-]$ for a neutral solution? Compare your answer to Exercise 6. Does this make sense?
7. Which substances in Table 12.7.1 are acidic?
8. Which substances in Table 12.7.1 are basic?
9. What is the pH of a solution when $[H^+]$ is 3.44×10^{-4} M?
10. What is the pH of a solution when $[H^+]$ is 9.04×10^{-13} M?
11. What is the pH of a solution when $[OH^-]$ is 6.22×10^{-7} M?
12. What is the pH of a solution when $[OH^-]$ is 0.0222 M?
13. What is the pOH of a solution when $[H^+]$ is 3.44×10^{-4} M?
14. What is the pOH of a solution when $[H^+]$ is 9.04×10^{-13} M?
15. What is the pOH of a solution when $[OH^-]$ is 6.22×10^{-7} M?
16. What is the pOH of a solution when $[OH^-]$ is 0.0222 M?
17. If a solution has a pH of 0.77, what is its pOH, $[H^+]$, and $[OH^-]$?
18. If a solution has a pOH of 13.09, what is its pH, $[H^+]$, and $[OH^-]$?

Answers

1. pH is the negative logarithm of $[H^+]$ and is equal to 14 − pOH.
3. pH < 7
5. 1.0×10^{-7} M
7. Every entry above pure water is acidic.
9. 3.46
11. 7.79
13. 10.546.21
15. pOH = 13.23; $[H^+] = 1.70 \times 10^{-1}$ M; $[OH^-] = 5.89 \times 10^{-14}$ M

Exercises (Buffers)

1. Define *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 combinations of compounds can make a buffer? Assume aqueous solutions.
   a. HCl and NaCl
   b. HNO_2 and $NaNO_2$
   c. NH_4NO_3 and HNO_3
   d. NH_4NO_3 and NH_3
4. Which combinations of compounds can make a buffer? Assume aqueous solutions.
   a. H_3PO_4 and Na_3PO_4
   b. $NaHCO_3$ and Na_2CO_3
   c. $NaNO_3$ and $Ca(NO_3)_2$
   d. 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 reactions 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. Two solutions are made containing the same concentrations of solutes. One solution is composed of H_3PO_4 and Na_3PO_4, while the other is composed of HCN and NaCN. Which solution should have the larger capacity as a buffer?

10. Two solutions are made containing the same concentrations of solutes. One solution is composed of NH_3 and NH_4NO_3, while the other is composed of H_2SO_4 and Na_2SO_4. Which solution should have the larger capacity as a buffer?

Answers

1. A buffer is the combination of a weak acid or base and a salt of that weak acid or base.

3.

a. no
b. yes
c. no
d. yes

5. 3b: strong acid: $NO_2^- + H^+ \rightarrow HNO_2$; strong base: $HNO_2 + OH^- \rightarrow NO_2^- + H_2O$; 3d: strong base: $NH_4^+ + OH^- \rightarrow NH_3 + H_2O$; strong acid: $NH_3 + H^+ \rightarrow NH_4^+$

7. Buffers can be made from three combinations: (1) H_3PO_4 and $H_2PO_4^-$, (2) $H_2PO_4^-$and HPO_4^{2-}, and (3) HPO_4^{2-} and PO_4^{3-}. (Technically, a buffer can be made from any two components.)

9. The phosphate buffer should have the larger capacity.

Additional Exercises

1. Write the balanced chemical equation between Zn metal and $HCl(aq)$. The other product is $ZnCl_2$.

2. Write the neutralization reaction in which $ZnCl_2$, also found in Exercise 1, is the salt product.

3. Why isn't an oxide compound like CaO considered a salt? (Hint: what acid-base combination would be needed to make it if it were a salt?)

4. Metal oxides are considered basic because they react with H_2O to form OH compounds. Write the chemical equation for a reaction that forms a base when CaO is combined with H_2O.

5. Write the balanced chemical equation between aluminum hydroxide and sulfuric acid.

6. Write the balanced chemical equation between phosphoric acid and barium hydroxide.

7. Write the equation for the chemical reaction that occurs when caffeine ($C_8H_{10}N_4O_2$) acts as a Brønsted-Lowry base.

8. Citric acid ($C_6H_8O_7$) is the acid found in citrus fruits. It can lose a maximum of three H^+ions in the presence of a base. Write the chemical equations for citric acid acting stepwise as a Brønsted-Lowry acid.

9. Can an amphiprotic substance be a strong acid and a strong base at the same time? Explain your answer.

10. Can an amphiprotic substance be a weak acid and a weak base at the same time? If so, explain why and give an example.

11. Under what conditions will the equivalence point of a titration be slightly acidic?

12. Under what conditions will the equivalence point of a titration be slightly basic?

13. Write the chemical equation for the autoionization of $\mathbf{NH_3}$.

14. Write the chemical equation for the autoionization of HF.

15. What is the $\mathbf{pOH}$ range for an acidic solution?

16. What is the pOH range for a basic solution?

17. The concentration of commercial $\mathbf{HCl}$ is about $\mathbf{12M}$. What is its $\mathbf{pH}$ and $\mathbf{pOH}$?

18. The concentration of concentrated $\mathbf{H_2SO_4}$ is about 18 M. Assuming only one $\mathbf{H^+}$ comes off the $\mathbf{H_2SO_4}$ molecule, what is its $\mathbf{pH}$ and $\mathbf{pOH}$? What would the $\mathbf{pH}$ and pOH be if the second $\mathbf{H^+}$were also ionized?

Answers

1. $\mathbf{Zn + 2HCl \rightarrow ZnCl_2 + H_2}$

3. The $\mathbf{O^{2-}}$ ion would come from $\mathbf{H_2O}$, which is not considered a classic acid in the Arrhenius sense.

5. $\mathbf{2Al(OH)_3 + 3H_2SO_4 \rightarrow Al_2\,(SO_4)_3 + 6H_2O}$

7. $\mathbf{C_8H_{10}\ N_4O_2 + H_2O \rightarrow C_8H_{10}\ N_4O_2H^+ + OH^-}$; the $\mathbf{H^+}$ion attaches to one of the $\mathbf{N}$ atoms in the caffeine molecule.

9. As a strong acid or base, an amphiprotic substance reacts $\mathbf{100\%}$ as an acid or a base, so it cannot be a base or an acid at the same time.

11. if the salt produced is an acidic salt

13. $\mathbf{NH_3 + NH_3 \rightarrow NH_4^+ + NH_2^-}$

15. $\mathbf{pOH > 7}$

17. $\mathbf{pH = -1.08; pOH = 15.08}$

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CHAPTER OVERVIEW

9: Oxidation and Reduction

One important type of chemical reaction is the oxidation-reduction reaction, also known as the redox reaction. Although we introduced redox reactions in Section 4.7, it is worth reviewing some basic concepts.

9.1: Introduction to Oxidation and Reduction
9.2: Oxidation-Reduction Reactions
9.3: Applications of Redox Reactions - Voltaic Cells
9.4: Electrolysis
9.E: Oxidation-Reduction Reaction (Exercises)

Thumbnail: Copper from a wire is displaced by silver in a silver nitrate solution it is dipped into, and solid silver precipitates out. (CC SA-BY 3.0 au; Toby Hudson).

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9.1: Introduction to Oxidation and Reduction

Most of us are familiar with rusty iron: metal that has a dark red-brown scale that falls off an object, ultimately weakening it. Although we usually attribute rusting exclusively to iron, this process occurs with many materials. The more formal term for rusting is *corrosion*. Corrosion is defined as the disintegration of a material due to chemical reactions with other substances in the environment. In many cases, oxygen in the air causes the disintegration. Corrosion is not uniformly destructive. Although the corrosion of iron is generally considered bad, the corrosion of aluminum and copper forms a protective barrier on the surface of the metal, protecting it from further reaction with the environment.



Figure **9.1.1**: Corroded beams on the Nandu River Iron Bridge. These support beams on the bridge are obviously rusted. If the rusting becomes too bad, it will compromise the integrity of the bridge, requiring replacement. (Public Domain; Anna Frodesiak.)

Having said that, it has been estimated that as much as 5% of expenditures in the United States apply to fixing problems caused by corrosion. The replacement of structures built with iron, steel, aluminum, and concrete must be performed regularly to keep these structures safe. As an example of what might happen, consider the story of the Silver Bridge on US Interstate 35, connecting West Virginia and Ohio. On December 15, 1967, the 39-year-old bridge collapsed, killing 46 people. The ultimate cause of the collapse was determined to be corrosion of a suspension chain on the Ohio side of the bridge.

Corrosion is an example of the type of chemical reaction discussed in this chapter. Although we usually think of corrosion as bad, the reaction it typifies can actually be put to good use.

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9.2: Oxidation-Reduction Reactions

Learning Objectives

- Define *oxidation* and *reduction*.
- Assign oxidation numbers to atoms in simple compounds.
- Recognize a reaction as an oxidation-reduction reaction.

Consider this chemical reaction:

$$\mathrm{Mg\,(s) + Cl_2\,(g) \longrightarrow MgCl_2}$$

The reactants are two electrically neutral elements; they have the same number of electrons as protons. The product, however, is ionic; it is composed of Mg^{2+} and Cl^- ions. Somehow, the individual Mg atoms lose two electrons to make the Mg^{2+} ion, while the Cl atoms gain an electron to become Cl^- ions. This reaction involves the *transfer of electrons* between atoms.

The process of losing and gaining electrons occurs simultaneously. However, mentally we can separate the two processes. **Oxidation** is defined as the loss of one or more electrons by an atom. **Reduction** is defined as the gain of one or more electrons by an atom. So oxidation and reduction always occur together; it is only mentally that we can separate them. Chemical reactions that involve the transfer of electrons are called **oxidation-reduction (or redox) reactions**.

Redox reactions require that we keep track of the electrons assigned to each atom in a chemical reaction. How do we do that? We use **oxidation numbers** to keep track of electrons in atoms. Oxidation numbers are assigned to atoms based on four rules. Oxidation numbers are not necessarily equal to the charge on the atom (although sometimes they can be); we must keep the concepts of charge and oxidation numbers separate.

Assigning Oxidation Numbers

The rules for assigning oxidation numbers to atoms are as follows:

1. Atoms in their elemental state are assigned an oxidation number of 0.
2. Atoms in monatomic (i.e., one-atom) ions are assigned an oxidation number equal to their charge. Oxidation numbers are usually written with the sign first, then the magnitude, to differentiate them from charges.
3. In compounds, fluorine is assigned a −1 oxidation number; oxygen is usually assigned a −2 oxidation number (except in peroxide compounds [where it is −1] and in binary compounds with fluorine [where it is positive]); and hydrogen is usually assigned a +1 oxidation number (except when it exists as the hydride ion [H^-], in which case rule 2 prevails).
4. In compounds, all other atoms are assigned an oxidation number so that the sum of the oxidation numbers on all the atoms in the species equals the charge on the species (which is zero if the species is neutral).

Here are some examples for practice. In H_2, both H atoms have an oxidation number of 0 by rule 1. In $MgCl_2$, magnesium has an oxidation number of +2, while chlorine has an oxidation number of −1 by rule 2. In H_2O, the H atoms each have an oxidation number of +1, while the O atom has an oxidation number of −2, even though hydrogen and oxygen do not exist as ions in this compound (rule 3). By contrast, by rule 3, each H atom in hydrogen peroxide (H_2O_2) has an oxidation number of +1, while each O atom has an oxidation number of −1. We can use rule 4 to determine oxidation numbers for the atoms in SO_2. Each O atom has an oxidation number of −2; for the sum of the oxidation numbers to equal the charge on the species (which is zero), the S atom is assigned an oxidation number of +4. Does this mean that the sulfur atom has a 4+ charge on it? No, it means only that the S atom is assigned a +4 oxidation number by our rules of apportioning electrons among the atoms in a compound.

Example 9.2.1

Assign oxidation numbers to the atoms in each substance.

a. $\mathrm{Cl_2}$
b. $\mathrm{GeO_2}$
c. $\mathrm{Ca(NO_3)_2}$

Solution

1. Cl_2 is the elemental form of chlorine. Rule 1 states each atom has an oxidation number of 0.
2. By rule 3, oxygen is normally assigned an oxidation number of −2. For the sum of the oxidation numbers to equal the charge on the species (zero), the Ge atom is assigned an oxidation number of +4.
3. $Ca(NO_3)_2$ can be separated into two parts: the Ca^{2+} ion and the NO_3^- ion. Considering these separately, the Ca^{2+} ion has an oxidation number of +2 by rule 2. Now consider the NO_3^- ion. Oxygen is assigned an oxidation number of −2, and there are three of them. According to rule 4, the sum of the oxidation numbers on all atoms must equal the charge on the species, so we have the simple algebraic equation x + 3(−2) = −1 where x is the oxidation number of the N atom and the −1 represents the charge on the species. Evaluating for x,

$$x + (-6) = -1$$
$$x = +5$$

Thus the oxidation number on the N atom in the NO_3^- ion is +5.

? Exercise 9.2.1: Phosphoric Acid

Assign oxidation numbers to the atoms in H_3PO_4.

Answer

H: +1; O: −2; P: +5

All redox reactions occur with a simultaneous change in the oxidation numbers of some atoms. At least two elements must change their oxidation numbers. When an oxidation number of an atom is increased in the course of a redox reaction, that atom is being *oxidized*. When an oxidation number of an atom is decreased in the course of a redox reaction, that atom is being *reduced*. Oxidation and reduction can also be defined in terms of increasing or decreasing oxidation numbers, respectively.

✓ Example 9.2.2

Identify what is being oxidized and reduced in this redox reaction.

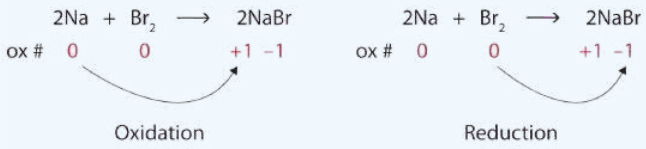
$$2\,Na + Br_2 \longrightarrow 2\,NaBr$$

Solution

Both reactants are the elemental forms of their atoms, so the Na and Br atoms have oxidation numbers of 0. In the ionic product, the Na^+ ions have an oxidation number of +1, while the Br^- ions have an oxidation number of −1.

$$\overset{0}{2\,Na} + \overset{0}{Br_2} \rightarrow \overset{+1-1}{2\,NaBr}$$

Sodium is increasing its oxidation number from 0 to +1, so it is being oxidized; bromine is decreasing its oxidation number from 0 to −1, so it is being reduced:



Because oxidation numbers are changing, this is a redox reaction. The total number of electrons being lost by sodium (two, one lost from each Na atom) is gained by bromine (two, one gained for each Br atom).

? Exercise 9.2.2

Identify what is being oxidized and reduced in this redox reaction.

$$C + O_2 \longrightarrow CO_2$$

Answer

C is being oxidized from 0 to +4.

O is being reduced from 0 to −2.

Oxidation reactions can become quite complex, as attested by the following redox reaction:

$$6\,H^+(aq) + 2\,\underset{+7}{MnO_4}^-(aq) + 5\,\underset{-1}{H_2O_2}(l) \longrightarrow 2\,\underset{+2}{Mn^{2+}}(aq) + 5\,\underset{0}{O_2}(g) + 8\,H_2O(l)$$

To demonstrate that this is a redox reaction, the oxidation numbers of the species being oxidized and reduced are listed; can you determine what is being oxidized and what is being reduced? This is also an example of a net ionic reaction; spectator ions that do not change oxidation numbers are not displayed in the equation. Eventually, we will need to learn techniques for writing correct (i.e., balanced) redox reactions.

Food and Drink Application: Fortifying Food with Iron

Iron is an essential mineral in our diet; iron-containing compounds like the heme protein in hemoglobin could not function without it. Most biological iron has the form of the Fe^{2+} ion; iron with other oxidation numbers is almost inconsequential in human biology (although the body does contain an enzyme to reduce Fe^{3+} to Fe^{2+}, so Fe^{3+} must have some biological significance, albeit minor). To ensure that we ingest enough iron, many foods are enriched with iron. Although Fe^{2+} compounds are the most logical substances to use, some foods use "reduced iron" as an ingredient (bread and breakfast cereals are the most well-known examples). Reduced iron is simply iron metal; iron is added as a fine metallic powder. The metallic iron is oxidized to Fe^{2+} in the digestive system and then absorbed by the body, but the question remains: Why are we ingesting metallic iron? Why not just use Fe^{2+} salts as an additive?



Figure **9.2.1** Ingredients. Many prepared foods list reduced iron in their ingredients list.

Although it is difficult to establish conclusive reasons, a search of scientific and medical literature suggests a few reasons. One reason is that fine iron filings do not affect the taste of the product. The size of the iron powder (several dozen micrometers) is not noticeable when chewing iron-supplemented foods, and the tongue does not detect any changes in flavor that can be detected when using Fe^{2+} salts. Fe^{2+} compounds can affect other properties of foodstuffs during preparation and cooking, like dough pliability, yeast growth, and color. Finally, of the common iron substances that might be used, metallic iron is the least expensive. These factors appear to be among the reasons why metallic iron is the supplement of choice in some foods.

Key Takeaways

- Oxidation-reduction (redox) reactions involve the transfer of electrons from one atom to another.
- Oxidation numbers are used to keep track of electrons in atoms.
- There are rules for assigning oxidation numbers to atoms.
- Oxidation is an increase in oxidation number (loss of electrons); reduction is a decrease in oxidation number (gain of electrons).

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9.3: Applications of Redox Reactions - Voltaic Cells

Learning Objectives

- Learn the parts of a voltaic cell.
- Combine half reactions to determine the voltage of a voltaic cell.
- Understand how voltaic cells are used as batteries.

Consider this redox reaction:

$$\mathrm{Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu}$$

If you were to mix zinc metal and copper ions in a container, this reaction would proceed by itself; we say that this reaction is *spontaneous*.

Suppose, however, we set up this reaction in a way depicted in Fig 14.4.1 - A Redox Reaction in Which the Two Half Reactions Are Physically Separated. Zinc and zinc ions are on one side of the system, while copper and copper ions are on the other side of the system. The two parts are connected with a wire.

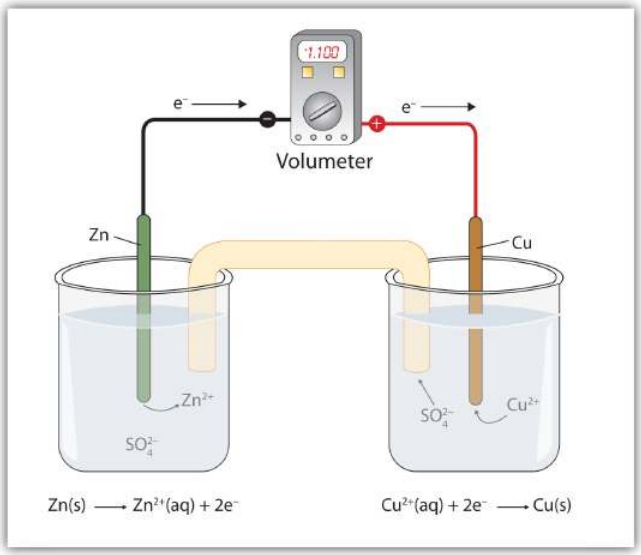


Figure **9.3.1** A Redox Reaction in Which the Two Half Reactions Are Physically Separated. One application of redox reactions requires that they be physically separated.

Even though the two half reactions are physically separated, a spontaneous redox reaction still occurs. However, in this case, the electrons transfer through the wire connecting the two half reactions; that is, this setup becomes a source of electricity. Useful work can be extracted from the electrons as they transfer from one side to the other. For example, a light bulb can be lit, or a motor can be operated. The apparatus as a whole, which allows useful electrical work to be extracted from a redox reaction, is called a **voltaic (galvanic) cell**.

Each individual system that contains a half reaction is called a **half cell**. The half cell that contains the oxidation reaction is called the **anode**, while the half cell that contains the reduction reaction is called the **cathode**. The cathode and anode collectively are the **electrodes** of the voltaic cell. Because electrons are coming from the anode, the anode is considered the *negative* electrode of the cell, while the cathode is considered the *positive* electrode of the cell. Finally, because electrons are moving from one half cell to the other, a charge imbalance builds up as the reaction proceeds. To counter that, a **salt bridge** is used; the salt bridge contains a solution of some ionic compound whose ions migrate to either side of the voltaic cell to maintain the charge balance.

The tendency for electrons to go from one half cell to another is called the **voltage** of the voltaic cell, represented by *E*. Sometimes the term *potential* is used to represent the voltage of a cell. Voltage is expressed in volts (V). The voltage of a voltaic cell is determined by the *difference* in the tendencies of the individual half cells and is characteristic of a given redox reaction when

concentrations are specific (1.0 M for dissolved species and 1.0 atm for gases). Because the voltage of a redox reaction is determined by the difference of the tendencies of the individual half reactions, absolute voltages are unnecessary; only relative voltages of each half reaction are needed. The relative voltage of each half cell is represented as $E_{1/2}$ and is based on the standard that the $E_{1/2}$ for the reaction

$$H^+ + e^- \rightarrow \frac{1}{2} H_2$$

is assigned to be exactly 0.000 V under standard conditions of pressure and concentration. Table **9.3.1** - Standard Reduction Potentials of Half Reactions, lists some relative $E_{1/2}$ values for some half reactions. Note that all half reactions are listed as reduction reactions, so these values are called the **standard reduction potentials** of each half reaction.

Reduction Half Reaction	$E_{1/2}$ (V)
$F_2 + 2e^- \rightarrow 2F^-$	2.87
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.61
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23
$Br_2 + 2e^- \rightarrow 2Br^-$	1.06
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96
$Ag^+ + e^- \rightarrow Ag$	0.80
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77
$I_2 + 2e^- \rightarrow 2I^-$	0.54
$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$AgCl + e^- \rightarrow Ag + Cl^-$	0.222
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	0.15
$2H^+ + 2e^- \rightarrow H_2$	0.000
$Pb^{2+} + 2e^- \rightarrow Pb$	−0.126
$Ni^{2+} + 2e^- \rightarrow Ni$	−0.25
$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.41
$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
$Cr^{3+} + 3e^- \rightarrow Cr$	−0.74
$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$Cr^{2+} + 2e^- \rightarrow Cr$	−0.91
$Ba^{2+} + 2e^- \rightarrow Ba$	−1.57
$Al^{3+} + 3e^- \rightarrow Al$	−1.66
$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
$Na^+ + e^- \rightarrow Na$	−2.714
$Li^+ + e^- \rightarrow Li$	−3.045

Table **9.3.1** *Standard Reduction Potentials of Half Reactions*

The above table lists only reduction reactions, but a redox reaction has a reduction *and* an oxidation. To make the oxidation reaction, simply reverse the reduction reaction in the above table and change the sign on the $E_{1/2}$ value. If the reduction potential is negative, make the voltage for the oxidation positive; if the reduction potential is positive, make the voltage for the oxidation negative.

Example 9.3.1

What is the value of $E_{1/2}$ for this half reaction?

$Ag + Cl^- \rightarrow AgCl + e^-$

Solution

The given reaction is the reverse of this reaction:

$AgCl + e^- \rightarrow Ag + Cl^- \; E_{1/2} = 0.222 \text{ V}$

Therefore, the $E_{1/2}$ of the given reaction is −0.222 V.

Exercise 9.3.1

What is the value of $E_{1/2}$ for this half reaction?

$Na \rightarrow Na^+ + e^-$

Answer

2.714 V

To determine the overall voltage of a particular voltaic cell, simply combine the voltages of the oxidation and reduction half reactions. Even if you need to take a multiple of a half reaction for the electrons to cancel, do not take the multiple of the $E_{1/2}$. Use the values directly as is from Table **9.3.1** - Standard Reduction Potentials of Half Reactions.

Spontaneous redox reactions have positive overall voltages. If the voltage of the reaction as written is negative, it is not spontaneous in that direction. Rather, the reverse reaction is the spontaneous redox reaction.

Example 9.3.2

What is the voltage of a voltaic cell based on this reaction? Is the reaction spontaneous as written?

$2NO_3^- + 8H^+ + 3Cu \rightarrow 2NO + 4H_2O + 3Cu^{2+}$

Solution

The overall redox reaction is formed from these two half reactions:

$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O \; E_{1/2} = 0.96 \text{ V} Cu^{2+} + 2 \, e^- \rightarrow Cu \; E_{1/2} = 0.34 \text{ V}$

The second reaction is reversed in the overall redox reaction, so its voltage changes sign from the reduction reaction:

$Cu \rightarrow Cu^{2+} + 2 \, e^- \; E_{1/2} = -0.34 \text{ V}$

To obtain the voltage of the voltaic cell based on the overall reaction, we simply combine the two voltages of the half reactions:

$E = 0.96 + (-0.34) = 0.62 \text{ V}$

Because the overall voltage is positive, the reaction is spontaneous as written.

? Exercise 9.3.2

What is the voltage of a voltaic cell based on this reaction? Is the reaction spontaneous as written?

$5Ni + 2MnO_4^- + 16H^+ \rightarrow 3Mn^{2+} + 8H_2O + 5Ni^{2+}$

Answer

1.76 V; spontaneous

Technically, any redox reaction can be set up to make a voltaic cell. In modern society, however, only certain redox reactions are put to practical use. A portable voltaic cell that generates electricity to power devices for our convenience is called a **battery**. All batteries are based on redox reactions.

The first battery (called a "voltaic pile") was constructed by the Italian scientist Alessandro Volta in 1800 and was based on the copper/zinc reaction depicted in Figure **9.3.1** - A Redox Reaction in Which the Two Half Reactions Are Physically Separated. Unfortunately, it was messy, requiring quantities of copper and zinc salts dissolved in water. In 1866, the French scientist Georges Leclanché invented the **dry cell,** a precursor to today's modern battery. A schematic of a dry cell is shown in Figure **9.3.2** - Dry Cell. The zinc case and the central carbon rod serve as the anode and cathode, respectively. The other reactants are combined into a moist paste that minimizes free liquid, so the battery is less messy (hence the name *dry cell*).

The actual redox reaction is complex but can be represented by the following redox reaction:

$$Zn + 2MnO_2 + 2NH_4^+ \rightarrow Zn^{2+} + Mn_2O_3 + 2NH_3 + H_2O$$

A dry cell has a voltage of about 1.56 V. While common and useful, dry cells have relatively short lifetimes and contain acidic components. They also cannot be recharged, so they are one-use only. Batteries that can be used only once are called **primary batteries**.

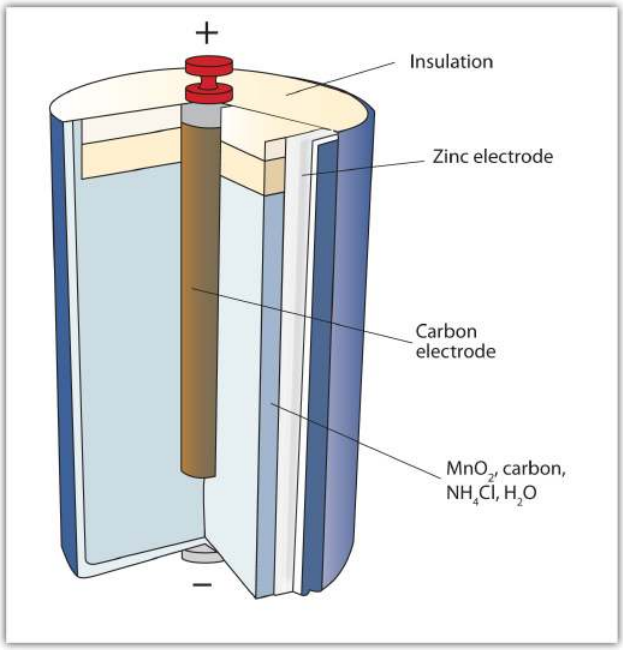


Figure **9.3.2** Dry Cell. The Leclanché dry cell is a common type of battery.

In the late 1950s, Lewis Urry of the Eveready Battery Company in Ohio invented the **alkaline battery** (still marketed today under the trade name *Energizer*). Alkaline batteries are similar to dry cells, but they use a basic moist paste rather than an acidic one. Moreover, the net amount of base does not change during the course of the redox reaction. The overall redox reaction is as follows:

$$Zn + 2MnO_2 \rightarrow ZnO + Mn_2O_3$$

Alkaline batteries have the advantage of being longer lasting and holding their voltage better—about 1.54 V—throughout their lifetime.

A common type of battery, especially with the increased popularity of personal electronic devices, is the button battery (Figure **9.3.3** - Button Battery). A button battery is a small battery that can power small electronic devices; the batteries can be as small as 5 mm across. Two popular redox reactions used for button batteries are the alkaline dry-cell reaction and a silver oxide-based reaction:

$$Zn + Ag_2O \rightarrow ZnO + 2Ag$$

Some button batteries use a lithium-based redox reaction, typified by this anode reaction:

$$Li \rightarrow Li^+ + e^- \quad E_{1/2} = 3.045 \text{ V}$$

The actual redox reaction depends on the composition of the cathode and is variable depending on voltage. Lithium batteries can also be used for applications that require more energy, such as portable computers and electric vehicles. Some lithium-based batteries are rechargeable and can be used over and over again; such batteries are called **secondary batteries**.

An important secondary battery is the lead storage battery, shown in the Figure **9.3.4** - Lead Storage Batteries. The lead storage battery is based on this redox reaction:

$$Pb + PbO_2 + 4H^+ + SO_4^{2-} \rightarrow 2PbSO_4 + 2H_2O$$

The redox reaction produces about 2 V, but it is typical to tie several individual batteries together to generate a larger voltage. The lead storage battery has the distinction that the product of both half reactions is $PbSO_4$, which as a solid that accumulates on the many plates within each cell. The lead storage battery is a secondary battery, as it can be recharged and reused many times. Because it is based on lead, these batteries are rather heavy. They should also be recycled when replaced so that potentially dangerous lead does not escape into the environment. Because of their characteristics, lead storage batteries are used to start large engines in automobiles, boats, and airplanes.

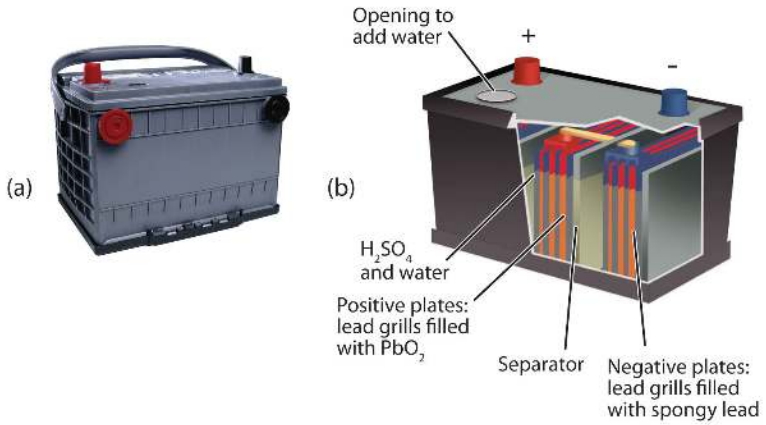


Figure14.4.4 Lead Storage Batteries Photo © Thinkstock. (a) A photo of a lead storage battery. (b) A schematic diagram of a lead storage battery.

Chemistry is Everywhere: Fuel Cells

A *fuel cell* is a type of battery in which reactants flow continuously into a specialized reaction chamber, and products flow out continuously while electrons are extracted from the reaction. Because all reactions in a fuel cell consist of a fuel and an oxidizer undergoing a redox reaction, an introduction of fuel cells is at home in a discussion of redox chemistry.

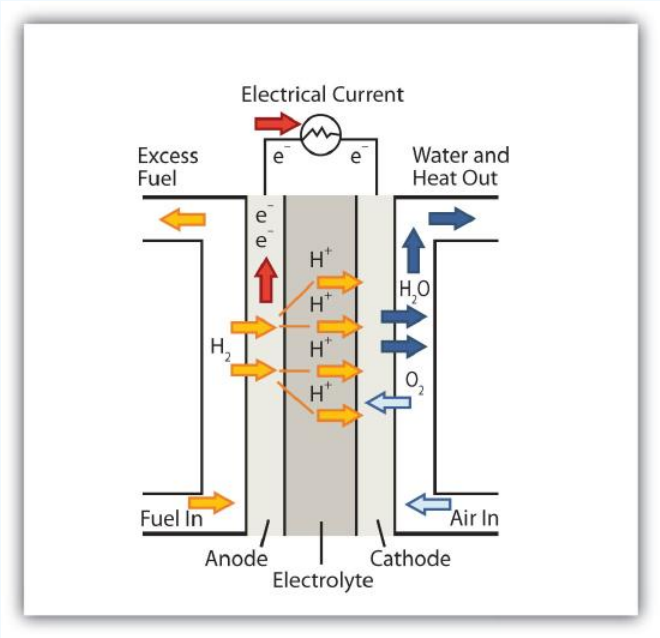


Figure **9.3.5** Fuel Cells. *This fuel cell uses H_2 as the fuel and O_2 as the oxidizer*.

By far the most common fuel cell reaction is based on hydrogen and oxygen:

$$2H_2 + O_2 \rightarrow 2H_2O \; E = 1.23 \text{ V under standard conditions}$$

However, fuel cells typically do not work under standard nor even optimal conditions, so they typically generate about 0.6–0.7 V. In this fuel cell, the only two products are water and electricity, so the fuel cell not only does not create pollution, but also makes a by-product that in some environments is a valuable commodity (water). Other fuels can be used besides hydrogen; fuel cells have been developed that work on methane, methyl alcohol, ethyl alcohol, carbon-rich materials, and even magnesium metal.

Hydrogen-based fuel cells were and are used to provide electricity for manned space vehicles, partly because their only chemical product is water, which could be used for drinking. However, there has been a recent resurgence in interest in fuel cells because of their potential use in electric cars. Most electric cars run on conventional batteries, which can be very heavy and expensive to replace. It is thought that fuel cells, rather than conventional batteries, might be better sources of electricity for automobiles.

Several current barriers to fuel cell use in electric cars include capacity, cost, and overall energy efficiency. The 2008 Honda FCX, the first production model of a vehicle powered with a fuel cell, can hold 4.1 kg (just under 9 lb) of highly pressured H_2 gas and has a range of 450 km (280 mi). It costs about $120,000–$140,000 to build, making the vehicle beyond the ability of most people to own. Finally, it always requires more energy to produce elemental hydrogen as a fuel than can be extracted from hydrogen as a fuel. As such, hydrogen is described as an energy carrier (like electricity) rather than an energy source (like oil and gas). This distinction points out a fundamental argument against fuel cells as a "better" power source.



Figure **9.3.6** Honda FCX. Source: Photo courtesy of vernieman, commons.wikimedia.org/wiki/File:Honda_FCX_2006_KLIMS_front.jpg.

The 2008 Honda FCX was the first production car to use a fuel cell as a power source. Nonetheless, the car is in very limited service because of its need for relatively large quantities of elemental hydrogen as fuel.

The limitations notwithstanding, there is a lot of interest in fuel cell research. If ways can be found to circumvent their current limitations, fuel cells may become more and more common as power sources.

Key Takeaways

- A voltaic cell produces electricity as a redox reaction occurs.
- The voltage of a voltaic cell can be determined by the reduction potentials of the half reactions.
- Voltaic cells are fashioned into batteries, which are a convenient source of electricity.

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9.4: Electrolysis

Learning Objectives

- Describe electrolysis from a perspective of redox reactions.
- Give examples of electrolysis applications.

Up to this point, we have considered redox reactions for processes that are spontaneous. When set up as a voltaic cell or battery, such reactions can be used as a source of electricity. However, it is possible to go in the other direction. By forcing electricity into a cell, we can make a redox reaction occur that normally would not be spontaneous. Under these circumstances, the cell is called an **electrolytic cell**, and the process that occurs in the cell is called **electrolysis** (Figure 9.4.1).

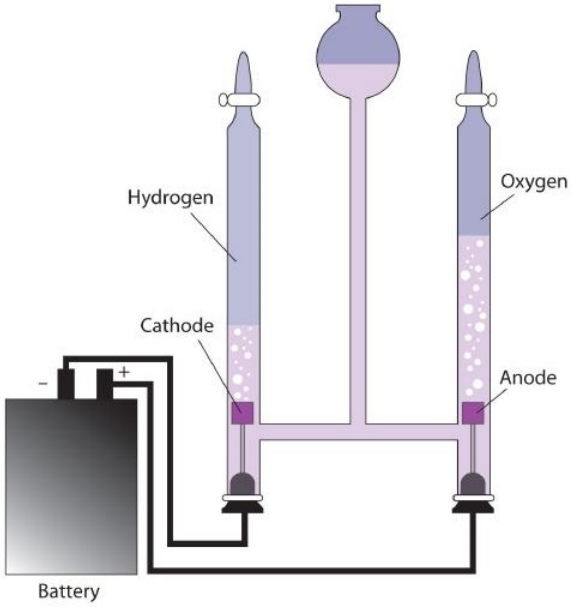


Figure 9.4.1: Electrolysis. In an electrolytic cell, electricity is forced through the cell to induce a non-spontaneous redox reaction. Here, the redox reaction $2H_2O \rightarrow 2H_2 + O_2$ is being caused by the introduction of electricity, which is supplied by the battery.

Electrolysis has many applications. For example, if NaCl is melted at about 800°C in an electrolytic cell and an electric current is passed through it, elemental sodium will appear at the cathode and elemental chlorine will appear at the anode as the following two reactions occur:

$$Na^+ + e^- \rightarrow Na$$

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

Normally we expect elemental sodium and chlorine to react spontaneously to make NaCl. However, by using an input of electricity, we can force the opposite reaction to occur and generate the elements. Lithium, potassium, and magnesium can also be isolated from compounds by electrolysis.

Another element that is isolated by electrolysis is aluminum. Aluminum formerly was a difficult metal to isolate in its elemental form; in fact, the top of the Washington Monument has a 2.8 kg cap of aluminum metal, which at the time (1884) was the largest piece of elemental aluminum ever isolated. However, in 1886, the American Charles Hall and the Frenchman Paul Héroult almost simultaneously worked out an electrolytic process for isolating aluminum from bauxite—an ore of aluminum whose chemical formula is $AlO_x(OH)_{3-2x}$. The basic reactions are as follows:

$$Al^{3+} + 3e^- \rightarrow Al_2O^{2-} \rightarrow O_2 + 4e^-$$

With the development of the Hall-Héroult process, the price of aluminum dropped by a factor of over 200, and aluminum metal became common. So much elemental aluminum is produced in the United States each year that it has been estimated that the

electrolysis of aluminum uses 5% of all the electricity in the country. (Recycling aluminum requires about 1/70th the energy of refining aluminum from ore, which illustrates the tremendous energy savings that recycling provides.)

Another application of electrolysis is electroplating, which is the deposition of a thin layer of metal on an object for protective or decorative purposes (Figure **9.4.2**). Essentially, a metal object is connected to the cathode of an electrolytic cell and immersed in a solution of a particular metal cation. When the electrolytic cell is operated, a thin coating of the metal cation is reduced to the elemental metal on the surface of the object; the thickness of the coating can be as little as a few micrometers (10^{-6} m). Jewelry, eating utensils, electrical contacts, and car parts like bumpers are common items that are electroplated. Gold, silver, nickel, copper, and chromium are common metals used in electroplating.

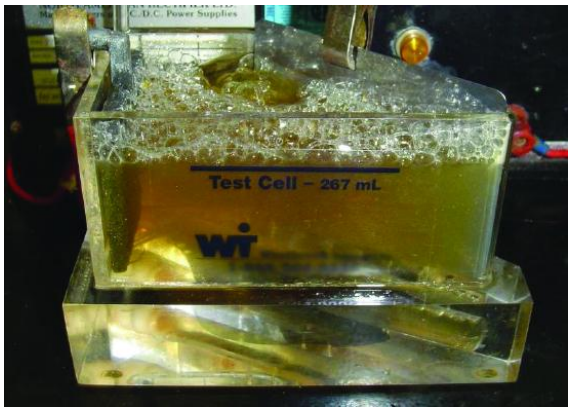


Figure **9.4.2**: Electroplating Source. Photo courtesy of Fstep, http://commons.wikimedia.org/wiki/File:Hullcell.jpg(opens in new window).

Key Takeaways

- Electrolysis is a forced non-spontaneous redox occurence by the introduction of electricity into a cell from an outside source.
- Electrolysis is used to isolate elements and electroplate objects.

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9.E: Oxidation-Reduction Reaction (Exercises)

Exercises (Oxidation-Reduction Reactions)

1. Is this reaction a redox reaction? Explain your answer. $2K(s) + Br_2(\ell) \rightarrow 2KBr(s)$

2. Is this reaction a redox reaction? Explain your answer. $2NaCl(aq) + Pb(NO_3)_2(aq) \rightarrow 2NaNO_3(aq) + PbCl_2(s)$

3. Which substance loses electrons and which substance gains electrons in this reaction? $2Mg(s) + O_2(g) \rightarrow 2MgO$

4. Which substance loses electrons and which substance gains electrons in this reaction? $16Fe(s) + 3S_8(s) \rightarrow 8Fe_2S_3(s)$

5. Which substance is oxidized and which substance is reduced in this reaction? $2Li(s) + O_2(g) \rightarrow Li_2O_2(s)$

6. Which substance is oxidized and which substance is reduced in this reaction? $2Fe(s) + 3I_2(s) \rightarrow 2FeI_3(s)$

7. What are two different definitions of oxidation?

8. What are two different definitions of reduction?

9. Assign oxidation numbers to the atoms in each substance.
   a. P_4
   b. SO_3
   c. SO_3^{2-}
   d. $Ca_3(PO_3)_2$

10. Assign oxidation numbers to the atoms in each substance.
    a. PCl_5
    b. $(NH_4)_2Se$
    c. Ag
    d. Li_2O_2

11. Assign oxidation numbers to the atoms in each substance.
    a. NO
    b. NO_2
    c. $CrCl_2$
    d. $CrCl_3$

12. Assign oxidation numbers to the atoms in each substance.
    a. NaH
    b. N_2O_3
    c. NO_2^-
    d. $CuNO_3$

13. Assign oxidation numbers to the atoms in each substance.
    a. CH_2O
    b. NH_3
    c. Rb_2SO_4

d. $Zn(C_2H_3O_2)_2$

14. Assign oxidation numbers to the atoms in each substance.
    a. C_6H_6
    b. $B(OH)_3$
    c. Li_2S
    d. Au

15. Identify what is being oxidized and reduced in this redox reaction by assigning oxidation numbers to the atoms. $2NO + Cl_2 \rightarrow 2NOCl$

16. Identify what is being oxidized and reduced in this redox reaction by assigning oxidation numbers to the atoms. $Sr + SO_3 \rightarrow SrSO_3$

17. Identify what is being oxidized and reduced in this redox reaction by assigning oxidation numbers to the atoms. $2KrF_2 + 2H_2O \rightarrow 2Kr + 4HF + O_2$

18. Identify what is being oxidized and reduced in this redox reaction by assigning oxidation numbers to the atoms. $SO_3 + SCl_2 \rightarrow SOCl_2 + SO_2$

19. Identify what is being oxidized and reduced in this redox reaction by assigning oxidation numbers to the atoms. $2Rb + MgCl_2 \rightarrow 2RbCl + Mg$

20. Identify what is being oxidized and reduced in this redox reaction by assigning oxidation numbers to the atoms. $2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$

Answers

1. yes because oxidation numbers are changing

3. lose: Mg; gain: O

5. oxidized: Li; reduced: O

7. increase in oxidation number; loss of electrons

9.
    a. P: 0
    b. S: +6; O: −2
    c. S: +4; O: −2
    d. Ca: +2; P: +3; O: −2

11.
    a. N: +2; O: −2
    b. N: +4; O: −2
    c. Cr: +2; Cl: −1
    d. Cr: +3; Cl: −1

13.
    a. C: 0; H: +1; O: −2
    b. N: −3; H: +1
    c. Rb: +1; S: +6; O: −2

d. Zn: +2; C: 0; H: +1; O: −2

15. oxidized: N; reduced: Cl

17. oxidized: O; reduced: Kr

19.oxidized: Rb; reduced: Mg

Exercises (Balancing Redox Reactions)

1. Balance these redox reactions by inspection.
   a. $Na + F_2 \rightarrow NaF$
   b. $Al_2O_3 + H_2 \rightarrow Al + H_2O$

2. Balance these redox reactions by inspection.
   a. $Fe_2S_3 + O_2 \rightarrow Fe_2O_3 + S$
   b. $Cu_2O + H_2 \rightarrow Cu + H_2O$

3. Balance these redox reactions by inspection.
   a. $CH_4 + O_2 \rightarrow CO_2 + H_2O$
   b. $P_2O_5 + Cl_2 \rightarrow PCl_3 + O_2$

4. Balance these redox reactions by inspection.
   a. $PbCl_2 + FeCl_3 \rightarrow PbCl_4 + FeCl_2$
   b. $SO_2 + F_2 \rightarrow SF_4 + OF_2$

5. Balance these redox reactions by the half reaction method.
   a. $Ca + H^+ \rightarrow Ca^{2+} + H_2$
   b. $Sn^{2+} \rightarrow Sn + Sn^{4+}$ (Hint: both half reactions will start with the same reactant.)

6. Balance these redox reactions by the half reaction method.
   a. $Fe^{3+} + Sn^{2+} \rightarrow Fe + Sn^{4+}$
   b. $Pb^{2+} \rightarrow Pb + Pb^{4+}$ (Hint: both half reactions will start with the same reactant.)

7. Balance these redox reactions by the half reaction method.
   a. $Na + Hg_2Cl_2 \rightarrow NaCl + Hg$
   b. $Al_2O_3 + C \rightarrow Al + CO_2$

8. Balance these redox reactions by the half reaction method.
   a. $Br^- + I_2 \rightarrow I^- + Br_2$
   b. $CrCl_3 + F_2 \rightarrow CrF_3 + Cl_2$

9. Balance these redox reactions that occur in aqueous solution. Use whatever water-derived species is necessary; there may be more than one correct balanced equation.
   a. $Cu + NO_3^- \rightarrow Cu^{2+} + NO_2$
   b. $Fe + MnO_4^- \rightarrow Fe^{3+} + Mn$

10. Balance these redox reactions that occur in aqueous solution. Use whatever water-derived species is necessary; there may be more than one correct balanced equation.

a. $CrO_3 + Ni^{2+} \rightarrow Cr^{3+} + Ni^{3+}$
b. $OsO_4 + C_2H_4 \rightarrow Os + CO_2$

11. Balance these redox reactions that occur in aqueous solution. Use whatever water-derived species is necessary; there may be more than one correct balanced equation.
a. $ClO^- + Ti^{2+} \rightarrow Ti^{4+} + Cl^-$
b. $BrO_3^- + Ag \rightarrow Ag^+ + BrO_2$

12. Balance these redox reactions that occur in aqueous solution. Use whatever water-derived species is necessary; there may be more than one correct balanced equation.
a. $H_2O_2 + NO \rightarrow N_2O_3 + H_2O$
b. $VO_2^+ + NO \rightarrow V^{3+} + NO_2$

13. Explain why this chemical equation is not balanced and balance it if it can be balanced: $Cr^{2+} + Cl_2 \rightarrow Cr^{3+} + 2Cl^-$

14. Explain why this equation is not balanced and balance it if it can be balanced: $O_2 + 2H_2O + Br_2 \rightarrow 4OH^- + 2Br^-$

Answers

1.
a. $2Na + F_2 \rightarrow 2NaF$
b. $Al_2O_3 + 3H_2 \rightarrow 2Al + 3H_2O$

3.
a. $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
b. $2P_2O_5 + 6Cl_2 \rightarrow 4PCl_3 + 5O_2$

5.
a. $Ca + 2H^+ \rightarrow Ca^{2+} + H_2$
b. $2Sn^{2+} \rightarrow Sn + Sn^{4+}$

7.
a. $2Na + Hg_2Cl_2 \rightarrow 2NaCl + 2Hg$
b. $2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$

9.
a. $4H^+ + Cu + 2NO_3^- \rightarrow Cu^{2+} + 2NO_2 + 2H_2O$ in acidic solution; $2H_2O + Cu + 2NO_3^- \rightarrow Cu^{2+} + 2NO_2 + 4OH^-$ in basic solution
b. $24H^+ + 3MnO_4^- + 7Fe \rightarrow 7Fe^{3+} + 3Mn + 12H_2O$ in acidic solution; $12H_2O + 3MnO_4^- + 7Fe \rightarrow 7Fe^{3+} + 3Mn + 24OH^-$ in basic solution

11.
a. $2H^+ + ClO^- + Ti^{2+} \rightarrow Cl^- + H_2O + Ti^{4+}$ in acidic solution; $H_2O + ClO^- + Ti^{2+} \rightarrow Cl^- + Ti^{4+} + 2OH^-$ in basic solution
b. $2H^+ + BrO_3^- + Ag \rightarrow BrO_2 + H_2O + Ag^+$ in acidic solution; $H_2O + BrO_3^- + Ag \rightarrow BrO_2 + Ag^+ + 2OH^-$ in basic solution

13. The charges are not properly balanced. The correct balanced equation is $2Cr^{2+} + Cl_2 \rightarrow 2Cr^{3+} + 2Cl^-$.

Exercises (Applications of Redox Reactions - Voltaic Cells)

1. Draw the voltaic cell represented by this reaction and label the cathode, the anode, the salt bridge, the oxidation half cell, the reduction half cell, the positive electrode, and the negative electrode. Use Fig. 14.4.1 as a guide. $Zn + 2Ag^+ \rightarrow Zn^{2+} + 2Ag$

2. Draw the voltaic cell represented by this reaction and label the cathode, the anode, the salt bridge, the oxidation half cell, the reduction half cell, the positive electrode, and the negative electrode. Use Fig. 14.4.1 as a guide. $3Mg + 2Cr^{3+} \rightarrow 3Mg^{2+} + 2Cr$

3. What is the voltage of this half reaction? $2F^- \rightarrow F_2 + 2e^-$

4. What is the voltage of this half reaction? $Na \rightarrow Na^+ + e^-$

5. What is the voltage of the voltaic cell in Exercise 1? Consult Table 14.4.1.

6. What is the voltage of the voltaic cell in Exercise 2? Consult Table 14.4.1.

7. Balance this redox reaction and determine its voltage. Is it spontaneous? $Li^+ + Al \rightarrow Li + Al^{3+}$

8. Balance this redox reaction and determine its voltage. Is it spontaneous? $Pb^{2+} + Ni \rightarrow Pb + Ni^{2+}$

9. Balance this redox reaction and determine its voltage. Is it spontaneous? $Cu^{2+} + Ag + Cl^- \rightarrow Cu + AgCl$

10. Balance this redox reaction and determine its voltage. Is it spontaneous? $Mn^{2+} + Br_2 \rightarrow MnO_4^- + Br^-$

11. Which reaction represents the cathode reaction in Exercise 7? The anode reaction?

12. Which reaction represents the cathode reaction in Exercise 8? The anode reaction?

13. Which reaction represents the cathode reaction in Exercise 9? The anode reaction?

14. Which reaction represents the cathode reaction in Exercise 10? The anode reaction?

15. A voltaic cell is based on this reaction: $Ni + 2Au^+ \rightarrow Ni^{2+} + 2Au$; If the voltage of the cell is 0.33 V, what is the standard reduction potential of the $Au^+ + e^- \rightarrow Au$ half reaction?

16. A voltaic cell is based on this reaction: $3Pb + 2V^{3+} \rightarrow 3Pb^{2+} + 2V$; If the voltage of the cell is −0.72 V, what is the standard reduction potential of the $V^{3+} + 3e^- \rightarrow V$ half reaction?

17. What species is being oxidized and what species is being reduced in a dry cell?

18. What species is being oxidized and what species is being reduced in an alkaline battery?

19. What species is being oxidized and what species is being reduced in a silver oxide button battery?

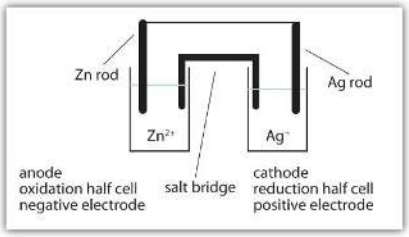
20. What species is being oxidized and what species is being reduced in a lead storage battery?

21. Based on the data in Table 14.4.1, what is the highest voltage battery you can construct?

22. Based on the data in Table 14.4.1, what is the lowest voltage battery you can construct? (This may be more challenging to answer than Exercise 21.)

Answers

1.



3. −2.87 V

5. 1.56 V

7. $3Li^{+} + Al \rightarrow 3Li + Al^{3+}$; −1.39 V; not spontaneous

9. $Cu^{2+} + 2Ag + 2Cl^{-} \rightarrow Cu + 2AgCl$; 0.12 V; spontaneous

11. cathode reaction: $Li^{+} + e^{-} \rightarrow Li$; anode reaction: $Al \rightarrow Al^{3+} + 3e^{-}$

13. cathode reaction: $Cu^{2+} + 2e^{-} \rightarrow Cu$; anode reaction: $Ag + Cl^{-} \rightarrow AgCl + e^{-}$

15. 0.08 V

17. oxidized: Zn; reduced: Mn

19. oxidized: Zn; reduced: Ag

21. 5.92 V from the reaction of F_2 and Li

Exercises (Electrolysis)

1. Define *electrolytic cell*.

2. How does the operation of an electrolytic cell differ from a voltaic cell?

3. List at least three elements that are produced by electrolysis.

4. Write the half reactions for the electrolysis of the elements listed in Exercise 3.

5. Based on Table 14.4.1, what voltage must be applied to an electrolytic cell to electroplate copper from Cu^{2+}?

6. Based on Table 14.4.1, what voltage must be applied to an electrolytic cell to electroplate aluminum from Al^{3+}?

Answers

1. an electrochemical cell in which charge is forced through and a nonspontaneous reaction occurs

3 any three of the following: Al, K, Li, Na, Cl_2, or Mg

5. 0.34 V

Additional Exercises

1. Oxidation was once defined as chemically adding oxygen to a substance. Use this reaction to argue that this definition is consistent with the modern definition of oxidation: $2Mg + O_2 \rightarrow 2MgO$

2. Reduction was once defined as chemically adding hydrogen to a substance. Use this reaction to argue that this definition is consistent with the modern definition of reduction: $C_2H_2 + 2H_2 \rightarrow C_2H_6$

3. Assign oxidation numbers to the atoms in each substance.
   a. Kr (krypton)
   b. krypton tetrafluoride (KrF_4)
   c. dioxygen difluoride (O_2F_2)

4. Assign oxidation numbers to the atoms in each substance.
   a. lithium hydride (LiH)
   b. potassium peroxide (K_2O_2)
   c. potassium fluoride (KF)

5. N atoms can have a wide range of oxidation numbers. Assign oxidation numbers for the N atom in each compound, all of which are known compounds.
   a. N_2O_5
   b. N_2O_4
   c. NO_2
   d. NO
   e. N_2H_4
   f. NH_3

6. Cr atoms can have a wide range of oxidation numbers. Assign oxidation numbers for the Cr atom in each compound, all of which are known compounds.
   a. Na_2CrO_4
   b. $Na_2Cr_2O_7$
   c. CrF_5
   d. $CrCl_3$
   e. $CrCl_2$

7. Balance this redox reaction by inspection: $S_8 + O_2 \rightarrow SO_2$

8. Balance this redox reaction by inspection: $C_{18}H_{38} + O_2 \rightarrow CO_2 + H_2O$

9. Balance this redox reaction by the half reaction method by assuming an acidic solution: $Cr_2O_7^{2-} + Fe \rightarrow Cr^{3+} + Fe^{3+}$

10. Balance the redox reaction in Exercise 9 by the half reaction method by assuming a basic solution.

11. The uranyl ion (UO_2^{2+}) is a fairly stable ion of uranium that requires strong reducers to reduce the oxidation number of uranium further. Balance this redox reaction using the half reaction method by assuming an acidic solution.$UO_2^{2+} + HN_3 \rightarrow U + N_2$

12. Balance the redox reaction in Exercise 11 by the half reaction method by assuming a basic solution.

13. Zinc metal can be dissolved by acid, which contains H^+ ions. Demonstrate that this is consistent with the fact that this reaction has a spontaneous voltage: $Zn + 2H^+ \rightarrow Zn^{2+} + H_2$

14. Copper metal cannot be dissolved by acid, which contains H^+ ions. Demonstrate that this is consistent with the fact that this reaction has a nonspontaneous voltage: $Cu + 2H^+ \rightarrow Cu^{2+} + H_2$

15. A disproportionation reaction occurs when a single reactant is both oxidized and reduced. Balance and determine the voltage of this disproportionation reaction. Use the data in Table 14.4.1 - Standard Reduction Potentials of Half Reactions: $Cr^{2+} \rightarrow Cr + Cr^{3+}$

16. A disproportionation reaction occurs when a single reactant is both oxidized and reduced. Balance and determine the voltage of this disproportionation reaction. Use the data in Table 14.4.1 - Standard Reduction Potentials of Half Reactions: $Fe^{2+} \rightarrow Fe + Fe^{3+}$

17. What would be overall reaction for a fuel cell that uses CH_4 as the fuel?

18. What would be overall reaction for a fuel cell that uses gasoline (general formula C_8H_{18}) as the fuel?

19. When NaCl undergoes electrolysis, sodium appears at the cathode. Is the definition of cathode the same for an electrolytic cell as it is for a voltaic cell?

20. When NaCl undergoes electrolysis, chlorine appears at the anode. Is the definition of anode the same for an electrolytic cell as it is for a voltaic cell?

21. An award is being plated with pure gold before it is presented to a recipient. If the area of the award is 55.0 cm^2 and will be plated with 3.00 µm of Au, what mass of Au will be plated on the award? The density of Au is 19.3 g/cm^3.

22. The unit of electrical charge is called the coulomb (C). It takes 96,500 coulombs of charge to reduce 27.0 g of Al from Al^{3+} to Al metal. At 1,040 cm^3, how many coulombs of charge were needed to reduce the aluminum in the cap of the Washington monument, assuming the cap is pure Al? The density of Al is 2.70 g/cm^3.

Answers

1. As oxygen is added to magnesium, it is being oxidized. In modern terms, the Mg atoms are losing electrons and being oxidized, while the electrons are going to the O atoms.

3.

a. Kr: 0
b. Kr: +4; F: −1
c. O: +1; F: −1

5.

a. +5
b. +4
c. +4
d. +2
e. −2
f. −3

7. $S_8 + 8O_2 \rightarrow 8SO_2$

9. $14H^+ + Cr_2O_7^{2-} + 2Fe \rightarrow 2Cr^{3+} + 7H_2O + 2Fe^{3+}$

11. $6HN_3 + UO_2^{2+} \rightarrow U + 2H_2O + 9N_2 + 2H^+$

13. The voltage of the reaction is +0.76 V, which implies a spontaneous reaction.

15. $3Cr^{2+} \rightarrow Cr + 2Cr^{3+}$; −0.50 V

17. $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

19. yes because reduction occurs at the cathode

21. 0.318 g

a.

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CHAPTER OVERVIEW

10: Organic Chemistry

Organic chemistry is the study of the chemistry of carbon compounds. Why focus on carbon? Carbon has properties that give its chemistry unparalleled complexity. It forms four covalent bonds, which give it great flexibility in bonding. It makes fairly strong bonds with itself (a characteristic called *catenation*), allowing for the formation of large molecules; it also forms fairly strong bonds with other elements, allowing for the possibility of a wide variety of substances. No other element demonstrates the versatility of carbon when it comes to making compounds. So an entire field of chemistry is devoted to the study of the compounds and reactivity of one element.

Because of the potential for complexity, chemists have defined a rather rigorous system to describe the chemistry of carbon. We will introduce some of that system in this chapter. Should you continue your study of chemistry beyond this text, you will find a much larger world of organic chemistry than we can cover in a single chapter.

10.1: Prelude to Organic Chemistry
10.2: Hydrocarbons
10.3: Branched Hydrocarbons
10.4: Alkyl Halides and Alcohols
10.5: Other Oxygen-Containing Functional Groups
10.6: Other Functional Groups
10.7: Polymers
10.E: Organic Chemistry (Exercises)

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10.1: Prelude to Organic Chemistry

All life on Earth is ultimately based on photosynthesis. Photosynthesis is the process by which plants absorb CO_2 and H_2O from their environment and, in the presence of sunlight, convert those substances into a simple sugar (glucose) and ultimately starches and other building blocks of life. The net photosynthesis chemical reaction is as follows:

$$6CO_2 + 6H_2O \overset{light}{\rightarrow} C_6H_{12}O_6 + 6O_2$$

Oxygen is also a product of photosynthesis. Most forms of animal life (including people) depend on oxygen to breathe, which makes plants indispensable. Virtually all food sources come from plants, eaten either directly (as fruits, vegetables, or grains) or indirectly (as feedstock for meat animals such as cattle, poultry, pigs, sheep, goats, and the like). Plants are absolutely necessary for life to exist.



Figure **10.1.1**: Photosynthesis. In the presence of the sun, plants perform photosynthesis, the chemical reactions that convert CO_2 and H_2O to glucose. The reaction also produces O_2, which is necessary for animal life. Virtually all life on Earth depends on photosynthesis.

The net reaction for photosynthesis is misleadingly simple. A series of reactions, called light-dependent reactions, start by the absorption of light by pigments (not just chlorophyll, as commonly misunderstood) in plant cells. This is followed by a series of light-independent reactions, so named not because they happen in the dark, but because they do not directly involve light. However, light-independent reactions involve the products of reactions stimulated by light, so they ultimately depend on light. The whole series of reactions involves many chemicals, enzymes, breaking and making chemical bonds, the transfer of electrons and H^+ ions, and other chemical processes. The elucidation of the actual steps of photosynthesis—a process still unduplicated artificially—is a major achievement of modern chemistry.

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10.2: 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:

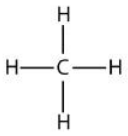


Figure **10.2.1** - Three-Dimensional Representation of Methane.

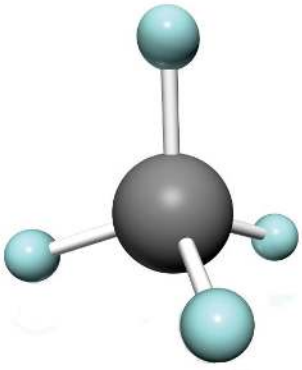
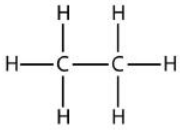
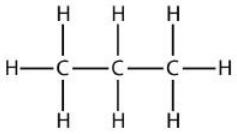


Figure **10.2.1** Three-Dimensional Representation of Methane © Thinkstock. The methane molecule is three dimensional, with the H atoms in the positions of the four corners of a tetrahedron.

The next-largest alkane has two C atoms that are covalently bonded to each other. For each C atom to make four covalent bonds, each C atom must be bonded to three H atoms. The resulting molecule, whose formula is C_2H_6, is ethane:



Propane has a backbone of three C atoms surrounded by H atoms. You should be able to verify that the molecular formula for propane is C_3H_8:



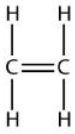
The diagrams representing alkanes are called **structural formulas** because they show the structure of the molecule. As molecules get larger, structural formulas become more and more complex. One way around this is to use a **condensed structural formula**, which lists the formula of each C atom in the backbone of the molecule. For example, the condensed structural formula for ethane is CH_3CH_3, while for propane it is $CH_3CH_2CH_3$. Table **10.2.1** - The First 10 Alkanes, gives the molecular formulas, the condensed structural formulas, and the names of the first 10 alkanes.

Table **10.2.1** The First 10 Alkanes

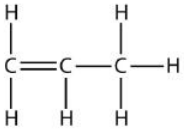
Molecular Formula	Condensed Structural Formula	Name
CH_4	CH_4	methane
C_2H_6	CH_3CH_3	ethane
C_3H_8	$CH_3CH_2CH_3$	propane
C_4H_{10}	$CH_3CH_2CH_2CH_3$	butane
C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	pentane
C_6H_{14}	$CH_3(CH_2)_4CH_3$	hexane
C_7H_{16}	$CH_3(CH_2)_5CH_3$	heptane
C_8H_{18}	$CH_3(CH_2)_6CH_3$	octane
C_9H_{20}	$CH_3(CH_2)_7CH_3$	nonane
$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	decane

Because alkanes have the maximum number of H atoms possible according to the rules of covalent bonds, alkanes are also referred to as **saturated hydrocarbons**.

Alkenes have a C–C double bond. Because they have less than the maximum number of H atoms possible, they are **unsaturated hydrocarbons**. The smallest alkene—ethene—has two C atoms and is also known by its common name ethylene:

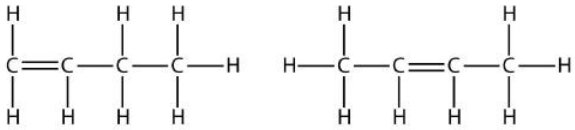


The next largest alkene—propene—has three C atoms with a C–C double bond between two of the C atoms. It is also known as propylene:



What do you notice about the names of alkanes and alkenes? The names of alkenes are the same as their corresponding alkanes except that the ending is *-ene*, rather than *-ane*. Using a stem to indicate the number of C atoms in a molecule and an ending to represent the type of organic compound is common in organic chemistry, as we shall see.

With the introduction of the next alkene, butene, we begin to see a major issue with organic molecules: choices. With four C atoms, the C–C double bond can go between the first and second C atoms or between the second and third C atoms:



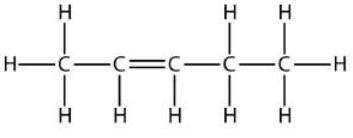
2 structural formulas for butene, with the first butene having the double bond on the first and second carbon from the left and the latter having its double bond on the second and third carbon from the left.

(A double bond between the third and fourth C atoms is the same as having it between the first and second C atoms, only flipped over.) The rules of naming in organic chemistry require that these two substances have different names. The first molecule is named *1-butene*, while the second molecule is named *2-butene*. The number at the beginning of the name indicates where the double bond originates. The lowest possible number is used to number a feature in a molecule; hence, calling the second molecule 3-butene would be incorrect. Numbers are common parts of organic chemical names because they indicate which C atom in a chain contains a distinguishing feature.

The compounds 1-butene and 2-butene have different physical and chemical properties, even though they have the same molecular formula—C_4H_8. Different molecules with the same molecular formula are called **isomers**. Isomers are common in organic chemistry and contribute to its complexity.

Example 10.2.1

Based on the names for the butene molecules, propose a name for this molecule.



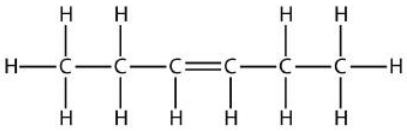
A structural formula of a five carbon molecule with a double bond on the third and fourth carbon from the left. There are ten hydrogen atoms in total.

Solution

With five C atoms, we will use the *pent-* stem, and with a C–C double bond, this is an alkene, so this molecule is a pentene. In numbering the C atoms, we use the number *2* because it is the lower possible label. So this molecule is named 2-pentene.

Exercise 10.2.1

Based on the names for the butene molecules, propose a name for this molecule.



A structural formula of a six carbon molecule with a double bond on the third and fourth carbon from the left. There are twelve hydrogen atoms in total.

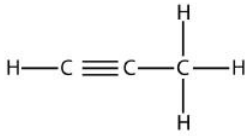
Answer

3-hexene

Alkynes, with a C–C triple bond, are named similarly to alkenes except their names end in *-yne*. The smallest alkyne is ethyne, which is also known as acetylene:

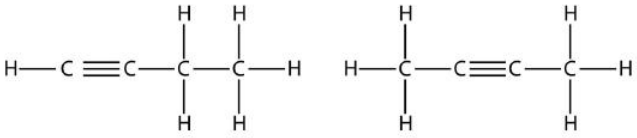


Propyne has the structure



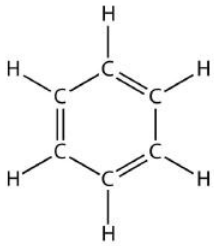
Structural formula showing three carbon molecules with a triple bond present between the first and second carbon atom. The appropriate number of hydrogen atoms is attached to each carbon atom.

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.

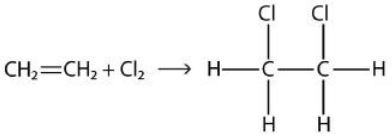
The alternating single and double C–C bonds give the benzene ring a special stability, and it does not react like an alkene as might be suspected. Benzene has the molecular formula C_6H_6; in larger aromatic compounds, a different atom replaces one or more of the H atoms.

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 **10.2.2** - Combustion). The combustion reaction for gasoline, for example, which can be represented by C_8H_{18}, is as follows:

$$2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O + \sim 5060kJ$$



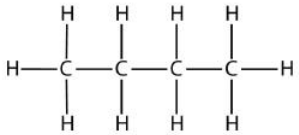
Figure **10.2.2** Combustion © Thinkstock. The combustion of hydrocarbons is a primary source of energy in our society.

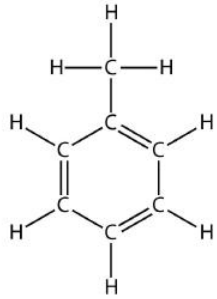
Key Takeaways

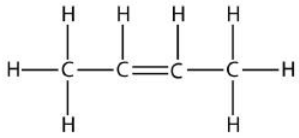
- The simplest organic compounds are hydrocarbons and are composed of carbon and hydrogen.
- Hydrocarbons can be aliphatic or aromatic; aliphatic hydrocarbons are divided into alkanes, alkenes, and alkynes.
- The combustion of hydrocarbons is a primary source of energy for our society.

Exercise 10.2.2

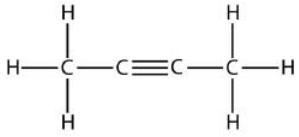
1. Define *hydrocarbon*. What are the two general types of hydrocarbons?
2. What are the three different types of aliphatic hydrocarbons? How are they defined?
3. Indicate whether each molecule is an aliphatic or an aromatic hydrocarbon; if aliphatic, identify the molecule as an alkane, an alkene, or an alkyne.

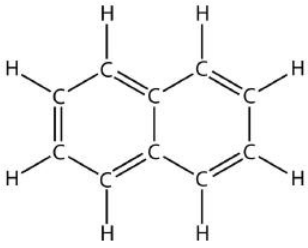
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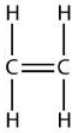
b. 

c. 

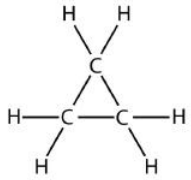
4. Indicate whether each molecule is an aliphatic or an aromatic hydrocarbon; if aliphatic, identify the molecule as an alkane, an alkene, or an alkyne.

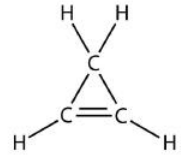
a. 

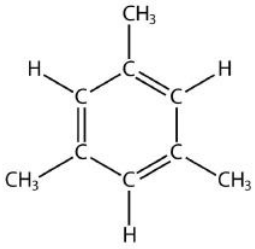
b. 

c. 

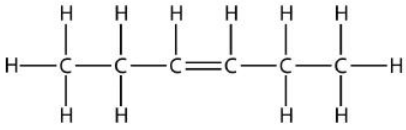
5. Indicate whether each molecule is an aliphatic or an aromatic hydrocarbon; if aliphatic, identify the molecule as an alkane, an alkene, or an alkyne.

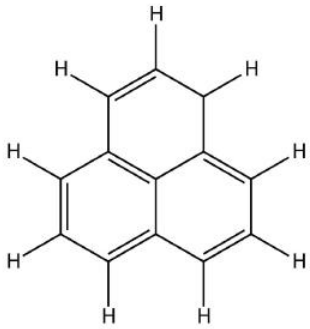
a. 

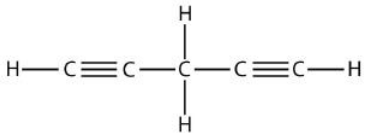
b. 

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. 

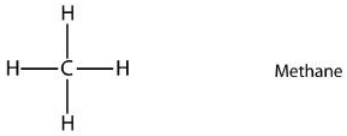
7. Name and draw the structural formulas for the four smallest alkanes.
8. Name and draw the structural formulas for the four smallest alkenes.
9. What does the term *aromatic* imply about an organic molecule?
10. What does the term *normal* imply when used for alkanes?
11. Explain why the name *1-propene* 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.

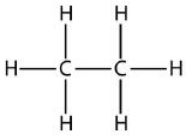
17. Draw the structure of the product of the reaction of bromine with propene.
18. Draw the structure of the product of the reaction of chlorine with 2-butene.
19. Draw the structure of the product of the reaction of hydrogen with 1-butene.
20. Draw the structure of the product of the reaction of hydrogen 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.

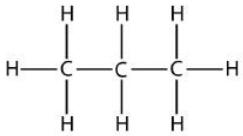
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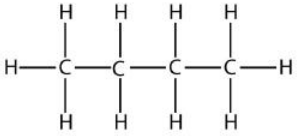
Answers

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.

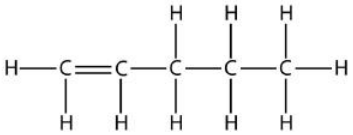

Methane


Ethane

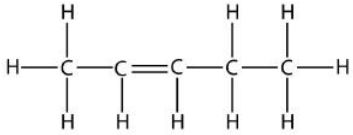

Propane


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



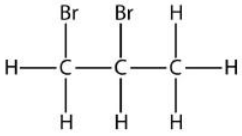
2-Pentene

13.

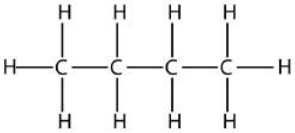
14.

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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10.3: Branched Hydrocarbons

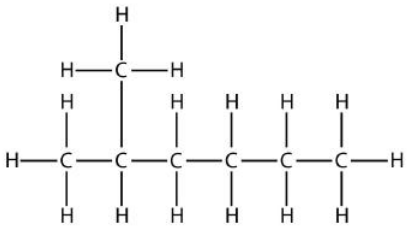
Learning Objectives

- Name a branched hydrocarbon from its structure.
- Draw the structural formula of a branched hydrocarbon from its name.

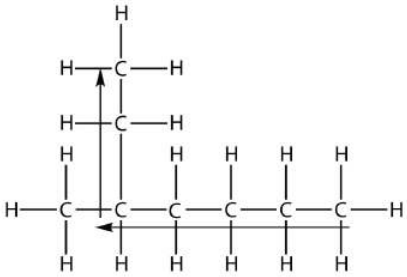
Not all hydrocarbons are straight chains. Many hydrocarbons have branches of C atoms attached to a chain. These branched alkanes are isomers of straight-chain alkanes having the same number of C atoms. However, they are different compounds with different physical and chemical properties. As such, they 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



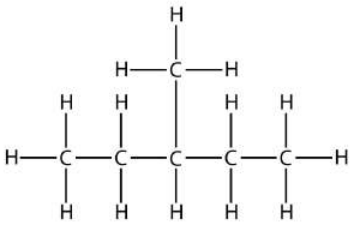
the longest chain of C atoms is not six, but seven, as shown. So this molecule will be named as a heptane.

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 **10.3.1** - Substituent Names, lists the substituent names for the five smallest substituents.

Table **10.3.1** Substituent Names

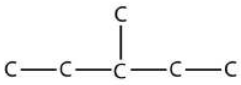
Substituent Formula	Number of C Atoms	Name of Substituent
CH_3	1	*methyl-*
CH_3CH_2	2	*ethyl-*
$CH_3CH_2CH_2$	3	*propyl-*
$CH_3CH_2CH_2CH_2$	4	*butyl-*
$CH_3CH_2CH_2CH_2CH_2$	5	*pentyl-*
and so forth	and so forth	and so forth

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!

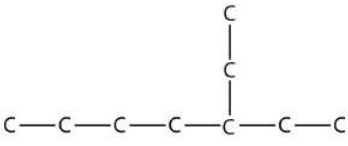
It is common to write the structural formula of a hydrocarbon without the H atoms, for clarity. So we can also represent 3-methylpentane as



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 10.3.1

Name this molecule.

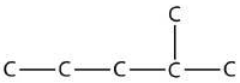


Solution

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 10.3.1

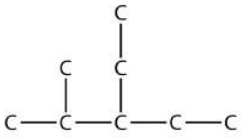
Name this molecule.



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



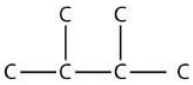
is 3-ethyl-2-methylpentane.

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 **10.3.2** - Numerical Prefixes to Use for Multiple Substituents. The number of the position values must agree with the numerical prefix before the substituent.

Table **10.3.2**: 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

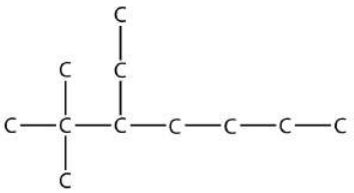
Consider this molecule:



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 10.3.2

Name this molecule.

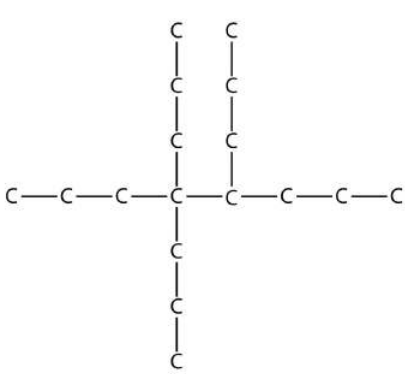


Solution

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 10.3.2

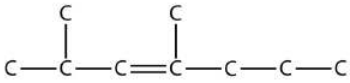
Name this molecule.



Answer

4,4,5-tripropyloctane

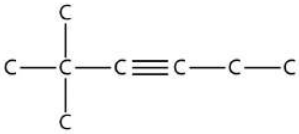
Alkenes and alkynes are named in a similar fashion. The biggest difference is that when identifying the longest carbon chain, it *must* contain the C–C double or triple bond. Furthermore, when numbering the main chain, the double or triple bond gets the lowest possible number. This means that there may 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 10.3.3

Name this molecule.



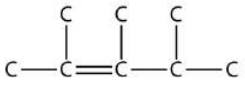
Solution

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 10.3.3

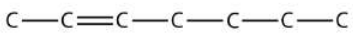
Name this molecule.



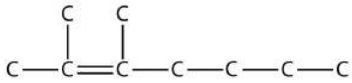
Answer

2,3,4-trimethyl-2-pentene

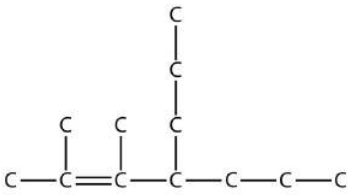
Once you master naming hydrocarbons from their given structures, it is rather easy to draw a structure from a given name. Just draw the parent chain with the correct number of C atoms (putting the double or triple bond in the right position, as necessary) and add the substituents in the proper positions. 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:



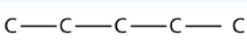
If we so choose, we can add H atoms to each C atom to give each carbon four covalent bonds, being careful to note that the C atoms in the double bond already have an additional covalent bond. (How many H atoms do you think are required? There will need to be 24 H atoms to complete the molecule.)

✓ Example 10.3.4

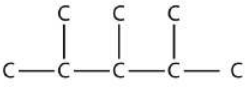
Draw the carbon backbone for 2,3,4-trimethylpentane.

Solution

First, we draw the five-carbon backbone that represents the pentane chain:



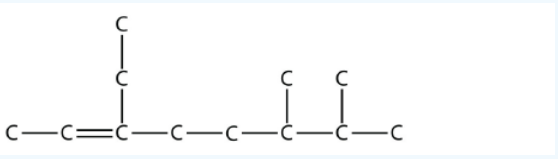
According to the name, there are three one-carbon methyl groups attached to the second, the third, and the fourth C atoms in the chain. We finish the carbon backbone by putting the three methyl groups on the pentane main chain:



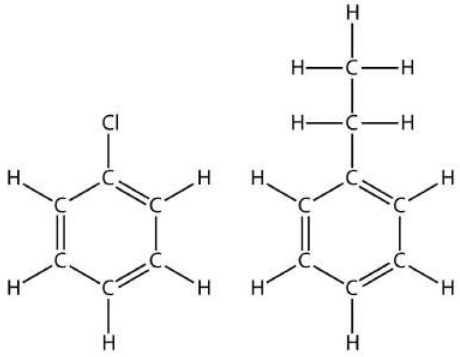
Exercise 10.3.4

Draw the carbon backbone for 3-ethyl-6,7-dimethyl-2-octene.

Answer

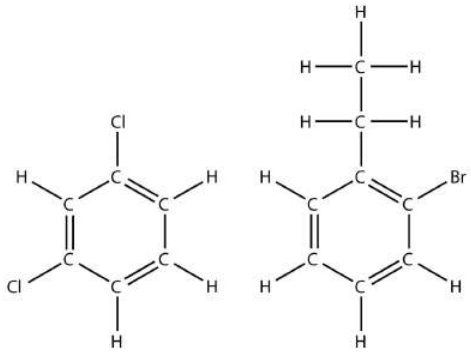


Naming substituted benzene molecules is straightforward. If there is only one substituent, the substituent is named as a side chain on a benzene molecule, like this:



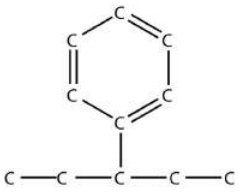
Chlorobenzene Ethylbenzene

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:



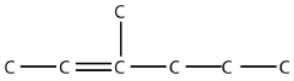
where the H atoms have been omitted for clarity.

Summary

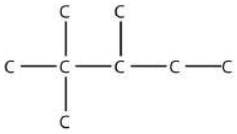
A unique name can be given to branched hydrocarbons. A unique structure can be drawn for the name of a hydrocarbon.

Exercise 10.3.5

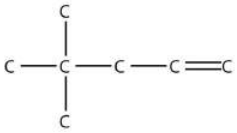
1. How does a branched hydrocarbon differ from a normal hydrocarbon?
2. How does a substituent get its unique name?
3. Name this molecule.



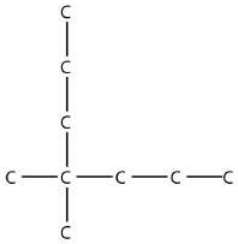
4. Name this molecule.



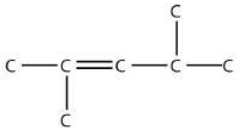
5. Name this molecule.



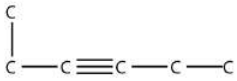
6. Name this molecule.



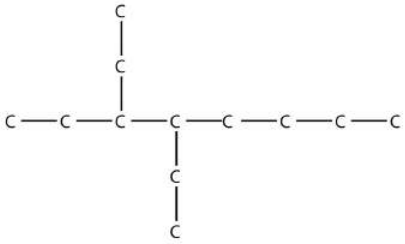
7. Name this molecule.



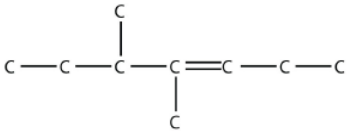
8. Name this molecule.



9. Name this molecule.

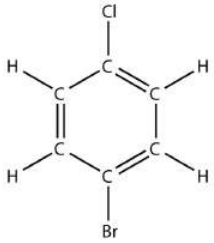


10. Name this molecule.

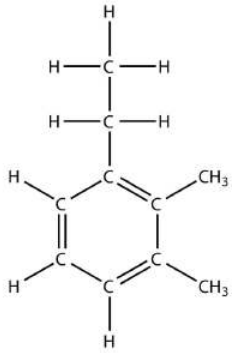


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11. Name this molecule.



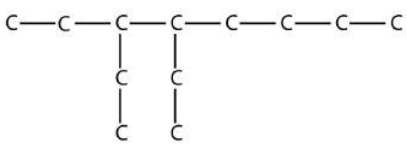
12. Name this molecule.

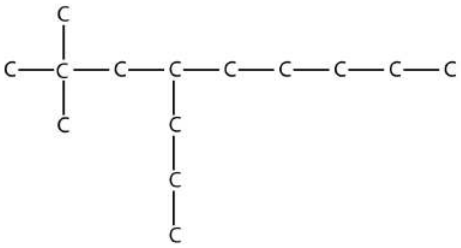


13. Draw the carbon backbone for each molecule.
    a. 3,4-diethyloctane
    b. 2,2-dimethyl-4-propylnonane
14. Draw the carbon backbone for each molecule.
    a. 3-ethyl-4-methyl-3-heptene
    b. 3,3-diethyl-1-pentyne
15. Draw the carbon backbone for each molecule.
    a. 4-ethyl-4-propyl-2-octyne
    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.

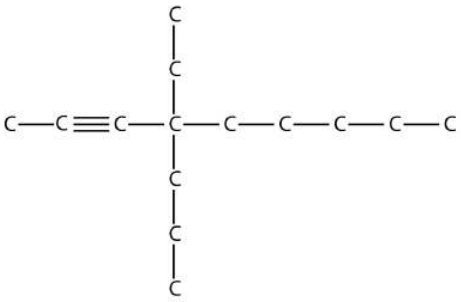
Answers

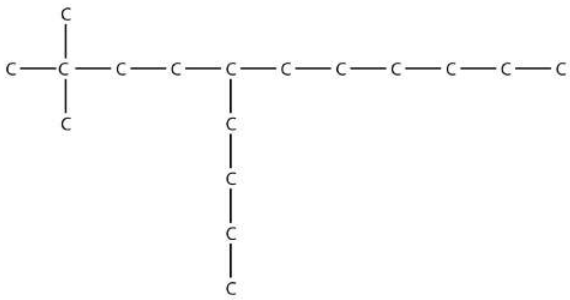
1. A branched hydrocarbon does not have all of its C atoms in a single row.
2.
3. 3-methyl-2-hexene
4.
5. 4,4-dimethyl-1-pentene
6.
7. 2,4-dimethyl-2-pentene
8.
9. 3,4-diethyloctane
10.
11. 1-bromo-4-chlorobenzene
12.

13. a. 

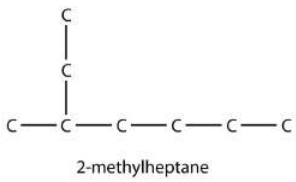
b. 

14.

15. a. 

b. 

16.

17. 

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10.4: Alkyl Halides and Alcohols

Learning Objectives

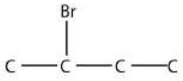
- Define *functional group*.
- Identify and name a simple alkyl halide.
- Identify and name a simple alcohol.
- Predict the product(s) of an elimination reaction of an alkyl halide or an alcohol.

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.

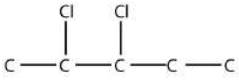
The presence of a halogen atom (F, Cl, Br, or I; also, X is used to represent any halogen atom) is one of the simplest functional groups. Organic compounds that contain a halogen atom are called **alkyl halides.** We have already seen some examples of alkyl halides when the addition of halogens across 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



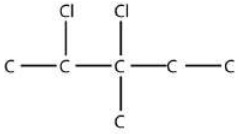
is 2-bromobutane, while this molecule



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 10.4.1

Name this molecule.



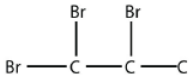
Solution

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 10.4.1

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 **10.4.1** - Isopropyl Alcohol).

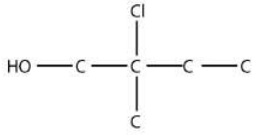


Figure **10.4.1** Isopropyl Alcohol. What you find labeled **isopropyl alcohol** in a medicine cabinet is more formally called 2-propanol.
Source: Photo courtesy of Craig Spurrier, en.Wikipedia.org/wiki/File:Rubbing.

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 10.4.2

Name this molecule as an alcohol and as a substituted alkane.

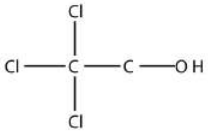


Solution

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 10.4.2

Name this molecule as an alcohol and as a substituted alkane.

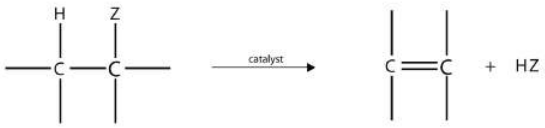


Answer

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.

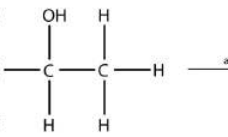
One reaction common to alcohols and alkyl halides is **elimination**, the removal of the functional group (either X or OH) and an H atom from an adjacent carbon. The general reaction can be written as follows:



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.

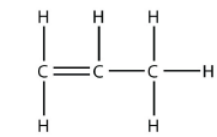
Example 10.4.3

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

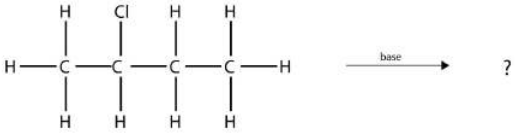


which is propene.

Exercise 10.4.3

Predict the organic product(s) of this reaction.

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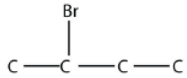
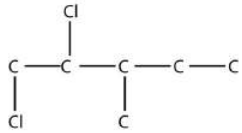
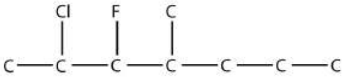
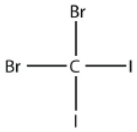
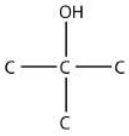
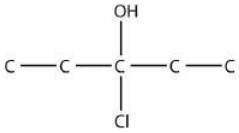
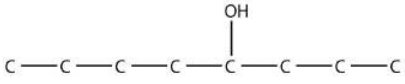
Answer

1-butene and 2-butene

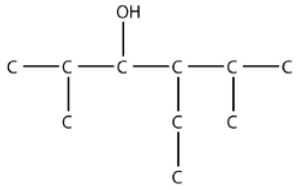
Key Takeaways

- 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.

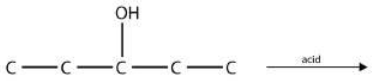
Exercise 10.4.4

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. 

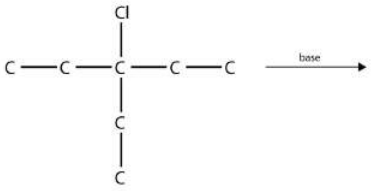
10. Name this molecule.



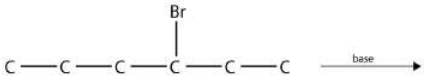
11. Predict the product(s) of this elimination reaction.



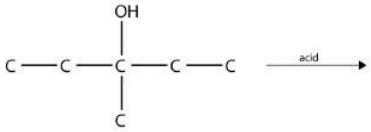
12. Predict the product(s) of this elimination reaction.



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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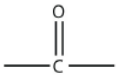
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10.5: Other Oxygen-Containing Functional Groups

Learning Objective

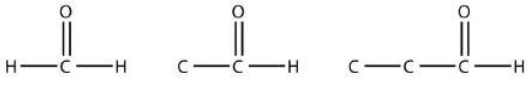
- Identify the aldehyde, ketone, acid, ester, and ether functional groups.

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:



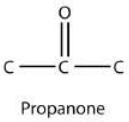
The other two bonds on the C atom are attached to other atoms. It is the identities of these other atoms that define what specific type of compound an organic molecule is.

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:



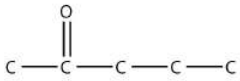
There is another way to name ketones: name the alkyl groups that are attached to the carbonyl group and add the word *ketone* to the name. So propanone can also be called dimethyl ketone, while 2-butanone is called methyl ethyl ketone.

Example 10.5.1

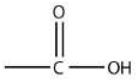
Draw the structure of 2-pentanone.

Solution

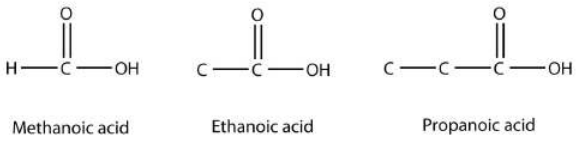
This molecule has five C atoms in a chain, with the carbonyl group on the second C atom. Its structure is as follows:



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 10.5.1). 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.

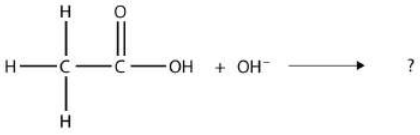
As their name suggests, however, carboxylic acids do act like acids in the presence of bases. The H atom in the carboxyl group comes off as the H^+ ion, leaving a **carboxylate anion**:



Carboxylate ions are named from the acid name: the *-oic acid* is replaced with *-oate* to name the ion.

Example 10.5.2:

Complete the chemical reaction. Can you name the carboxylate ion formed?



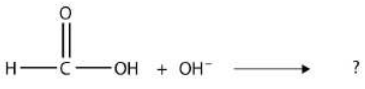
Solution

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 10.5.1

Complete the chemical reaction. Can you name the carboxylate ion formed?

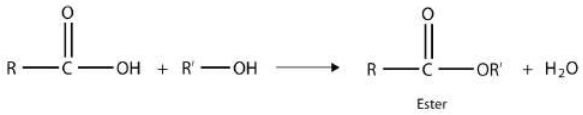


Answer



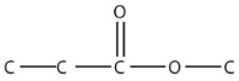
The anion is the methanoate ion, which is commonly called the formate ion.

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′

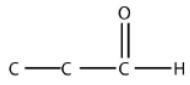
The two R groups may be the same or different. Naming ethers is like the alternate way of naming ketones. In this case, the R groups are named sequentially, and the word *ether* is appended. The molecule CH_3OCH_3 is dimethyl ether, while $CH_3OCH_2CH_3$ is methyl ethyl ether. Diethyl ether, another 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.

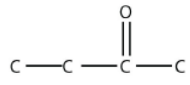
Key Takeaway

- Aldehydes, ketones, carboxylic acids, esters, and ethers have oxygen-containing functional groups.

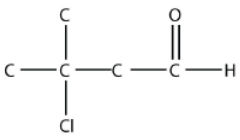
Exercise 10.5.2

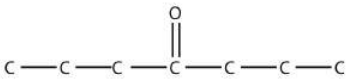
1. Name a similarity between the functional groups found in aldehydes and ketones. Can you name a difference between them?
2. Explain how a carboxylic acid is used to make an ester.
3. Name each molecule.

a. 

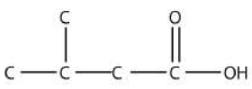
b. 

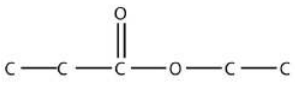
4. Name each molecule.

a. 

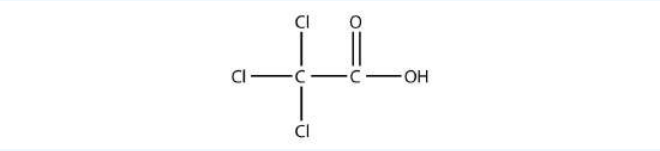
b. 

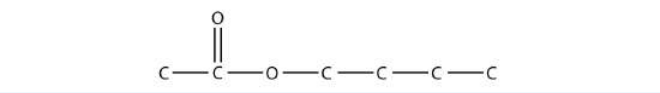
5. Name each molecule.

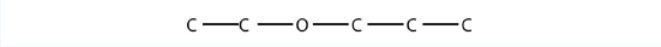
a. 

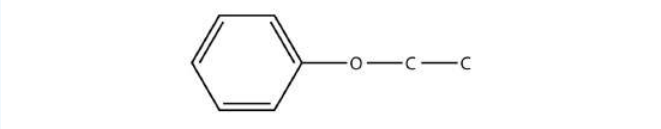
b. 

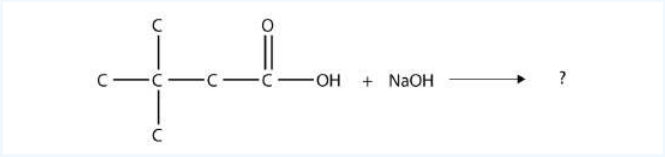
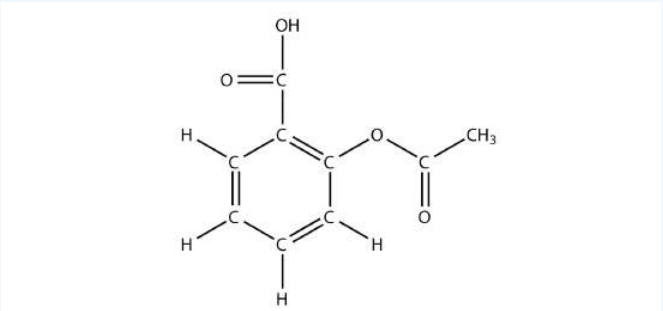
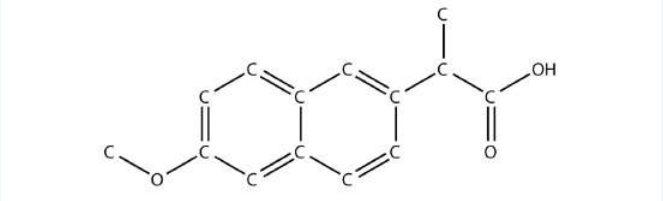
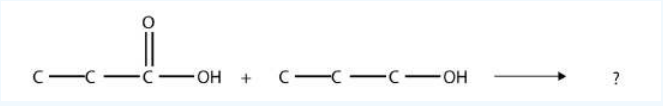
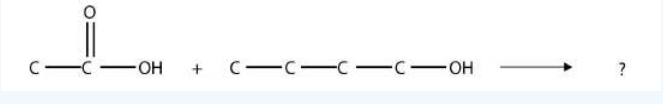
6. Name each molecule.

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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10.6: Other 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.

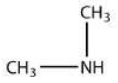
Nitrogen-Containing Compounds

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:



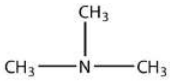
Methylamine

A *secondary* amine has two H atoms substituted with R groups:



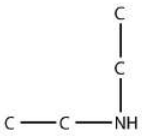
Dimethylamine

A *tertiary* amine has all three H atoms substituted with R groups:

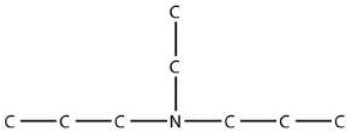


Trimethylamine

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



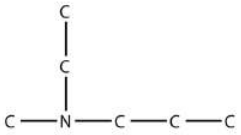
is diethylamine (the H atoms on the C atoms are omitted for clarity), while this amine



is ethyldipropylamine.

Example 10.6.1

Name this amine.

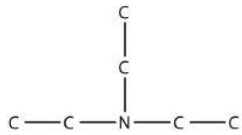


Solution

This amine has a methyl group, an ethyl group, and a propyl group. Listing the names in alphabetical order, this amine is ethylmethylpropylamine.

? Exercise 10.6.1

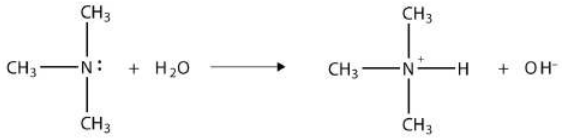
Name this amine.



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 **10.6.1** - Some Naturally Occurring N-Containing Compounds, shows some N-containing substances that you may recognize.

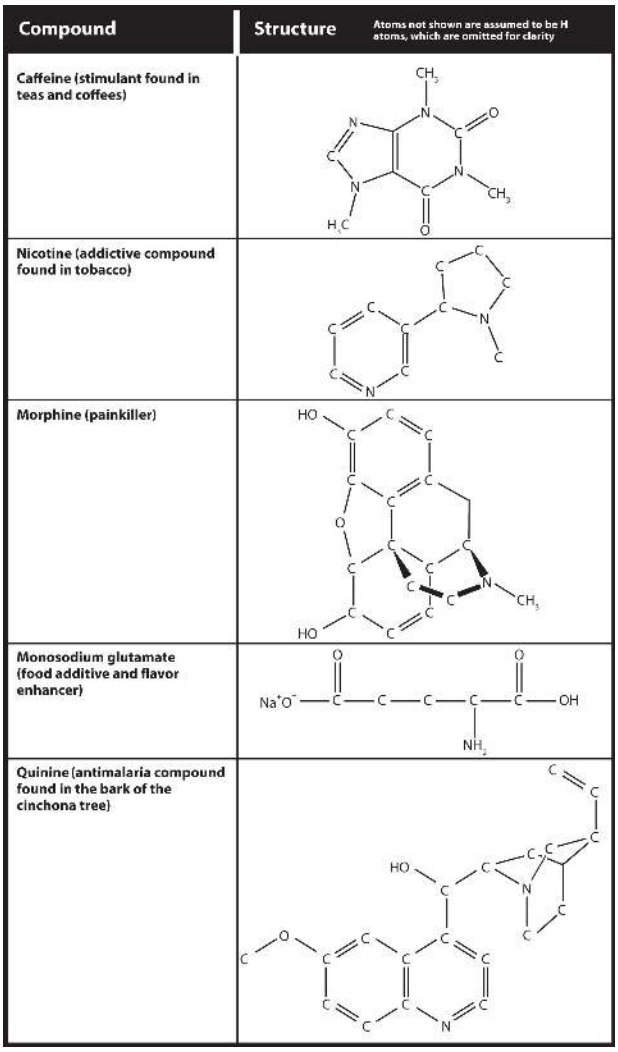


Figure **10.6.1** Some Naturally Occurring N-Containing Compounds.

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:



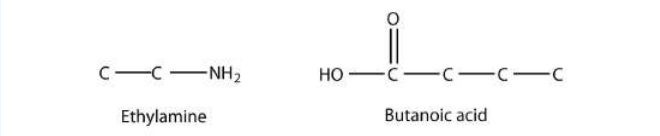
The bond between the N of the amine group and the C of the carbonyl group is called an **amide bond.** Amide bonds are particularly important in biological molecules called proteins, which are composed of strings of amino acids—molecules that have an amine group and a carboxylic acid group within them. 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 10.6.2

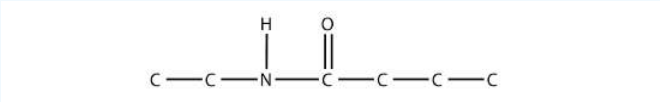
Draw the structure of the amide formed by the combination of ethylamine and butanoic acid.

Solution

The structures of ethylamine and butanoic acid are as follows:



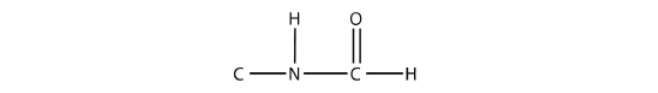
When they come together to make an amide, an H_2O molecule is lost, and the N of the amine group bonds to the C of the carboxyl group. The resulting molecule is as follows:



Exercise 10.6.2

Draw the structure of the amide formed by the combination of methylamine and formic acid.

Answer

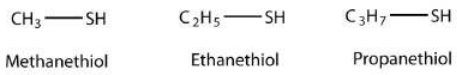


Sulfur-Containing Compounds

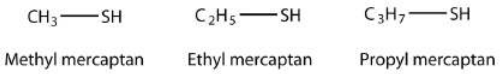
Sulfur is below oxygen on the periodic table, and it occasionally shows some similar chemistry. One similarity is that an S atom can take the place of an O atom in an alcohol, to make a molecule that looks like this:

R-SH

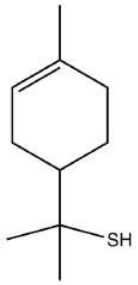
The sulfur analog of an alcohol is called a **thiol**. The formal way of naming a thiol is similar to that of alcohols, except that instead of using the *suffix-ol*, you use *-thiol* as the suffix. The following illustrates *thiol* nomenclature:



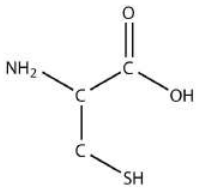
An older system uses the word *mercaptan* in naming simple thiols, much like the word *alcohol* is used with small alcohols. These thiols can also be named like this:



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.

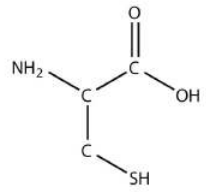
Because of the existence of essential amino acids, a diet that is properly balanced in protein is necessary. Rice and beans, a very popular food dish in Latin cuisines, actually provides all of the essential amino acids in one dish; without one component, the dish would be nutritionally incomplete. Corn (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.

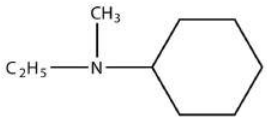
Key Takeaway

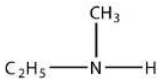
- Other functional groups include amine, amide, and thiol functional groups.

Exercise 10.6.3

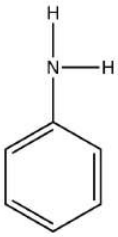
1. What are the structure and name of the smallest amine?
2. What are the structure and name of the smallest thiol?
3. Identify each compound as a primary, secondary, or tertiary amine.

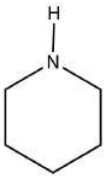
a. 

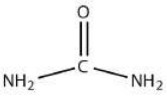
b. 

c. 

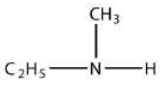
4. Identify each compound as a primary, secondary, or tertiary amine.

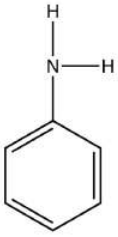
a. 

b. 

c. 

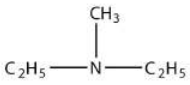
5. Write the chemical reaction between each amine in Exercise 3 and HCl.
6. Write the chemical reaction between each amine in Exercise 4 and HNO_3.
7. Name each amine.

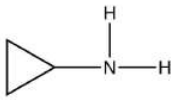
a. 

b. 

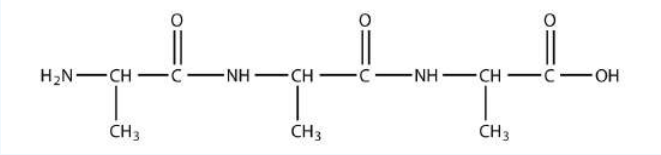
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8. Name each amine.

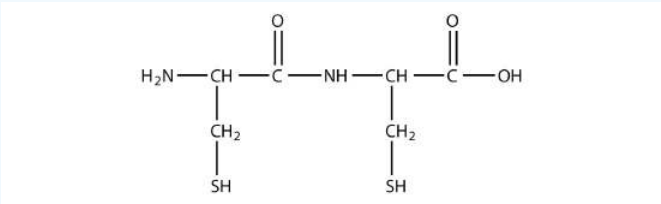
a. 

b. 

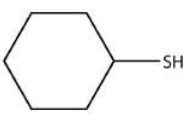
9. A *peptide* is a short chain of amino acids connected by amide bonds. How many amide bonds are present in this peptide?



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. 

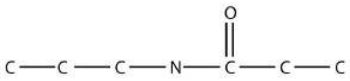
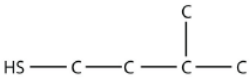
b. $C_4H_9–SH$

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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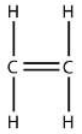
- **16.6: Other Functional Groups** by Anonymous is licensed CC BY-NC-SA 3.0. Original source: https://2012books.lardbucket.org/books/beginning-chemistry.

10.7: Polymers

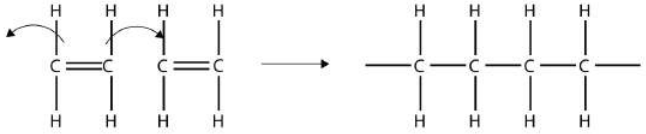
Learning Objectives

- 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:

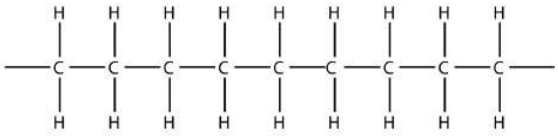


Imagine the bond between the carbons opening up and attacking another ethylene molecule:



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 **10.7.1** - 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.

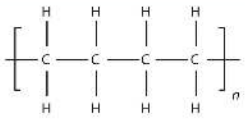
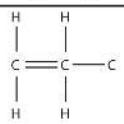
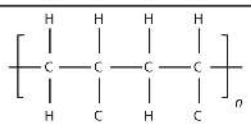
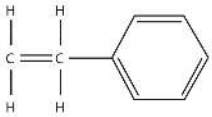
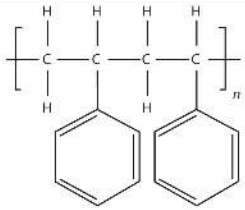
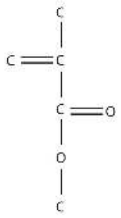
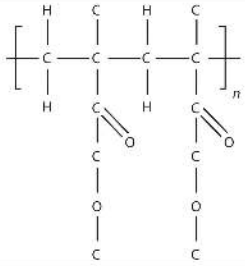
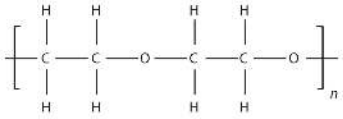
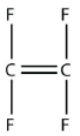
Monomer	Monomer Name	Polymer	Polymer Name
	ethylene		poly(ethylene)
	propylene		poly(propylene)
	styrene		poly(styrene)
	methyl methacrylate		poly(methyl methacrylate)
	ethylene oxide		poly(ethylene oxide)

Figure 10.7.1: Some Monomers and Their Addition Polymers

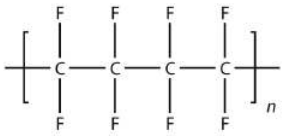
Example 10.7.1

Draw the polymer that results from the polymerization of tetrafluoroethylene.



Solution

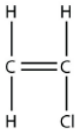
In the case of this monomer, the double bond opens up and joins to other monomers, just as with ethylene. The polymer that is made has this structure:



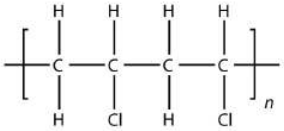
Exercise 10.7.1

Draw the polymer that results from the polymerization of vinyl chloride.

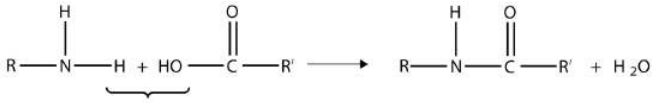
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Answer

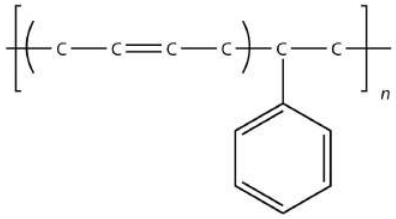


Another type of polymer is the *condensation polymer*, which is a polymer made when two different monomers react together and release some other small molecule as a product. We have already seen an example of this, in the formation of an amide bond:



Here, H_2O is released when the ends of the molecules react to form a polymer.

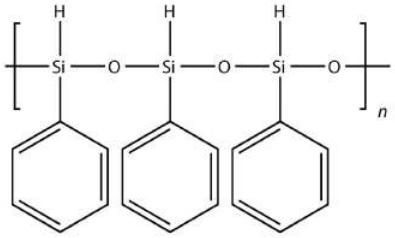
Related to condensation polymers are the *copolymers*, polymers made from more than one type of monomer. For example, ethylene and propylene can be combined into a polymer that is a mixture of the two monomers. A common form of synthetic rubber called styrene butadiene rubber (SBR) is made from two monomers: 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.

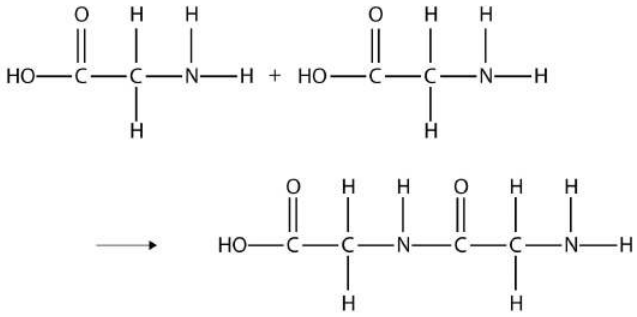
The uses of polymers are almost too numerous to consider. Anything that you might describe as "plastic" is likely a polymer. Polymers are used to make everything from toothbrushes to computer cases to automobile parts. Many epoxy-based adhesives are condensation polymers that adhere strongly to other 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:



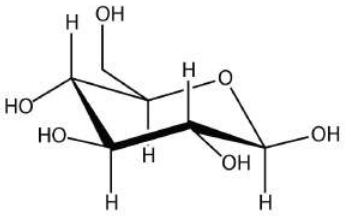
Silicones are used to make oils and lubricants; they are used as sealants for glass objects (such as aquariums) and films for waterproofing objects. Solid silicones are heat resistant and rubbery and are used to make cookware and electrical insulation.

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:

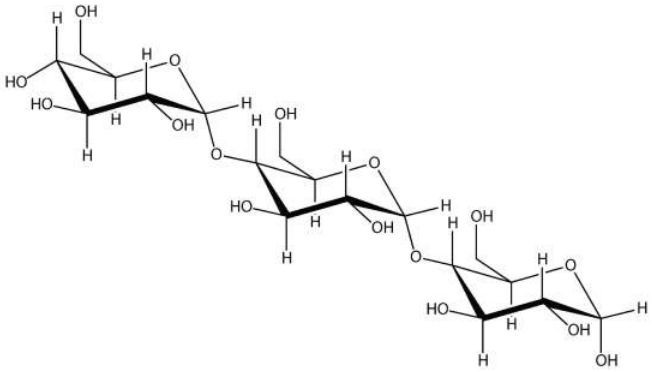


Proteins are formed when hundreds or even thousands of amino acids form amide bonds to make polymers. Proteins play a crucial role in living organisms.

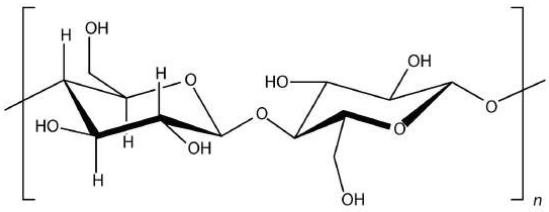
A *carbohydrate* is a compound that has the general formula $C_n(H_2O)_n$. Many carbohydrates are relatively small molecules, such as glucose:



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 **10.7.2**). DNA is the fundamental material in chromosomes and is directly responsible for heredity, while RNA is an essential substance in protein synthesis.

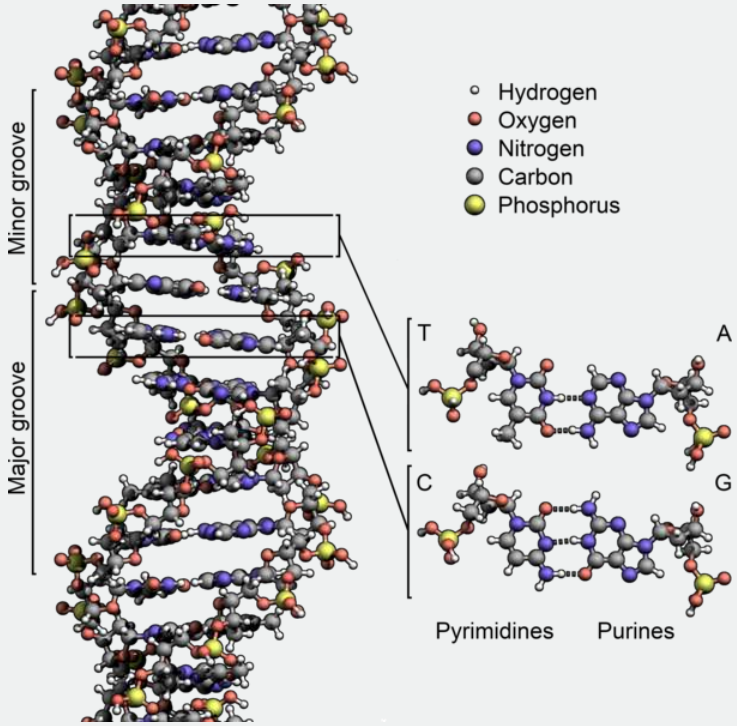


Figure **10.7.2**: The DNA in our cells is a polymer of nucleotides, each of which is composed of a phosphate group, a sugar, and a nitrogen-containing base. (CC BY-SA 3.0 Unported; Zephyris via Wikipedia)

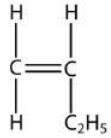
Key Takeaways

- Polymers are long molecules composed of chains of units called monomers.
- Several important biological polymers include proteins, starch, cellulose, and DNA.

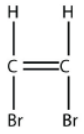
Exercise 10.7.2

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.

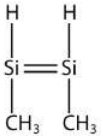
3. Draw the polymer made from this monomer.



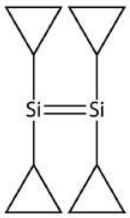
4. Draw the polymer made from this monomer.



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.



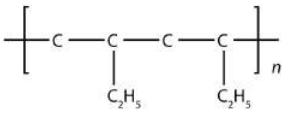
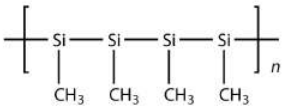
10. Draw the silicone made from this monomer.



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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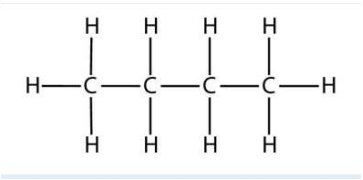
10.E: Organic Chemistry (Exercises)

Exercises (Hydrocarbons)

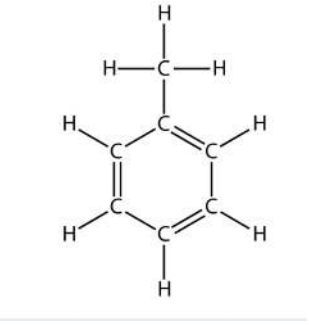
1. Define hydrocarbon. What are the two general types of hydrocarbons?

2. What are the three different types of aliphatic hydrocarbons? How are they defined?

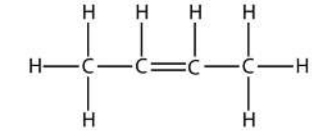
3. Indicate whether each molecule is an aliphatic or an aromatic hydrocarbon; if aliphatic, identify the molecule as an alkane, an alkene, or an alkyne.

a. 

<smiles>CCCC</smiles>

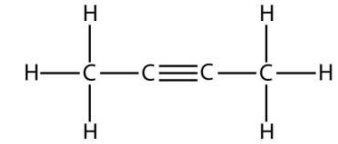
b. 

<smiles>Cc1ccccc1</smiles>

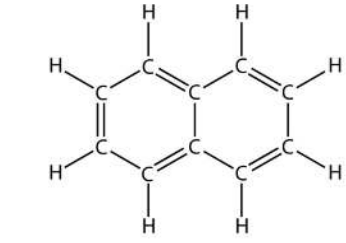
c. 

<smiles>C/C=C\C</smiles>

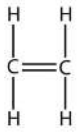
4. Indicate whether each molecule is an aliphatic or an aromatic hydrocarbon; if aliphatic, identify the molecule as an alkane, an alkene, or an alkyne.

a. 

<smiles>CC#CC</smiles>

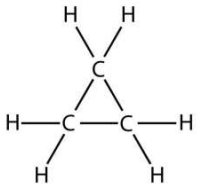
b. 

<smiles>c1ccc2ccccc2c1</smiles>

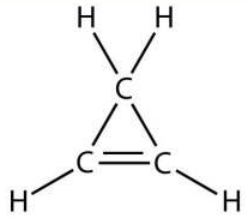
c. 

<smiles>C=C</smiles>

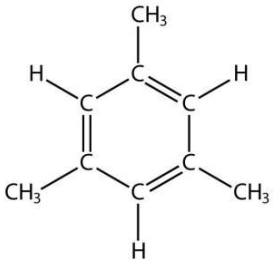
5. Indicate whether each molecule is an aliphatic or an aromatic hydrocarbon; if aliphatic, identify the molecule as an alkane, an alkene, or an alkyne.

a. 

<smiles>C1CC1</smiles>

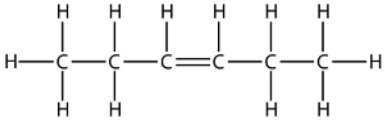
b. 

<smiles>C1=CC1</smiles>

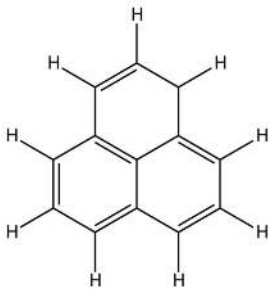
c. 

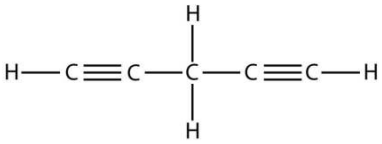
<smiles>Cc1cccc(C)c1</smiles>

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

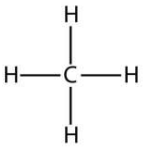
3.

a. aliphatic; alkane
b. aromatic
c. aliphatic; alkene

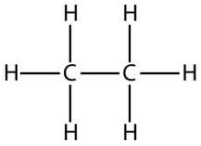
5.

a. aliphatic; alkane
b. aliphatic; alkene
c. aromatic

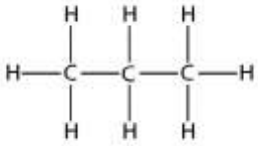
7.

a.  Methane

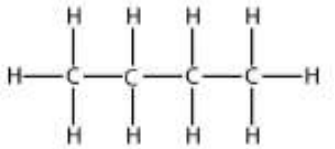
<smiles>C</smiles>

b.  Ethane

<smiles>CC</smiles>

c.  Propane

<smiles>CCC</smiles>

d.  Butane

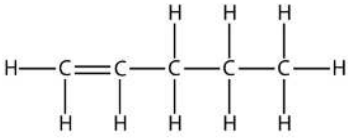
<smiles>CCCC</smiles>

9. Aromatic means that the molecule has a benzene ring.

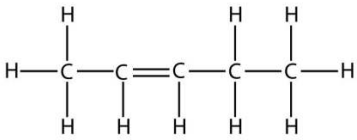
11. The 1 is not necessary. The name of the compound is simply propene.

<smiles>C=CCCC</smiles>

13.

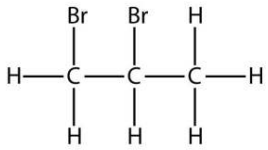
a.  1-Pentene

<smiles>C=CCCC</smiles>

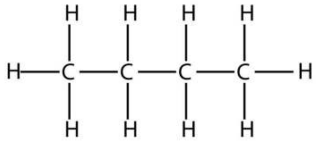
b.  2-Pentene

<smiles>CC=CCC</smiles>

15. $CH_4 + Br_2 \rightarrow CH_3Br + HBr$

17. 

<smiles>CC(Br)CBr</smiles>

19. 

<smiles>CCCC</smiles>

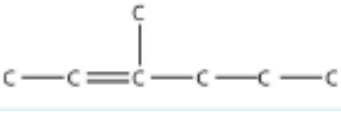
21. $C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O$

Exercises (Branched Hydrocarbons)

1. How does a branched hydrocarbon differ from a normal hydrocarbon?

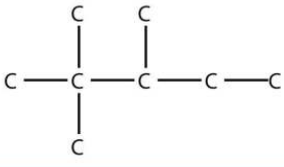
2. How does a substituent get its unique name?

3. Name this molecule.



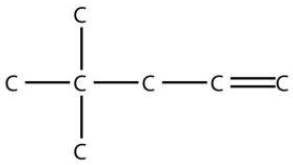
<smiles>CC=C(C)CCC</smiles>

4. Name this molecule.



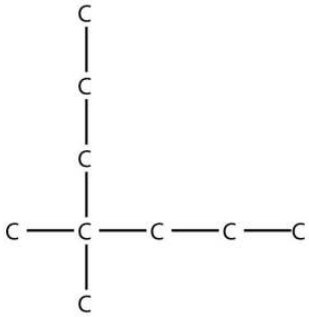
<smiles>CC(C)C(C)(C)C</smiles>

5. Name this molecule.



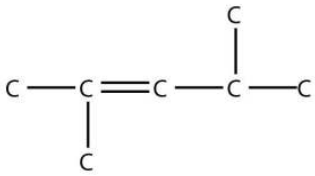
<smiles>C=CCC(C)(C)C</smiles>

6. Name this molecule.



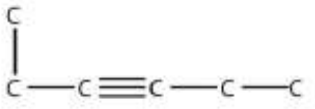
<smiles>CCCC(C)(C)CCCl</smiles>

7. Name this molecule.



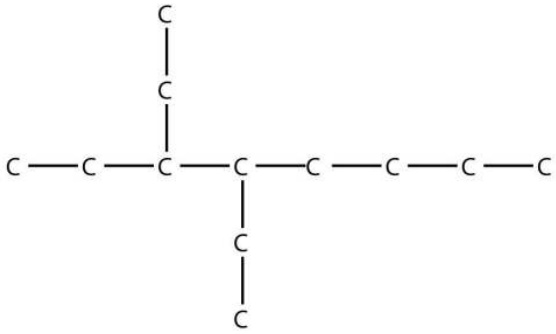
<smiles>CC(C)=CC(C)C</smiles>

8. Name this molecule.



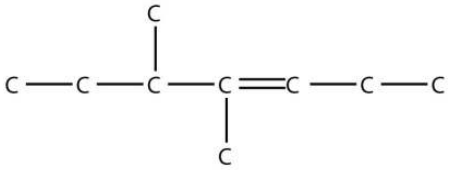
<smiles>CCC#CCC</smiles>

9. Name this molecule.



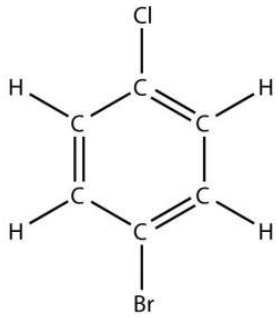
<smiles>CCCCC(CC)C(CC)CC</smiles>

10. Name this molecule.



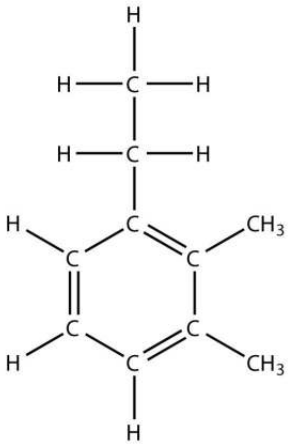
<smiles>CCC=C(C)C(C)CC</smiles>

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

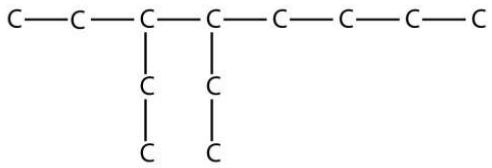
5. 4,4-dimethyl-1-pentene

7. 2,4-dimethyl-2-pentene

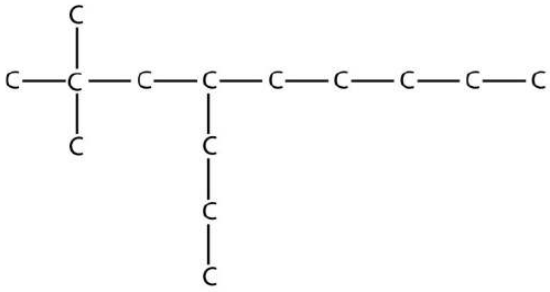
9. 3,4-diethyloctane

11. 1-bromo-4-chlorobenzene

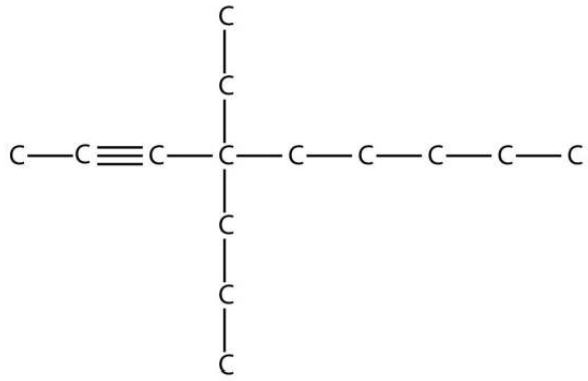
13.

a. 

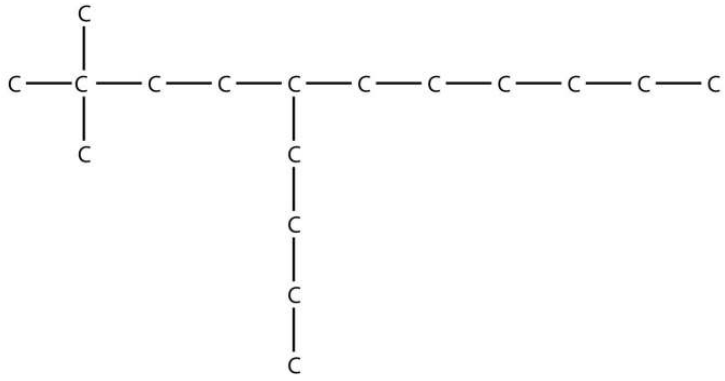
<smiles>CCCCC(CC)C(CC)CC</smiles>

b. 

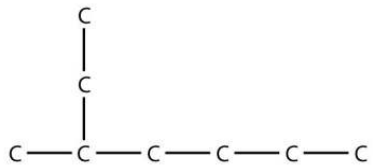
<smiles>CCCCCC(CCC)CC(C)(C)C</smiles>

15. a. 

<smiles>CC#CC(CC)(CCC)CCCCC</smiles>

b. 

<smiles>CCCCCCC(CCCC)CCC(C)(C)C</smiles>

17.  2-methylheptane

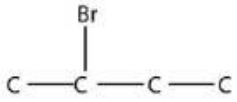
<smiles>CCCCC(C)CC</smiles>

Exercises (Alkyl Halides and Alcohols)

1. Define functional group and give two examples.

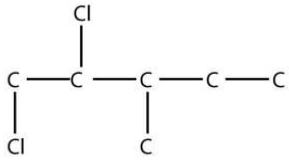
2. What is elimination? How does it differ for alkyl halides and alcohols?

3. Name this molecule.



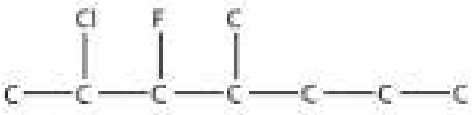
<smiles>CC(C)Br</smiles>

4. Name this molecule.



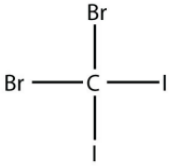
<smiles>CCC(C)C(Cl)CCl</smiles>

5. Name this molecule.



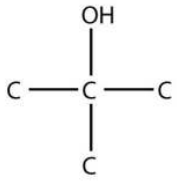
<smiles>CCCC(C)C(F)C(C)Cl</smiles>

6. Name this molecule.



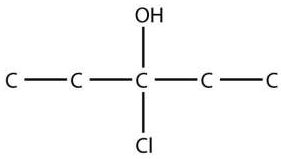
<smiles>BrC(Br)(I)I</smiles>

7. Name this molecule.



<smiles>CC(C)(C)O</smiles>

8. Name this molecule.



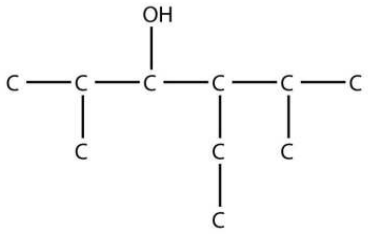
<smiles>CCC(O)(Cl)CC</smiles>

9. Name this molecule.



<smiles>CCCCC(O)CCCl</smiles>

10. Name this molecule.



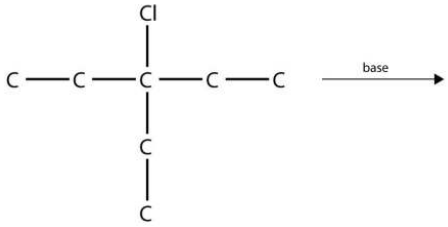
<smiles>CCC(C(C)C)C(O)C(C)C</smiles>

11. Predict the product(s) of this elimination reaction.



<smiles>CCC(O)CC</smiles>

12. Predict the product(s) of this elimination reaction.



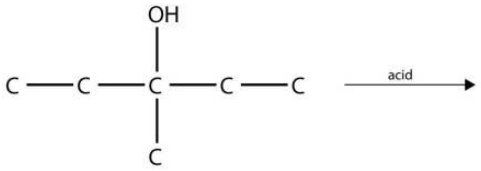
<smiles>CCC(Cl)(CC)CC</smiles>

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

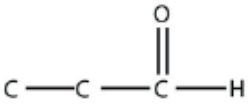
13. 2-hexene and 3-hexene

Exercises (Other Oxygen-Containing Functional Groups)

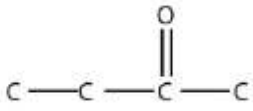
1. Name a similarity between the functional groups found in aldehydes and ketones. Can you name a difference between them?

2. Explain how a carboxylic acid is used to make an ester.

3. Name each molecule.

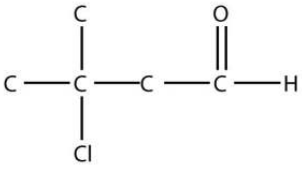
a. 

<smiles>CCC=O</smiles>

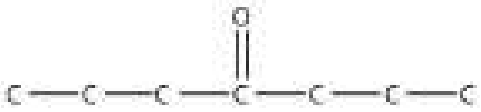
b. 

<smiles>CCC(=O)Cl</smiles>

4. Name each molecule.

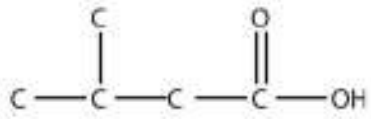
a. 

<smiles>CC(C)(Cl)CC=O</smiles>

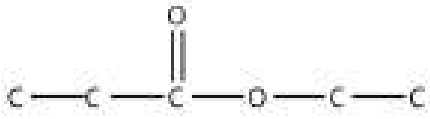
b. 

<smiles>CCCC(=O)CCC</smiles>

5. Name each molecule.

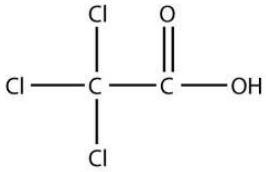
a. 

<smiles>CC(C)CC(=O)O</smiles>

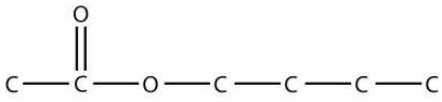
b. 

<smiles>CCC(=O)OCCl</smiles>

6. Name each molecule.

a. 

<smiles>O=C(O)C(Cl)(Cl)Cl</smiles>

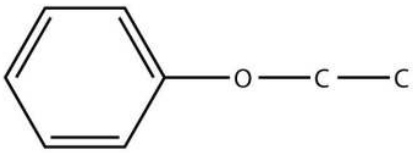
b. 

<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.

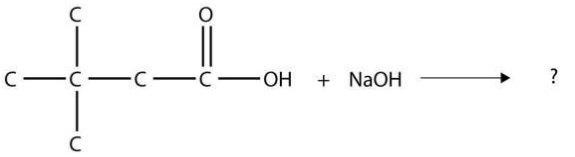
10. Give an alternate but acceptable name to the molecule in Exercise 4 b.

11. Complete this chemical reaction.



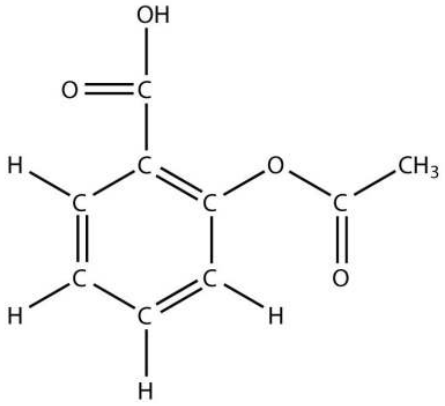
<smiles>CCC(=O)[OH2+]</smiles>

12. Complete this chemical reaction.



<smiles>CC(C)(C)CC(=O)O</smiles>

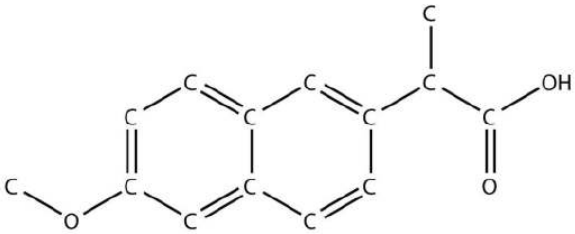
13. The drug known as aspirin has this molecular structure:



<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>

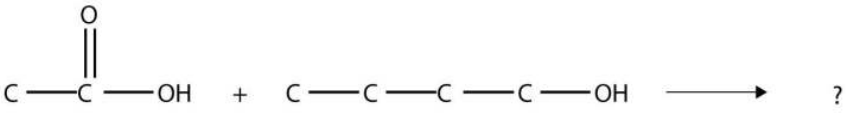
(The extra **H** atoms are omitted for clarity.) Identify the functional group(s) i this molecule.

15. Identify the ester made by reacting these molecules.



<smiles>CCC(=O)[OH2+]</smiles>

16. Identify the ester made by reacting these molecules.



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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. $\mathbf{H_2O + KCH_3CH_2CO_2}$

13. acid, ester, and aromatic (benzene ring)

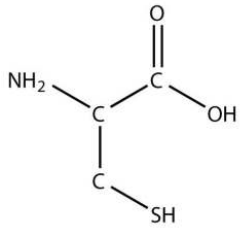
15. propyl propionate

Exercises (Other Functional Groups)

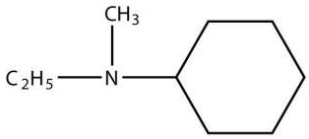
1. What are the structure and name of the smallest amine?

2. What are the structure and name of the smallest thiol?

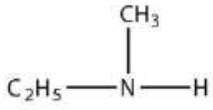
3. Identify each compound as a primary, secondary, or tertiary amine.

a. 

<smiles>NC(CS)C(=O)O</smiles>

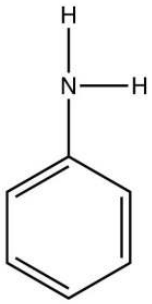
b. 

<smiles>CCN(C)C1CCCCC1</smiles>

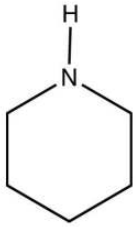
c. 

<smiles>CCNC</smiles>

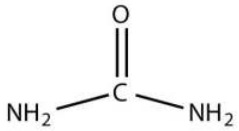
4. Identify each compound as a primary, secondary, or tertiary amine.

a. 

<smiles>Nc1ccccc1</smiles>

b. 

<smiles>C1CCNCC1</smiles>

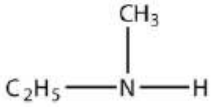
c. 

<smiles>NC(N)=O</smiles>

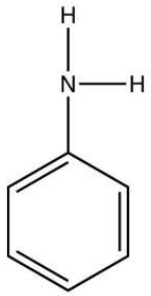
5. Write the chemical reaction between each amine in Exercise 3 and **HCl**.

6. Write the chemical reaction between each amine in Exercise 4 and $\mathbf{HNO_3}$.

7. Name each amine.

a. 

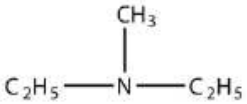
<smiles>CCNC</smiles>

b. 

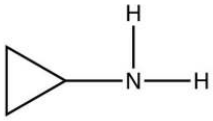
<smiles>Nc1ccccc1</smiles>

8. Name each amine.

https://chem.libretexts.org/@go/page/303929

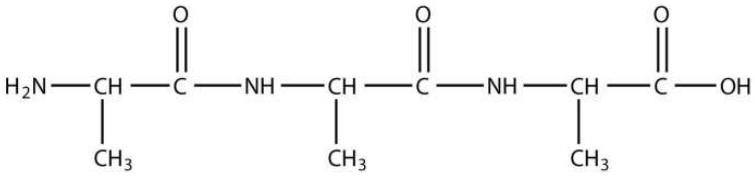
a. 

<smiles>CCN(C)CC</smiles>

b. 

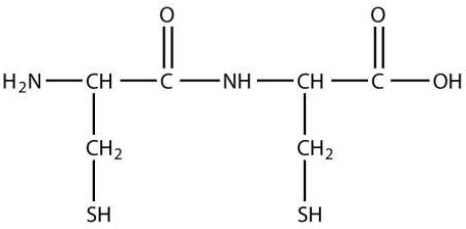
<smiles>CNC1CC1</smiles>

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.)

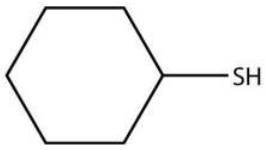


<smiles>NC(CS)C(=O)NC(CS)C(=O)O</smiles>

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. $\mathbf{C_4H_9 - SH}$

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. $\mathbf{CH_3NH_2}$; 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.

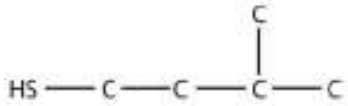


<smiles>CCCNC(=O)CC</smiles>

13.

a. cyclohexanethiol
b. butanethiol

15.



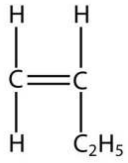
<smiles>CC(C)CCS</smiles>

Exercises (Polymers)

1. Explain the relationship between a monomer and a polymer.

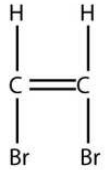
2. Must a monomer have a double bond to make a polymer? Give an example to illustrate your answer.

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>

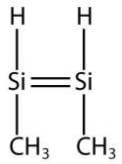
5. What is the difference between an addition polymer and a condensation polymer?

6. What is the difference between a condensation polymer and a copolymer?

7. List three properties of polymers that vary widely with composition.

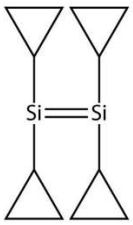
8. List three uses of polymers.

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.

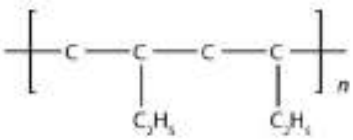
12. What is the difference between starch and cellulose?

13. Explain how protein is a polymer.

14. What are the parts that compose DNA?

Answers

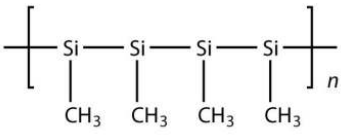
1. A polymer is many monomers bonded together.

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 $\mathrm{C-C}$ 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.

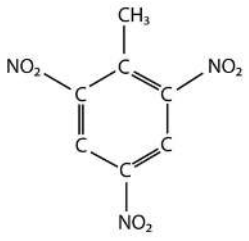
15. What is the maximum number of methyl groups that can be on a propane backbone before the molecule cannot be named as a propane compound?

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>

https://chem.libretexts.org/@go/page/303929

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?

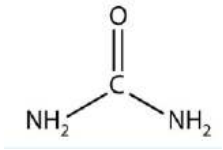
24. Draw the structure of the final product of the double elimination of 1,3-dibromopropane.

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.

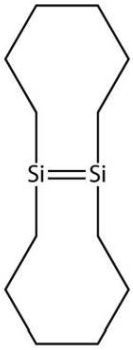
33. The odor of fish is caused by the release of small amine molecules, which vaporize easily and are detected by the nose. Lemon juice contains acids that react with the amines and make them not as easily vaporized, which is one reason why adding lemon juice to seafood is so popular. Write the chemical 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:

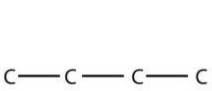


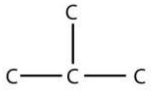
38. One of the ingredients in the original Silly Putty was a silicone polymer with two methyl groups on each Si atom. Draw this silicone.

Answers

1. cyclopropane, cyclobutane, and cyclopentane

3.

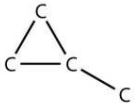




<smiles>CC(C)C</smiles>

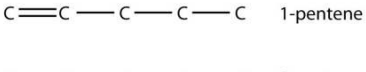
5.



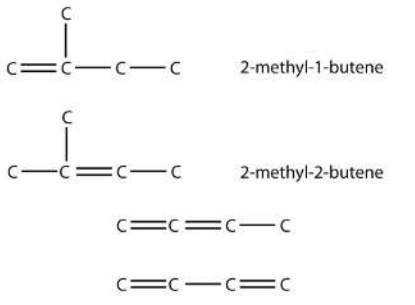


<smiles>C1CCC1</smiles> <smiles>CC1CC1</smiles>

7.



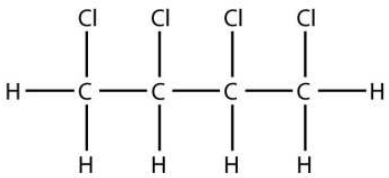
9.



Both molecular formulas are C_4H_6.

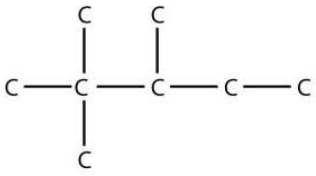
11. $C_2H_6 + 6Cl_2 \rightarrow C_2Cl_6 + 6HCl$

13.

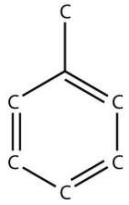


<smiles>CCl</smiles>

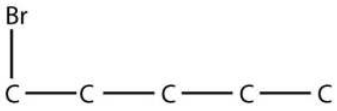
15. two

17. 

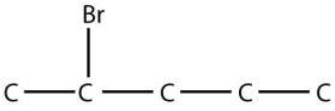
<smiles>CCC(C)C(C)(C)C</smiles>

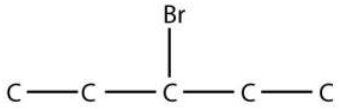
19. 

<smiles>CCCCCBr</smiles>



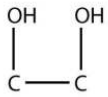
<smiles>CCCC(C)Br</smiles>



21. 

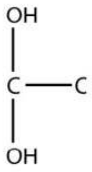
<smiles>CCC(Br)CC</smiles>

23. ethyne



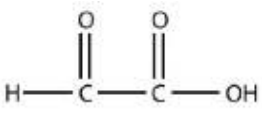
<smiles>OCCO</smiles>

or

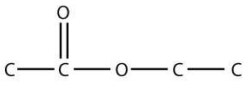


<smiles>OC(O)Cl</smiles>

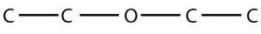
25. The names are 1,2-dihydroxyethane and 1,1-dihydroxyethane, respectively.

27. 

<smiles>O=CC(=O)O</smiles>

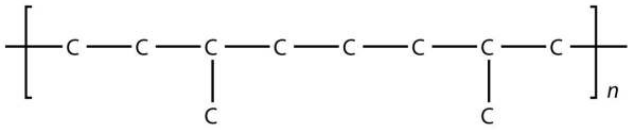
29. 

<smiles>CCOC(C)=O</smiles>

31. 

33. $(CH_3)_3\ N + HCl \rightarrow (CH_3)_3\,NHCl$

35. (answers will vary)

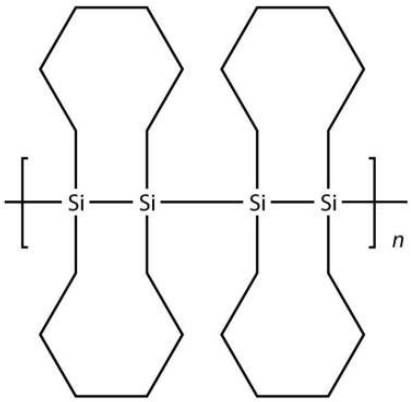


<smiles>CC(CCCCC(C)(C)C)CCC(C)(C)C</smiles>

or



<smiles>CC(CCCCC(C)CC(C)(C)C)CC(C)(C)C</smiles>

37. 

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CHAPTER OVERVIEW

11: Biochemistry

11.1: Energy and the Living Cell
11.2: Carbohydrates- A Storehouse of Energy
11.3: Fats and Other Lipids
11.4: Proteins- Polymers of Amino Acids
11.5: Structure and Function of Proteins
11.6: Nucleic Acids- Parts, Structure, and Function
11.7: RNA Protein Synthesis and the Genetic Code
11.8: Carbohydrates (Exercises)
11.9: Lipids (Exercises)
11.10: Amino Acids, Proteins and Enzymes (Exercise)
11.11: Nucleic Acids (Exercises)

Thumbnail: DNA double helix. (public domain; NIH - Genome Research Institute).

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11.1: Energy and the Living Cell

Learning Objective

- Know the similarities and differences between plant and animal cells.
- Know the functions of the major parts of plant and animal cells.

Biochemistry, sometimes called **biological chemistry**, is the study of chemical processes within and relating to living organisms. Biochemical processes give rise to the complexity of life. Biochemistry focuses on understanding how biological molecules give rise to the processes that occur within living cells and between cells, which in turn relates greatly to the study and understanding of tissues, organs, and organism structure and function. Much of biochemistry deals with the structures, functions and interactions of biological macromolecules, such as proteins, nucleic acids, carbohydrates and lipids, which provide the structure of cells and perform many of the functions associated with life. The mechanisms by which cells harness energy from their environment via chemical reactions are known as metabolism. The findings of biochemistry are applied primarily in medicine, nutrition, and agriculture. In medicine, biochemists investigate the causes and cures of diseases. In nutrition, they study how to maintain health wellness and study the effects of nutritional deficiencies. In agriculture, biochemists investigate soil and fertilizers, and try to discover ways to improve crop cultivation, crop storage and pest control.

The major parts of plant and animal cells (Figure **11.1.1**) include the plasma membrane, nucleus, ribosomes, and mitochondria.

The plasma membrane is made up of a phospholipid bilayer with embedded proteins that separates the internal contents of the cell from its surrounding environment. A phospholipid is a lipid molecule composed of two fatty acid chains, a glycerol backbone, and a phosphate group. The plasma membrane regulates the passage of some substances, such as organic molecules, ions, and water, preventing the passage of some to maintain internal conditions, while actively bringing in or removing others. Other compounds move passively across the membrane.

Nucleus

Typically, the **nucleus** is the most prominent organelle in a cell . The nucleus (plural = nuclei) houses the cell's DNA in the form of chromatin and directs the synthesis of ribosomes and proteins.

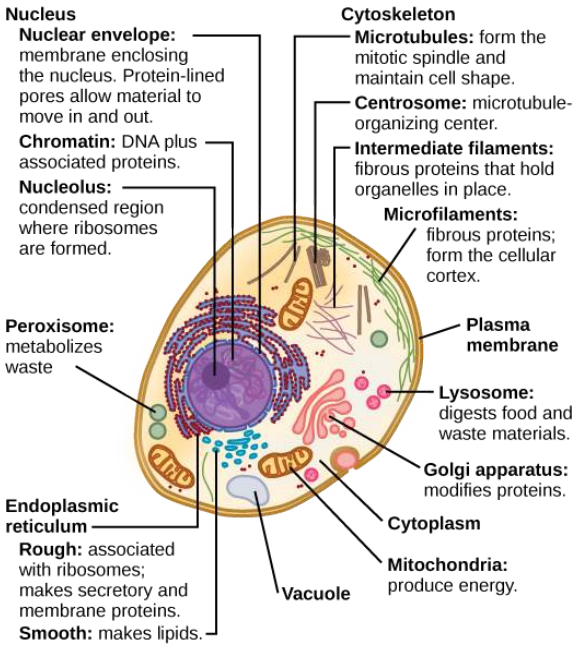
Ribosomes

Ribosomes are the cellular structures responsible for protein synthesis. When viewed through an electron microscope, free ribosomes appear as either clusters or single tiny dots floating freely in the cytoplasm. Ribosomes may be attached to either the cytoplasmic side of the plasma membrane or the cytoplasmic side of the endoplasmic reticulum. Electron microscopy has shown that ribosomes consist of large and small subunits. Ribosomes are enzyme complexes that are responsible for protein synthesis.

Because protein synthesis is essential for all cells, ribosomes are found in practically every cell, although they are smaller in prokaryotic cells. They are particularly abundant in immature red blood cells for the synthesis of hemoglobin, which functions in the transport of oxygen throughout the body.

Mitochondria

Mitochondria (singular = mitochondrion) are often called the "powerhouses" or "energy factories" of a cell because they are responsible for making adenosine triphosphate (ATP), the cell's main energy-carrying molecule. The formation of ATP from the breakdown of glucose is known as cellular respiration. In keeping with our theme of form following function, it is important to point out that muscle cells have a very high concentration of mitochondria because muscle cells need a lot of energy to contract.



(a)

Figure_03_03_01b_new.png?revision=1&size=bestfit&width=519&height=476" style="width: 490.994px; height: 450px;" />

Figure* 11.1.1*: *This figure shows (a) a typical animal cell and (b) a typical plant cell.*

Animal Cells versus Plant Cells

Despite their fundamental similarities, there are some striking differences between animal and plant cells. Animal cells have centrioles, centrosomes (discussed under the cytoskeleton), and lysosomes, whereas plant cells do not. Plant cells have a cell wall (made of cellulose), chloroplasts, plasmodesmata, and plastids used for storage, and a large central vacuole, whereas animal cells do not.

Energy in Biological Systems

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:

$$6\,CO_2 + 6\,H_2O + 686\ \text{kcal} \rightarrow C_6H_{12}O_6 + 6\,O_2 \tag{11.1.1}$$

(The 686 kcal come from solar energy.) Chloroplasts function in photosynthesis and can be found in cells of plants and algae. The chloroplasts contain a green pigment called chlorophyll, which captures the energy of sunlight for photosynthesis. 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. This is the major difference between plants and animals: Plants are able to make their own food, like glucose, whereas animals must rely on other organisms for their organic compounds or food source.

Summary

The major parts of plant and animal cells (Figure **11.1.1**) include the plasma membrane, nucleus, ribosomes, and mitochondria.

Animal cells have centrioles, centrosomes (discussed under the cytoskeleton), and lysosomes, whereas plant cells do not.

Plant cells have a cell wall (made of cellulose), chloroplasts, plasmodesmata, and plastids used for storage, and a large central vacuole, whereas animal cells do not.

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Contributors and Attributions

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- Wikipedia
- Marisa Alviar-Agnew (Sacramento City College)

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11.2: Carbohydrates- A Storehouse of Energy

Learning Objective

- Know the difference between starch, cellulose and glycogen.
- List the key steps in carbohydrate digestion.

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. Different carbohydrates that will be discussed below include the simple sugars, oligosaccharides and polysaccharides (Figure **11.2.1**.

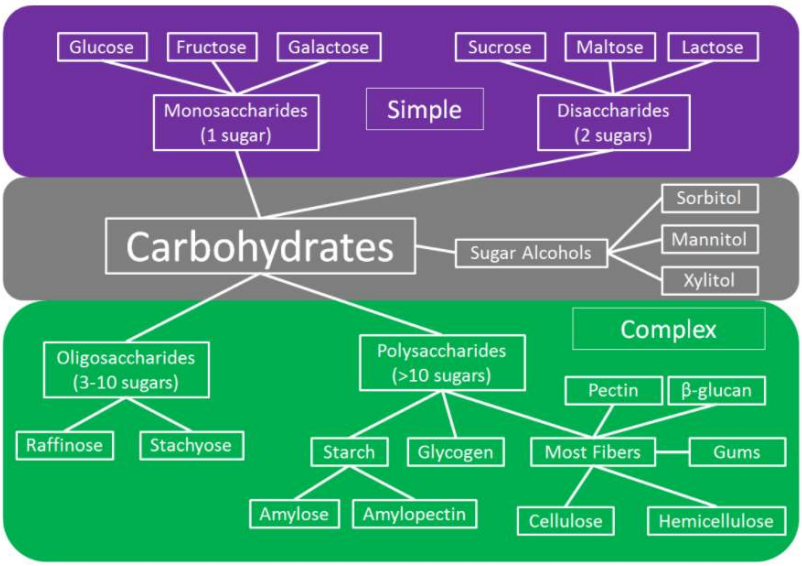
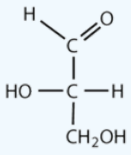
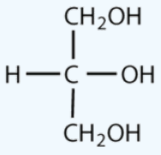


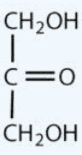
Figure **11.2.1** *Overview of carbohydrates*

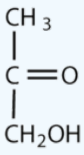
Example 11.2.1

Which compounds would be classified as carbohydrates?

a. 

b. 

c. 

d. 

Solution

a. This is a carbohydrate because the molecule contains an aldehyde functional group with OH groups on the other two carbon atoms.

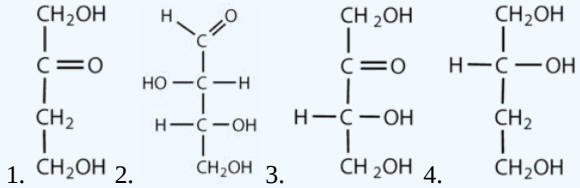
b. This is not a carbohydrate because the molecule does not contain an aldehyde or a ketone functional group.

c. This is a carbohydrate because the molecule contains a ketone functional group with OH groups on the other two carbon atoms.

d. This is not a carbohydrate; although it has a ketone functional group, one of the other carbons atoms does not have an OH group attached.

Exercise 11.2.1

Which compounds would be classified as carbohydrates?



Some Simple Sugars

The naturally occurring **monosaccharides** contain three to seven carbon atoms per molecule (one sugar unit) . Monosaccharides (or simple sugars) 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.

Although a variety of monosaccharides are found in living organisms, three hexoses are particularly abundant: D-glucose, D-galactose, and D-fructose (Figure **11.2.2**). Glucose and galactose are both aldohexoses, while fructose is a ketohexose.

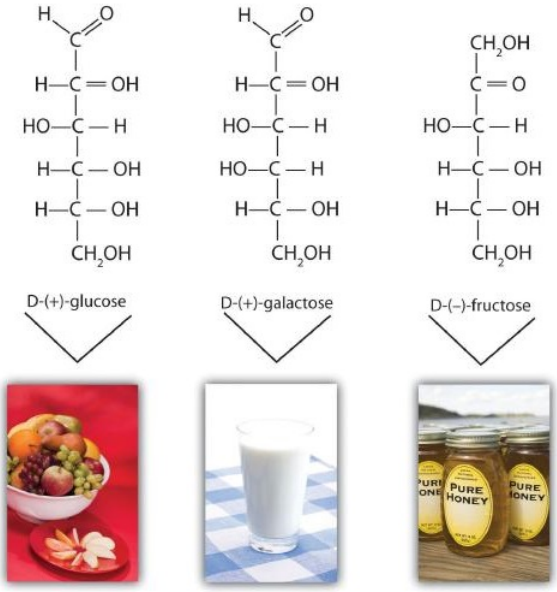


Figure **11.2.2**: Structures of Three Important Hexoses. Each hexose is pictured with a food source in which it is commonly found. Source: Photos © Thinkstock.

In aqueous solution, the predominant forms are not the straight-chain structure shown above. Rather, they adopt a cyclic structure. The representative ring structures of glucose, fructose, and galactose are shown in Figure **11.2.3**. Notice that all are 6-carbon sugars (hexoses). However, fructose has a five member ring, while glucose and galactose have 6 member rings. Also notice that the only structural difference between glucose and galactose is the position of the alcohol (OH) group that is shown in red.

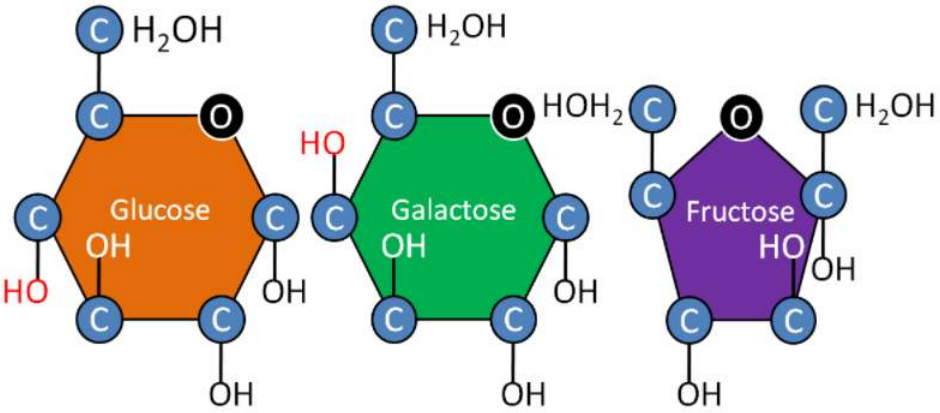


Figure **11.2.3** *The ring structures of glucose, galactose, and fructose.*

A **disaccharide** contains two monosaccharides joined together. Examples include and . They are composed of two monosaccharide units bound together by a bond known as a formed via a , resulting in the loss of a atom from one monosaccharide and a from the other. The of unmodified disaccharides is $C_{12}H_{22}O_{11}$. Although there are numerous kinds of disaccharides, a handful of disaccharides are particularly notable.

Sucrose, which may be obtained by condensing a molecule of α-glucose with one of the cyclic forms of fructose called β-fructose. The structure of sucrose is shown in Figure **11.2.4**.

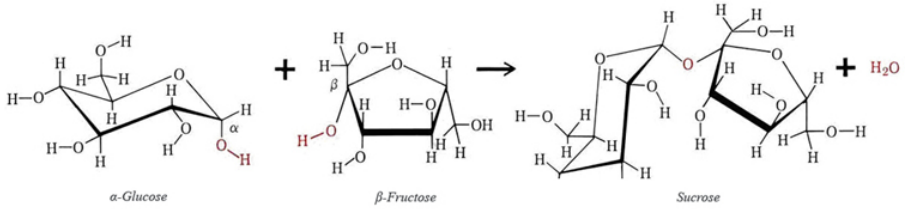


Figure **11.2.4** *The formation of sucrose from glucose and fructose.*

Other, less familiar, examples of disaccharides are lactose, which occurs in milk, and maltose, which are shown in Figure **11.2.5**. In order to digest a disaccharide like sucrose or lactose, the human body must have an enzyme which can catalyze hydrolysis of the linkage between the two monosaccharide units. Many Asians, Africans, and American Indians are incapable of synthesizing lactase, the enzyme that speeds hydrolysis of lactose. If such persons drink milk, the undigested lactose makes them sick.

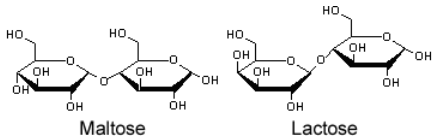


Figure **11.2.5** Two other common disaccharides, maltose and lactose.

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 **11.2.6**). 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 **11.2.6**). 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.

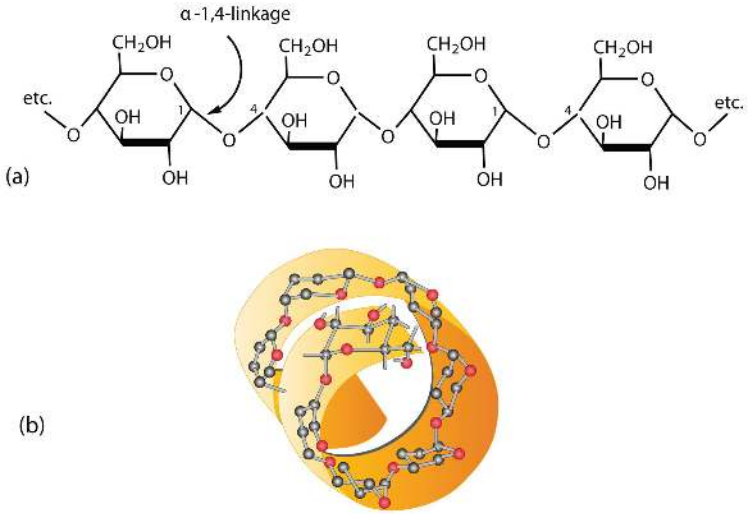


Figure **11.2.6** Amylose. (a) Amylose is a linear chain of α-D-glucose units joined together by α-1,4-glycosidic bonds. (b) Because of hydrogen bonding, amylose acquires a spiral structure that contains six glucose units per turn.

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 **11.2.7**). 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.

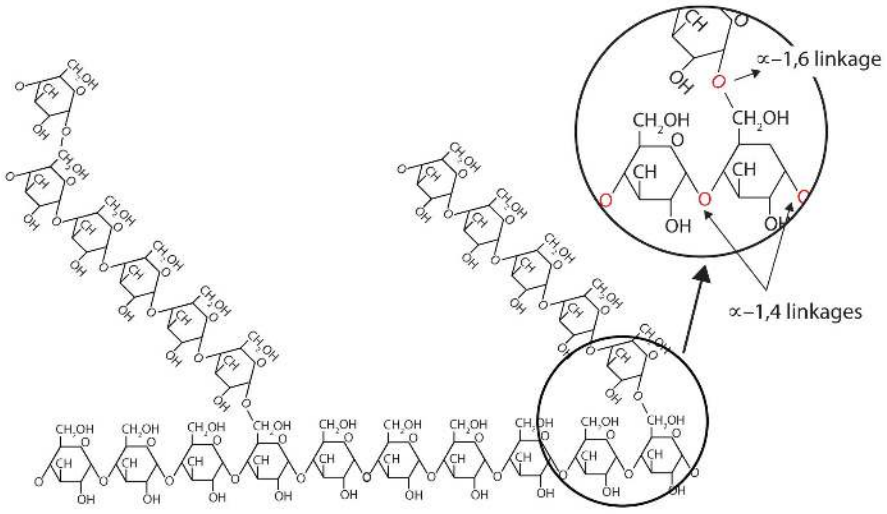


Figure **11.2.7** Representation of the Branching in Amylopectin and Glycogen. Both amylopectin and glycogen contain branch points that are linked through α-1,6-linkages. These branch points occur more often in glycogen.

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 **11.2.8**). 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 **11.2.8**). 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.

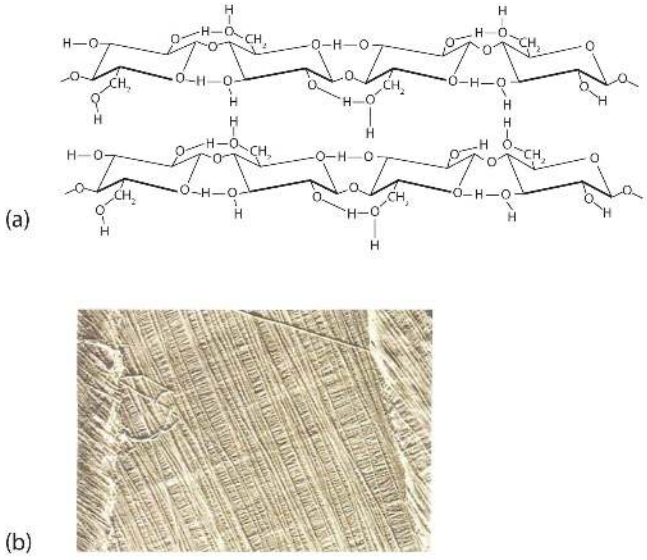


Figure **11.2.8** Cellulose. (a) There is extensive hydrogen bonding in the structure of cellulose. (b) In this electron micrograph of the cell wall of an alga, the wall consists of successive layers of cellulose fibers in parallel arrangement.

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.

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.

Sources

Wikipedia

Contributors and Attributions

- Template:ContribLindshield
- Libretext: The Basics of GOB Chemistry (Ball et al.)
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- Marisa Alviar-Agnew (Sacramento City College)

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11.3: Fats and Other Lipids

Learning Objectives

- Recognize the structures of common fatty acids.
- Describe the structure of fats and oils and classify them as saturated, monounsaturated, or polyunsaturated.

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 **11.3.1** 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.

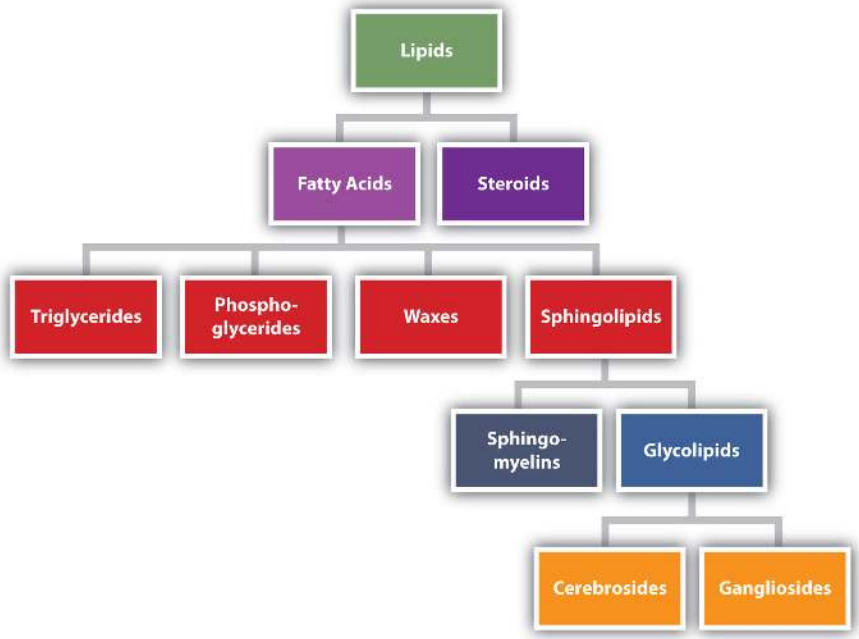


Figure **11.3.1** *Lipid organization based on structural relationships*

Fatty Acids

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.

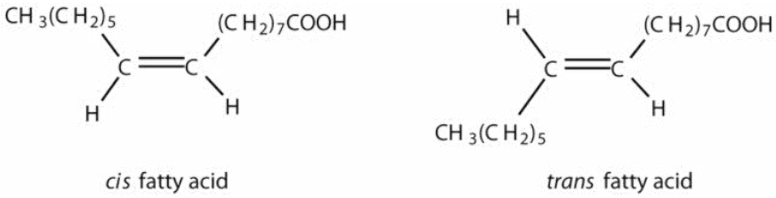


Table **11.3.1** lists some common fatty acids and one important source for each. The atoms or groups around the double bonds in unsaturated fatty acids can be arranged in either the cis or trans isomeric form. Naturally occurring fatty acids are generally in the cis configuration.

Table **11.3.1** 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.

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. Although we often draw the carbon atoms in a straight line, they actually have more of a zigzag configuration (Figure **11.3.2*a***). Viewed as a whole, however, the saturated fatty acid molecule is relatively straight (Figure **11.3.2*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.

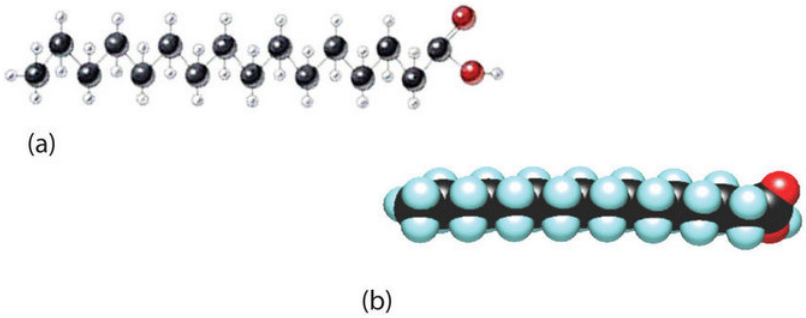
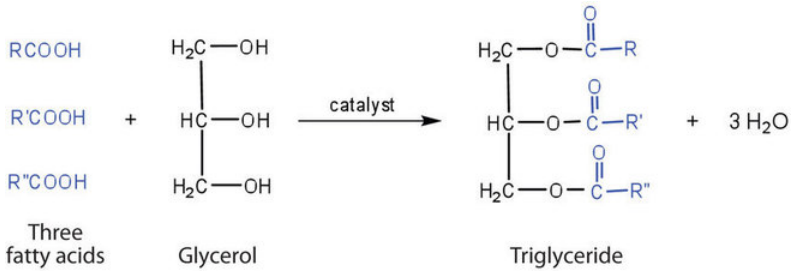


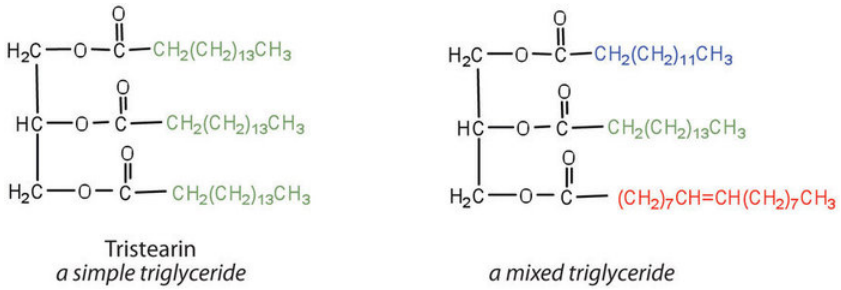
Figure **11.3.2** The Structure of Saturated Fatty Acids. (a) There is a zigzag pattern formed by the carbon-to-carbon single bonds in the ball-and-stick model of a palmitic acid molecule. (b) A space-filling model of palmitic acid shows the overall straightness of a saturated fatty acid molecule.

Structures of Fats and Oils

Fats and oils are called triglycerides (or *triacylcylgerols*) because they are esters composed of three fatty acid units joined to *glycerol*, a trihydroxy alcohol:



If all three OH groups on the glycerol molecule are esterified with the same fatty acid, the resulting ester is called a *simple triglyceride*. Although simple triglycerides have been synthesized in the laboratory, they rarely occur in nature. Instead, a typical triglyceride obtained from naturally occurring fats and oils contains two or three different fatty acid components and is thus termed a *mixed triglyceride*.



A triglyceride is called a fat if it is a solid at 25°C; it is called an oil if it is a liquid at that temperature. These differences in melting points reflect differences in the degree of unsaturation and number of carbon atoms in the constituent fatty acids. Triglycerides obtained from animal sources are usually solids, while those of plant origin are generally oils. Therefore, we commonly speak of animal fats and vegetable oils.

No single formula can be written to represent the naturally occurring fats and oils because they are highly complex mixtures of triglycerides in which many different fatty acids are represented. Table **11.3.2** 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 **11.3.2** 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

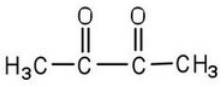
*Totals less than 100% indicate the presence of fatty acids with fewer than 12 carbon atoms or more than 18 carbon atoms.

†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.

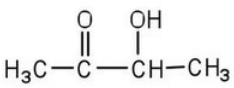
Terms such as ***saturated fat*** or *unsaturated oil* are often used to describe the fats or oils obtained from foods. **Saturated fats** contain a high proportion of saturated fatty acids, while **unsaturated oils** contain a high proportion of unsaturated fatty acids. The high consumption of saturated 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

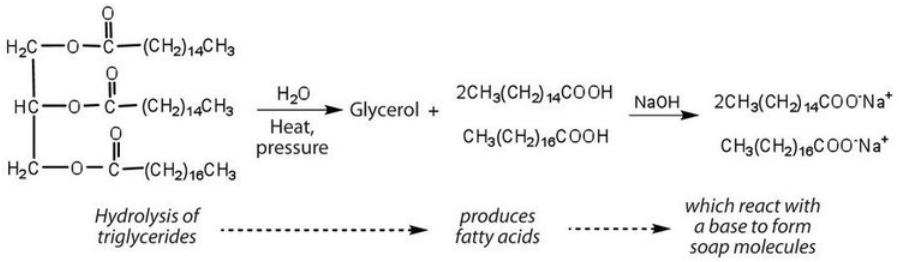


3-hydroxy-2-butanone

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):



Iodine Value

The **iodine value** (or **iodine adsorption value** or **iodine number** or **iodine index**, commonly abbreviated as **IV**) in chemistry is the mass of iodine in grams that is consumed by 100 grams of a chemical substance. Iodine numbers are often used to determine the amount of unsaturation in fats, oils and waxes. In fatty acids, unsaturation occurs mainly as double bonds which are very reactive towards halogens, the iodine in this case. Thus, the higher the iodine value, the more unsaturations are present in the fat. It can be seen from the table that coconut oil is very saturated, which means it is good for making soap. On the other hand, linseed oil is highly unsaturated, which makes it a drying oil, well suited for making oil paints.

Table **11.3.1** *Iodine Numbers of Common Fats and Oils. Source Wikipedia*

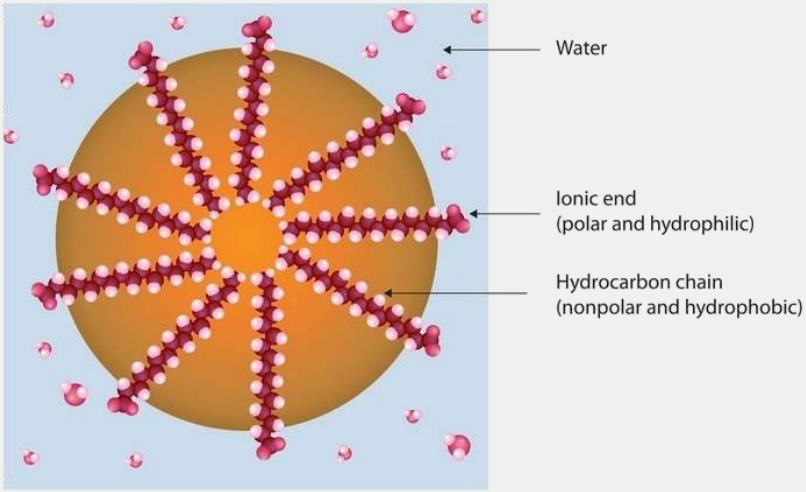
Fat	Iodine Value (g/100g)
Beef tallow	42-48
Butter	25-42
Canola Oil	110-126
Coconut Oil	6-11
Fish oil	190-205
Linseed Oil	170-204
Olive Oil	75-94
Safflower Oil	135-150
Walnut Oil	132-162

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.

Summary

- Fatty acids are carboxylic acids that are the structural components of many lipids.
- 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.
- Fats and oils are composed of molecules known as triglycerides, which are esters composed of three fatty acid units linked to glycerol.
- 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.
- Animal fats and oils which are made up mostly of saturated fatty acids have low iodine values (numbers), while those oils with high degree of unsaturation (with more C=C bonds) have high iodine values.

Contributors and Attributions

- Libretext: The Basics od GOB Chemistry (Ball et al.)
- Wikipedia

- Marisa Alviar-Agnew (Sacramento City College)

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11.4: Proteins- Polymers of Amino Acids

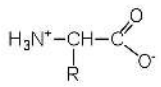
Learning Objectives

- Identify different amino acids.
- Describe how short chain proteins (polypeptides) are formed from amino acids.

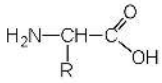
Proteins may be defined as compounds of high molar mass consisting largely or entirely of chains of amino acids. Their masses range from several thousand to several million daltons (Da). In addition to carbon, hydrogen, and oxygen atoms, all proteins contain nitrogen and sulfur atoms, and many also contain phosphorus atoms and traces of other elements. Proteins serve a variety of roles in living organisms and are often classified by these biological roles. Muscle tissue is largely protein, as are skin and hair. Proteins are present in the blood, in the brain, and even in tooth enamel. Each type of cell in our bodies makes its own specialized proteins, as well as proteins common to all or most cells. We begin our study of proteins by looking at the properties and reactions of amino acids, which is followed by a discussion of how amino acids link covalently to form peptides and proteins. We end the chapter with a discussion of enzymes—the proteins that act as catalysts in the body.

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

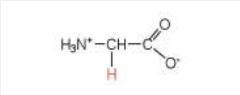
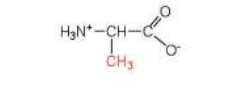
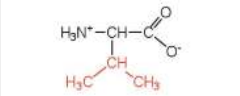
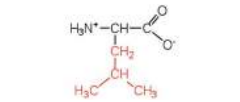
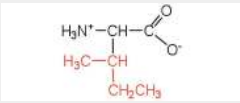
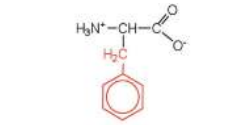
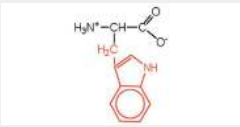
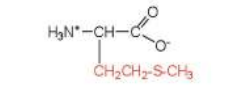
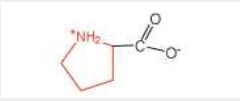
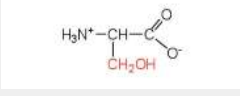
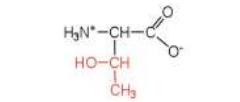
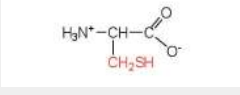


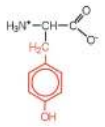
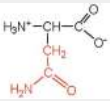
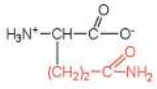
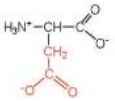
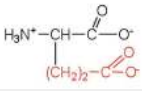
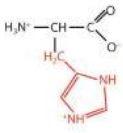
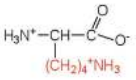
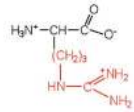
α-Amino acid drawn as an uncharged molecule; not an accurate respresentation of amino acid structure

Classification

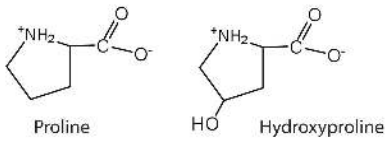
In addition to the amino and carboxyl groups, amino acids have a side chain or R group attached to the α-carbon. Each amino acid has unique characteristics arising from the size, shape, solubility, and ionization properties of its R group. As a result, the side chains of amino acids exert a profound 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 **11.4.1**.

Table **11.4.1**: 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*

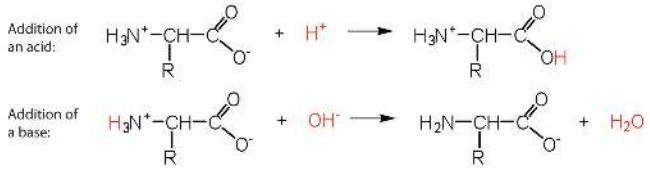
Common Name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
tyrosine	tyr (Y)		181	also classified as an aromatic amino acid
asparagine	asn (N)		132	the amide of aspartic acid
glutamine	gln (Q)		146	the amide of glutamic acid
Amino acids with a negatively charged R group				
aspartic 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.



Zwitterions

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.



The Peptide Bond: Peptides and Proteins

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 as shown in Figure 11.4.1

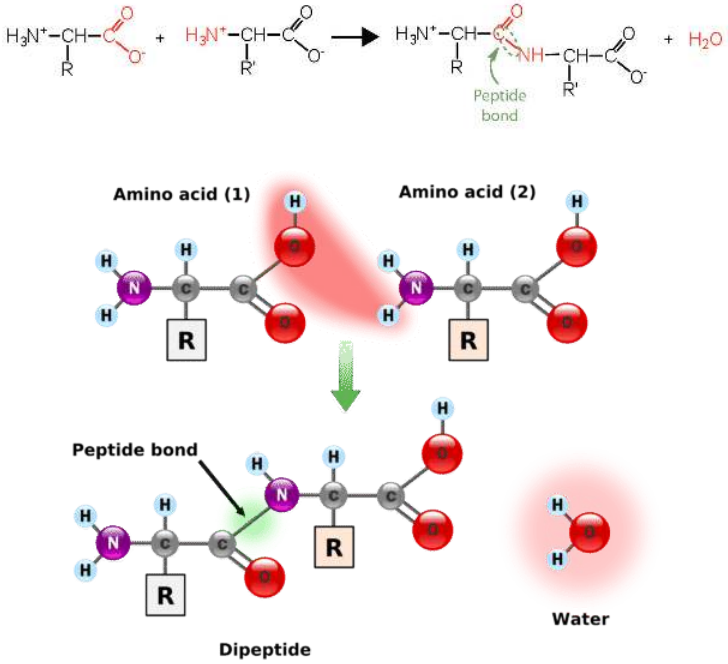
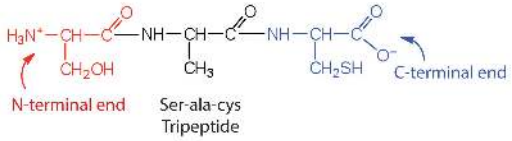


Figure 11.4.1 *Amino acids undergo condensation to form a molecule called a dipeptide. The* C—N *bond is called a peptide bond.*

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.

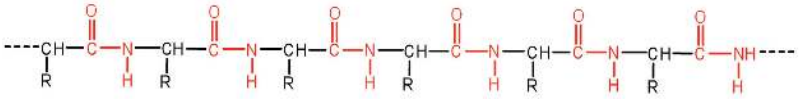


The general term *peptide* refers to an amino acid chain of unspecified length. However, chains of about 50 amino acids or more are usually called proteins or polypeptides. In its physiologically active form, a protein may be composed of one or more polypeptide chains.

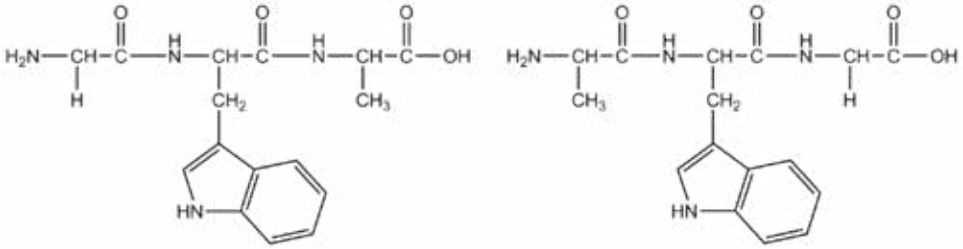
Peptide cells in our bodies have an intricate mechanism for the manufacture of proteins. Humans have to use other techniques in order to synthesize the same proteins in a lab. The chemistry of peptide synthesis is complicated. Both active groups on an amino acid can react and the amino acid sequence must be a specific one in order for the protein to function. Robert Merrifield developed the first synthetic approach for making proteins in the lab, a manual approach which was lengthy and tedious (and, he won the Nobel Prize in Chemistry in 1984 for his work). Today, however, automated systems can crank out a peptide in a very short period of time.

The Sequence of Amino Acids

The particular sequence of amino acids in a longer chain is called an amino acid sequence. By convention, the amino acid sequence is listed in the order such that the free amine group is on the left end of the molecule and the free carboxyl group is on the right end of the molecule.



For example, suppose that a sequence of the amino acids glycine, tryptophan, and alanine is formed with the free amine group as part of the glycine and the free carboxyl group as part of the alanine. The amino acid sequence can be easily written using the abbreviations as Gly-Trp-Ala. This is a different sequence from Ala-Trp-Gly because the free amine and carboxyl groups would be on different amino acids in that case.



Bradykinin

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 **11.4.2**) 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.

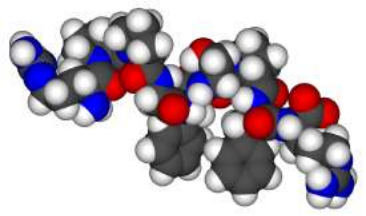


Figure **11.4.2** Space-filling model of bradykinin. (Public Domain; Fvasconcellos)

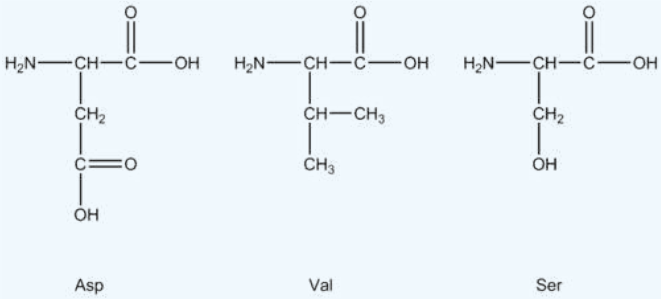
Just as millions of different words are spelled with our 26-letter English alphabet, millions of different proteins are made with the 20 common amino acids. However, just as the English alphabet can be used to write gibberish, amino acids can be put together in the *wrong sequence* to produce nonfunctional 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.

Example 11.4.1

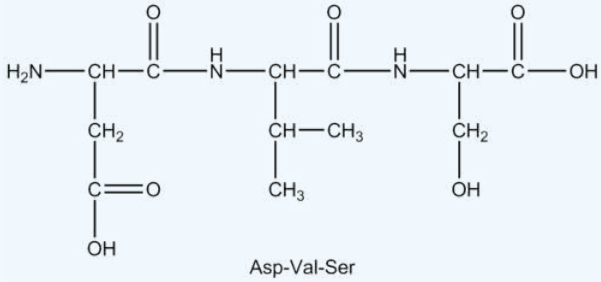
Draw the polypeptide Asp-Val-Ser.

Solution

1. Identify the structures of each of the three given amino acids and draw them in the same order as given in the name.



2. Leaving the order the same, connect the amino acids to one another by forming peptide bonds. Note that the order given in the name is the same way the amino acids are connected in the molecule. The first one listed is always the **N**-terminus of the polypeptide.



Asp-Val-Ser

Example 11.4.2

List all of the possible polypeptides that can be formed from cysteine (Cys), leucine (Leu), and arginine (Arg).

Solution

Although there are only three amino acids, the order in which they are bonded changes the identity, properties, and function of the resulting polypeptide. There are six possible polypeptides formed from these three amino acids.

Cys-Leu-Arg

Cys-Arg-Leu

Leu-Cys-Arg

Leu-Arg-Cys

Arg-Cys-Leu

Arg-Leu-Cys

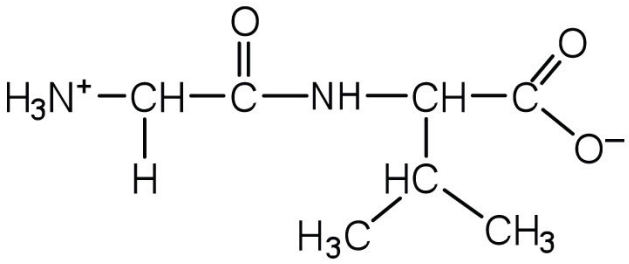
Exercise 11.4.1

Draw the structure for each peptide.

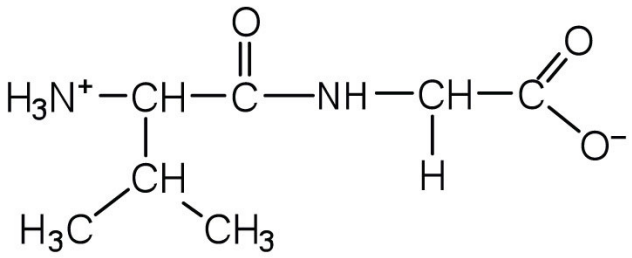
a. gly-val
b. val-gly

Answers

a.



b.



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 chain consisting of only two amino acid units is called a *dipeptide*; a chain consisting of three is a *tripeptide*.
- Chains of about 50 amino acids or more are usually called proteins or polypeptides.
- 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).
- The order, or *sequence*, in which the amino acids are connected is also of critical importance in order for a peptide or protein to be physiologically active.

Contributors and Attributions

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-
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11.5: Structure and Function of Proteins

Learning Objectives

- Describe the four levels of protein structure.
- Identify the types of attractive interactions that hold proteins in their most stable three-dimensional structure
- Explain the role of an enzyme in the body.

Each of the thousands of naturally occurring proteins has its own characteristic amino acid composition and sequence that result in a unique three-dimensional shape. Since the 1950s, scientists have determined the amino acid sequences and three-dimensional conformation of numerous proteins and thus obtained important clues on how each protein performs its specific function in the body.

Proteins are compounds of high molar mass consisting largely or entirely of chains of amino acids. Because of their great complexity, protein molecules cannot be classified on the basis of specific structural similarities, as carbohydrates and lipids are categorized. The two major structural classifications of proteins are based on far more general qualities: whether the protein is (1) fiberlike and insoluble or (2) globular and soluble. Some proteins, such as those that compose hair, skin, muscles, and connective tissue, are fiberlike. These fibrous proteins are insoluble in water and usually serve structural, connective, and protective functions. Examples of fibrous proteins are keratins, collagens, myosins, and elastins. Hair and the outer layer of skin are composed of keratin. Connective tissues contain collagen. Myosins are muscle proteins and are capable of contraction and extension. Elastins are found in ligaments and the elastic tissue of artery walls.

Globular proteins, the other major class, are soluble in aqueous media. In these proteins, the chains are folded so that the molecule as a whole is roughly spherical. Familiar examples include egg albumin from egg whites and serum albumin in blood. Serum albumin plays a major role in transporting fatty acids and maintaining a proper balance of osmotic pressures in the body. Hemoglobin and myoglobin, which are important for binding oxygen, are also globular proteins.

Levels of Protein Structure

The structure of proteins is generally described as having four organizational levels. The first of these is the **primary structure**, which is the number and sequence of amino acids in a protein's polypeptide chain or chains, beginning with the free amino group and maintained by the peptide bonds connecting each amino acid to the next. The primary structure of insulin, composed of 51 amino acids, is shown in Figure **11.5.1**.

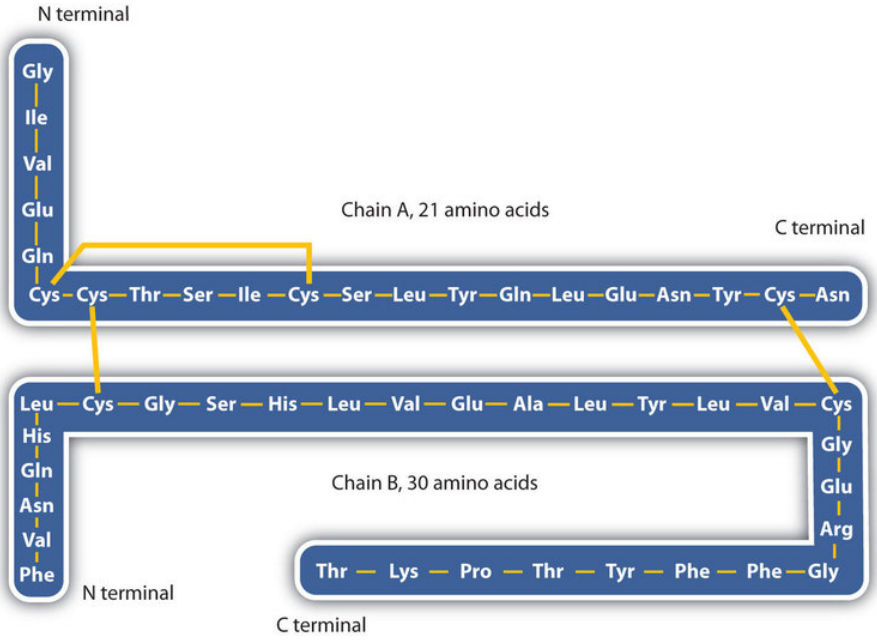


Figure **11.5.1** Primary Structure of Human Insulin. Human insulin, whose amino acid sequence is shown here, is a hormone that is required for the proper metabolism of glucose.

A protein molecule is not a random tangle of polypeptide chains. Instead, the chains are arranged in unique but specific conformations. The term **secondary structure** refers to the fixed arrangement of the polypeptide backbone. On the basis of X ray studies, Linus Pauling and Robert Corey postulated that certain proteins or portions of proteins twist into a spiral or a helix. This helix is stabilized by *intrachain* hydrogen bonding between the carbonyl oxygen atom of one amino acid and the amide hydrogen atom four amino acids up the chain (located on the next turn of the helix) and is known as a right-handed α-helix. X ray data indicate that this helix makes one turn for every 3.6 amino acids, and the side chains of these amino acids project outward from the coiled backbone (Figure **11.5.2**). The α-keratins, found in hair and wool, are exclusively α-helical in conformation. Some proteins, such as gamma globulin, chymotrypsin, and cytochrome c, have little or no helical structure. Others, such as hemoglobin and myoglobin, are helical in certain regions but not in others.

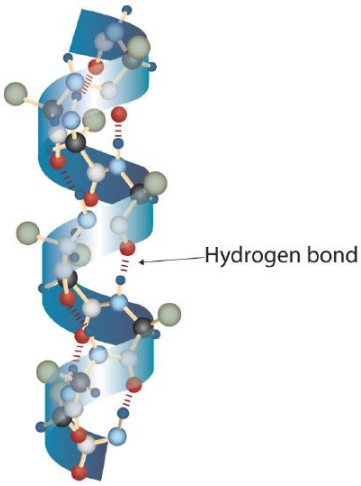


Figure **11.5.2** A Ball-and-Stick Model of an α-Helix. This ball-and-stick model shows the intrachain hydrogen bonding between carbonyl oxygen atoms and amide hydrogen atoms. Each turn of the helix spans 3.6 amino acids. Note that the side chains (represented as green spheres) point out from the helix.

Another common type of secondary structure, called the *β-pleated sheet conformation*, is a sheetlike arrangement in which two or more extended polypeptide chains (or separate regions on the same chain) are aligned side by side. The aligned segments can run either parallel or antiparallel—that is, the N-terminals can face in the same direction on adjacent chains or in different directions—

and are connected by *interchain* hydrogen bonding (Figure **11.5.3**). The β-pleated sheet is particularly important in structural proteins, such as silk fibroin. It is also seen in portions of many enzymes, such as carboxypeptidase A and lysozyme.

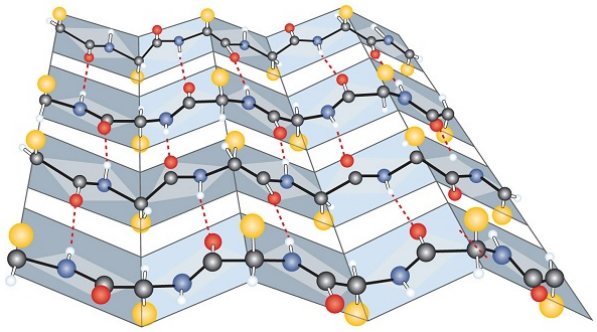


Figure **11.5.3** A Ball-and-Stick Model of the β-Pleated Sheet Structure in Proteins. The side chains extend above or below the sheet and alternate along the chain. The protein chains are held together by interchain hydrogen bonding.

Tertiary structure refers to the unique three-dimensional shape of the protein as a whole, which results from the folding and bending of the protein backbone. The tertiary structure is intimately tied to the proper biochemical functioning of the protein. Figure **11.5.4** shows a depiction of the three-dimensional structure of insulin.

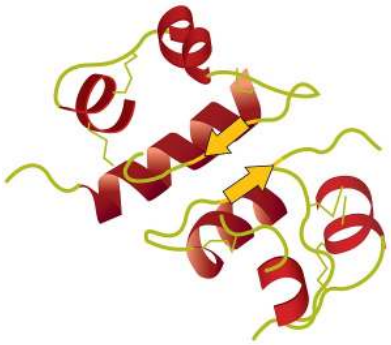
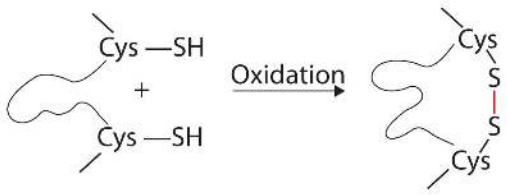


Figure **11.5.4** A Ribbon Model of the Three-Dimensional Structure of Insulin. The spiral regions represent sections of the polypeptide chain that have an α-helical structure, while the broad arrows represent β-pleated sheet structures.

Four major types of attractive interactions determine the shape and stability of the tertiary structure of proteins.

You studied several of them previously.

1. Ionic bonding. Ionic bonds result from electrostatic attractions between positively and negatively charged side chains of amino acids. For example, the mutual attraction between an aspartic acid carboxylate ion and a lysine ammonium ion helps to maintain a particular folded area of a protein (part (a) of Figure **11.5.5**).
2. Hydrogen bonding. Hydrogen bonding forms between a highly electronegative oxygen atom or a nitrogen atom and a hydrogen atom attached to another oxygen atom or a nitrogen atom, such as those found in polar amino acid side chains. Hydrogen bonding (as well as ionic attractions) is extremely important in both the intra- and intermolecular interactions of proteins (part (b) of Figure **11.5.5**).
3. Disulfide linkages. Two cysteine amino acid units may be brought close together as the protein molecule folds. Subsequent oxidation and linkage of the sulfur atoms in the highly reactive sulfhydryl (SH) groups leads to the formation of cystine (part (c) of Figure **11.5.5**). Intrachain disulfide linkages are found in many proteins, including insulin (yellow bars in Figure **11.5.1**) and have a strong stabilizing effect on the tertiary structure.



4. Dispersion forces. Dispersion forces arise when a normally nonpolar atom becomes momentarily polar due to an uneven distribution of electrons, leading to an instantaneous dipole that induces a shift of electrons in a neighboring nonpolar atom. Dispersion forces are weak but can be important when other types of interactions are either missing or minimal (part (d) of Figure **11.5.5**). This is the case with fibroin, the major protein in silk, in which a high proportion of amino acids in the protein have nonpolar side chains. The term *hydrophobic interaction* is often misused as a synonym for dispersion forces. Hydrophobic interactions arise because water molecules engage in hydrogen bonding with other water molecules (or groups in proteins capable of hydrogen bonding). Because nonpolar groups cannot engage in hydrogen bonding, the protein folds in such a way that these groups are buried in the interior part of the protein structure, minimizing their contact with water.

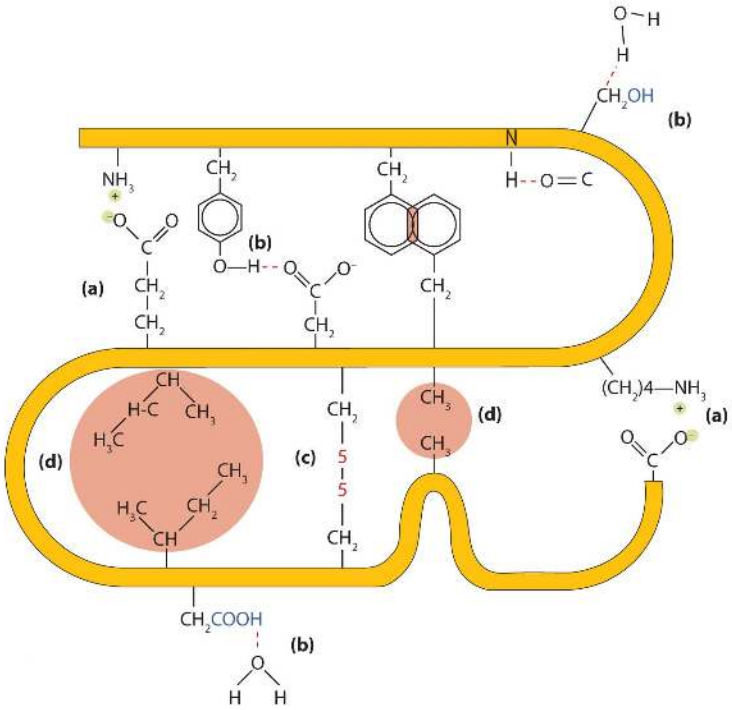


Figure **11.5.5** Tertiary Protein Structure Interactions. Four interactions stabilize the tertiary structure of a protein: (a) ionic bonding, (b) hydrogen bonding, (c) disulfide linkages, and (d) dispersion forces.

When a protein contains more than one polypeptide chain, each chain is called a *subunit*. The arrangement of multiple subunits represents a fourth level of structure, the quaternary structure of a protein. Hemoglobin, with four polypeptide chains or subunits, is the most frequently cited example of a protein having quaternary structure (Figure **11.5.6**). The quaternary structure of a protein is produced and stabilized by the same kinds of interactions that produce and maintain the tertiary structure. A schematic representation of the four levels of protein structure is in Figure **11.5.7**.

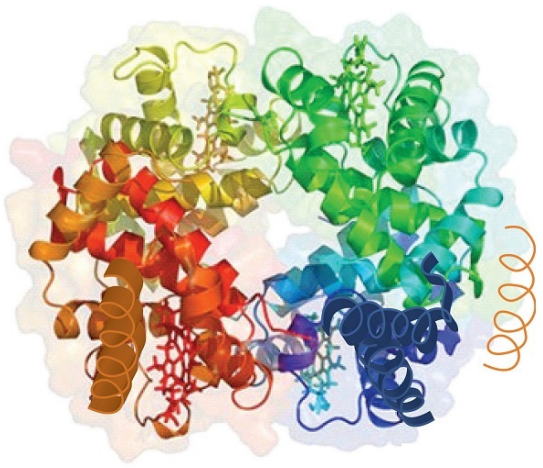


Figure **11.5.6** The Quaternary Structure of Hemoglobin. Hemoglobin is a protein that transports oxygen throughout the body.

Source: Image from the RCSB PDB (www.pdb.org) of PDB ID 1I3D (R.D. Kidd, H.M. Baker, A.J. Mathews, T. Brittain, E.N. Baker (2001) Oligomerization and ligand binding in a homotetrameric hemoglobin: two high-resolution crystal structures of hemoglobin Bart's (gamma(4)), a marker for alpha-thalassemia. Protein Sci. 1739–1749).

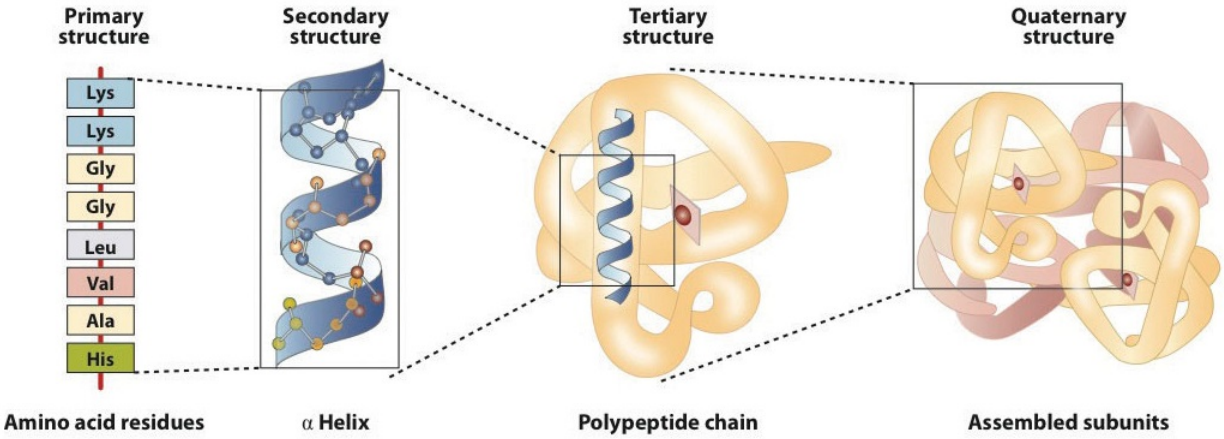


Figure **11.5.7** Levels of Structure in Proteins.

The *primary structure* consists of the specific amino acid sequence. The resulting peptide chain can twist into an α-helix, which is one type of *secondary structure*. This helical segment is incorporated into the *tertiary structure* of the folded polypeptide chain. The single polypeptide chain is a subunit that constitutes the *quaternary structure* of a protein, such as hemoglobin that has four polypeptide chains.

Globular and Fibrous Proteins

Once proteins form and have developed all levels of their structure, they can be classified as either fibrous or globular. These classifications give the basic shape of the entire protein molecule. While many proteins are **globular proteins** (see figure below), keratin proteins are **fibrous** (see figure below) and make up the hair, nails, and the outer layer of skin.

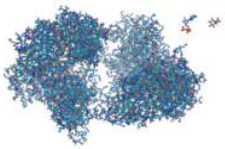


Figure **11.5.8** Globular protein.

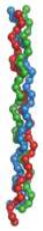


Figure **11.5.9** Fibrous protein.

Enzymes: Exquisite Precision Machines

The first enzyme to be isolated was discovered in 1926 by American chemist James Sumner, who crystallized the protein. The enzyme was urease, which catalyzes the hydrolytic decomposition of urea, a component of urine, into ammonia and carbon dioxide.

$$\mathrm{H_2NCON_2}\,(aq) + \mathrm{H_2O}\,(l) \overset{\text{urease}}{\rightarrow} 2\mathrm{NH_3}\,(g) + \mathrm{CO_2}\,(g)$$

His discovery was ridiculed at first because nobody believed that enzymes would behave the same way that other chemicals did. Sumner was eventually proven right and won the Nobel Prize in Chemistry in 1946.

Enzymes and Biochemical Reactions

Most chemical reactions within organisms would be impossible under the conditions in cells. For example, the body temperature of most organisms is too low for reactions to occur quickly enough to carry out life processes. Reactants may also be present in such low concentrations that it is unlikely they will meet and collide. Therefore, the rate of most biochemical reactions must be increased by a catalyst. A **catalyst** is a chemical that speeds up chemical reactions. In organisms, catalysts are called **enzymes**. Essentially, enzymes are biological catalysts.

Like other catalysts, enzymes are not reactants in the reactions they control. They help the reactants interact but are not used up in the reactions. Instead, they may be used over and over again. Unlike other catalysts, enzymes are usually highly specific for particular chemical reactions. They generally catalyze only one or a few types of reactions.

Enzymes are extremely efficient in speeding up reactions. They can catalyze up to several million reactions per second. As a result, the difference in rates of biochemical reactions with and without enzymes may be enormous. A typical biochemical reaction might take hours or even days to occur under normal cellular conditions without an enzyme, but less than a second with an enzyme.

Figure **11.5.10** diagrams a typical enzymatic reaction. A **substrate** is the molecule or molecules on which the enzyme acts. In the urease catalyzed reaction, urea is the substrate.

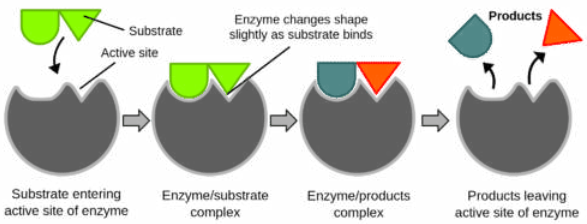


Figure **11.5.10** The sequence of steps for a substrate binding to an enzyme in its active site, reacting, then being released as products.

The first step in the reaction is that the substrate binds to a specific part of the enzyme molecule, known as the active site. The binding of the substrate is dictated by the shape of each molecule. Side chains on the enzyme interact with the substrate in a specific way, resulting in the making and breaking of bonds. The **active site** is the place on an enzyme where the substrate binds. An enzyme folds in such a way that it typically has one active site, usually a pocket or crevice formed by the folding pattern of the protein. Because the active site of an enzyme has such a unique shape, only one particular substrate is capable of binding to that enzyme. In other words, each enzyme catalyzes only one chemical reaction with only one substrate. Once the enzyme/substrate complex is formed, the reaction occurs and the substrate is transformed into products. Finally, the product molecule or molecules

are released from the active site. Note that the enzyme is left unaffected by the reaction and is now capable of catalyzing the reaction of another substrate molecule.

For many enzymes, the active site follows a **lock and key** (Figure **11.5.11*A***) model where the substrate fits exactly into the active site. The enzyme and substrate must be a perfect match so the enzyme only functions as a catalyst for one reaction. Other enzymes have an **induced fit** (Figure **11.5.11*B***) model. In an induced fit model, the active site can make minor adjustments to accommodate the substrate. This results in an enzyme that is capable of interacting with a small group of similar substrates. Look at the shape of the active site compared to the shape of the substrate in B of the figure below. The active site adjusts to accommodate the substrate.

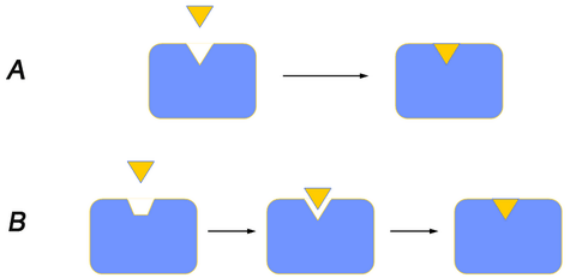


Figure **11.5.11** (A) Lock and key enzyme model and (B) induced fit enzyme model.

Inhibitors

An **inhibitor** is a molecule which interferes with the function of an enzyme, either by slowing or stopping the chemical reaction. Inhibitors can work in a variety of ways, but one of the most common is illustrated in the figure below.

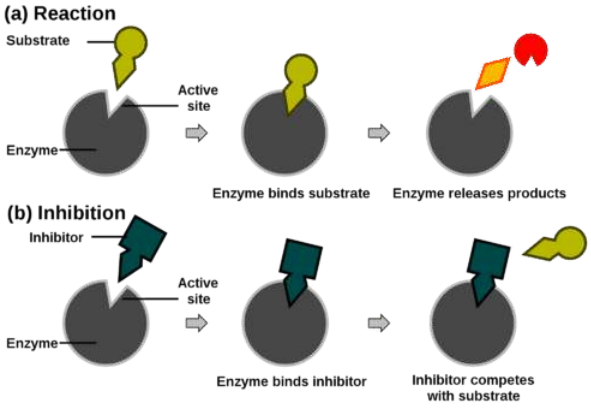


Figure **11.5.12** A competitive inhibitor is a molecule that binds to the active site of an enzyme without reacting, thus preventing the substrate from binding.

A **competitive inhibitor** binds competitively at the active site and blocks the substrate from binding. Since no reaction occurs with the inhibitor, the enzyme is prevented from catalyzing the reaction.

A **non-competitive inhibitor** does not bind at the active site. It attaches at an **allosteric site**, which is some other site on the enzyme, and changes the shape of the protein. The allosteric site is any site on the enzyme that is not the active site. The attachment of the non-competitive inhibitor to the allosteric site results in a shift in three-dimensional structure that alters the shape of the active site so that the substrate will no longer fit in the active site properly (see figure below).

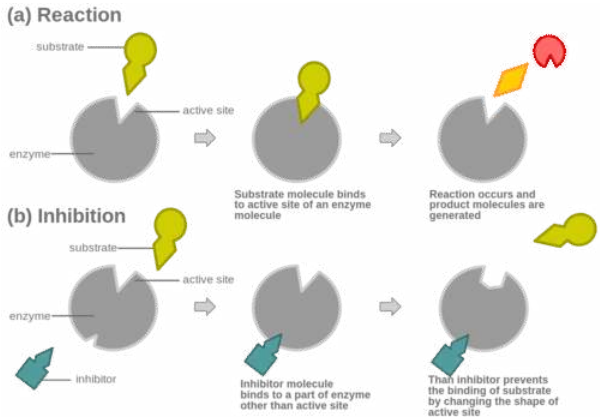


Figure 11.5.13 Non-competitive inhibition.

Cofactors and Coenzymes

Some enzymes require the presence of another substrate as a "helper" molecule in order to function properly. **Cofactors** and **coenzymes** serve in this role. Cofactors are inorganic species and coenzymes are small organic molecules. Many vitamins, such as B vitamins, are coenzymes. Some metal ions which function as cofactors for various enzymes include zinc, magnesium, potassium, and iron.

Catalytic Activity of Enzymes

Enzymes generally lower activation energy by reducing the energy needed for reactants to come together and react. One way that enzymes act is to bring reactants (substrates) together so they don't have to expend energy moving about until they collide at random. Enzymes bind both reactant molecules (substrates), tightly and specifically, at a site on the enzyme's active site. Enzymes can also bring molecules to the active site to break them apart. For example, sucrase is the enzyme for the breakdown of sucrose which enters the active site of the enzyme and helps weaken the interactions between the fructose and glucose that make up sucrose. Sucrase is specific to the breakdown of sucrose as are most enzymes. The active site is specific for the reactants of the biochemical reaction the enzyme catalyzes. Similar to puzzle pieces fitting together, the active site can only bind certain substrates. The activities of enzymes also depend on the temperature, concentration, and the pH of the surroudings.

Concentration

As with most reactions, the concentration of the reactant(s) affects the reaction rate. This is also true in enzyme concentration. When either substrate or enzyme concentration is low, the rate of the reaction will be slower than where there are higher concentrations. The two species must interact for a reaction to occur and higher concentrations of one or both will result in more effective interactions between the two.

However, continuing to increase the substrate's concentration will not always increase the reaction rate. This is because at some point, all of the enzymes will be occupied and unavailable to bind with another substrate molecule until the substrate forms a product molecule and is released from the enzyme.

pH

Some enzymes work best at acidic pHs, while others work best in neutral environments. For example, digestive enzymes secreted in the acidic environment (low pH) of the stomach help break down proteins into smaller molecules. The main digestive enzyme in the stomach is **pepsin**, which works best at a pH of about 1.5. These enzymes would not work optimally at other pHs. Trypsin is another enzyme in the digestive system, which breaks protein chains in food into smaller particles. **Trypsin** works in the small intestine, which is not an acidic environment. Trypsin's optimum pH is about 8.

Different reactions and different enzymes will achieve their maximum rate at certain pH values. As shown in the figure below, the enzyme achieves a maximum reaction rate at a pH of 4. Notice that the reaction will continue at lower and higher pH values because the enzyme will still function at other pH values but will not be as effective. At very high or very low pH values, denaturation will occur because an enzyme is just a protein with a specific function.

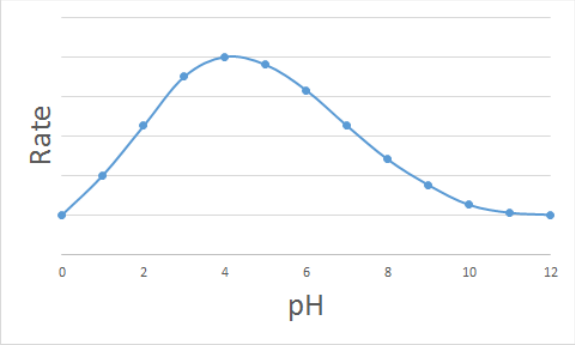


Figure **11.5.14** Relationship between rate and pH.

Temperature

As with pH, reactions also have an ideal temperature where the enzyme functions most effectively. It will still function at higher and lower temperatures, but the rate will be less. For many biological reactions, the ideal temperature is at physiological conditions which is around **37°C** which is normal body temperature. Many enzymes lose function at lower and higher temperatures. At higher temperatures, an enzyme's shape deteriorates. Only when the temperature comes back to normal does the enzyme regain its shape and normal activity unless the temperature was so high that it caused irreversible damage.

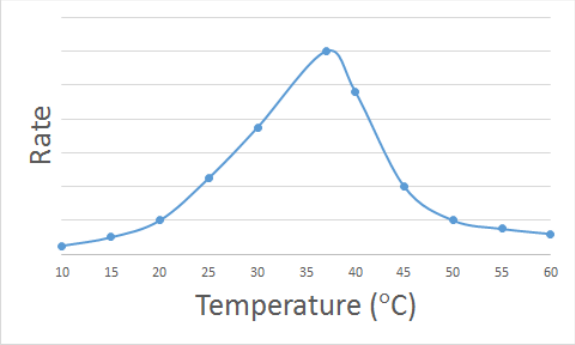


Figure **11.5.15** *Relationship between temperature and rate*.

Applications of Enzymes

Enzymes are used in the and other industrial applications when extremely specific catalysts are required (Table **11.5.1**). Enzymes in general are limited in the number of reactions they have evolved to catalyze and also by their lack of stability in and at high temperatures. As a consequence, is an active area of research and involves attempts to create new enzymes with novel properties, either through rational design or *in vitro* evolution. These efforts have begun to be successful, and a few enzymes have now been designed "from scratch" to catalyze reactions that do not occur in nature.

Table **11.5.1** *Uses of Enzymes in Various Industries. Source: Wikipedia*

Application	Enzymes used	Uses
Biofuel industry	Cellulases	Break down cellulose into sugars that can be fermented to produce cellulosic ethanol.
	Ligninases	Pretreatment of biomass for biofuel production.
Biological detergent	Proteases, amylases, lipases	Remove protein, starch, and fat or oil stains from laundry and dish ware.
	Mannanases	Remove food stains from the common food additive guar gum.
Brewing industry	Amylase, glucanases, proteases	Split polysaccharides and proteins in the malt.
	Betaglucanases	Improve the wort and beer filtration characteristics.
	Amyloglucosisdase and pullulanases	Make low-calorie beer and adjust fermentability.
	Acetolacatate deacrboxylase (ALDC)	Increase fermentation efficiency by reducing diacetyl formation.
Culinary uses	Papain	Tenderize meat for cooking.
Dairy industry	Renin	Hydrolyze protein in the manufacture of cheese.
	Lipases	Produce Camembert cheese and blue cheese such as Roquefort.
Food processing	Amylases	Produce sugars from starch, such as in making high-fructose corn syrup.
	Proteases	Lower the protein level of flour, as in biscuit-making.
	Trypsin	Manufacture hypoallergenic baby foods.
	Cellulases, pectinases	Clarify fruit juices.
Molecular biology	Nucleases, DNA ligase, and polymerases	Use restriction digestion and the polymerase chain reaction to create recombinant DNA.
Paper industry	Xylanases, hemicellulases, and lignin peroxidases	Remove lignin from Kraft pulp.
Personal care	Proteases	Remove proteins on cotact lenses to prevent infections.
Starch industry	Amylases	Convert starch into glucose and various syrups.



https://www.youtube.com/watch?v=E90D4BmaVJM

Summary

- Proteins can be divided into two categories: fibrous, which tend to be insoluble in water, and globular, which are more soluble in water. A protein may have up to four levels of structure.
- The primary structure consists of the specific amino acid sequence.
- The resulting peptide chain can form an α-helix or β-pleated sheet (or local structures not as easily categorized), which is known as secondary structure. These segments of secondary structure are incorporated into the tertiary structure of the folded polypeptide chain.
- The quaternary structure describes the arrangements of subunits in a protein that contains more than one subunit. Four major types of attractive interactions determine the shape and stability of the folded protein: ionic bonding, hydrogen bonding, disulfide linkages, and dispersion forces.
- An enzyme is an organic catalyst produced by a living cell. Enzymes are such powerful catalysts that the reactions they promote occur rapidly at body temperature.
- The molecule or molecules on which an enzyme acts are called its substrates.
- An enzyme has an active site where its substrate or substrates bind to form an enzyme-substrate complex.
- The original lock and key model of enzyme and substrate binding pictured a rigid enzyme of unchanging configuration binding to the appropriate substrate. The newer induced fit model describes the enzyme active site as changing its conformation after binding to the substrate.
- Enzymes have numerous applications in the food and dairy industry, biofuel industry, paper industry etc.

Contributors and Attributions

- Libretext: The Basics of GOB Chemistry (Ball et al.)
-
- Allison Soult, Ph.D. (Department of Chemistry, University of Kentucky)
- Wikipedia
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11.6: Nucleic Acids- Parts, Structure, and Function

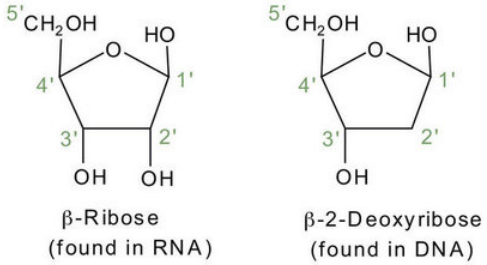
Learning Objectives

- Describe the two types of nucleic acids and the function of each type.
- Describe the secondary structure of DNA and the importance of complementary base pairing.
- Describe how a new copy of DNA is synthesized.

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 **11.6.1**).

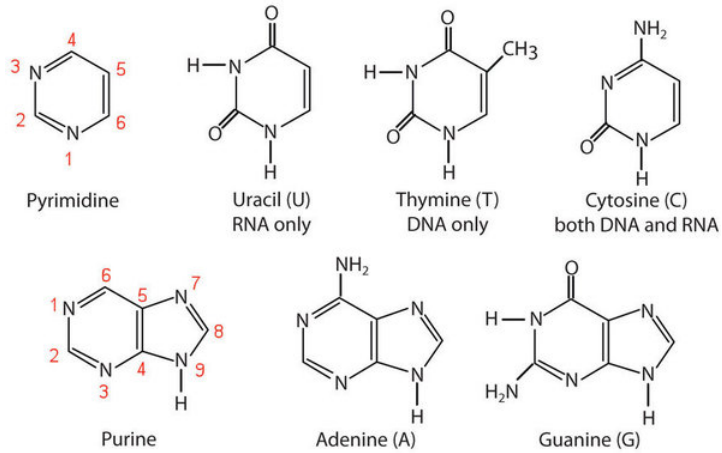


Figure **11.6.1** The Nntrogenous bases found in DNA and RNA.

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 **11.6.1** 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 **11.6.1** 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 **11.6.2**.

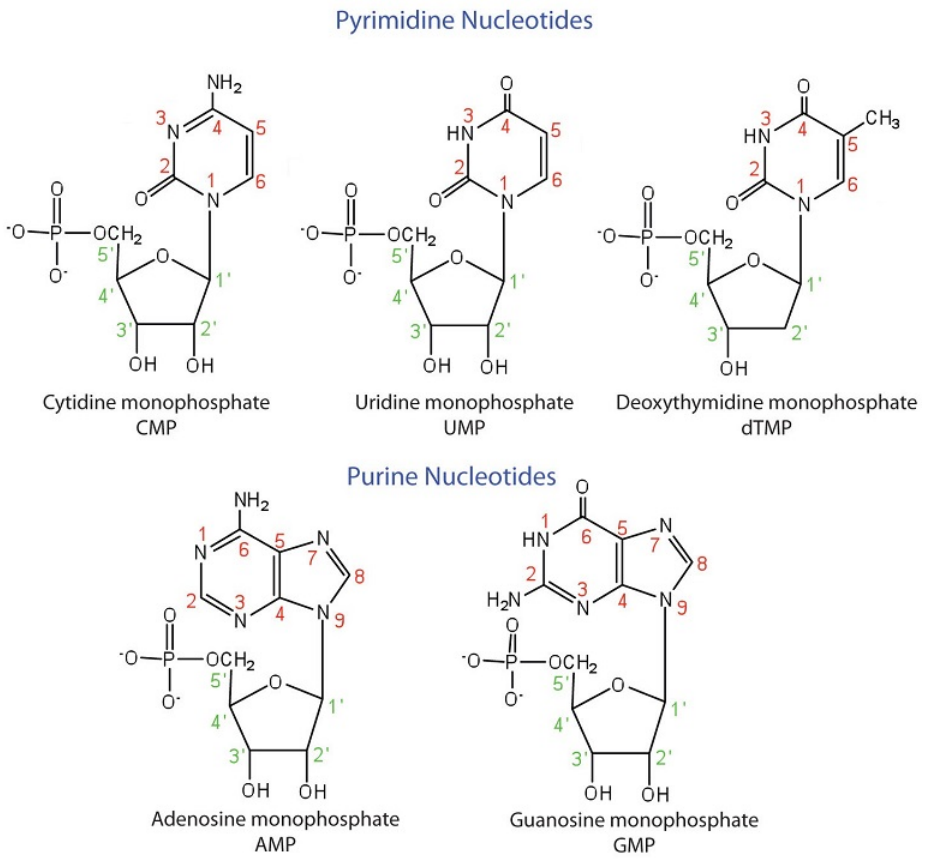


Figure **11.6.2** The pyrimidine and purine nucleotides

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 **11.6.3**, 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.

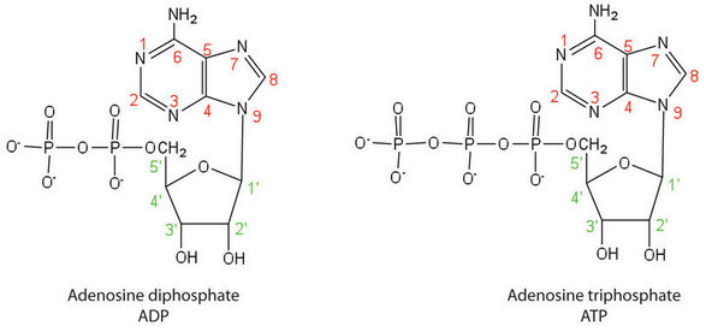


Figure **11.6.3** *Structures of two important adenine-containing nucleotides.*

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 **11.6.4**). 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.*

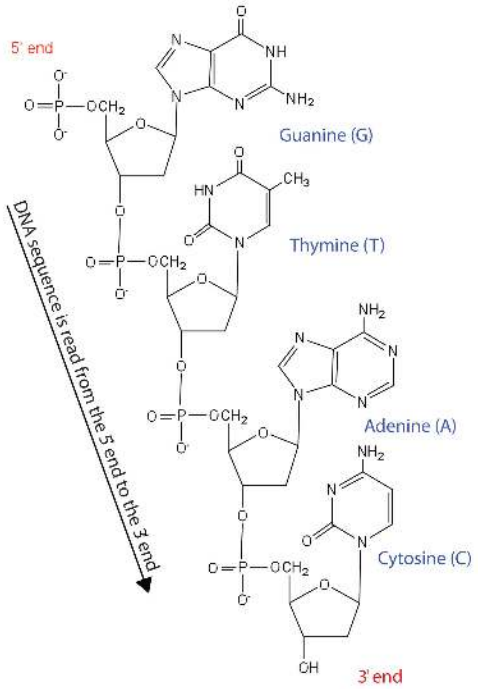


Figure **11.6.4** Structure of a segment of DNA. A similar segment of RNA would have OH groups on each C2′, and uracil would replace thymine.

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 **11.6.4**) 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 **11.6.4** 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 **11.6.5**).

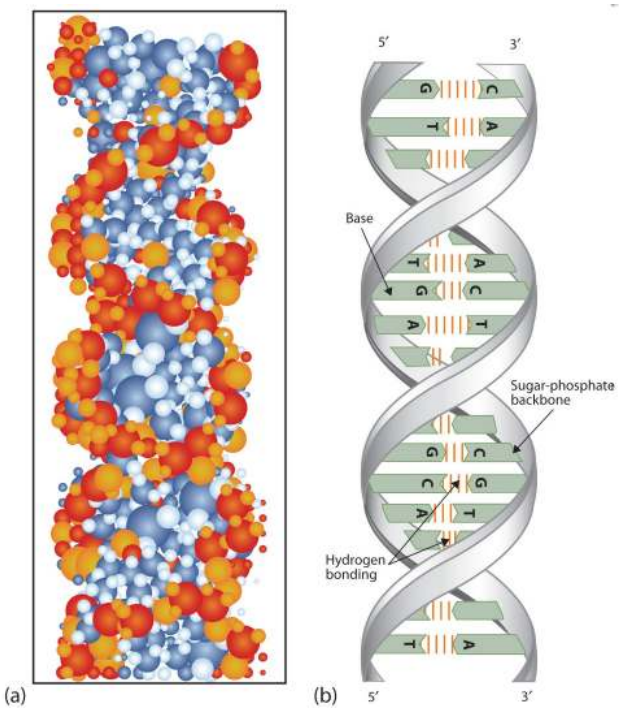


Figure **11.6.5** DNA Double Helix. (a) This represents a computer-generated model of the DNA double helix. (b) This represents a schematic representation of the double helix, showing the complementary bases.

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 **11.6.6** 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).

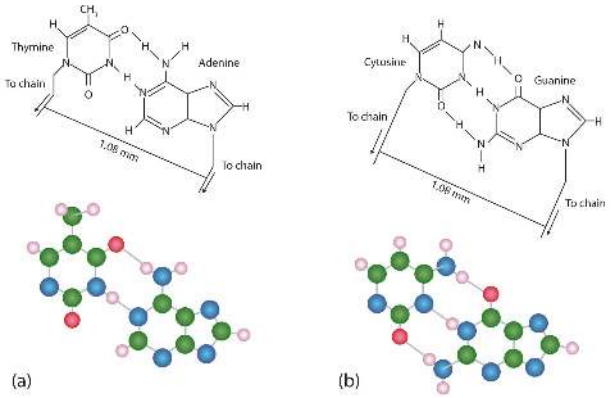


Figure **11.6.6** Complementary Base Pairing. Complementary bases engage in hydrogen bonding with one another: (a) thymine and adenine; (b) cytosine and guanine.

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 **11.6.7**. 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 **11.6.6** 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.

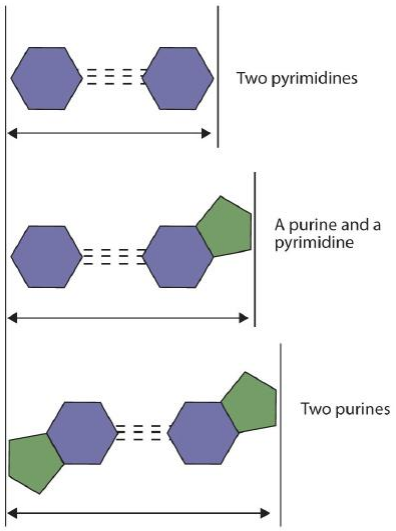


Figure **11.6.7** Difference in Widths of Possible Base Pairs

We previously stated that deoxyribonucleic acid (DNA) stores genetic information, while ribonucleic acid (RNA) is responsible for transmitting or expressing genetic information by directing the synthesis of thousands of proteins found in living organisms. But how do the nucleic acids perform these functions? Three processes are required: (1) *replication*, in which new copies of DNA are made; (2) *transcription*, in which a segment of DNA is used to produce RNA; and (3) *translation*, in which the information in RNA is translated into a protein sequence.

DNA: Self-Replication

New cells are continuously forming in the body through the process of cell division. For this to happen, the DNA in a dividing cell must be copied in a process known as replication. The complementary base pairing of the double helix provides a ready model for how genetic replication occurs. If the two chains of the double helix are pulled apart, disrupting the hydrogen bonding between base pairs, each chain can act as a *template*, or pattern, for the synthesis of a new complementary DNA chain.

The nucleus contains all the necessary enzymes, proteins, and nucleotides required for this synthesis. A short segment of DNA is “unzipped,” so that the two strands in the segment are separated to serve as templates for new DNA. DNA polymerase, an enzyme,

recognizes each base in a template strand and matches it to the complementary base in a free nucleotide. The enzyme then catalyzes the formation of an ester bond between the 5′ phosphate group of the nucleotide and the 3′ OH end of the new, growing DNA chain. In this way, each strand of the original DNA molecule is used to produce a duplicate of its former partner (Figure **11.6.8**). Whatever information was encoded in the original DNA double helix is now contained in each replicate helix. When the cell divides, each daughter cell gets one of these replicates and thus all of the information that was originally possessed by the parent cell.

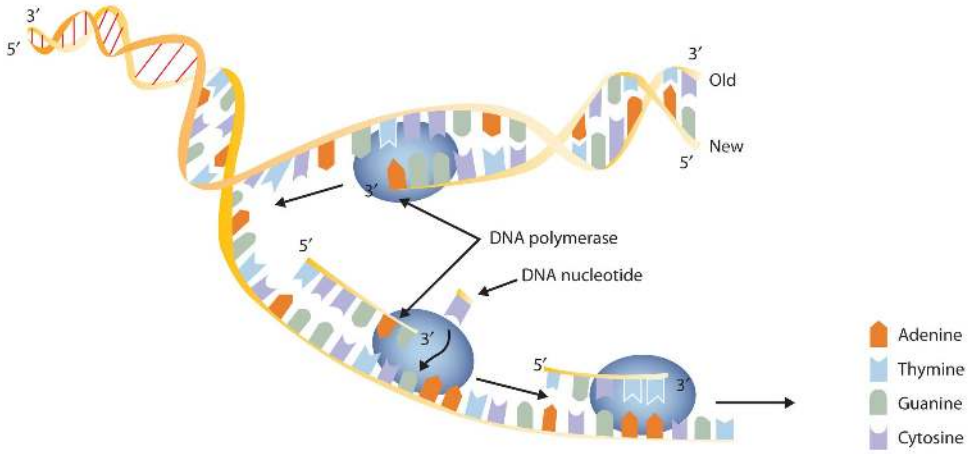


Figure **11.6.8** A Schematic Diagram of DNA Replication. DNA replication occurs by the sequential unzipping of segments of the double helix. Each new nucleotide is brought into position by DNA polymerase and is added to the growing strand by the formation of a phosphate ester bond. Thus, two double helixes form from one, and each consists of one old strand and one new strand, an outcome called *semiconservative replications*. (This representation is simplified; many more proteins are involved in replication.)

✔ Example 11.6.1

A segment of one strand from a DNA molecule has the sequence 5′-TCCATGAGTTGA-3′. What is the sequence of nucleotides in the opposite, or complementary, DNA chain?

Solution

Knowing that the two strands are antiparallel and that T base pairs with A, while C base pairs with G, the sequence of the complementary strand will be 3′-AGGTACTCAACT-5′.

? Exercise 11.6.1

A segment of one strand from a DNA molecule has the sequence 5′-CCAGTGAATTGCCTAT-3′. What is the sequence of nucleotides in the opposite, or complementary, DNA chain?

Answer

3′-GGTCACTTAACGGATA-5′.

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.
- 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.
- 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.
- In DNA replication, each strand of the original DNA serves as a template for the synthesis of a complementary strand.
- DNA polymerase is the primary enzyme needed for replication.

Contributors and Attributions

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11.7: RNA Protein Synthesis and the Genetic Code

Learning Objectives

- Describe the characteristics of the genetic code.
- Describe how a protein is synthesized from mRNA.

One of the definitions of a gene is as follows: a segment of deoxyribonucleic acid (DNA) carrying the code for a specific polypeptide. Each molecule of messenger RNA (mRNA) is a transcribed copy of a gene that is used by a cell for synthesizing a polypeptide chain. If a protein contains two or more different polypeptide chains, each chain is coded by a different gene. We turn now to the question of how the sequence of nucleotides in a molecule of ribonucleic acid (RNA) is translated into an amino acid sequence.

How can a molecule containing just 4 different nucleotides specify the sequence of the 20 amino acids that occur in proteins? If each nucleotide coded for 1 amino acid, then obviously the nucleic acids could code for only 4 amino acids. What if amino acids were coded for by groups of 2 nucleotides? There are 4^2, or 16, different combinations of 2 nucleotides (AA, AU, AC, AG, UU, and so on). Such a code is more extensive but still not adequate to code for 20 amino acids. However, if the nucleotides are arranged in groups of 3, the number of different possible combinations is 4^3, or 64. Here we have a code that is extensive enough to direct the synthesis of the primary structure of a protein molecule.



***Video**: NDSU Virtual Cell Animations project animation "Translation". For more information, see http://vcell.ndsu.nodak.edu/animations*

The genetic code can therefore be described as the identification of each group of three nucleotides and its particular amino acid. The sequence of these triplet groups in the mRNA dictates the sequence of the amino acids in the protein. Each individual three-nucleotide coding unit, as we have seen, is called a *codon*.

Protein synthesis is accomplished by orderly interactions between mRNA and the other ribonucleic acids (transfer RNA [tRNA] and ribosomal RNA [rRNA]), the ribosome, and more than 100 enzymes. The mRNA formed in the nucleus during transcription is transported across the nuclear membrane into the cytoplasm to the ribosomes—carrying with it the genetic instructions. The process in which the information encoded in the mRNA is used to direct the sequencing of amino acids and thus ultimately to synthesize a protein is referred to as translation.

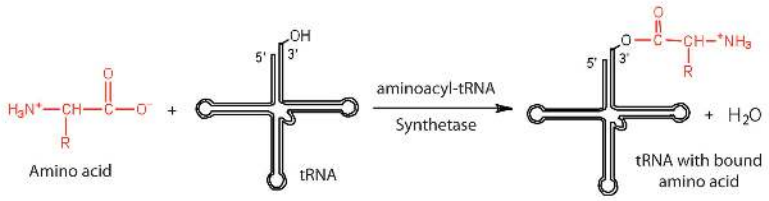
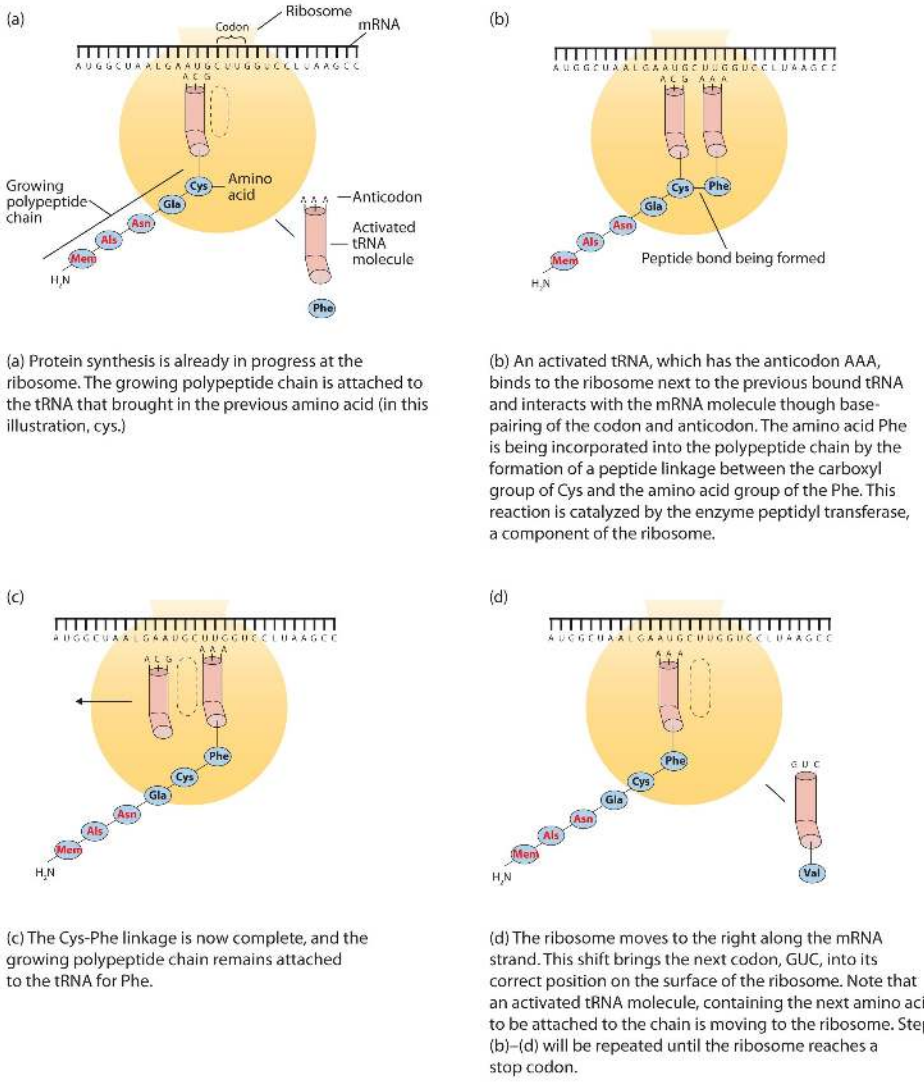


Figure **11.7.1**: Binding of an Amino Acid to Its tRNA

Before an amino acid can be incorporated into a polypeptide chain, it must be attached to its unique tRNA. This crucial process requires an enzyme known as aminoacyl-tRNA synthetase (Figure **11.7.1**). There is a specific aminoacyl-tRNA synthetase for each amino acid. This high degree of specificity is vital to the incorporation of the correct amino acid into a protein. After the amino acid molecule has been bound to its tRNA carrier, protein synthesis can take place. Figure **11.7.2** depicts a schematic stepwise representation of this all-important process.



(a) Protein synthesis is already in progress at the ribosome. The growing polypeptide chain is attached to the tRNA that brought in the previous amino acid (in this illustration, cys.)

(b) An activated tRNA, which has the anticodon AAA, binds to the ribosome next to the previous bound tRNA and interacts with the mRNA molecule though base-pairing of the codon and anticodon. The amino acid Phe is being incorporated into the polypeptide chain by the formation of a peptide linkage between the carboxyl group of Cys and the amino acid group of the Phe. This reaction is catalyzed by the enzyme peptidyl transferase, a component of the ribosome.

(c) The Cys-Phe linkage is now complete, and the growing polypeptide chain remains attached to the tRNA for Phe.

(d) The ribosome moves to the right along the mRNA strand. This shift brings the next codon, GUC, into its correct position on the surface of the ribosome. Note that an activated tRNA molecule, containing the next amino acid to be attached to the chain is moving to the ribosome. Steps (b)–(d) will be repeated until the ribosome reaches a stop codon.

Figure **11.7.2**: The Elongation Steps in Protein Synthesis

Early experimenters were faced with the task of determining which of the 64 possible codons stood for each of the 20 amino acids. The cracking of the genetic code was the joint accomplishment of several well-known geneticists—notably Har Khorana, Marshall Nirenberg, Philip Leder, and Severo Ochoa—from 1961 to 1964. The genetic dictionary they compiled, summarized in Figure **11.7.3**, shows that 61 codons code for amino acids, and 3 codons serve as signals for the termination of polypeptide synthesis (much

like the period at the end of a sentence). Notice that only methionine (AUG) and tryptophan (UGG) have single codons. All other amino acids have two or more codons.

First base	Second base: U	Second base: C	Second base: A	Second base: G	Third base
U	Phe	Ser	Tyr	Cys	U
	Phe	Ser	Tyr	Cys	C
	Leu	Ser	Stop	Stop	A
	Leu	Ser	Stop	Trp	G
C	Leu	Pro	His	Arg	U
	Leu	Pro	His	Arg	C
	Leu	Pro	Gln	Arg	A
	Leu	Pro	Gln	Arg	G
A	Ile	Thr	Asn	Ser	U
	Ile	Thr	Asn	Ser	C
	Ile	Thr	Lys	Arg	A
	Met	Thr	Lys	Arg	G
G	Val	Ala	Asp	Gly	U
	Val	Ala	Asp	Gly	C
	Val	Ala	Glu	Gly	A
	Val	Ala	Glu	Gly	G

Figure **11.7.3**: The Genetic Code

Example 11.7.1: Using the Genetic Code

A portion of an mRNA molecule has the sequence 5′-AUGCCACGAGUUGAC-3′. What amino acid sequence does this code for?

Solution

Use Figure **11.7.3** to determine what amino acid each set of three nucleotides (codon) codes for. Remember that the sequence is read starting from the 5′ end and that a protein is synthesized starting with the N-terminal amino acid. The sequence 5′-AUGCCACGAGUUGAC-3′ codes for met-pro-arg-val-asp.

Exercise 11.7.1

A portion of an mRNA molecule has the sequence 5′-AUGCUGAAUUGCGUAGGA-3′. What amino acid sequence does this code for?

met-leu-asn-cys-val-gly

The Nature of the Genetic Code

Further experimentation threw much light on the nature of the genetic code, as follows:

1. The code is virtually universal; animal, plant, and bacterial cells use the same codons to specify each amino acid (with a few exceptions).
2. The code is “degenerate”; in all but two cases (methionine and tryptophan), more than one triplet codes for a given amino acid.
3. The first two bases of each codon are most significant; the third base often varies. This suggests that a change in the third base by a mutation may still permit the correct incorporation of a given amino acid into a protein. The third base is sometimes called the “wobble” base.
4. The code is continuous and nonoverlapping; there are *no* nucleotides between codons, and adjacent codons do not overlap.
5. The three termination codons are read by special proteins called release factors, which signal the end of the translation process.

6. The codon AUG codes for methionine and is also the initiation codon. Thus methionine is the first amino acid in each newly synthesized polypeptide. This first amino acid is usually removed enzymatically before the polypeptide chain is completed; the vast majority of polypeptides do not begin with methionine.

Summary

- In transcription, a segment of DNA serves as a template for the synthesis of an RNA sequence.
- RNA polymerase is the primary enzyme needed for transcription.
- In translation, the information in mRNA directs the order of amino acids in protein synthesis. A set of three nucleotides (codon) codes for a specific amino acid.

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11.8: Carbohydrates (Exercises)

16.1: Carbohydrates

Concept Review Exercises

1. Why is photosynthesis important?
2. Identify the differences among monosaccharides, disaccharides, and polysaccharides.

Answers

1. Photosynthesis is the process by which solar energy is used to reduce carbon dioxide to carbohydrates, which are needed for energy by plants and other living organisms that eat plants.
2. A monosaccharide is the simplest carbohydrate and cannot be hydrolyzed to produce a smaller carbohydrate; a disaccharide is composed of two monosaccharide units; and a polysaccharide contains many saccharide units.

Exercises

1. When an aqueous solution of trehalose is heated, two molecules of glucose are produced for each molecule of trehalose. Is trehalose a monosaccharide, a disaccharide, or a polysaccharide?
2. When an aqueous solution of arabinose is heated, no other molecules are produced. Is arabinose a monosaccharide, a disaccharide, or a polysaccharide?

Answer

1. Trehalose is a disaccharide because it is hydrolyzed into two molecules of glucose (a monosaccharide).

16.2: Classes of Monosaccharides

Concept Review Exercises

1. What is a chiral carbon?
2. Describe how enantiomers differ.

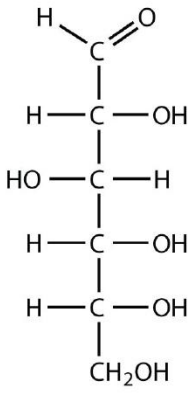
Answers

1. A chiral carbon is a carbon atom with four different groups attached to it.
2. Enantiomers are mirror images of each other; they differ in the arrangements of atoms around a chiral carbon.

Exercises

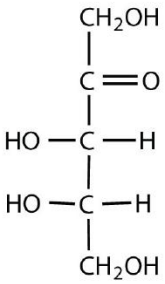
1. Identify each sugar as an aldose or a ketose and then as a triose, tetrose, pentose, or hexose.

   a. D-glucose

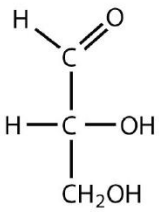


   b. L-ribulose

b. L-ribulose

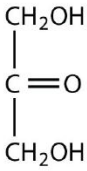


c. D-glyceraldehyde

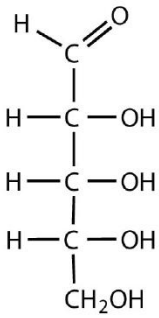


2. Identify each sugar as an aldose or a ketose and then as a triose, tetrose, pentose, or hexose.

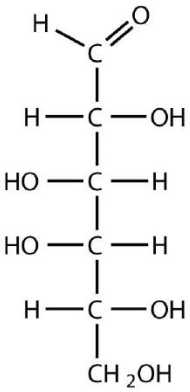
a. dihydroxyacetone



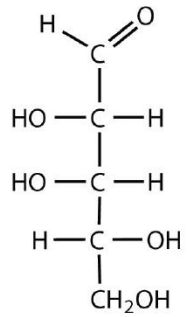
b. D-ribose

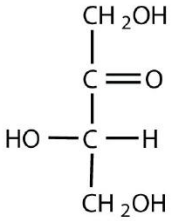


c. D-galactose

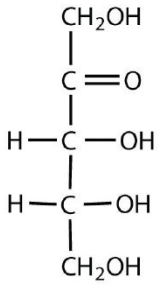


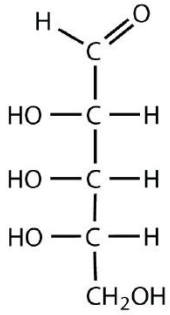
3. Identify each sugar as an aldose or a ketose and then as a D sugar or an L sugar.

a. 

b. 

4. Identify each sugar as an aldose or a ketose and then as a D sugar or an L sugar.

a. 

b. 

Answers

1. a. aldose; hexose
   b. ketose; pentose
   c. aldose; triose

3. a. aldose; D sugar
   b. ketose; L sugar

16.3: Important Hexoses

Concept Review Exercises

1. Describe the similarities and differences in the structures of D-glucose and D-galactose.
2. Describe similarities and differences in the structures of D-glucose and D-fructose.

Answers

1. Both monosaccharides are aldohexoses. The two monosaccharides differ in the configuration around the fourth carbon atom.
2. Both monosaccharides are hexoses. D-glucose is an aldohexose, while D-fructose is a ketohexose.

Exercises

1. Identify each sugar by its common chemical name.
    1. blood sugar
    2. levulose
2. Identify each sugar by its common chemical name.
    1. dextrose
    2. brain sugar
3. Identify each sugar as an aldohexose or a ketohexose.
    1. glucose
    2. galactose
    3. fructose
4. What hexose would you expect to be most abundant in each food?
    1. honey
    2. milk
    3. cornstarch

Answers

1. 1. D-glucose
    2. D-fructose
3. 1. aldohexose
    2. aldohexose
    3. ketohexose

16.4: Cyclic Structures of Monosaccharides

Concept Review Exercises

1. Define each term.

a. mutarotation
b. anomer
c. anomeric carbon

2. How can you prove that a solution of α-D-glucose exhibits mutarotation?

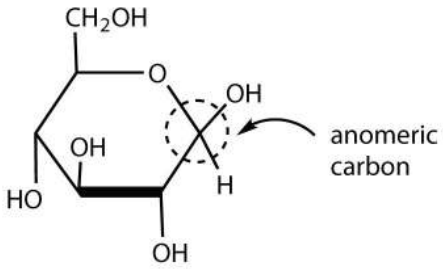
Answers

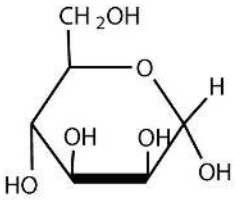
1. a. the ongoing interconversion between anomers of a particular carbohydrate to form an equilibrium mixture
   b. a stereoisomer that differs in structure around what was the carbonyl carbon atom in the straight-chain form of a monosaccharide
   c. the carbon atom that was the carbonyl carbon atom in the straight-chain form of a monosaccharide
2. Place a sample of pure α-D-glucose in a polarimeter and measure its observed rotation. This value will change as mutarotation occurs.

Exercises

1. Draw the cyclic structure for β-D-glucose. Identify the anomeric carbon.
2. Draw the cyclic structure for α-D-fructose. Identify the anomeric carbon.
3. Given that the aldohexose D-mannose differs from D-glucose only in the configuration at the second carbon atom, draw the cyclic structure for α-D-mannose.
4. Given that the aldohexose D-allose differs from D-glucose only in the configuration at the third carbon atom, draw the cyclic structure for β-D-allose.

Answers

1. 

3. 

16.5 Properties of Monosaccharides

Concept Review Exercises

1. Why are monosaccharides soluble in water?
2. What is a reducing sugar?

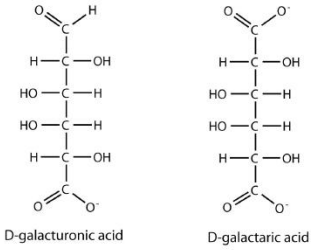
Answers

1. Monosaccharides are quite soluble in water because of the numerous OH groups that readily engage in hydrogen bonding with water.
2. any carbohydrate capable of reducing a mild oxidizing agent, such as Tollens' or Benedict's reagents, without first undergoing hydrolysis

Exercises

1. Which gives a positive Benedict's test—L-galactose, levulose, or D-glucose?
2. Which gives a positive Benedict's test—D-glyceraldehyde, corn sugar, or L-fructose?
3. D-Galactose can be oxidized at the sixth carbon atom to yield D-galacturonic acid and at both the first and sixth carbon atoms to yield D-galactaric acid. Draw the Fischer projection for each oxidation product.
4. D-Glucose can be oxidized at the first carbon atom to form D-gluconic acid, at the sixth carbon atom to yield D-glucuronic acid, and at both the first and sixth carbon atoms to yield D-glucaric acid. Draw the Fischer projection for each oxidation product.

Answers

1. All three will give a positive Benedict's test because they are all monosaccharides.
3. 

16.6 Disaccharides

Concept Review Exercise

1. What monosaccharides are obtained by the hydrolysis of each disaccharide?
    1. sucrose
    2. maltose
    3. lactose

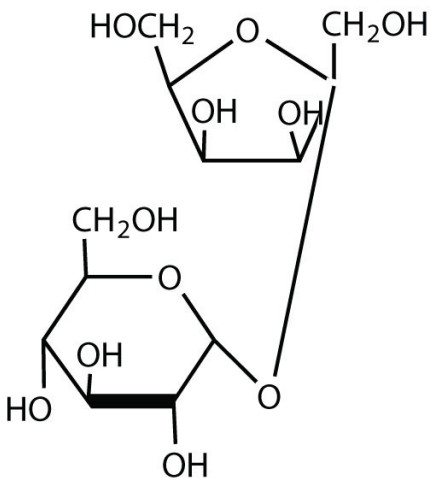
Answer

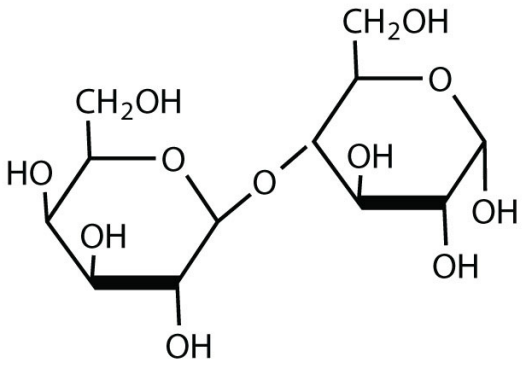
1. 1. D-glucose and D-fructose
    2. two molecules of D-glucose
    3. D-glucose and D-galactose

Exercises

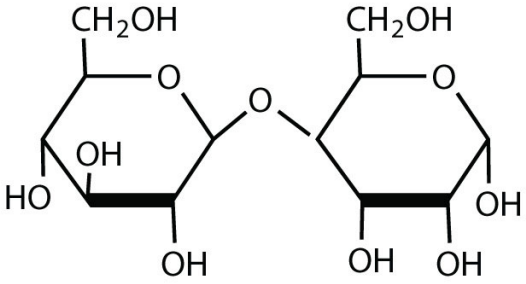
1. Identify each sugar by its common chemical name.
    1. milk sugar
    2. table sugar
2. Identify each sugar by its common chemical name.
    1. cane sugar
    2. malt sugar

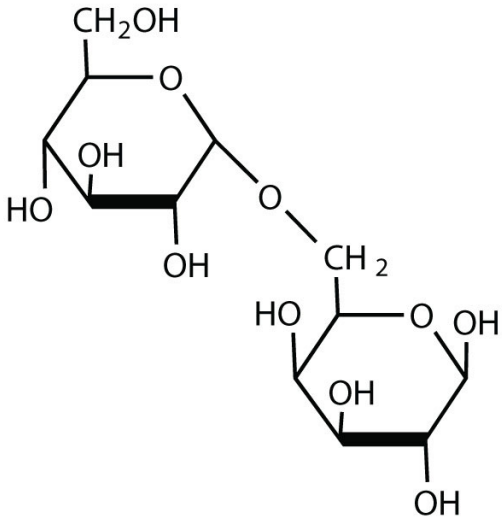
3. For each disaccharide, indicate whether the glycosidic linkage is α or β.

1. 

2. 

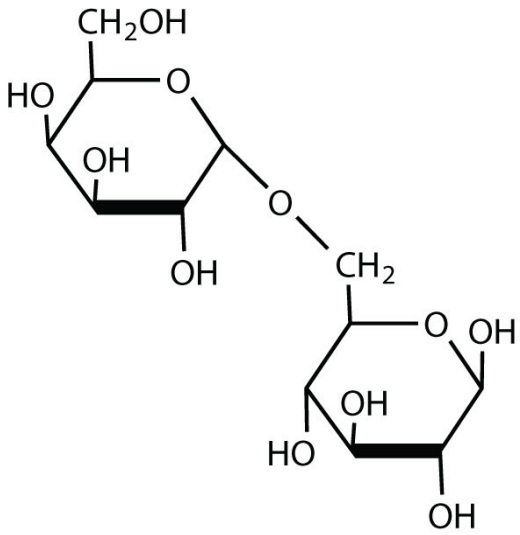
4. For each disaccharide, indicate whether the glycosidic linkage is α or β.

1. 



2.

5. Identify each disaccharide in Exercise 3 as a reducing or nonreducing sugar. If it is a reducing sugar, draw its structure and circle the anomeric carbon. State if the OH group at the anomeric carbon is in the α or the β position.
6. Identify each disaccharide in Exercise 4 as a reducing or nonreducing sugar. If it is a reducing sugar, draw its structure and circle the anomeric carbon. State if the OH group at the anomeric carbon is in the α or β position.
7. Melibiose is a disaccharide that occurs in some plant juices. Its structure is as follows:

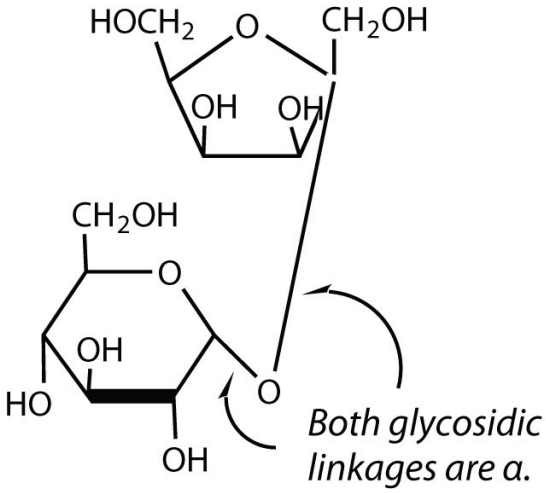


   1. What monosaccharide units are incorporated into melibiose?
   2. What type of linkage (α or β) joins the two monosaccharide units of melibiose?
   3. Melibiose has a free anomeric carbon and is thus a reducing sugar. Circle the anomeric carbon and indicate whether the OH group is α or β.
8. Cellobiose is a disaccharide composed of two glucose units joined by a β-1,4-glycosidic linkage.
   1. Draw the structure of cellobiose.
   2. Is cellobiose a reducing or nonreducing sugar? Justify your answer.

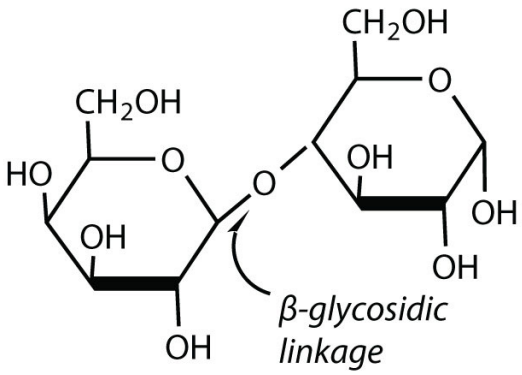
Answers

1. 1. lactose
   2. sucrose

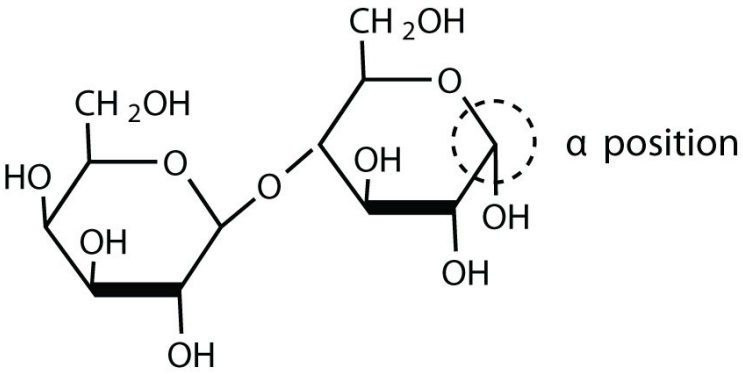
3. 1.



   2.

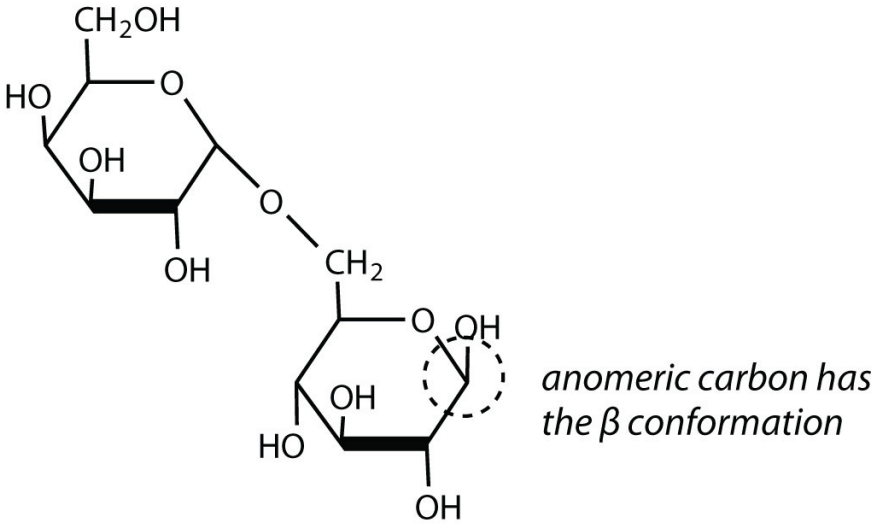


5. 3a: nonreducing; 3b: reducing



7. 1. galactose and glucose
   2. α-glycosidic linkage

3.



16.7 Polysaccharides

Concept Review Exercises

1. What purposes do starch and cellulose serve in plants?
2. What purpose does glycogen serve in animals?

Answers

1. Starch is the storage form of glucose (energy) in plants, while cellulose is a structural component of the plant cell wall.
2. Glycogen is the storage form of glucose (energy) in animals.

Exercises

1. What monosaccharide is obtained from the hydrolysis of each carbohydrate?
    1. starch
    2. cellulose
    3. glycogen
2. For each carbohydrate listed in Exercise 1, indicate whether it is found in plants or mammals.
3. Describe the similarities and differences between amylose and cellulose.
4. Describe the similarities and differences between amylopectin and glycogen.

Answers

1. 1. glucose
   2. glucose
   3. glucose

3. Amylose and cellulose are both linear polymers of glucose units, but the glycosidic linkages between the glucose units differ. The linkages in amylose are α-1,4-glycosidic linkages, while the linkages in cellulose they are β-1,4-glycosidic linkages.

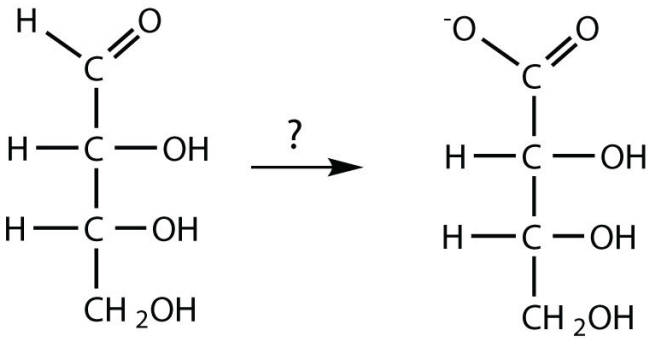
ADDITIONAL EXERCISES

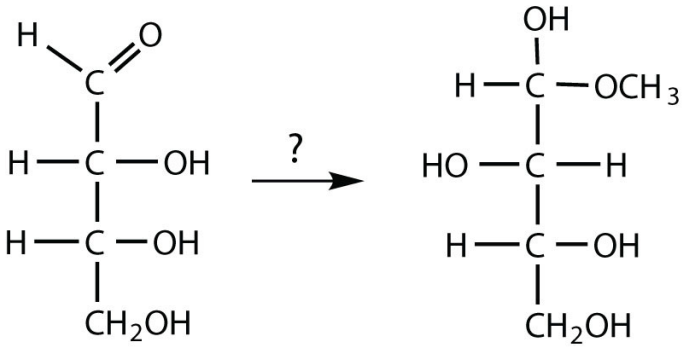
1. Draw the Fischer projections for D-glucose and D-ribose. Identify all the functional groups in each structure.
2. Draw the Fischer projections for D-galactose and D-fructose. Identify all the functional groups in each structure.
3. L-Fucose is an aldohexose that is often incorporated into oligosaccharides attached to cell membranes. It is also known as 6-deoxy-L-galactose. Draw the structure of L-fucose.
4. D-glucitol, also known as sorbitol, is added to shredded coconut to keep it soft and to pharmaceutical products to increase the absorption of nutrients. It is prepared industrially by the reduction of D-glucose. Propose a structure for D-glucitol.
5. Which would give a positive Benedict's test—lactose, amylopectin, D-ribose, sucrose, D-glyceraldehyde, or amylose?
6. Which enzyme hydrolyzes each carbohydrate?

   1. maltose
   2. lactose
   3. cellulose
   4. sucrose

7. What structural characteristics are necessary if a disaccharide is to be a reducing sugar? Draw the structure of a hypothetical reducing disaccharide composed of two aldohexoses.
8. Raffinose, a trisaccharide found in beans and sugar beets, contains D-galactose, D-glucose, and D-fructose. The enzyme α-galactase catalyzes the hydrolysis of raffinose to galactose and sucrose. Draw the structure of raffinose. (The linkage from galactose to the glucose unit is α-1,6).
9. What reagent(s) could be used to carry out each conversion?

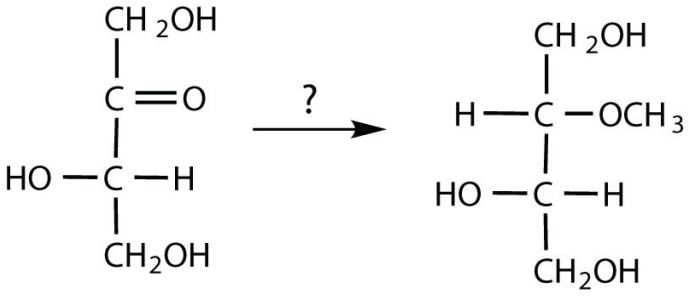
1.



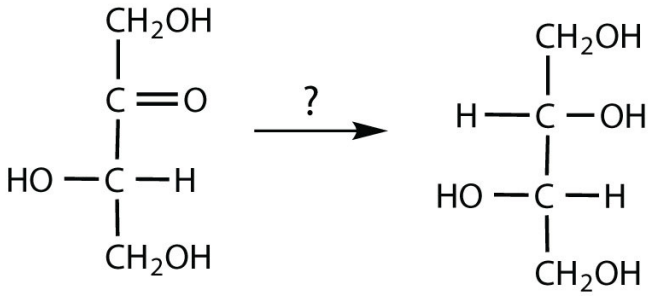


2.

10. What reagents are necessary to carry out each conversion?

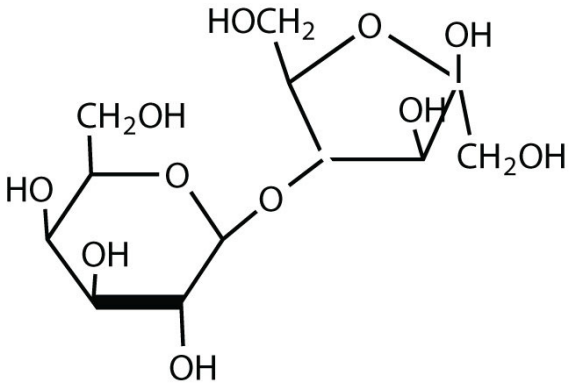


1.

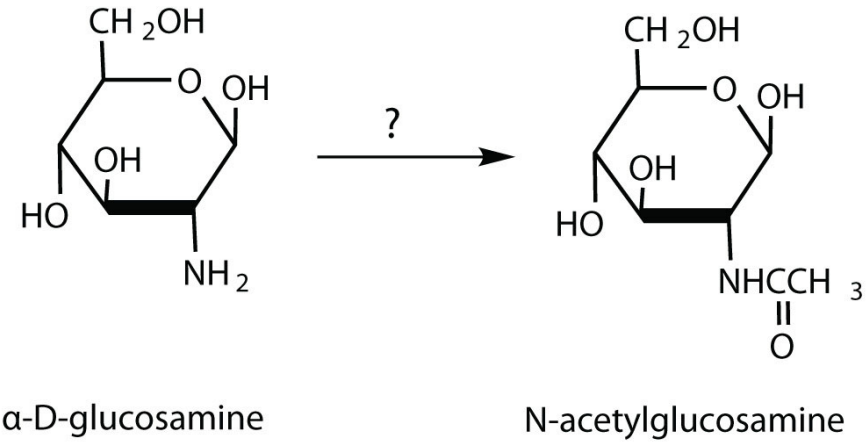


2.

11. The structure of lactulose is shown here. What monosaccharide units compose this disaccharide?

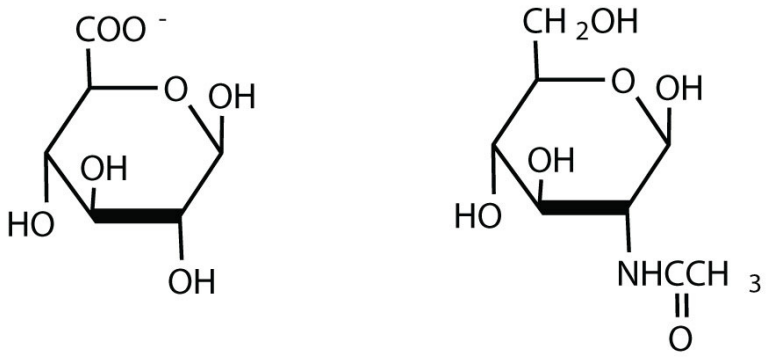


12. N-acetylglucosamine is synthesized from D-glucosamine, which in turn is obtained from D-glucose. What reagents are needed for the conversion of D-glucosamine to N-acetylglucosamine?



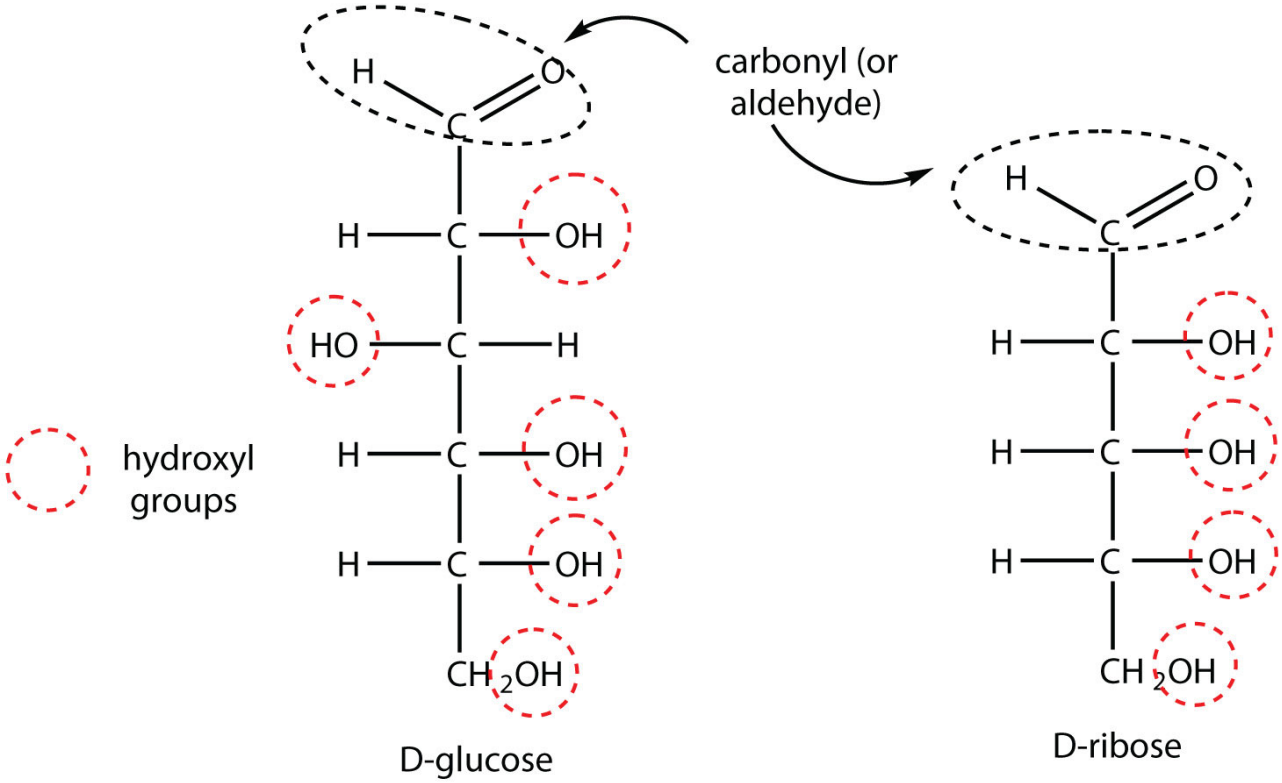
α-D-glucosamine N-acetylglucosamine

13. Hyaluronic acid is a heteropolymer that acts as a lubricating agent in the fluids of joints and the eyes. Its structure consists of repeating disaccharide units containing glucuronic acid and N-acetylglucosamine connected by a β-1,3-linkage. Draw the structure of the disaccharide unit found in hyaluronic acid.



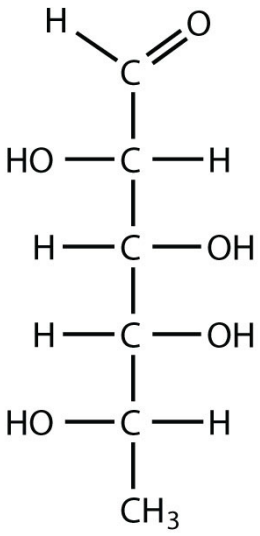
Glucuronic acid N-acetylglucosamine

14. Several artificial sweeteners are discussed in this chapter.
    1. Which are currently approved for use in the United States?
    2. Which has (or have) a bitter, metallic aftertaste?
    3. Which was (or were) most recently approved for use in the United States?
    4. Which contain(s) potassium?
15. If 3.0 mmol (3.0×10^{-3} mol) samples of saccharin, cyclamate, aspartame, and acesulfame K were each dissolved in separate beakers containing 500 mL of pure water, which solution would have the sweetest taste? Which solution would have the least sweet taste? Justify your answers.
16. Identify two functional groups found in aspartame, acesulfame K, and sucralose.
17. Why does a deficiency of lactase lead to cramps and diarrhea?
18. How does galactosemia differ from lactose intolerance in terms of the cause of the disease and its symptoms and severity?



1.

2.



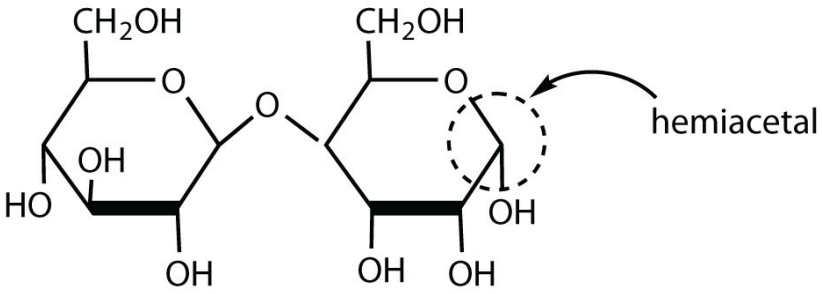
3.

4.

5. Lactose, D-ribose, and D-glyceraldehyde would give a positive Benedict's test.

6.

7. To be a reducing sugar, a disaccharide must contain an anomeric carbon atom that can open up to form an aldehyde functional group, as shown in this disaccharide (answers will vary).



8.

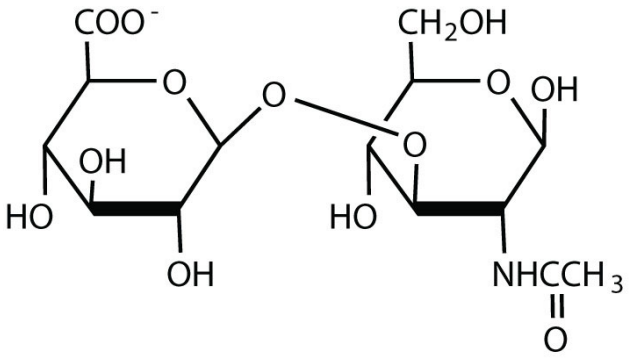
9.

1. The carbohydrate is being oxidized; Tollens' or Benedict's reagent could be used.
2. To form the compound shown, an aldehyde must react with methanol (CH_3OH) and an acid catalyst.

10.

11. galactose and fructose

12.



13.

14.

15. Sucralose would be expected to have the sweetest taste because its relative sweetness is the highest. Lactose would have the least sweet taste because it has the lowest relative sweetness.

16.

17. Intestinal bacteria can act on the lactose present in the intestine to produce organic acids and gases. The buildup of water and bacterial decay products leads to cramps and diarrhea.

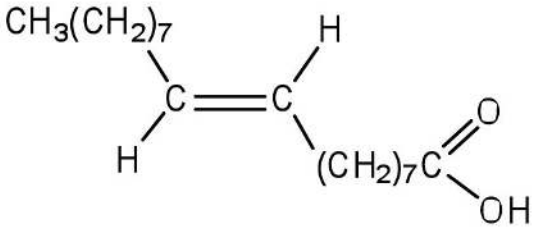
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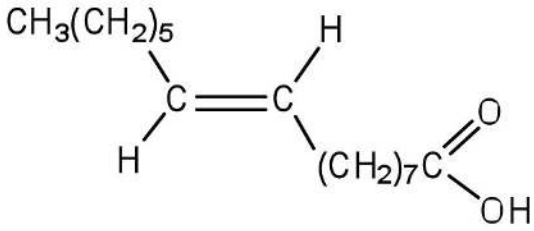
11.9: Lipids (Exercises)

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.

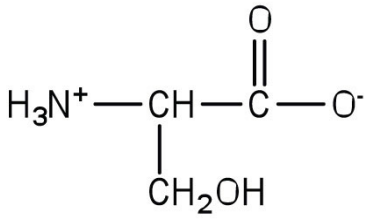


Elaidic acid



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.

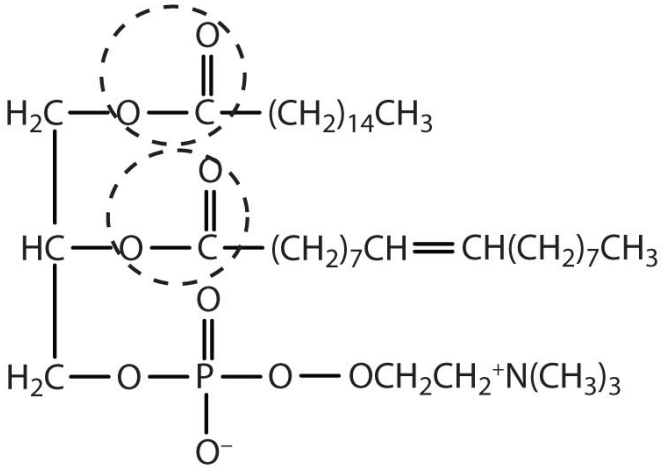


6. Explain whether each compound would be expected to diffuse through the lipid bilayer of a cell membrane.
   a. potassium chloride
   b. $CH_3CH_2CH_2CH_2CH_2CH_3$
   c. fructose
7. Identify the role of each steroid hormone in the body.
   a. progesterone
   b. aldosterone
   c. testosterone
   d. 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?

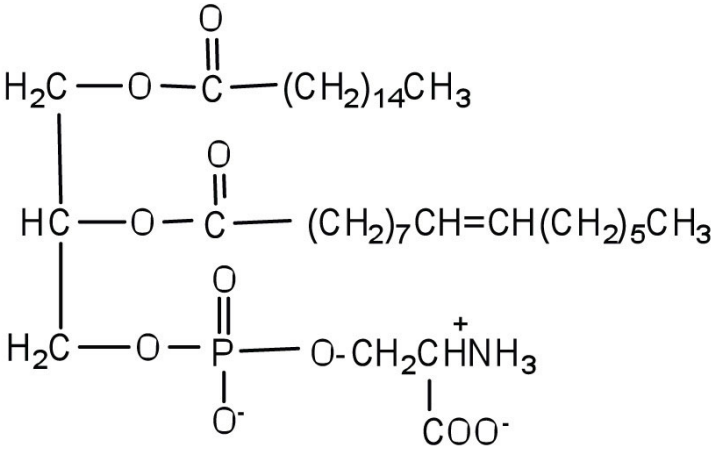
Answers

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

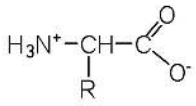
9. a. arachidonic acid
   b. induce smooth muscle contraction, lower blood pressure, and contribute to the inflammatory response

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11.10: Amino Acids, Proteins and Enzymes (Exercise)

18.1: Properties of Amino Acids

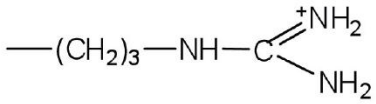
Concept Review Exercises

1. What is the general structure of an α-amino acid?
2. Identify the amino acid that fits each description.
   a. also known as aspartate
   b. almost as strong a base as sodium hydroxide
   c. does not have a chiral carbon
3. 

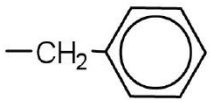
4. a. aspartic acid
   b. arginine
   c. glycine
5. Write the side chain of each amino acid.
   a. serine
   b. arginine
   c. phenylalanine
6. Write the side chain of each amino acid.
   a. aspartic acid
   b. methionine
   c. valine
7. Draw the structure for each amino acid.
   a. alanine
   b. cysteine
   c. histidine
8. Draw the structure for each amino acid.
   a. threonine
   b. glutamic acid
   c. leucine
9. Identify an amino acid whose side chain contains a(n)
   a. amide functional group.
   b. aromatic ring.
   c. carboxyl group.
10. Identify an amino acid whose side chain contains a(n)
    a. OH group
    b. branched chain
    c. amino group

1. a. CH_2OH^-

b.

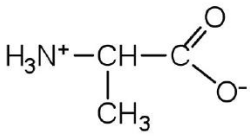


c.

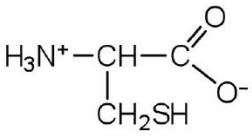


2.

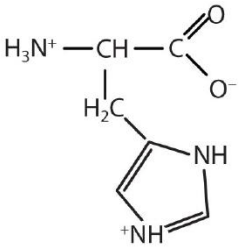
3. a.



b.



c.



4.

5. a. asparagine or glutamine
   b. phenylalanine, tyrosine, or tryptophan
   c. aspartic acid or glutamic acid

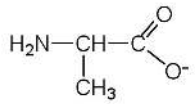
18.2: Reactions of Amino Acids

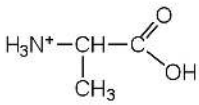
Concept Review Exercises

1. Define each term.
   a. zwitterion
   b. isoelectric point
2. Draw the structure for the anion formed when alanine (at neutral pH) reacts with a base.
3. Draw the structure for the cation formed when alanine (at neutral pH) reacts with an acid.

Answers

1. a. an electrically neutral compound that contains both negatively and positively charged groups
   b. the pH at which a given amino acid exists in solution as a zwitterion

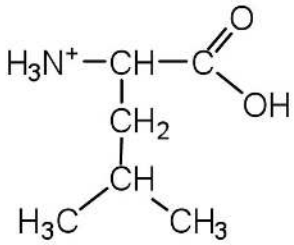
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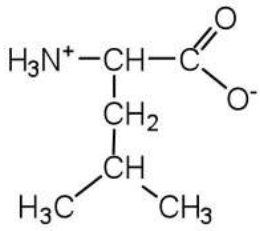
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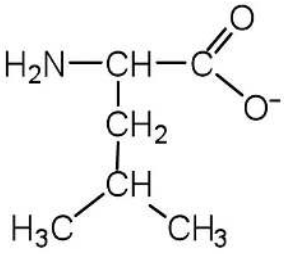
Exercises

1. Draw the structure of leucine and determine the charge on the molecule in a(n)
   a. acidic solution (pH = 1).
   b. neutral solution (pH = 7).
   c. a basic solution (pH = 11)
2. Draw the structure of isoleucine and determine the charge on the molecule in a(n)
   a. acidic solution (pH = 1).
   b. neutral solution (pH = 7).
   c. basic solution (pH = 11).

Answer

1. a. 

   b. 

   c. 

18.3: Peptides

Concept Review Exercises

1. Distinguish between the N-terminal amino acid and the C-terminal amino acid of a peptide or protein.
2. Describe the difference between an amino acid and a peptide.
3. Amino acid units in a protein are connected by peptide bonds. What is another name for the functional group linking the amino acids?

Answers

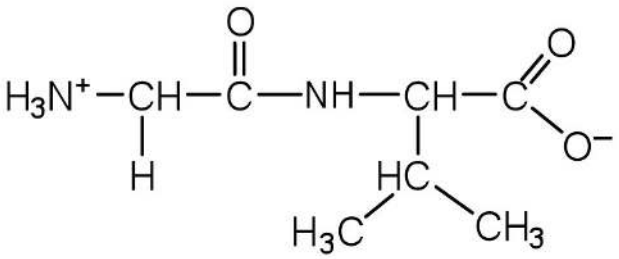
1. The N-terminal end is the end of a peptide or protein whose amino group is free (not involved in the formation of a peptide bond), while the C-terminal end has a free carboxyl group.
2. A peptide is composed of two or more amino acids. Amino acids are the building blocks of peptides.
3. amide bond

Exercises

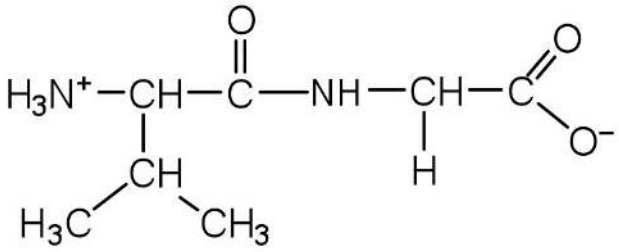
1. Draw the structure for each peptide.
   a. gly-val
   b. val-gly
2. Draw the structure for cys-val-ala.
3. Identify the C- and N-terminal amino acids for the peptide lys-val-phe-gly-arg-cys.
4. Identify the C- and N-terminal amino acids for the peptide asp-arg-val-tyr-ile-his-pro-phe.

Answers

1. a.



   b.



3. C-terminal amino acid: cys; N-terminal amino acid: lys

18.4: Proteins

Concept Review Exercises

1. What is the predominant attractive force that stabilizes the formation of secondary structure in proteins?
2. Distinguish between the tertiary and quaternary levels of protein structure.
3. Briefly describe four ways in which a protein could be denatured.

Answers

1. hydrogen bonding
2. Tertiary structure refers to the unique three-dimensional shape of a single polypeptide chain, while quaternary structure describes the interaction between multiple polypeptide chains for proteins that have more than one polypeptide chain.
3. (1) heat a protein above 50°C or expose it to UV radiation; (2) add organic solvents, such as ethyl alcohol, to a protein solution; (3) add salts of heavy metal ions, such as mercury, silver, or lead; and (4) add alkaloid reagents such as tannic acid

Exercises

1. Classify each protein as fibrous or globular.
   a. albumin
   b. myosin
   c. fibroin
2. Classify each protein as fibrous or globular.
   a. hemoglobin
   b. keratin
   c. myoglobin
3. What name is given to the predominant secondary structure found in silk?
4. What name is given to the predominant secondary structure found in wool protein?
5. A protein has a tertiary structure formed by interactions between the side chains of the following pairs of amino acids. For each pair, identify the strongest type of interaction between these amino acids.
   a. aspartic acid and lysine
   b. phenylalanine and alanine
   c. serine and lysine
   d. two cysteines
6. A protein has a tertiary structure formed by interactions between the side chains of the following pairs of amino acids. For each pair, identify the strongest type of interaction between these amino acids.
   a. valine and isoleucine
   b. asparagine and serine
   c. glutamic acid and arginine
   d. tryptophan and methionine
7. What level(s) of protein structure is(are) ordinarily disrupted in denaturation? What level(s) is(are) not?
8. Which class of proteins is more easily denatured—fibrous or globular?

Answers

1. a. globular
   b. fibrous
   c. fibrous
3. β-pleated sheet
5. a. ionic bonding
   b. dispersion forces
   c. dispersion forces
   d. disulfide linkage
7. Protein denaturation disrupts the secondary, tertiary, and quaternary levels of structure. Only primary structure is unaffected by denaturation.

18.5: Enzymes

Concept Review Exercise

In the small intestine, sucrose is hydrolyzed to form glucose and fructose in a reaction catalyzed by sucrase.

1. Identify the substrate in this reaction.
2. Name the enzyme.

Answers

1. sucrose
2. sucrase

Exercises

1. Identify the substrate catalyzed by each enzyme.
    a. lactase
    b. cellulase
    c. peptidase
2. Identify the substrate catalyzed by each enzyme.
    a. lipase
    b. amylase
    c. maltase
3. Identify each type of enzyme.
    a. decarboxylase
    b. protease
    c. transaminase
4. Identify each type of enzyme.
    a. dehydrogenase
    b. isomerase
    c. lipase

Answers

1. a. lactose
    b. cellulose
    c. peptides
3. a. lyase
    b. hydrolase
    c. transferase

18.6: Enzyme Action

Concept Review Exercises

1. Distinguish between the lock-and-key model and induced-fit model of enzyme action.
2. Which enzyme has greater specificity—urease or carboxypeptidase? Explain.

Answers

1. The lock-and-key model portrays an enzyme as conformationally rigid and able to bond only to substrates that exactly fit the active site. The induced fit model portrays the enzyme structure as more flexible and is complementary to the substrate only after the substrate is bound.
2. Urease has the greater specificity because it can bind only to a single substrate. Carboxypeptidase, on the other hand, can catalyze the removal of nearly any amino acid from the carboxyl end of a peptide or protein.

Exercises

1. What type of interaction would occur between each group present on a substrate molecule and a functional group of the active site in an enzyme?
   a. COOH
   b. NH_3^+
   c. OH
   d. $CH(CH_3)_2$
2. What type of interaction would occur between each group present on a substrate molecule and a functional group of the active site in an enzyme?
   a. SH
   b. NH_2
   c. C_6H_5
   d. COO^-
3. For each functional group in Exercise 1, suggest an amino acid whose side chain might be in the active site of an enzyme and form the type of interaction you identified.
4. For each functional group in Exercise 2, suggest an amino acid whose side chain might be in the active site of an enzyme and form the type of interaction you identified.

Answers

1. a. hydrogen bonding
   b. ionic bonding
   c. hydrogen bonding
   d. dispersion forces
3. a. The amino acid has a polar side chain capable of engaging in hydrogen bonding; serine (answers will vary).
   b. The amino acid has a negatively charged side chain; aspartic acid (answers will vary).
   c. The amino acid has a polar side chain capable of engaging in hydrogen bonding; asparagine (answers will vary).
   d. The amino acid has a nonpolar side chain; isoleucine (answers will vary).

18.7: Enzyme Activity

Concept Review Exercises

1. The concentration of substrate X is low. What happens to the rate of the enzyme-catalyzed reaction if the concentration of X is doubled?
2. What effect does an increase in the enzyme concentration have on the rate of an enzyme-catalyzed reaction?

Answers

1. If the concentration of the substrate is low, increasing its concentration will increase the rate of the reaction.
2. An increase in the amount of enzyme will increase the rate of the reaction (provided sufficient substrate is present).

Exercises

1. In non-enzyme-catalyzed reactions, the reaction rate increases as the concentration of reactant is increased. In an enzyme-catalyzed reaction, the reaction rate initially increases as the substrate concentration is increased but then begins to level off, so that the increase in reaction rate becomes less and less as the substrate concentration increases. Explain this difference.
2. Why do enzymes become inactive at very high temperatures?
3. An enzyme has an optimum pH of 7.4. What is most likely to happen to the activity of the enzyme if the pH drops to 6.3? Explain.
4. An enzyme has an optimum pH of 7.2. What is most likely to happen to the activity of the enzyme if the pH increases to 8.5? Explain.

Answers

1. In an enzyme-catalyzed reaction, the substrate binds to the enzyme to form an enzyme-substrate complex. If more substrate is present than enzyme, all of the enzyme binding sites will have substrate bound, and further increases in substrate concentration cannot increase the rate.
3. The activity will decrease; a pH of 6.3 is more acidic than 7.4, and one or more key groups in the active site may bind a hydrogen ion, changing the charge on that group.

18.8: Enzyme Inhibition

Concept Review Exercises

1. What is the difference between a cofactor and a coenzyme?
2. How are vitamins related to coenzymes?

Answers

1. A coenzyme is one type of cofactor. Coenzymes are organic molecules required by some enzymes for activity. A cofactor can be either a coenzyme or an inorganic ion.
2. Coenzymes are synthesized from vitamins.

Exercises

1. Identify each vitamin as water soluble or fat soluble.
    a. vitamin D
    b. vitamin C
    c. vitamin B_{12}
2. Identify each vitamin as water soluble or fat soluble.
    a. niacin
    b. cholecalciferol
    c. biotin
3. What vitamin is needed to form each coenzyme?
    a. pyridoxal phosphate
    b. flavin adenine dinucleotide
    c. coenzyme A
    d. nicotinamide adenine dinucleotide
4. What coenzyme is formed from each vitamin?
    a. niacin
    b. thiamine
    c. cyanocobalamin
    d. pantothenic acid

5. What is the function of each vitamin or coenzyme?
   a. flavin adenine dinucleotide
   b. vitamin A
   c. biotin
6. What is the function of each vitamin or coenzyme?
   a. vitamin K
   b. pyridoxal phosphate
   c. tetrahydrofolate

Answers

1. a. fat soluble
   b. water soluble
   c. water soluble
3. a. vitamin B_6 or pyridoxine
   b. vitamin B_2 or riboflavin
   c. pantothenic acid
   d. vitamin B_3 or niacin
5. a. needed by enzymes that catalyze oxidation-reduction reactions in which two hydrogen atoms are transferred
   b. needed for the formation of vision pigments
   c. needed by enzymes that catalyze carboxylation reactions

18.9: Enzyme Cofactors and Vitamins

Concept Review Exercises

1. What are the characteristics of an irreversible inhibitor?
2. In what ways does a competitive inhibitor differ from a noncompetitive inhibitor?

Answers

1. It inactivates an enzyme by bonding covalently to a particular group at the active site.
2. A competitive inhibitor structurally resembles the substrate for a given enzyme and competes with the substrate for binding at the active site of the enzyme. A noncompetitive inhibitor binds at a site distinct from the active site and can bind to either the free enzyme or the enzyme-substrate complex.

Exercises

1. What amino acid is present in the active site of all enzymes that are irreversibly inhibited by nerve gases such as DIFP?
2. Oxaloacetate (OOCCH2COCOO) inhibits succinate dehydrogenase. Would you expect oxaloacetate to be a competitive or noncompetitive inhibitor? Explain.

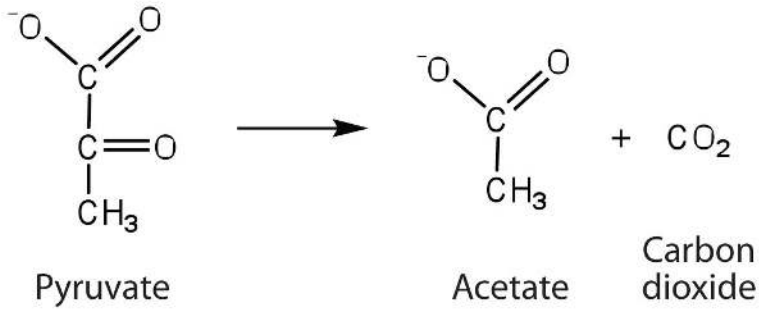
Answer

1. serine

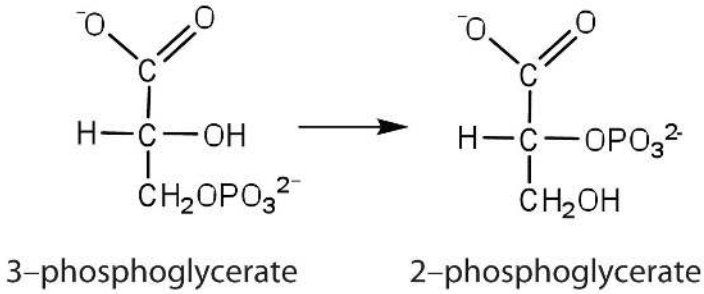
Additional Exercises

1. Draw the structure of the amino acid γ-aminobutyric acid (GABA). Would you expect to find GABA in the amino acid sequence of a protein? Explain.
2. Draw the structure of the amino acid homocysteine (R group = CH_2CH_2SH). Would you expect to find homocysteine in the amino acid sequence of a protein? Justify your answer.
3. Write equations to show how leucine can act as a buffer (that is, how it can neutralize added acid or base).

4. Write equations to show how isoleucine can act as a buffer (that is, how it can neutralize added acid or base).
5. Glutathione (γ-glutamylcysteinylglycine) is a tripeptide found in all cells of higher animals. It contains glutamic acid joined in an unusual peptide linkage involving the carboxyl group of the R group (known as γ-carboxyl group), rather than the usual carboxyl group (the α-carboxyl group). Draw the structure of glutathione.
6. Draw the structure of the pentapeptide whose sequence is arg-his-gly-leu-asp. Identify which of the amino acids have R groups that can donate or gain hydrogen ions.
7. Bradykinin is a peptide hormone composed of nine amino acids that lowers blood pressure. Its primary structure is arg-pro-pro-gly-phe-ser-pro-phe-arg. Would you expect bradykinin to be positively charged, negatively charged, or neutral at a pH of 6.0? Justify your answer.
8. One of the neurotransmitters involved in pain sensation is a peptide called substance P, which is composed of 11 amino acids and is released by nerve-cell terminals in response to pain. Its primary structure is arg-pro-lys-pro-gln-gln-phe-phe-gly-leu-met. Would you expect this peptide to be positively charged, negatively charged, or neutral at a pH of 6.0? Justify your answer.
9. Carbohydrates are incorporated into *glycoproteins*. Would you expect the incorporation of sugar units to increase or decrease the solubility of a protein? Justify your answer.
10. Some proteins have phosphate groups attached through an ester linkage to the OH groups of serine, threonine, or tyrosine residues to form *phosphoproteins*. Would you expect the incorporation of a phosphate group to increase or decrease the solubility of a protein? Justify your answer.
11. Refer to Table 18.5 and determine how each enzyme would be classified.
    a. the enzyme that catalyzes the conversion of ethanol to acetaldehyde
    b. the enzyme that catalyzes the breakdown of glucose 6-phosphate to glucose and inorganic phosphate ion (water is also a reactant in this reaction)
12. Refer to Table 18.5 and determine how each enzyme would be classified.
    a. the enzyme that catalyzes the removal of a carboxyl group from pyruvate to form acetate

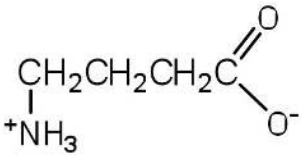


    b. the enzyme that catalyzes the rearrangement of 3-phosphoglycerate to form 2-phosphoglycerate



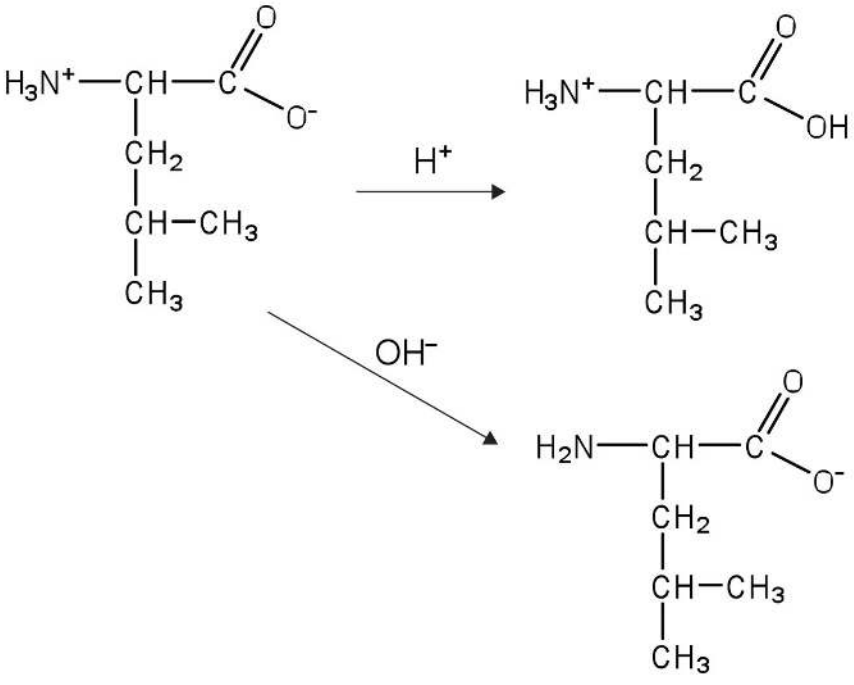
13. The enzyme lysozyme has an aspartic acid residue in the active site. In acidic solution, the enzyme is inactive, but activity increases as the pH rises to around 6. Explain why.
14. The enzyme lysozyme has a glutamic acid residue in the active site. At neutral pH (6–7), the enzyme is active, but activity decreases as the pH rises. Explain why.
15. The activity of a purified enzyme is measured at a substrate concentration of 1.0 μM and found to convert 49 μmol of substrate to product in 1 min. The activity is measured at 2.0 μM substrate and found to convert 98 μmol of substrate to product/minute.
    a. When the substrate concentration is 100 μM, how much substrate would you predict is converted to product in 1 min? What if the substrate concentration were increased to 1,000 μM (1.0 mM)?
    b. The activities actually measured are 676 μmol product formed/minute at a substrate concentration of 100 μM and 698 μmol product formed/minute at 1,000 μM (1.0 mM) substrate. Is there any discrepancy between these values and those you predicted in Exercise 15a? Explain.
16. A patient has a fever of 39°C. Would you expect the activity of enzymes in the body to increase or decrease relative to their activity at normal body temperature (37°C)?
17. Using your knowledge of factors that influence enzyme activity, describe what happens when milk is pasteurized.

Answers

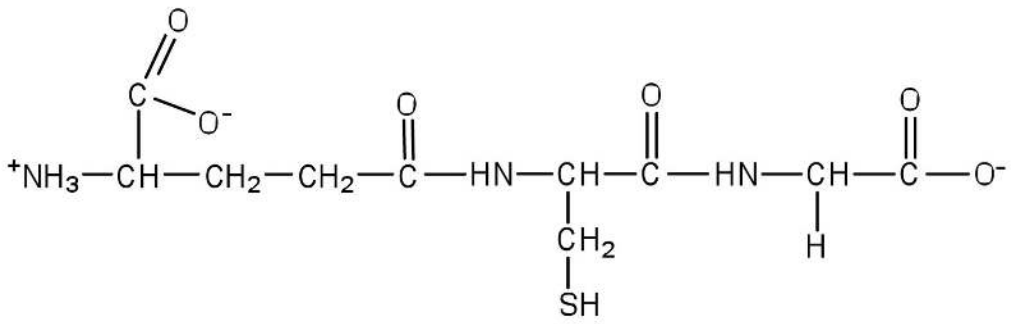


1.

This amino acid would not be found in proteins because it is not an α-amino acid.



3.

5. 

7. Bradykinin would be positively charged; all of the amino acids, except for arginine, have R groups that do not become either positively or negatively charged. The two arginines are R groups that are positively charged at neutral pH, so the peptide would have an overall positive charge.

9. Carbohydrates have many OH groups attached, which can engage in hydrogen bonding with water, which increases the solubility of the proteins.

11.

a. oxidoreductase
b. hydrolase

13. The enzyme is active when the carboxyl group in the R group of aspartic acid does not have the hydrogen attached (forming COO^-); the hydrogen is removed when the pH of the solution is around pH 6 or higher.

15.

a. at 100 µM, you would predict that the rate would increase 100 times to 4,900 µmol of substrate to product in 1 min; at 1.0 mM, you would predict an increase to 49,000 µmol of substrate to product in 1 min.
b. There is a great discrepancy between the predicted rates and actual rates; this occurs because the enzyme becomes saturated with substrate, preventing a further increase in the rate of the reaction (the reaction is no longer linear with respect to substrate concentration because it is at very low concentrations).

17. When milk is pasteurized, it is heated to high temperatures. These high temperatures denature the proteins in bacteria, so they cannot carry out needed functions to grow and multiply.

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11.11: 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

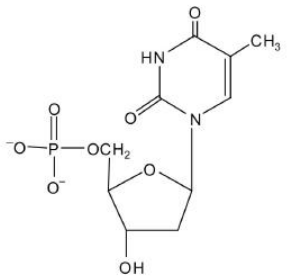
Answers

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

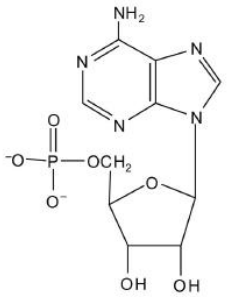
Exercises

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.

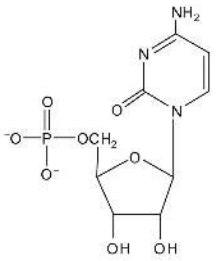


b.

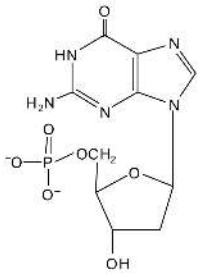


4. For each structure, circle the sugar unit and identify the nucleotide as a ribonucleotide or a deoxyribonucleotide.

a.

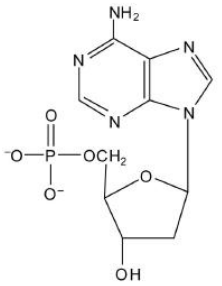


b.

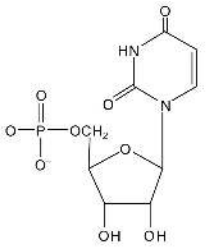


5. For each structure, circle the nitrogenous base and identify it as a purine or pyrimidine.

a.

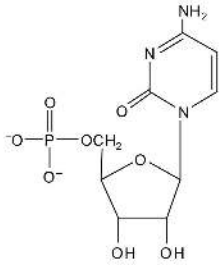


b.

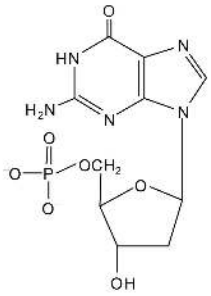


6. For each structure, circle the nitrogenous base and identify it as a purine or pyrimidine.

a.



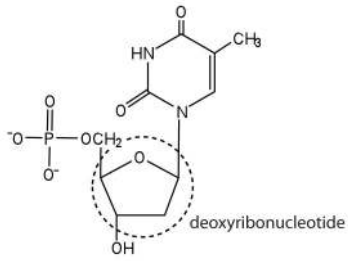
b.



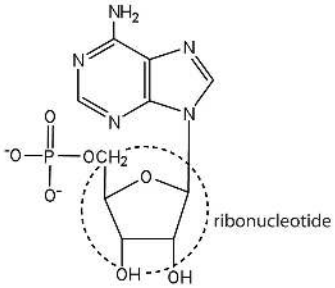
Answers

1. a. ribose
   b. deoxyribose

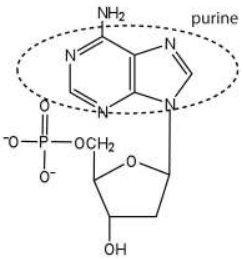
3. a.



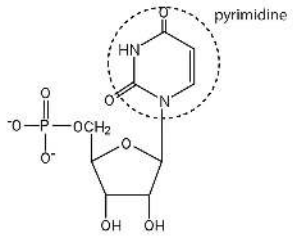
b.



a.



b.



19.2: Nucleic Acid Structure

Concept Review Exercises

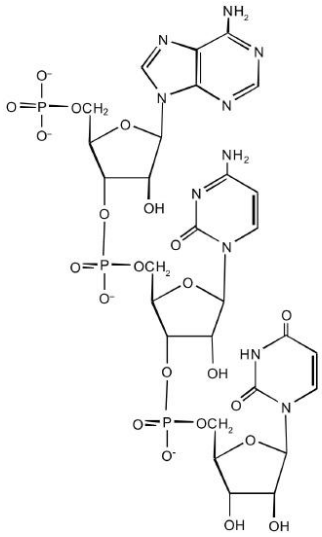
1. a. Name the two kinds of nucleic acids.
   b. Which type of nucleic acid stores genetic information in the cell?
2. What are complementary bases?
3. Why is it structurally important that a purine base always pair with a pyrimidine base in the DNA double helix?

Answers

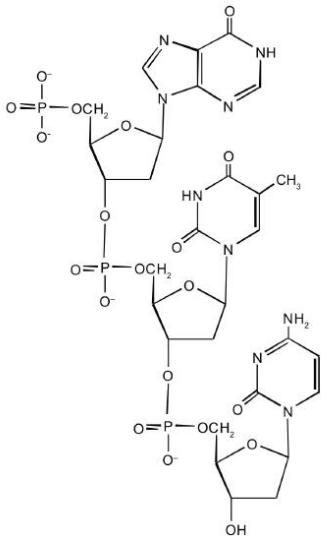
1. a. deoxyribonucleic acid (DNA) and ribonucleic acid (RNA)
   b. DNA
2. the specific base pairings in the DNA double helix in which guanine is paired with cytosine and adenine is paired with thymine
3. The width of the DNA double helix is kept at a constant width, rather than narrowing (if two pyrimidines 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.

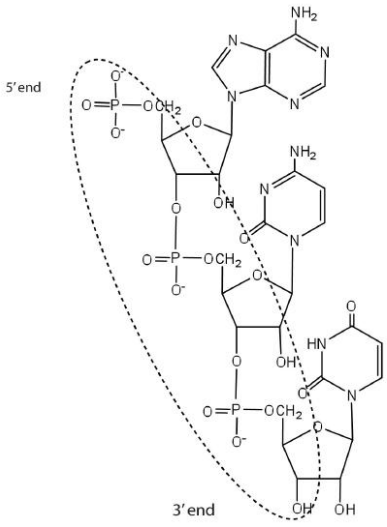


3. Which nitrogenous base in DNA pairs with each nitrogenous base?
    a. cytosine
    b. adenine
    c. guanine
    d. thymine
4. Which nitrogenous base in RNA pairs with each nitrogenous base?
    a. cytosine
    b. adenine
    c. guanine
    d. thymine
5. How many hydrogen bonds can form between the 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 **11.11.3** to identify the amino acids carried by each tRNA molecule in Exercise 1.
6. Use Figure **11.11.3** to identify the amino acids carried by each tRNA molecule in Exercise 2.
7. Use Figure **11.11.3** to determine the amino acid sequence produced from this mRNA sequence: 5′-AUGAGCGACUUUGCGGGAUUA-3′.
8. Use Figure **11.11.3** 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

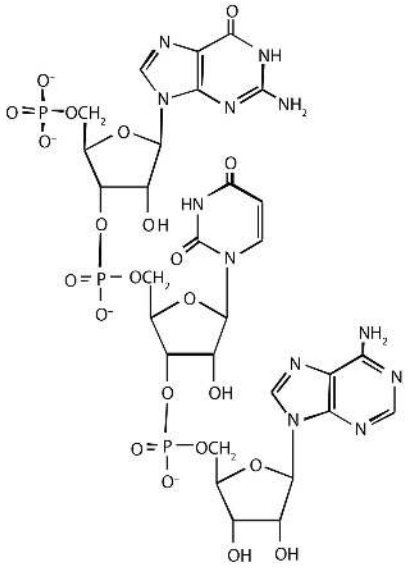
1. Describe the general structure of a virus.
2. How does a DNA virus differ from an RNA virus?
3. Why is HIV known as a retrovirus?
4. Describe how a DNA virus invades and destroys a cell.
5. a. Describe how an RNA virus invades and destroys a cell.
   b. How does this differ from a DNA virus?
6. What 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. -

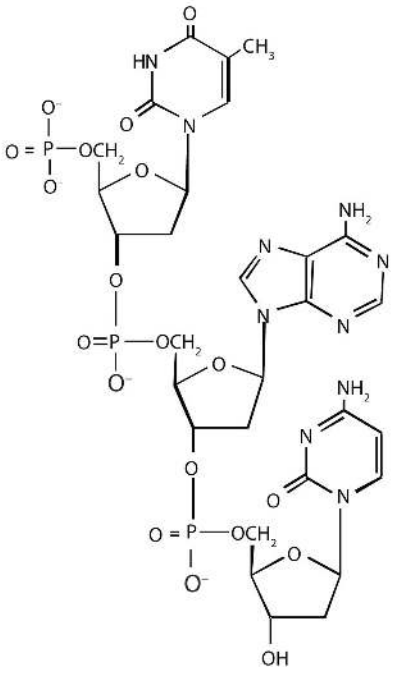
Additional Exercises

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

12: Air

12.1: Earth's Atmosphere- Divisions and Composition
12.2: Chemistry of the Atmosphere
12.3: Stratospheric Ozone- Earth's Vital Shield
12.4: Carbon Dioxide and Climate Change
12.5: Outdoor Air Pollution
12.6: Automobile Emissions
12.7: Photochemical Smog- Making Haze While the Sun Shines
12.8: Acid Rain- Air Pollution Water Pollution
12.9: Indoor Air Pollution
12.10: The Inside Story- Indoor Air Pollution
12.11: Who Pollutes? Who Pays?

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12.1: Earth's Atmosphere- Divisions and Composition

Learning Objectives

- Describe the different layers of the atmosphere.
- Know the composition of air.

The Earth's atmosphere is composed of several layers (Figure **12.1.1**). The lowest layer, the troposphere, extends from the Earth's surface up to about 6 miles or 10 kilometers (km) in altitude. Virtually all human activities occur in the troposphere. Mt. Everest, the tallest mountain on the planet, is only about 5.6 miles (9 km) high. The next layer, the stratosphere, continues from 6 miles (10 km) to about 31 miles (50 km). Most commercial airplanes fly in the lower part of the stratosphere.

Most atmospheric ozone is concentrated in a layer in the stratosphere, about 9 to 18 miles (15 to 30 km) above the Earth's surface (see the figure below). Ozone is a molecule that contains three oxygen atoms. At any given time, ozone molecules are constantly formed and destroyed in the stratosphere. The total amount has remained relatively stable during the decades that it has been measured.

The ozone layer in the stratosphere absorbs a portion of the radiation from the sun, preventing it from reaching the planet's surface. Most importantly, it absorbs the portion of UV light called UVB. UVB has been linked to many harmful effects, including skin cancers, cataracts, xand harm to some crops and marine life.

The mesosphere starts just above the stratosphere and extends to 85 kilometers (53 miles) high. Meteors burn up in this layer
The thermosphere starts just above the mesosphere and extends to 600 kilometers (372 miles) high. Aurora and satellites occur in this layer. The ionosphere is an abundant layer of electrons and ionized atoms and molecules that stretches from about 48 kilometers (30 miles) above the surface to the edge of space at about 965 km (600 mi), overlapping into the mesosphere and thermosphere. This dynamic region grows and shrinks based on solar conditions and divides further into the sub-regions: D, E and F; based on what wavelength of solar vvradiation is absorbed. The ionosphere is a critical link in the chain of Sun-Earth interactions. This region is what makes radio communications possible. The exosphere is is the upper limit of the atmosphere. It extends from the top of the thermosphere up to 10,000 km (6,200 mi).

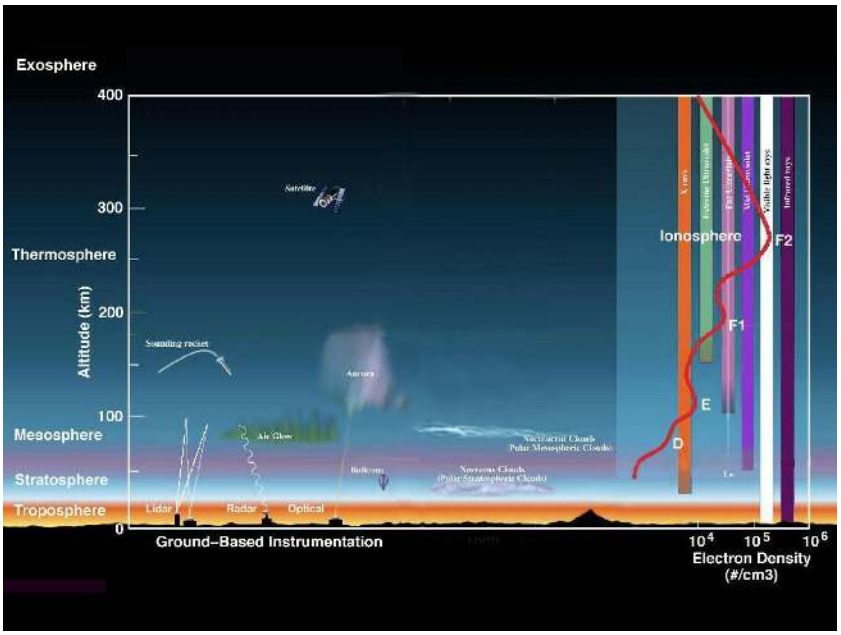


Figure* 12.1.1** *The Earth's atmosphere* ***Credit: *NASA/Goddard*

Composition of the Atmosphere

Except for water vapor, whose atmospheric abundance varies from practically zero up to 4%, the fractions of the major atmospheric components N_2, O_2, and Ar are remarkably uniform below about 100 km (Table **12.1.1**). At greater heights, diffusion becomes the principal transport process, and the lighter gases become relatively more abundant. In addition, photochemical processes result in the formation of new species whose high reactivities would preclude their existence in significant concentrations at the higher pressures found at lower elevations.

The atmospheric gases fall into three abundance categories: major, minor, and trace. Nitrogen, the most abundant component, has accumulated over time as a result of its geochemical inertness; a very small fraction of it passes into the other phases as a result of biological activity and natural fixation by lightning. It is believed that denitrifying bacteria in marine sediments may provide the

major route for the return of N_2 to the atmosphere. Oxygen is almost entirely of biological origin, and cycles through the hydrosphere, the biosphere, and sedimentary rocks. Argon consists mainly of Ar^{40} which is a decay product of K^{40} in the mantle and crust.

Table **12.1.1** *The Major Components of Clean Dry Air in the Lower Atmosphere*

nitrogen	N_2	78.08 %
oxygen	O_2	20.95 %
argon	Ar	0.93 %

The most abundant of the minor gases aside from water vapor is carbon dioxide (Table **12.1.2**). Next in abundance are neon and helium. Helium is a decay product of radioactive elements in the earth, but neon and the other inert gases are primordial, and have probably been present in their present relative abundances since the earth's formation. Two of the minor gases, ozone and carbon monoxide, have abundances that vary with time and location. A variable abundance implies an imbalance between the rates of formation and removal. In the case of carbon monoxide, whose major source is anthropogenic (a small amount is produced by biological action), the variance is probably due largely to localized differences in fuel consumption, particularly in internal combustion engines. The nature of the carbon monoxide sink (removal mechanism) is not entirely clear; it may be partly microbial.

Table **12.1.2** *The Minor Components of Air in the Lower Atmosphere.*

water	H_2O	0-4 %
carbon dioxide	CO_2	325 ppm
neon	Ne	18 ppm
helium	He	5 ppm
methane	CH_4	2 ppm
krypton	Kr	1 ppm
hydrogen	H_2	0.5 ppm
nitrous oxide	N_2O	0.3 ppm
carbon monoxide	CO	0.05-0.2 ppm
ozone	O_3	0.02 - 10 ppm
xenon	Xe	0.08 ppm

Summary

- The layers of the atmosphere include the trophosphere, stratosphere, mesosphere, thermosphere, and exosphere.
- The major components of dry clean air are N_2, O_2, and Ar.
- The most abundant of the minor gases are water vapor and CO_2

Contributors and Attributions

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12.2: Chemistry of the Atmosphere

Learning Objectives

- Describe the nitrogen cycle.
- Describe the oxygen cycle.
- Describe the conditions for temperature inversion.

The mix of gases in the atmosphere forms a complex system organized into layers that together support life on Earth. Although there are numerous gases, as shown in Table 13.1.1, the top four gases make up 99.998 % of the volume of *clean dry air* (unpolluted air that does not contain water vapor). Of this dry composition of the atmosphere **nitrogen**, by far, is the most common (78%). Nitrogen dilutes oxygen and prevents rapid or instantaneous burning at the Earth's surface, as oxygen gas is a necessary reactant of the combustion process. Nitrogen is also needed and used by living things to make proteins, though as nitrogen gas, N_2, it is unavailable to most living things. **Oxygen** is used by all living things to make molecules that are essential for life. It is also essential for aerobic respiration as well as combustion or burning.

Nitrogen Cycle

All life requires nitrogen-compounds, e.g., proteins and nucleic acids. Air, which is 79% nitrogen gas (N_2), is the major reservoir of nitrogen. But most organisms cannot use nitrogen in this form. Figure **12.2.1** illustrates the entire nitrogen cycle. Plants must secure their nitrogen in "fixed" form, i.e., incorporated in compounds such as: nitrate ions (NO_3^-), ammonium ions (NH_4^+) and urea $(NH_2)_2CO$. Animals secure their nitrogen (and all other) compounds from plants (or animals that have fed on plants).

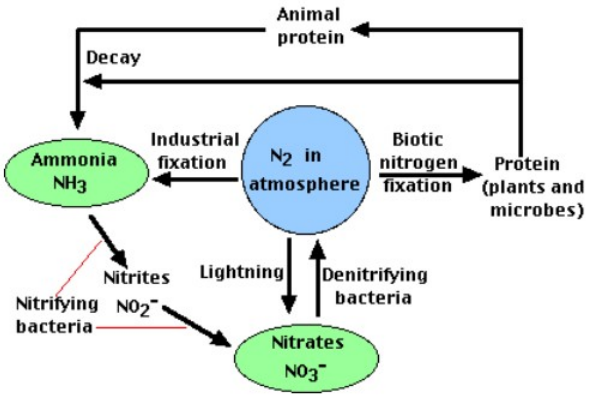


Figure **12.2.1** Nitrogen cycle

Four processes participate in the cycling of nitrogen through the biosphere: (1) nitrogen fixation, (2) decay, (3) nitrification, and (4) denitrification. Microorganisms play major roles in all four of these.

Nitrogen Fixation

The nitrogen molecule (N_2) is quite inert. To break it apart so that its atoms can combine with other atoms requires the input of substantial amounts of energy. Three processes are responsible for most of the nitrogen fixation in the biosphere:

- **atmospheric fixation** by lightning
- **biological fixation** by certain microbes alone or in a symbiotic relationship with some plants and animals
- **industrial fixation**

Atmospheric Fixation

The enormous energy of lightning breaks nitrogen molecules and enables their atoms to combine with oxygen in the air forming nitrogen oxides. These dissolve in rain, forming nitrates, that are carried to the earth. Atmospheric nitrogen fixation probably contributes some 5– 8% of the total nitrogen fixed.

Industrial Fixation

Under great pressure, at a temperature of 600°C, and with the use of a catalyst, atmospheric nitrogen and hydrogen (usually derived from natural gas or petroleum) can be combined to form ammonia (NH_3). Ammonia can be used directly as fertilizer, but most of its is further processed to urea and ammonium nitrate (NH_4NO_3).

Biological Fixation

The ability to fix nitrogen in the soil (Figure **12.2.2**) only in certain bacteria and archaea.

- Some live in a symbiotic relationship with plants of the legume family (e.g., soybeans, alfalfa).
- Some establish symbiotic relationships with plants other than legumes (e.g., alders).
- Some establish symbiotic relationships with animals, e.g., termites and "shipworms" (wood-eating bivalves).
- Some nitrogen-fixing bacteria live free in the soil.
- Nitrogen-fixing cyanobacteria are essential to maintaining the fertility of semi-aquatic environments like rice paddies.

Biological nitrogen fixation requires a complex set of enzymes and a huge expenditure of ATP. Although the first stable product of the process is ammonia, this is quickly incorporated into protein and other organic nitrogen compounds.

Decay

The proteins made by plants enter and pass through food webs just as carbohydrates do. At each trophic level, their metabolism produces organic nitrogen compounds that return to the environment, chiefly in excretions. The final beneficiaries of these materials are microorganisms of decay. They break down the molecules in excretions and dead organisms into **ammonia**.

Nitrification

Ammonia can be taken up directly by plants — usually through their roots. However, most of the ammonia produced by decay is converted into **nitrates**. Until recently this was thought always to be accomplished in two steps:

1. Bacteria of the genus *Nitrosomonas* oxidize $\mathbf{NH_3}$ to **nitrites** ($\mathbf{NO_2^-}$).
2. Bacteria of the genus *Nitrobacter* oxidize the nitrites to **nitrates** ($\mathbf{NO_3^-}$).

These two groups of autotrophic bacteria are called **nitrifying bacteria**. Through their activities (which supply them with all their energy needs), nitrogen is made available to the roots of plants. However, in 2015, two groups reported finding that bacteria in the genus *Nitrospira* were able to carry out both steps: ammonia to nitrite and nitrite to nitrate. This ability is called "comammox" (for complete ammonia oxidation).

In addition, both soil and the ocean contain **archaeal** microbes, assigned to the Crenarchaeota, that convert ammonia to nitrites. They are more abundant than the nitrifying bacteria and may turn out to play an important role in the nitrogen cycle.

Many legumes, in addition to fixing atmospheric nitrogen, also perform nitrification - converting some of their organic nitrogen to nitrites and nitrates. These reach the soil when they shed their leaves.

Denitrification

The three processes above remove nitrogen from the atmosphere and pass it through ecosystems. Denitrification reduces nitrates and nitrites to nitrogen gas, thus replenishing the atmosphere. In the process several intermediates are formed:

- nitric oxide (NO)
- nitrous oxide (N_2O)(a greenhouse gas 300 times as potent as CO_2)
- nitrous acid (HONO)

Once again, bacteria are the agents. They live deep in soil and in aquatic sediments where conditions are anaerobic. They use nitrates as an alternative to oxygen for the final electron acceptor in their respiration.

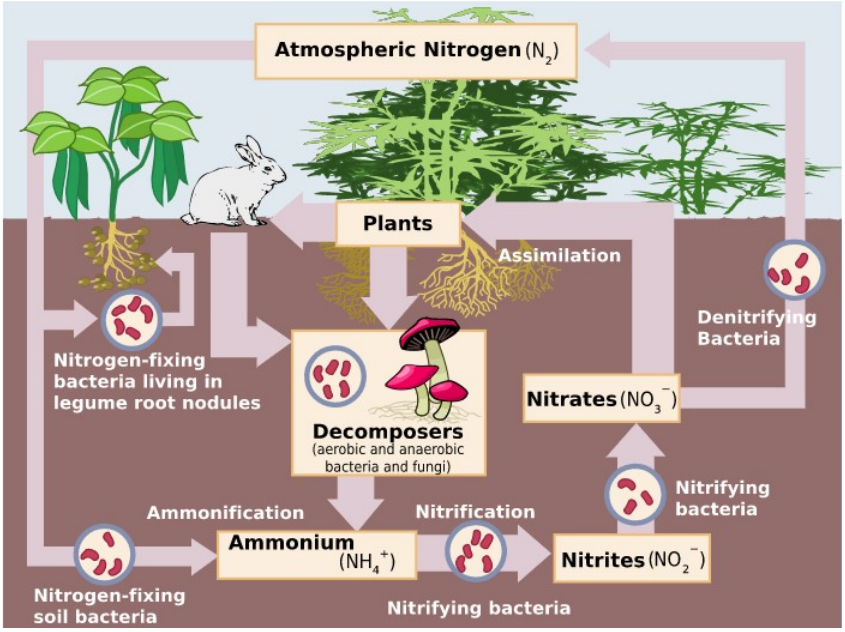


Figure **12.2.2** The role of soil bacteria in the Nitrogen cycle: Nitrogen transitions between various biologically useful forms.

Anammox (anaerobic ammonia oxidation)

Under anaerobic conditions in marine and freshwater sediments, other species of bacteria are able to oxidize ammonia (with NO_2^-) forming nitrogen gas.

$$NH_4^+ + NO_2^- \longrightarrow N_2 + 2\,H_2O$$

The anammox reaction may account for as much as 50% of the denitrification occurring in the oceans. All of these processes participate in closing the nitrogen cycle.

Are the denitrifiers keeping up?

Agriculture may now be responsible for one-half of the nitrogen fixation on earth through the use of fertilizers produced by industrial fixation and the the growing of legumes like soybeans and alfalfa. This is a remarkable influence on a natural cycle. Are the denitrifiers keeping up the nitrogen cycle in balance? Probably not. Certainly, there are examples of nitrogen enrichment in ecosystems. One troubling example: the "blooms" of algae in lakes and rivers as nitrogen fertilizers leach from the soil of adjacent farms (and lawns). The accumulation of dissolved nutrients in a body of water is called **eutrophication**.

Oxygen Cycle

Oxygen is the most abundant element on the earth's crust. The earth's surface is composed of the crust, atmosphere, and hydrosphere. About 50% of the mass of the earth's crust consists of oxygen (combined with other elements, principally silicon). Oxygen occurs as O_2 molecules and, to a limited extent, as O_3 (ozone) molecules in air. It forms about 20% of the mass of the air. About 89% of water by mass consists of combined oxygen. In combination with carbon, hydrogen, and nitrogen, oxygen is a large part of plants and animals.

Oxygen is a colorless, odorless, and tasteless gas at ordinary temperatures. It is slightly denser than air. Although it is only slightly soluble in water (49 mL of gas dissolves in 1 L at STP), oxygen's solubility is very important to aquatic life.

Oxygen is essential in combustion processes such as the burning of fuels. Plants and animals use the oxygen from the air in respiration (*Figure* **12.2.4**). The main way free oxygen is lost from the atmosphere is via and , mechanisms in which life and consume oxygen and release carbon dioxide.

The respiration process is represented as:

$$6\,O_2{}^{+}C_6H_{12}O_6 \longrightarrow 6\,CO_2{}^{+}6H_2O$$

Green plants continually replenish the oxygen in the atmosphere by a process called photosynthesis (*Figure* **12.2.3***)* . The products of photosynthesis may vary, but, in general, the process converts carbon dioxide and water into glucose (a sugar) and oxygen using the energy of light:

$$6\,CO_2(g) + 6\,H_2O(l) \xrightarrow[\text{light}]{\text{chlorophyll}} C_6H_{12}O_6(aq) + 6\,O_2(g) \tag{12.2.1}$$

$$\underset{\text{dioxide}}{\text{carbon}} \qquad \text{water} \qquad\qquad \text{glucose} \qquad\qquad \text{oxygen} \tag{12.2.2}$$

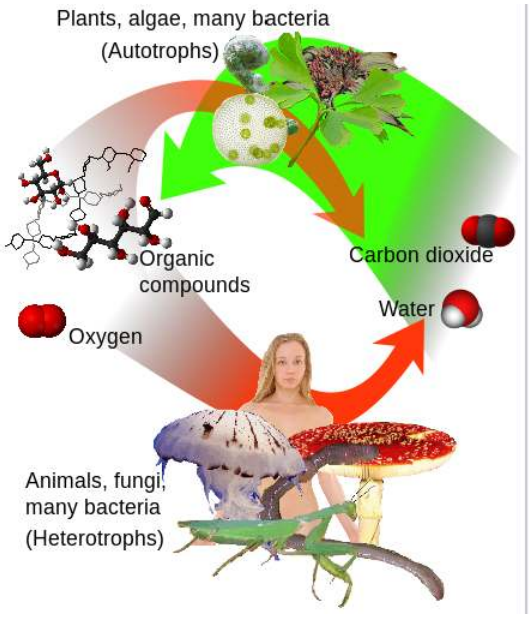


Figure **12.2.3**

Overview of and photosynthesis (green) and respiration (red).

Water (at right), together with carbon dioxide (CO_2), form oxygen and organic compounds (at left),

which can be respired to water and (CO_2). Source: Wikipedia

Thus, the oxygen that became carbon dioxide and water by the metabolic processes in plants and animals returns to the atmosphere by photosynthesis. Photosynthesizing organisms include the plant life of the land areas as well as the of the oceans. The tiny marine was discovered in 1986 and accounts for more than half of the photosynthesis of the open ocean.

Oxygen is a key reactant in various oxidation reactions mentioned in section 8.5. Atmospheric free oxygen is also consumed by chemical weathering and surface reactions. An example of surface weathering is formation of rust:

$$4\,FeO + O_2 \longrightarrow 2\,Fe_2O_3$$

Ozone forms naturally in the upper atmosphere by the action of ultraviolet light from the sun on the oxygen there. Most atmospheric ozone occurs in the stratosphere, a layer of the atmosphere extending from about 10 to 50 kilometers above the earth's surface. This ozone acts as a barrier to harmful ultraviolet light from the sun by absorbing it via a chemical decomposition reaction:

$$O_3(g) \xrightarrow{\text{ultraviolet light}} O(g) + O_2(g)$$

Temperature Inversions

In meteorology, an **inversion**, also known as a **temperature inversion**, is a deviation from the normal change of an amospheric property with altitude. It almost always refers to an inversion of the thermal lapse rate. Normally, air temperature decreases with an increase in altitude. During an inversion, warmer air is held above cooler air; the normal temperature profile with altitude is inverted.

An inversion traps air pollution, such as smog, close to the ground. An inversion can also suppress convection by acting as a "cap". If this cap is broken for any of several reasons, convection of any moisture present can then erupt into violent thunderstorms

Temperature inversion can notoriously result in freezing rain in cold climates.

Summary

- The different forms of nitrogen that can be used in metabolism are produced through the process of nitrogen fixation.
- Bacteria in the soil carry out a process known as denitrification which converts nitrates back to nitrogen gas.
- Oxygen is produced mainly through photosynthesis. An additional source of atmospheric free oxygen comes from , whereby high-energy radiation breaks down atmospheric water and nitrous oxide.
- Oxygen is utilized during cellular respiration and decay. As well as during chemical weathering and various oxidation reactions.
- Temperature inversion is when a layer of cool air is trapped under a layer of warmer air. The cool dense air can trap and accumulate air pollutants.

Contributors and Attributions

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12.3: Stratospheric Ozone- Earth's Vital Shield

Learning Objectives

- Describe the depletion of the ozone layer.
- Explain how chlorine and bromine atoms react with ozone that leads to the depletion of the ozone layer.

The earth's stratospheric ozone layer plays a critical role in absorbing ultraviolet radiation emitted by the sun. In the last thirty years, it has been discovered that stratospheric ozone is depleting as a result of anthropogenic pollutants. There are a number of chemical reactions that can deplete stratospheric ozone; however, some of the most significant of these involves the catalytic destruction of ozone by halogen radicals such as chlorine and bromine.

Introduction

The atmosphere of the Earth is divided into five layers. In order of closest and thickest to farthest and thinnest the layers are listed as follows: troposphere, stratosphere, mesosphere, thermosphere and exosphere. The majority of the ozone in the atmosphere resides in the stratosphere, which extends from six miles above the Earth’s surface to 31 miles. Humans rely heavily on the absorption of ultraviolet B rays by the ozone layer because UV-B radiation causes skin cancer and can lead to genetic damage. The ozone layer has historically protected the Earth from the harmful UV rays, although in recent decades this protection has diminished due to stratospheric ozone depletion.

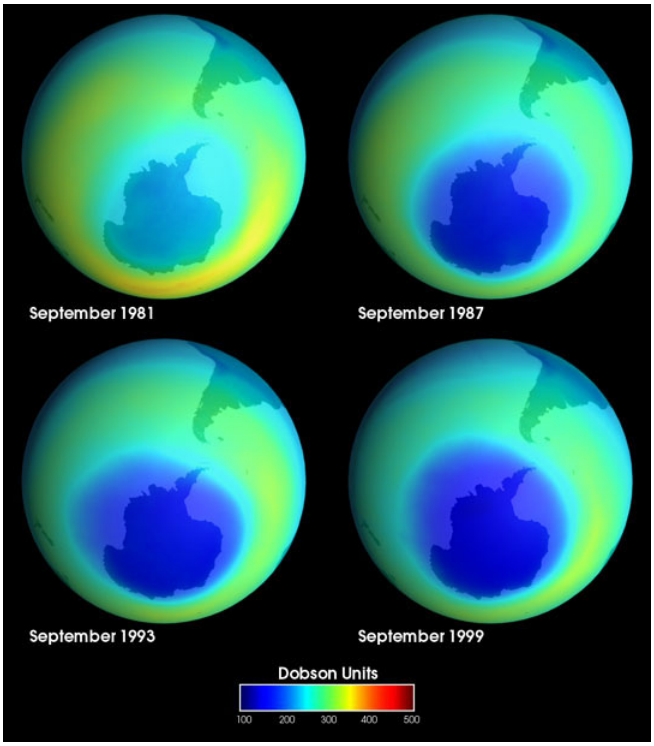


Figure courtesy of NASA.

Ozone depletion is largely a result of man-made substances. Humans have introduced gases and chemicals into the atmosphere that have rapidly depleted the ozone layer in the last century. This depletion makes humans more vulnerable to the UV-B rays which are known to cause skin cancer as well as other genetic deformities. The possibility of ozone depletion was first introduced by scientists in the late 1960's as dreams of super sonic transport began to become a reality. Scientists had long been aware that nitric oxide (NO) can catalytically react with ozone (O_3) to produce O_2 molecules; however, NO molecules produced at ground level have a half life far too short to make it into the stratosphere. It was not until the advent of commercial super sonic jets (which fly in the stratosphere and at an altitude much higher then conventional jets) that the potential for NO to react with stratospheric ozone became a possibility. The threat of ozone depletion from commercial super sonic transport was so great that it is often cited as the

main reason why the US federal government pulled support for its development in 1971. Fear of ozone depletion was abated until 1974 when Sherwood Rowland and Mario Molina discovered that chlorofluorocarbons could be photolyzed by high energy photons in the stratosphere. They discovered that this process could releasing chlorine radicals that would catalytically react with O_3 and destroy the molecule. This process is called the Rowland-Molina theory of O_3 depletion.

The Chapman Cycle

The stratosphere is in a constant cycle with oxygen molecules and their interaction with ultraviolet rays. This process is considered a cycle because of its constant conversion between different molecules of oxygen. The ozone layer is created when ultraviolet rays react with oxygen molecules (O_2) to create ozone (O_3) and atomic oxygen (O). This process is called the *Chapman cycle*.

Step 1: An oxygen molecules is photolyzed by solar radiation, creating two oxygen radicals:

$$h\nu + O_2 \rightarrow 2O^{\cdot}$$

Step 2: Oxygen radicals then react with molecular oxygen to produce ozone:

$$O_2 + O^{\cdot} \rightarrow O_3$$

Step 3: Ozone then reacts with an additional oxygen radical to form molecular oxygen:

$$O_3 + O^{\cdot} \rightarrow 2O_2$$

Step 4: Ozone can also be recycled into molecular oxygen by reacting with a photon:

$$O_3 + h\nu \rightarrow O_2 + O^{\cdot}$$

It is important to keep in mind that ozone is constantly being created and destroyed by the Chapman cycle and that these reactions are natural processes, which have been taking place for millions of years. Because of this, the thickness the ozone layer at any particular time can vary greatly. It is also important to know that O_2 is constantly being introduced into the atmosphere through photosynthesis, so the ozone layer has the capability of regenerating itself.

Chemistry of Ozone Depletion

CFC molecules are made up of chlorine, fluorine and carbon atoms and are extremely stable. This extreme stability allows CFC's to slowly make their way into the stratosphere (most molecules decompose before they can cross into the stratosphere from the troposphere). This prolonged life in the atmosphere allows them to reach great altitudes where photons are more energetic. When the CFC's come into contact with these high energy photons, their individual components are freed from the whole. The following reaction displays how Cl atoms have an ozone destroying cycle:

$$Cl + O_3 \rightarrow ClO + O_2 \qquad \textbf{(step 1)}$$

$$ClO + O^{\cdot} \rightarrow Cl + O_2 \qquad \textbf{(step 2)}$$

$$O_3 + O^{\cdot} \rightarrow 2O_2 \qquad \textbf{(Overall reaction)}$$

Chlorine is able to destroy so much of the ozone because it acts as a catalyst. Chlorine initiates the breakdown of ozone and combines with a freed oxygen to create two oxygen molecules. After each reaction, chlorine begins the destructive cycle again with another ozone molecule. One chlorine atom can thereby destroy thousands of ozone molecules. Because ozone molecules are being broken down they are unable to absorb any ultraviolet light so we experience more intense UV radiation at the earths surface.

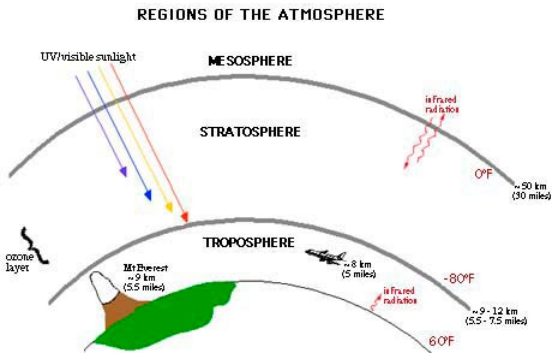


Figure courtesy of NOAA.

From 1985 to 1988, researchers studying atmospheric properties over the south pole continually noticed significantly reduced concentrations of ozone directly over the continent of Antarctica. For three years it was assumed that the ozone data was incorrect and was due to some type of instrument malfunction. In 1988, researchers finally realized their error and concluded that an enormous hole in the ozone layer had indeed developed over Antarctica. Examination of NASA satellite data later showed that the hole had begun to develop in the mid 1970's.

The ozone hole over Antarctica is formed by a slew of unique atmospheric conditions over the continent that combine to create an ideal environment for ozone destruction.

- Because Antarctica is surrounded by water, winds over the continent blow in a unique clockwise direction creating a so called "polar vortex" that effectively contains a single static air mass over the continent. As a result, air over Antarctica does not mix with air in the rest of the earth's atmosphere.
- Antarctica has the coldest winter temperatures on earth, often reaching -110 F. These chilling temperatures result in the formation of polar stratospheric clouds (PSC's) which are a conglomeration of frozen H_2O and HNO_3. Due to their extremely cold temperatures, PSC's form an electrostatic attraction with CFC molecules as well as other halogenated compounds

As spring comes to Antarctica, the PSC's melt in the stratosphere and release all of the halogenated compounds that were previously absorbed to the cloud. In the antarctic summer, high energy photons are able to photolyze the halogenated compounds, freeing halogen radicals that then catalytically destroy O_3. Because Antarctica is constantly surrounded by a polar vortex, radical halogens are not able to be diluted over the entire globe. The ozone hole develops as result of this process.

Resent research suggests that the strength of the polar vortex from any given year is directly correlated to the size of the ozone hole. In years with a strong polar vortex, the ozone hole is seen to expand in diameter, whereas in years with a weaker polar vortex, the ozone hole is noted to shrink

Ozone Depleting Substances

The following substances are listed as ozone depleting substances under Title VI of the United State Clean Air Act:

Table **12.3.1**: Ozone Depleting Substances And Their Ozone-Depletion Potential. Taken directly from the Clean Air Act, as of June 2010.

Substance	Ozone- depletion potential
chlorofluorocarbon-11 (CFC–11)	1.0
chlorofluorocarbon-12 (CFC–12)	1.0
chlorofluorocarbon-13 (CFC–13)	1.0
chlorofluorocarbon-111 (CFC–111)	1.0
chlorofluorocarbon-112 (CFC–112)	1.0
chlorofluorocarbon-113 (CFC–113)	0.8
chlorofluorocarbon-114 (CFC–114)	1.0
chlorofluorocarbon-115 (CFC–115)	0.6
chlorofluorocarbon-211 (CFC–211)	1.0
chlorofluorocarbon-212 (CFC–212)	1.0
chlorofluorocarbon-213 (CFC–213)	1.0
chlorofluorocarbon-214 (CFC–214)	1.0
chlorofluorocarbon-215 (CFC–215)	1.0
chlorofluorocarbon-216 (CFC–216)	1.0
chlorofluorocarbon-217 (CFC–217)	1.0
halon-1211	3.0
halon-1301	10.0
halon-2402	6.0
carbon tetrachloride	1.1
methyl chloroform	0.1
hydrochlorofluorocarbon-22 (HCFC–22)	0.05
hydrochlorofluorocarbon-123 (HCFC–123)	0.02
hydrochlorofluorocarbon-124 (HCFC–124)	0.02
hydrochlorofluorocarbon-141(b) (HCFC–141(b))	0.1
hydrochlorofluorocarbon-142(b) (HCFC–142(b))	0.06

Summary

- Any disruption of the balance that results in a higher rate of ozone destruction than ozone creation would result in depletion of ozone.
- Some compounds that release chlorine or bromine when they are exposed to intense UV light in the stratosphere contribute to ozone depletion, and are called ozone-depleting substances (ODS)
- The Montreal Protocol is an international agreement that committed all parties (signatory nations) to a schedule for phasing out the production and use of CFCs and other substances known to be harmful to the ozone layer.

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12.4: Carbon Dioxide and Climate Change

Learning Objectives

- Define global warming, climate change, the greenhouse effect, and greenhouse gases.
- Discuss strategies for reducing the intensity of the human influence on the greenhouse effect.

Global warming refers to the increase in the average temperature of the Earth's atmosphere due to elevated greenhouse gas concentrations, heightening the greenhouse effect. **Climate change** includes both global warming driven by human-induced emissions of greenhouse gases and the resulting large-scale shifts in weather patterns. Though there have been previous periods of climatic change, since the mid-20th century humans have had an unprecedented impact on Earth's climate system and caused change on a global scale.

The largest driver of warming is the emission of gases that create a greenhouse effect, of which more than 90% are carbon dioxide (CO_2) and methane. Fossil fuel burning (coal, oil, and natural gas) for energy consumption is the main source of these emissions, with additional contributions from agriculture, deforestation, and manufacturing. The human cause of climate change is not disputed by any scientific body of national or international standing. Temperature rise is accelerated or tempered by climate feedbacks, such as loss of sunlight-reflecting snow and ice cover, increased water vapour (a greenhouse gas itself), and changes to land and ocean carbon sinks.

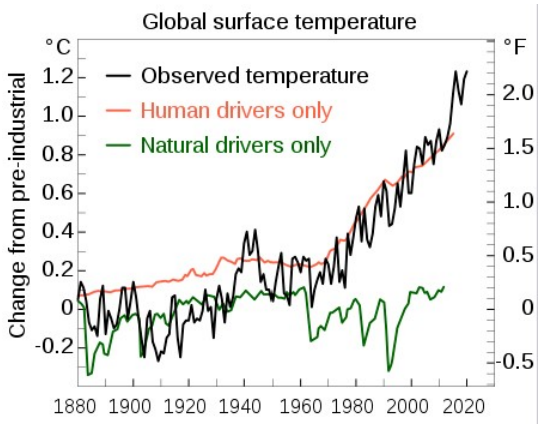


Figure **12.4.1** Observed temperature from NASA versus the 1850-1900 average as a pre-industrial baseline.

The **greenhouse effect** is the process by which radiation from a planet's atmosphere warms the planet's surface to a temperature above what it would be without this atmosphere (Figure **12.4.2**). Radiatively active gases (i.e. greenhouse gases) in a planet's atmosphere radiate energy in all directions. Part of this radiation is directed towards the surface, thus warming it. The intensity of downward radiation – that is, the strength of the greenhouse effect – depends on the amount of greenhouse gases that the atmosphere contains. The temperature rises until the intensity of upward radiation from the surface, thus cooling it, balances the downward flow of energy.

Earth's natural greenhouse effect is critical to supporting life and initially was a precursor to life moving out of the ocean onto land. Human activities, mainly the burning of fossil fuels and clear cutting of forests, have increased the greenhouse effect and caused global warming.

The term *greenhouse effect* is a slight misnomer in the sense that physical greenhouses warm via a different mechanism. The greenhouse effect as an atmospheric mechanism functions through radiative heat loss while a traditional greenhouse as a built structure blocks convective heat loss. The result, however, is an increase in temperature in both cases.

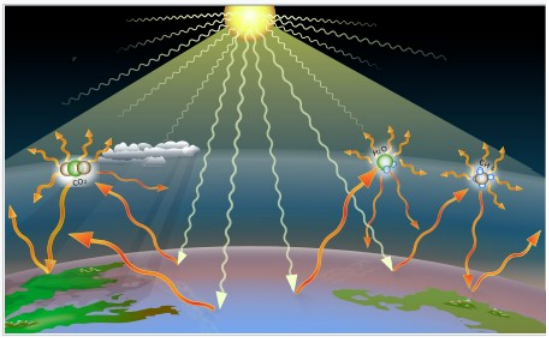


Figure 12.4.2 The greenhouse effect of solar radiation on the Earth's surface caused by emission of greenhouse gases. Source: Wikipedia

Greenhouse Gases and Global Warming

A **greenhouse gas** (sometimes abbreviated **GHG**) is a gas that absorbs and emits radiant energy within the thermal infrared range, causing the greenhouse effect. It's important to realize that **water vapor** (H_2O) is also a greenhouse gas. While humans have little direct impact on water vapor concentrations in the atmosphere, it is still an essential component of the natural greenhouse effect that occurs in our atmosphere. The four major categories of greenhouse gases that have been impacted by humans the most will be discussed in detail below. See Table **12.4.1** for a numeric comparison of these greenhouse gases.

• Carbon dioxide, CO_2

• Methane, CH_4

• Nitrous oxide, N_2O

• Synthetic **fluorinated gases**, including **hydrofluorocarbons** (HFCs), **perfluorocarbons** (PFCs), and **sulfur hexafluoride** (SF_6)

Carbon dioxide (CO_2) is the greenhouse gas responsible for most of the human-caused climate change in our atmosphere. It has the highest concentration in the atmosphere of any of the greenhouse gases that we'll discuss here. Remember that CO_2 is a direct product of both combustion and cellular respiration, causing it to be produced in great quantities both naturally and anthropogenically. Any time biomass or fossil fuels are burned, CO_2 is released. Major anthropogenic sources include: electricity production from coal-fired and natural gas power plants, transportation, and industry (Chapter 4). To get an idea of how CO_2 concentration has changed over time, watch this video compiled by the National Oceanic and Atmospheric Administration (NOAA): http://www.esrl.noaa.gov/gmd/ccgg/trends/history.html. This video contains atmospheric CO_2 concentrations measured directly, dating back to 1958, as well as atmospheric CO_2 concentrations measured indirectly from ice core data, dating back to 800,000 BCE. By 1990, a quantity of over seven billion tons of carbon (equivalent to 26 billion tons of carbon dioxide when the weight of the oxygen atoms are also considered) was being emitted into the atmosphere every year, much of it from industrialized nations. Similar to the action of the naturally existing greenhouse gases, any additional greenhouse gases leads to an increase in the surface temperature of the Earth.

While CO_2 is produced by aerobic cellular respiration, gases such as CH_4 and N_2O are often the products of anaerobic metabolisms. Agriculture is a major contributor to CH_4 emissions. In addition to anaerobic bacteria, methane is also a significant component of natural gas, and is commonly emitted through the mining and use of natural gas and petroleum, in addition to coal mining. Finally, landfills contribute significantly to CH_4 emissions, as the waste put into the landfill largely undergoes anaerobic decomposition as it is buried under many layers of trash and soil. Natural sources of CH_4 include swamps and wetlands, and volcanoes.

The vast majority of N_2O production by humans comes from agricultural land management. While some N_2O is naturally emitted to the atmosphere from soil as part of the nitrogen cycle, human changes in land management, largely due to agricultural practices, have greatly increased N_2O emissions. Some N_2O is also emitted from transportation and industry.

Due to their relatively high concentrations in the atmosphere compared to synthetic gases, CO_2, CH_4, and N_2O, are responsible for most of the human-caused global climate change over the past century. Figure **12.4.2** shows the increases in all three gases since

1750. Ice core data shows us that the atmospheric CO_2 concentration never exceeded 300 ppm before the industrial revolution. As of early 2015, the current atmospheric CO_2 concentration is 400 ppm.

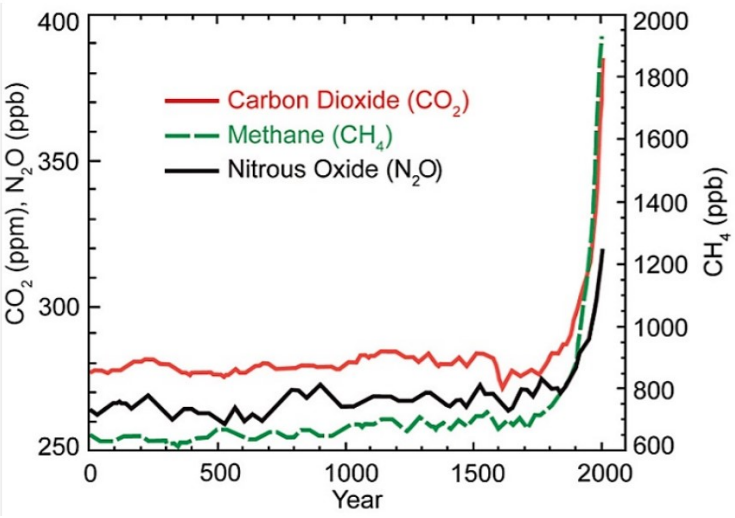


Figure **12.4.2**: Increase in greenhouse gas concentrations in the atmosphere over the last 2,000 years. Increases in concentrations of these gases since 1750 are due to human activities in the industrial era. Concentration units are parts per million (ppm) or parts per billion (ppb), indicating the number of molecules of the greenhouse gas per million or billion molecules of air. Source: USGCRP (2009)

One class of greenhouse gas chemicals that has no natural sources is the fluorinated gases. These include HFCs, PFCs, and SF6, among others. Because these are synthetic chemicals that are only created by humans, these gases were essentially non-existent before the industrial revolution. These synthetic gases are used for a wide variety of applications, from refrigerants to semiconductor manufacturing, and propellants to fire retardants. They tend to have a long lifetime in the atmosphere, as seen in Table **12.4.1**. Some of these chemicals, as well as the older **chlorofluorocarbons** (CFCs), have been phased out by international environmental legislation under the Montreal Protocol. Due to their long lifespan, many of these now banned CFCs remain in the atmosphere. Newer chemical replacements, such as HFCs, provide many of the same industrial applications, but unfortunately have their own environmental consequences.

Just as greenhouse gases differ in their sources and their residence time in the atmosphere, they also differ in their ability to produce the greenhouse effect. This is measured by the **global warming potential**, or GWP, of each greenhouse gas. The GWP of a greenhouse gas is based on its ability to absorb and scatter energy, as well as its lifetime in the atmosphere. Since CO_2 is the most prevalent greenhouse gas, all other greenhouse gases are measured relative to it. As the reference point, CO_2 always has a GWP of 1. Note the very high GWP values of the synthetic fluorinated gases in Table **12.4.1**. This is largely due to their very long residence time in the atmosphere. Also note the higher GWP values for CH_4 and N_2O compared to CO_2.

Table **12.4.1**. Comparision of Greenhouse Gases.

Greenhouse gas	Chemical formula or abbreviation	Lifetime in atmosphere	Global warming potential (100-year)
Carbon dioxide	CO_2	Variable	1
Methane	CH_4	12 years	28-36
Nitrous oxide	N_2O	114 years	298
Hydrofluorocarbons	Abbreviation: HFCs	1-270 years	12-14,800
Perfluorocarbons	Abbreviation: PFCs	2,600-50,000 years	7,390
Sulfur hexafluoride	SF6	3,200 years	22,800

Other climate influencers

In addition to greenhouse gases, other manmade changes may be forcing climate change. Increases in near-surface ozone from internal combustion engines, aerosols such as carbon black, mineral dust and aviation-induced exhaust are acting to raise the surface temperature. This primarily occurs due to a decrease in the **albedo** of light-colored surfaces by the darker-colored carbon black, soot, dust, or particulate matter. As you know, it is more comfortable to wear a white shirt on a hot summer day than a black shirt. Why is this? Because the lighter-colored material bounces more solar radiation back toward space than the darker-colored material does, allowing it to stay cooler. The darker-colored material absorbs more solar radiation, increasing its temperature. Just as the white shirt has a higher albedo than the black shirt, light-colored objects in nature (such as snow) have a higher albedo than dark-colored objects (such as soot or dust). As humans increase the amount of carbon black, soot, dust, and particulates in the atmosphere, we decrease the albedo of light-colored surfaces, causing them to absorb more solar radiation and become warmer than they would without human influence. An example of this can be seen in the snow on Figure **12.4.3**.



Figure **12.4.3**: A photograph of the extreme dust deposition from the deserts of the Colorado Plateau onto the Colorado Rockies snowpack in 2009. Taken from the high point of the Senator Beck Basin in the San Juan Mountains, it captures the extent of the impact of darkening in which the snow albedo dropped to about 30%, more than doubling the absorption of sunlight. Credit: S. McKenzie Skiles, Snow Optics Laboratory, NASA/JPL

Consequences of Climate Change

We will only discuss some of the consequences of climate change in this section, including changes in temperature, precipitation, ocean level, and ocean acidity. There are many more changes that have been seen, and are projected to continue in the future. These include: changes in the amount and distribution of ice and snow, changes in seasonality, ecosystem shift, and habitat changes of plant and animal populations, in addition to others. For more information about these consequence of climate change, visit this site: http://www.epa.gov/climatechange/sci...ors/index.html.

Temperature and precipitation

Temperature and **precipitation** are the two most direct impacts on the Earth's climate due to climate change. By now, you should already understand why an increase in greenhouse gas levels in the atmosphere causes an increase in temperature. But why does it also impact precipitation patterns? As you already know, water vapor is an important component of the Earth's atmosphere . As the air in the troposphere warms and cools, the amount of water vapor that it holds changes dramatically. Here in Georgia, we have very hot and humid summers. The high summer humidity in this region is possible due to the increased capability warm air has to

hold water vapor. Simply put, warmer air can hold more water than cooler air. As air cools, its ability to hold water vapor decreases, and any excess water will leave the air as liquid water. A great example of this is the formation of dew on surfaces overnight. During the day, the temperature is warmer than it is at night, and the air has a relatively high holding capacity for water vapor. When the sun sets, the air cools, decreasing its capacity to hold water vapor. That extra water must go somewhere, and it does that by accumulating on surfaces. Similarly, when warm and cool air fronts collide, the chances for rain and thunderstorms increase. Furthermore, an increase in temperature enhances evaporation occurring at the Earth's surface. This increased evaporation leads to greater concentrations of water vapor in the atmosphere which can lead to increased precipitation.

The change in temperature that we have already seen in the Earth's average atmospheric temperature is relatively small (about1.2 °C, according to Figure 7.5.1). However, as with many of the aspects of climate change, the potential for greater changes increases dramatically as time progresses in the future. This can be seen in Figure **12.4.4**, which displays a model of the predicted temperature increase. Notice that these changes occur relatively rapidly, and are not uniform across the globe. What might be some of the reasons for this?

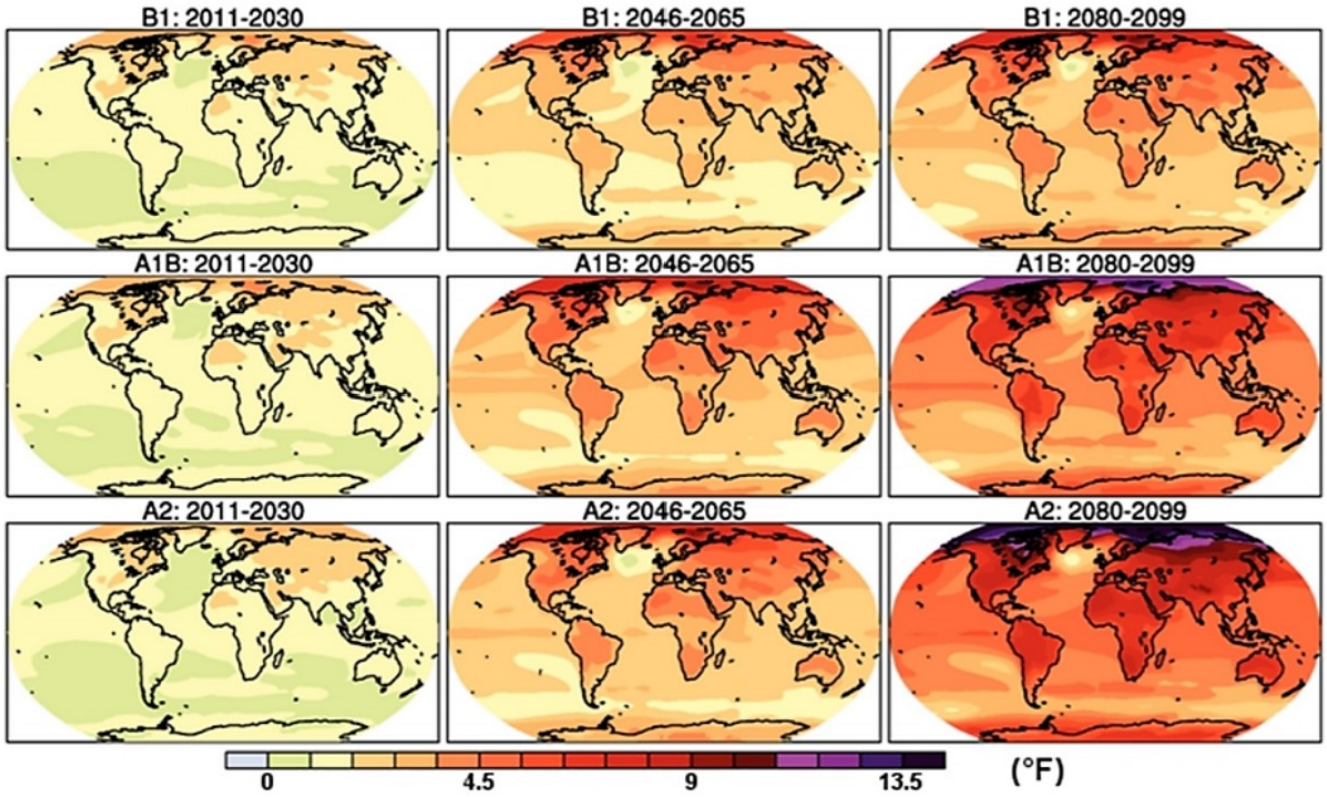


Figure **12.4.4**: Projected changes in global average temperatures under three emissions scenarios (rows) for three different time periods (columns). Changes in temperatures are relative to 1961- 1990 averages. The scenarios come from the IPCC Special Report on Emissions Scenarios: B1 is a low emissions scenario, A1B is a medium-high emissions scenario, and A2 is a high emissions scenario. Source: IPCC Working Group I: The Physical Science Basis, 2007.

Changes in precipitation occur due to a variety of factors, including changes in atmospheric water vapor content due to changing temperature, as discussed above. Also at play is the heightened **evaporation** rate of water on Earth's surface under warmer temperatures. More evaporation leads to more precipitation. Finally, shifts in wind patterns impact the distribution of precipitation events. As you can see in Figure **12.4.5**, there are some areas of the globe that are expected to have an increase in precipitation, while others are expected to have a dramatic decrease. Some major population centers projected to have a moderate to severe precipitation increase include (population estimates of the metropolitan area given in parentheses): New York, United States (20.1 million); Bogotá, Colombia (12.1 m.); and Manila, Philippines (11.9 m.). What sort of challenges might these cities face in the future as they deal with this change in their climate?

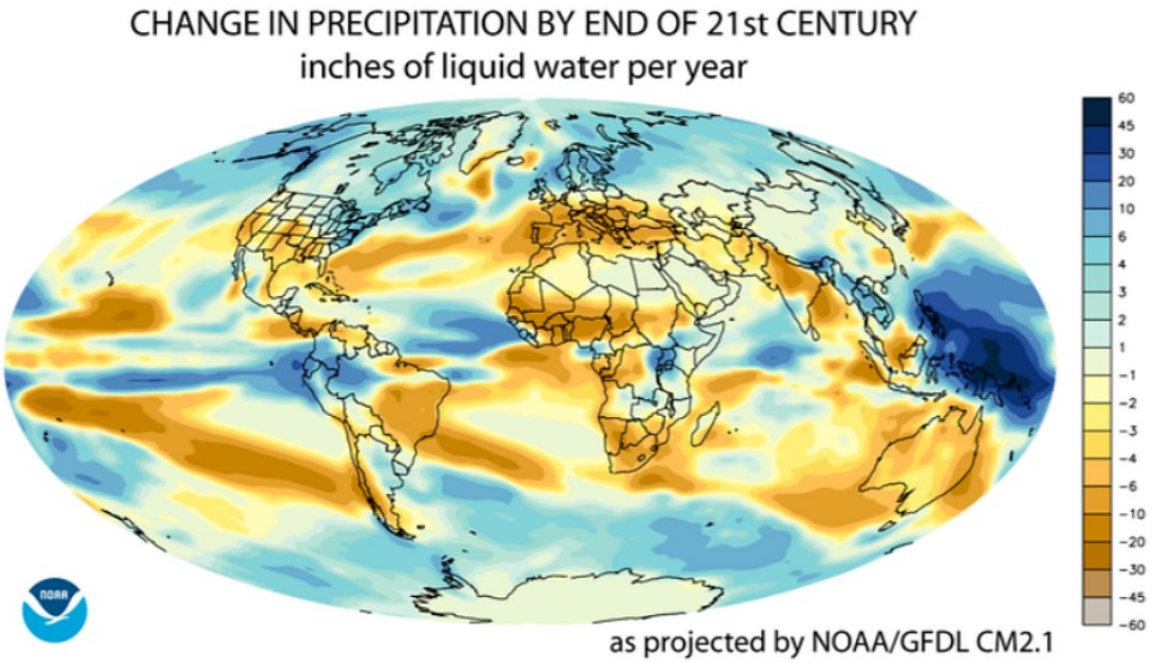


Figure **12.4.5** The plotted precipitation differences were computed as the difference between the 2081 to 2100 20-year averages minus the 1951 to 2000 50-year average. Blue areas project increases in precipitation; brown areas project decreases.

In contrast, many more major metropolitan areas are projected to have a moderate to severe precipitation decrease (droughts) by the end of the 21st century. These include Delhi, India (21.8 m.); Lagos, Nigeria (21 m.); São Paulo, Brazil (20.9 m.); Kolkata, India (14.6 m.); Istanbul, Turkey (14.4 m.); Los Angeles, United States (13.3 m.); Rio de Janeiro, Brazil (12 m.); Paris, France (12 m.); and Lahore, Pakistan (11.3 m.). The largest challenge that these areas are likely to face is a dwindling water supply for drinking and agriculture. See Chapter 8 for more detail on challenges faced by societies to supply clean, reliable water to their populations and farms.

Additional challenges may be felt by all areas of the world with regard to changes in the seasonality or timing of precipitation, as well the form in which precipitation falls (e.g., mist or downpour; rain, ice, or snow). All of these factors affect the availability of soil water for plants, the flow of rivers and streams, and the overall accessibility of water worldwide. Furthermore, scientists predict an increase in the number and severity of storms as climate change progresses. For a full discussion of the potential impacts of this, see the assigned article.

Sea level rise While we know that water continuously cycles around the world, and that the overall quantity of water on Earth will not change due to global climate change, the distribution of this water is changing. In particular, oceans are increasing in volume while land ice stores (such as **glaciers**) are decreasing. This contributes to an increase in sea level worldwide (Figure **12.4.6**).

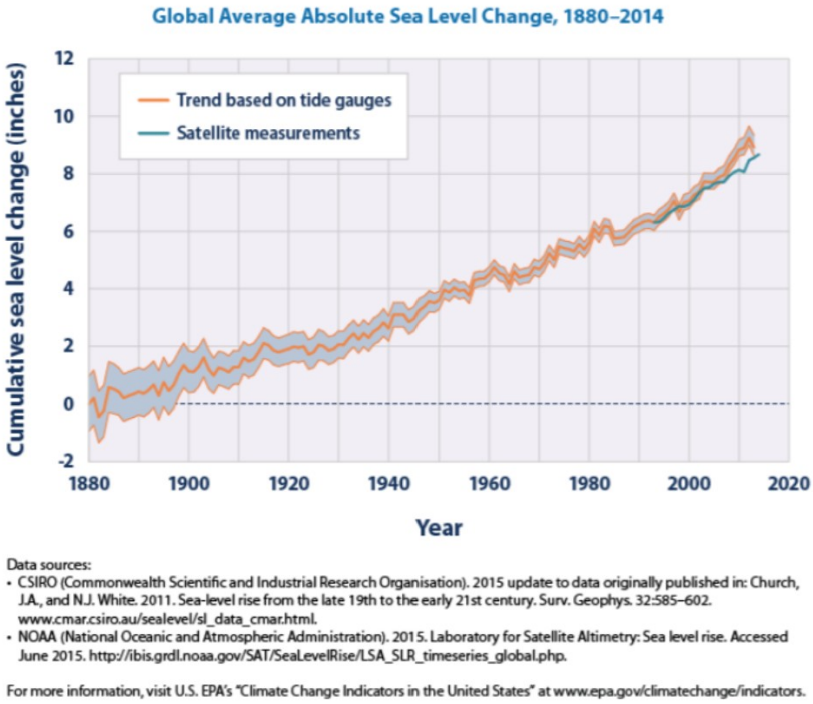


Figure **12.4.6**: *This graph shows average absolute cumulative changes in sea level for the world's oceans since 1880, based on a combination of tide gauge measurements and recent satellite measurements. The shaded band shows the likely range of values, based on the number of measurements collected and the precision of the methods used.*

From the data in Figure **12.4.6**, we see that sea level has increased at an average of 0.06 inches (0.15 cm) per year over the time period shown above. Most of this rise, however, has occurred within the most recent decades. The rate of increase has gone up to between 0.11 to 0.14 inches (0.28 to 0.36 cm) per year since 1993. There are two forces causing sea level to rise, both caused by climate change. First, the increased global temperature has caused increased ice melting in many regions of the globe. Melting **land ice** (such as the glacier shown in Figure **12.4.7**) contributes to sea level rise because water that used to be stored in ice sitting on top of land becomes running water which reaches the ocean through **runoff.** We also observe **sea ice** melting (see http://www.epa.gov/climatechange/sci ence/indicators/index.html for data and figures). Sea ice, such as the ice that covers the arctic regions of the Northern Hemisphere, has no land underneath it. When it melts, the water stays in the same locations, and the overall sea level does not change.



Figure 12.4.7: Glacier Retreat

The second factor that influences sea level rise is a phenomenon called thermal expansion. Due to the physical properties of water, as water warms, its density decreases. A less dense substance will have fewer molecules in a given area than a more dense substance (see Chapter 1 supplemental material). This means that as the overall temperature of the oceans increases due to global climate change, the same amount of water molecules will now occupy a slightly larger volume. This may not seem significant, but considering the 1.3 billion trillion liters (264 billion gallons) of water in the ocean, even a small change in density can have large effects on sea level as a whole.

Scientists have already documented sea level rise in some areas of the world, including one familiar to most of us: the Southeastern United States. Figure 12.4.8 depicts the measured land area lost due to increasing sea level since 1996. Note that the Southeast (defined here as the Atlantic coast of North Carolina south to Florida) is particularly susceptible to land area loss due to the gently sloping nature of our coastline. Moving northward into the Mid-Atlantic States (defined here as Virginia north to Long Island, New York), coastal habitats tend to have a steeper geography, which protects against some losses.

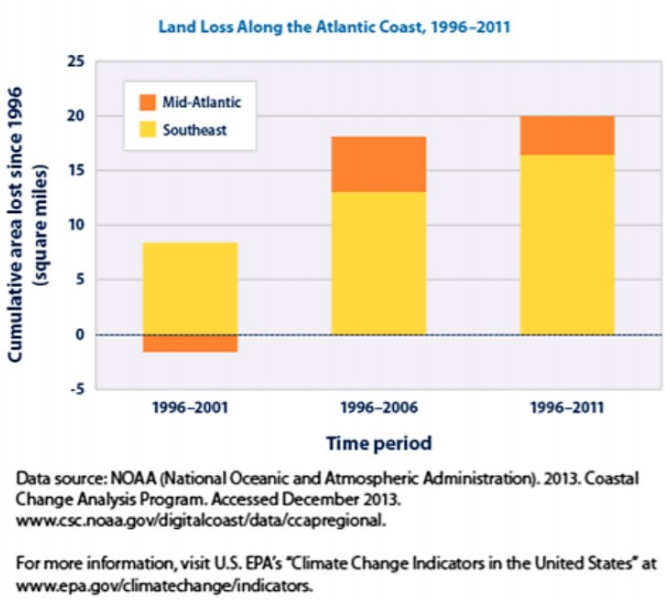


Figure 12.4.8: This graph shows the net amount of land converted to open water along the Atlantic coast during three time periods: 1996–2001, 1996–2006, and 1996–2011. The results are divided into two regions: the Southeast and the Mid-Atlantic. Negative numbers show where land loss is outpaced by the accumulation of new land.

While the ecological effects of sea level rise remain in the United States, we don't project any catastrophic loss of life, property, or livelihood for some time. This is, in part, due to large investments that we have made in infrastructure to protect our cities and farmlands. This is not the case in many areas of the world. For a discussion of the impacts of sea level rise on less industrialized nations of Bangladesh, Maldives, Kiribati, and Fiji, review the required article reading.

Ocean acidification

Dissolved CO_2 is essential for many organisms, including shell-building animals and other organisms that form a hard coating on their exterior (e.g., shellfish, corals, Haptophyte algae). This hard coating is built out of aragonite, a mineral form of the molecule calcium carbonate, $CaCO_3$. These organisms rely on the formation of carbonate ions (see Chapter 1 supplemental material for information on ions), CO_3^{2-}, from dissolved CO_2, through a natural, chemical reaction that occurs. This takes place through a chain-reaction equation, where bicarbonate (HCO_3^-) is formed as an intermediate, and hydrogen ions (H^+) are generated (equations 12.4.1 and 12.4.2).

$$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^-$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$$

To have a better visualization of this process, follow along with the interactive graphic at: http://www.whoi.edu/home/oceanus_ima...ification.html.

As you can see, both equations 12.4.1 and 12.4.2 each produce one H^+. This is significant to water chemistry because an increase in H+ concentration means a decrease in the pH of the water. You can see in Figure 12.4.9 that a lower pH means that the liquid is more acidic. As shown in the interactive graphic, an increase in CO_2 in the atmosphere causes additional CO_2 to be dissolved in the ocean. This means that more CO_2 in the atmosphere leads to more acidic ocean environments.

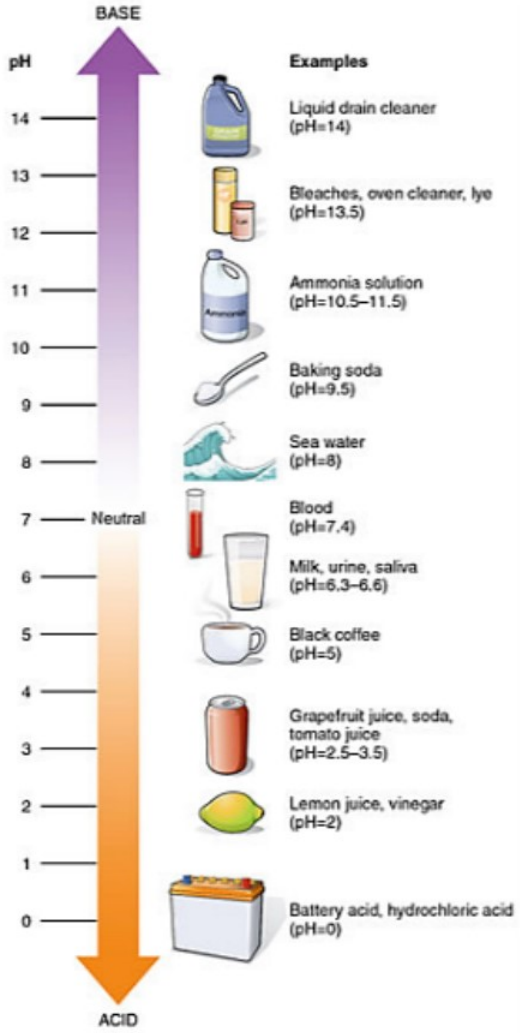


Figure **12.4.9**: The pH scale and relative acidity. Illustration from Anatomy & Physiology, Connexions Web site. http://cnx.org/content/col11496/1.6/, Jun 19, 2013.

Unfortunately for shell-building animals, the buildup of H^+ in the more acidic ocean environment blocks the absorption of calcium and CO_3^{2-}, and makes the formation of aragonite more difficult. An aragonite deficit is already being documented in many of the world's oceans, as shown in Figure **12.4.10**.

The increasing acidity of the world's oceans is resulting in habitat changes across the globe. This is only expected to worsen as atmospheric CO_2 levels continue to increase. Many organisms, including the corals that are the foundation species of the beautiful coral reefs, are very sensitive to changes in ocean pH. Scientists have documented cases of ecosystem destruction through coral bleaching, caused by the effects of climate change including ocean acidification and increased temperature. For more information, visit the NOAA Coral Reef Conservation Program website: coralreef.noaa.gov/threats/climate/.

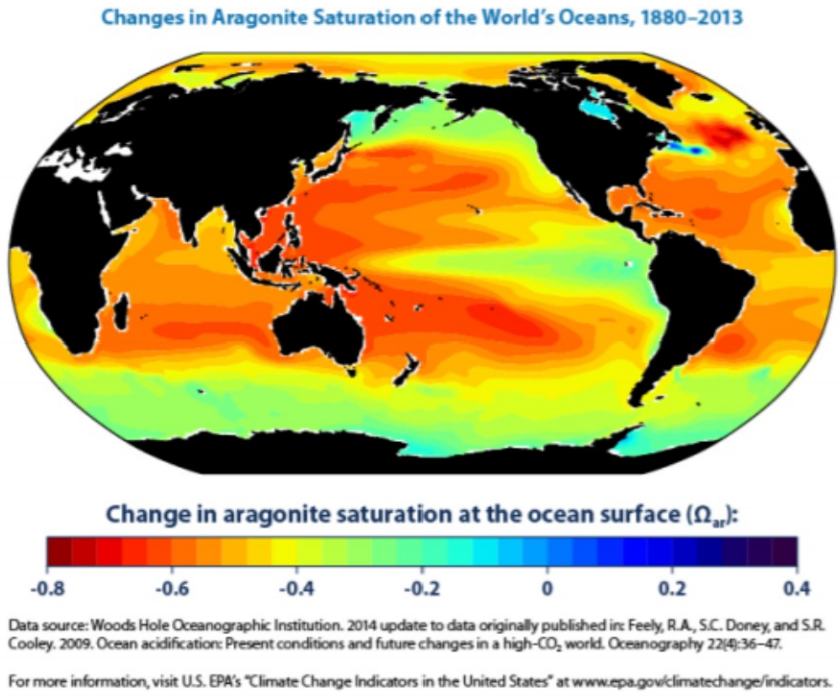


Figure **12.4.10**: This map shows changes in the aragonite saturation level of ocean surface waters between the 1880s and the most recent decade (2004–2013). Aragonite is a form of calcium carbonate that many marine animals use to build their skeletons and shells. A negative change represents a decrease in saturation.

Climate Strategies

While the situation surrounding global climate change is in serious need of our attention, it is important to realize that many scientists, leaders, and concerned citizens are making solutions to climate change part of their life's work. The two solutions to the problems caused by climate change are **mitigation** and **adaptation**, and we will likely need a combination of both in order to prosper in the future.

Adaptation strategies

We know that climate change is already occurring, as we can see and feel the effects of it. For this reason, it is essential to also adapt to our changing environment. This means that we must change our behaviors in response to the changing environment around us. Some adaptation strategies are discussed in the required article reading.

Adaption strategies will vary greatly by region, depending on the largest specific impacts in that area. For example, in the city of Delhi, India, a dramatic decrease in rainfall is projected over the next century (Figure 7.6.2). This city will likely need to implement policies and practices relating to conservation of water, for example: rainwater harvesting, water re-use, and increased irrigation efficiency. Rain-limited cities near oceans, such as Los Angeles, California may choose to use desalination to provide drinking water to their citizens. **Desalination** involves taking the salt out of seawater to make it potable (Chapter 14).

Cities with low elevations near oceans may need to implement adaptation strategies to rising sea levels, from seawalls and levees to relocation of citizens. One adaptations strategy gaining use is the creation or conservation of **wetlands**, which provide natural protection against storm surges and flooding.

Mitigation strategies

In general, a strategy to mitigate climate change is one that reduces the amount of greenhouse gases in the atmosphere or prevents additional emissions. Mitigations strategies attempt to "fix" the problems caused by climate change. Governmental regulations regarding fuel efficiency of vehicles is one example of an institutionalized mitigation strategy already in place in the United States and in many other countries around the world. Unlike some other countries, there are no **carbon taxes** or charges on burning fossil

fuels in the United States. This is another governmental mitigation strategy that has been shown to be effective in many countries including India, Japan, France, Costa Rica, Canada, and the United Kingdom.

In addition to government measures and incentives, technology can also be harnessed to mitigate climate change. One strategy for this is the use of **carbon capture and sequestration** (CCS). Through CCS, 80-90% of the CO_2 that would have been emitted to the atmosphere from sources such as a coal-fired power plant is instead captured and then stored deep beneath the Earth's surface. The CO_2 is often injected and sequestered hundreds of miles underground into porous rock formations sealed below an impermeable layer, where it is stored permanently (Figure 12.4.11).

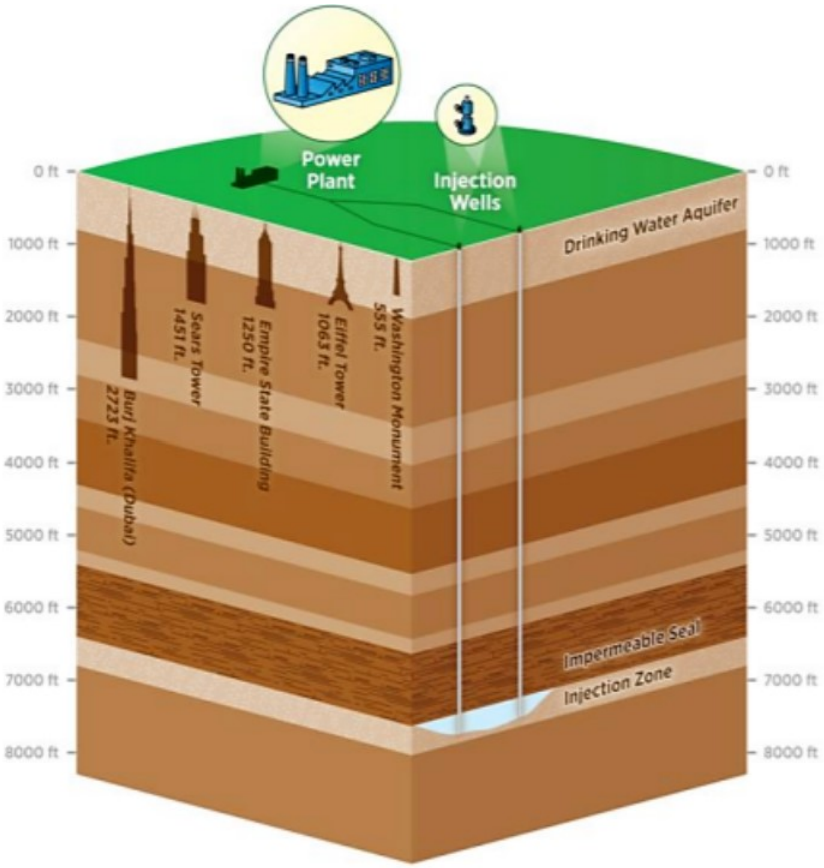


Figure 12.4.11: Carbon capture and sequestration schematic with landmarks shown to scale for depth reference. Source: US EPA.

Scientists are also looking into the use of soils and vegetation for carbon storage potential. Proper management of soil and forest ecosystems has been shown to create additional carbon sinks for atmospheric carbon, reducing the overall atmospheric CO_2 burden. Increasing soil carbon further benefits communities by providing better-quality soil for agriculture and cultivation.

Technologies related to alternative energy sources (Chapter 15) mitigate climate change by providing people with energy not derived from the combustion of fossil fuels. Finally, simple activities such as energy conservation, choosing to walk or bike instead of driving, and disposing of waste properly are activities that, when done by large numbers of people, actively mitigate climate change by preventing carbon emissions.

Take a moment to identify ways that you personally can be involved in the mitigation of or adaptation to climate change. What changes can you make in your own life to prevent excess carbon emissions? Similar to your ecological footprint, which you should have already calculated in lab, you can also calculate your carbon footprint. Use the EPA's carbon footprint calculator to do so, and investigate the Reduce Your Emissions section to find ways to decrease your carbon footprint.

Recommendations from the US Environmental Protection Agency

Figure 12.4.12 list various technologies and approaches that companies and individuals can adapt to reduce greenhouse gases. Technologies related to alternative energy sources mitigate climate change by providing people with energy not derived from the combustion of fossil fuels. Finally, simple activities such as energy conservation, choosing to walk or bike instead of driving, and disposing of waste properly are activities that, when done by large numbers of people, actively mitigate climate change by preventing carbon emissions.

Solutions for Transportation Air Pollution

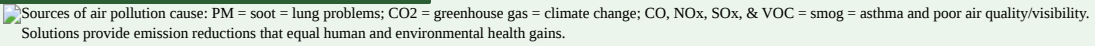


Figure 12.4.6 *Sources and solutions for transportation air pollution. Image: EPA*

Solutions for transportation air pollution, emission reductions, can lead to cleaner air and better health.

- Catalytic converters in conjunction with unleaded gasoline and low sulfur levels significantly reduce hydrocarbon and nitrogen oxide emissions.
- Fuel standards reduce exposure to pollutants like lead and benzene. Renewable fuels reduce CO_2 emissions.
- Engine technologies like computer controls, variable valve timing, multi-valve engines, turbo charging and gasoline direct injection improve fuel economy and reduce CO_2 emissions.
- Transmission technologies like 7+ speeds, dual clutch transmissions, (DCTs), and continuously variable transmissions (CVTs) improve fuel economy and reduce CO_2 emissions.
- Diesel filters reduce particulate matter from on road and off road diesel engines. Alternative vehicle technologies like plug-in electric vehicles and fuel cells equals zero tailpipe emissions.
- Better transportation planning for passengers and freight reduce emissions and fuel use.

Summary

- Gases that trap heat in the atmosphere are called greenhouse gases.
- The greenhouse effect is the process by which radiation from a planet's atmosphere warms the planet's surface to a temperature above what it would be without this atmosphere.
- Global warming refers to the increase in the average temperature of the Earth’s atmosphere due to elevated greenhouse gas concentrations, heightening the greenhouse effect.
- Climate change includes both global warming driven by human-induced emissions of greenhouse gasesand the resulting large-scale shifts in weather patterns.
- Greenhouse gases differ in their ability to produce the greenhouse effect as measured by the global warming potential, or GWP. A molecule of CH_4 is about 28 times more effective than one of CO_2 at absorbing infrared radiation, while N_2O is 298 times more effective . The synthetic fluorinated gases are evn much higher (in the thousands). This is largely due to their very long residence time in the atmosphere.

- Different technologies and approaches recommended by the US EPA to to reduce human greenhouse emmissions were provided.

Contributors and Attributions

- Marisa Alviar-Agnew (Sacramento City College)
- Libretext: Introduction to Environmental Science (Zendher et al.)
- US EPA
- Wikipedia

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12.5: Outdoor Air Pollution

Learning Objectives

- Define air pollution.
- Know the sources and effects of major outdoor pollutants

Air pollution refers to the introduction, into the atmosphere, of substances that have harmful effects on humans, other living organisms, and the environment either as solid particles, liquid droplets or gases. Air pollution can result from natural processes such as dust storms, forest fires, and volcanic eruptions, or from human activities such as biomass burning, vehicular emissions, mining, agriculture, and industrial processes. Improved technology and government policies have helped reduce most types of outdoor air pollution in many industrialized countries including the United States, in recent decades. However, outdoor air quality is still a problem in less industrialized nations, especially in megacities of rapidly industrializing nations such as China and India.

Outdoor pollutants can come from **stationary (point)** sources or **mobile (nonpoint)** sources (Figure 12.5.1). Stationary sources have a fixed location, for example power plant smokestacks, burning, construction sites, farmlands and surface mines among others. Mobile sources of air pollutants move from place to place while emitting pollutants. Examples of mobile sources include vehicles, aircrafts, ships, and trains.

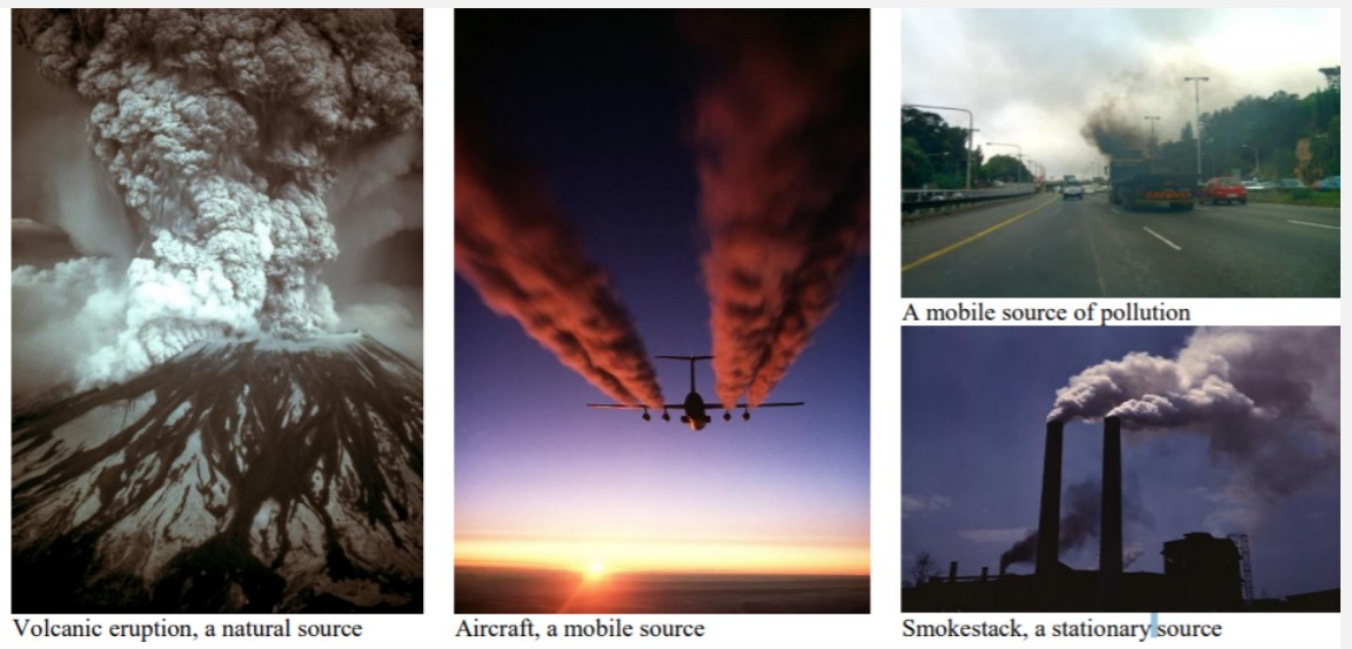


Figure 12.5.1: Images showing various sources of air pollution, including natural and anthropogenic, stationary and mobile. Source: All images obtained from Wiki Commons commons.wikimedia.org/wiki/Air_pollution

Pollutants are categorized into two major types based on how they originated namely primary and secondary pollutants. **Primary pollutants** are those released directly from the source into the air in a harmful form. The primary pollutants that account for nearly all air pollution problems are carbon monoxide (58%), volatile organic compounds (VOCs, 11%), nitrogen oxides (15%), sulfur dioxides (13%), and particulate material (3%). **Secondary pollutants** are produced through reactions between primary pollutants and normal atmospheric compounds. For example, ground-level ozone forms over urban areas through reactions, powered by sunlight, between primary pollutants (oxides of nitrogen) and other atmospheric gases such as VOCs.

Criteria pollutants

Under the Clean Air Act, the Environmental Protection Agency (EPA) establishes air quality standards to protect public health and the environment. EPA has set national air quality standards for six common air pollutants namely: 1) carbon monoxide; 2) ground-level ozone; 3) nitrogen dioxide; 4) Sulfur dioxide; 5) lead; and 6) particulate matter (also known as particle pollution). Of the six pollutants, particle pollution and ground-level ozone are the most widespread health threats. EPA calls these pollutants "criteria" air

pollutants because it regulates them by developing human health-based and/or environmentally-based criteria (science-based guidelines) for setting permissible levels. The set of limits based on human health is called primary standards. Another set of limits intended to prevent environmental and property damage is called secondary standards.

1. **Carbon Monoxide (CO)**: is a colorless, odorless gas emitted from combustion processes, specifically, the incomplete combustion of fuel. Nationally and, particularly in urban areas, the majority of CO emissions to ambient air come from mobile sources. CO can cause harmful health effects by reducing oxygen delivery to the body's organs (like the heart and brain) and tissues. At extremely high levels, CO can cause death.
2. **Ground-level ozone (O_3)**: is a colorless gas with a slightly sweet odor that is not emitted directly into the air, but is created by the interaction of sunlight, heat, oxides of nitrogen (NO_x) and volatile organic compounds (VOCs). Ozone is likely to reach unhealthy levels on hot sunny days in urban environments. Emissions from industrial facilities and electric utilities, motor vehicle exhaust, gasoline vapors, and chemical solvents are some of the major sources of NO_x and VOCs.
3. **Nitrogen dioxide (NO_2)**: is one of a group of highly reactive gasses known as "oxides of nitrogen," or "nitrogen oxides (NO_x)." Other nitrogen oxides include nitrous acid and nitric acid. NO_2 is a yellowish-brown to reddish-brown foul-smelling gas that is a major contributor to smog and acid rain. Nitrogen oxides result when atmospheric nitrogen and oxygen react at the high temperatures created by combustion engines. Most emissions in the U.S. result from combustion in vehicle engines, electrical utility, and industrial combustion.
4. **Sulfur dioxide (SO_2)**: Sulfur dioxide is one of a group of highly reactive gasses known as “oxides of sulfur.” The largest sources of SO_2 emissions are from fossil fuel combustion at power plants (73%) and other industrial facilities (20%). Smaller sources of SO_2 emissions include industrial processes such as extracting metals from their ores, and the burning of high sulfur containing fuels by locomotives, large ships, and non-road equipment.
5. **Lead (Pb)**: is a metal found naturally in the environment as well as in manufactured products. The major sources of lead emissions have historically been from fuels in motor vehicles (such as cars and trucks) and industrial sources. As a result of EPA's regulatory efforts to remove lead from gasoline, emissions of lead from the transportation sector dramatically declined by 95 percent between 1980 and 1999, and levels of lead in the air decreased by 94 percent during that time period. The major sources of lead emissions today are ore and metal processing and piston-engine aircraft operating on leaded aviation gasoline. Today, the highest levels of lead in air are usually found near lead smelters.
6. **Particulate material (PM)**, sometimes known simply as “**particulates**” refers to solid particles and liquid droplets suspended in the air we breathe. Particulate pollution is made up of a variety of components, including acids (nitrates and sulfates), organic chemicals, metals, soil or dust particles, and allergens (pollen and mold spores). The size of the particles in directly linked to their potential for causing health problems. Particles that are 10 micrometers in diameter or smaller generally pass through the throat and nose and enter the lungs. EPA groups these into two types: "**inhalable coarse particles**," with diameters larger than 2.5 micrometers and smaller than 10 micrometers and "**fine particles**," with diameters that are 2.5 micrometers and smaller. How small is 2.5 micrometers? Think about a single hair from your head. The average human hair is about 70 micrometers in diameter – making it 30 times larger than the largest fine particle (Figure 12.5.2). Our respiratory systems are equipped to filter larger particles out of the air once it is inhaled. However, the lungs are vulnerable to both coarse particles (PM_{10}), and fine particles ($PM_{2.5}$). These can slip past the respiratory system's natural defenses and get deep into the lungs and some may even get into the bloodstream. Coarse particles come from road dust while fine particles come from combustion processes.

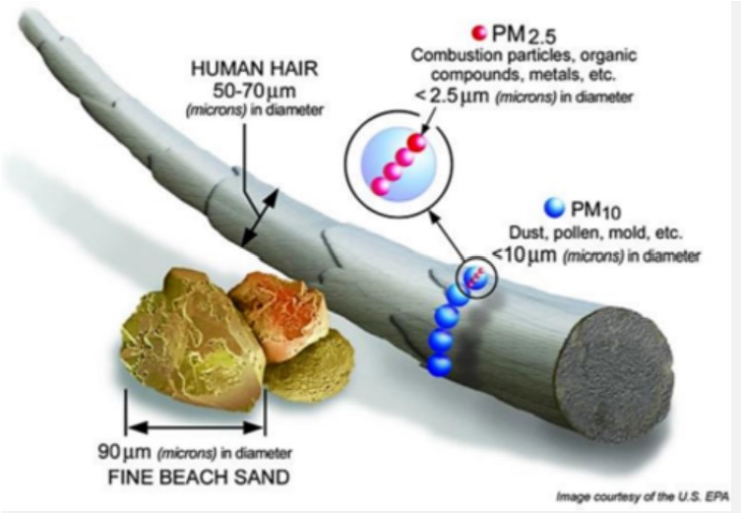


Figure **12.5.2** Graphic showing size comparison of particulate material (PM_{10} and $PM_{2.5}$) compared to fine beach sand and human hair. Source: US EPA http://www.epa.gov/air/particlepollution/basic.html

Volatile Organic Compounds

Volatile organic compounds (VOCs) are carbon-containing chemicals emitted as gases from natural and human-made sources. Natural sources of VOCs include plants, the largest source, and bacteria in the guts of termites and ruminant animals. These compounds are generally oxidized to carbon monoxide and carbon dioxide in the atmosphere. VOCs are of great concern because they are precursors for the formation of ozone, a secondary air pollutant.

A large number of synthetic organic chemicals such as benzene, toluene, formaldehyde, vinyl chloride, chloroform, and phenols are widely used as ingredients in countless household products. Paints, paint strippers, varnishes, many cleaning, disinfecting, cosmetic, degreasing, and hobby products all contain VOCs. Fuels are also made up of organic chemicals. All of these products can release organic compounds while you are using them, and, to some degree, when they are stored. The “new car smell” characteristic of new cars is from a complex mix of dozens of VOC. Also, concentrations of many VOCs are consistently higher indoors (up to ten times higher) than outdoors. They are often held responsible for sick building syndrome, an illness resulting from indoor pollution in which the specific cause is not identified.

Smog

Smog is a mixture of air pollutants (sulfur dioxide, nitrogen oxides, ozone, and particulates) that often form over urban areas as a result of fossil fuel combustion. The term was coined from the terms “smoke” and “fog” referring to a brownish haze that pollutes the air, greatly reducing visibility and making it difficult for some people to breathe (Figure **12.5.3** and **12.5.4**). There are two main types of smog: industrial and photochemical smog. **Industrial smog** is produced primarily by the burning of fossil fuels which produces carbon dioxide (from complete combustion), carbon monoxides (from partial combustion), sulfur, and mercury. The sulfur reacts with other chemicals in the atmosphere producing several sulfur compounds including sulfur dioxide. These compounds along with particulate material make up industrial smog. **Photochemical smog** is formed when sunlight drives chemical reactions between primary pollutants from automobiles and normal atmospheric compounds. The product is a mix of over 100 different chemicals with the most abundant being ground-level ozone. This type of smog will be discussed in more detail in section 13.5.



Figure 12.5.3: Smog over Almaty city, Kazakhstan. Photo by Igors Jefimovs. Source: Wikicommons commons.wikimedia.org/wiki/C...dia/File:Smog_ over_Almaty.jpg



Figure 12.5.4: Smog over Santiago in Chile. Source: German Wikipedia commons.wikimedia.org/wiki/C...#/media/File:Santiago30std.jpg

Industrial Smog

Industrial smog or London-type smog is mainly a product of burning large amounts of high sulfur coal. Clean air laws passed in 1956 have greatly reduced smog formation in the United Kingdom; however, in other parts of the world London-type smog is still very prevalent. The main constituent of London-type smog is soot; however, these smogs also contain large quantities of fly ash, sulfur dioxide, sodium chloride and calcium sulfate particles. If concentrations are high enough, sulfur dioxide can react with atmospheric hydroxide to produce sulfuric acid, which will precipitate as acid rain.

$$SO_2 + OH \rightarrow HOSO_2 \tag{12.5.1}$$

$$HOSO_2 + O_2 \rightarrow HO_2 + SO_3 \tag{12.5.2}$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \tag{12.5.3}$$

Concerns about the harmful effects of acid rain have led to strong pressure on industry to minimize the release of SO_2 and NO. For example, coal-burning power plants now use SO_2 "scrubbers," which trap SO_2 by its reaction with lime (CaO) to produce calcium sulfite dihydrate ($CaSO_3 \cdot 2H_2O$; Figure 12.5.5).

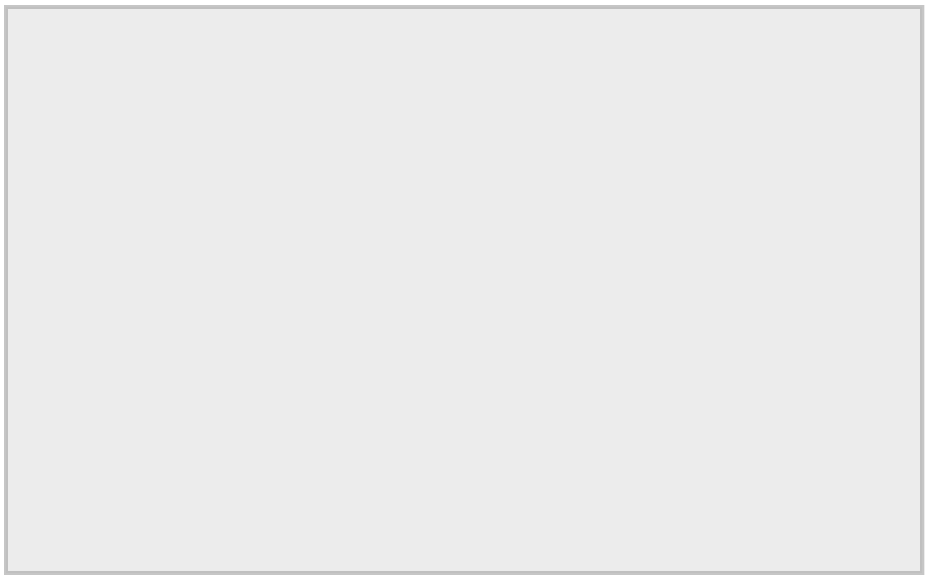


Figure 12.5.5: Schematic Diagram of a Wet Scrubber System. In coal-burning power plants, SO_2 can be removed ("scrubbed") from exhaust gases by its reaction with a lime (CaO) and water spray to produce calcium sulfite dihydrate ($CaSO_3 \cdot 2H_2O$). Removing SO_2 from the gases prevents its conversion to SO_3 and subsequent reaction with rainwater (acid rain). Scrubbing systems are now commonly used to minimize the environmental effects of large-scale fossil fuel combustion.

Toxic pollutants

Toxic air pollutants, also known as hazardous air pollutants, are those pollutants that are known or suspected to cause cancer or other serious health effects, such as reproductive effects or birth defects, or adverse environmental effects. Examples of toxic air pollutants include **benzene**, which is found in gasoline; **perchloroethylene,** which is emitted from some dry cleaning facilities; **methylene chloride**, which is used as a solvent and paint stripper by a number of industries; and others such as dioxin, asbestos, toluene, and metals such as cadmium, mercury, chromium, and lead compounds.

Most air toxics originate from human-made sources, including mobile sources (e.g., cars, trucks, buses) and stationary sources (e.g., factories, refineries, power plants), as well as indoor sources (e.g., some building materials and cleaning solvents). Some air toxics are also released from natural sources such as volcanic eruptions and forest fires. Exposure to air toxics is mainly through breathing but some toxic air pollutants such as mercury can deposit onto soils or surface waters, where they are taken up by plants and ingested by animals and are eventually magnified up through the food chain. Like humans, animals may experience health problems if exposed to sufficiently high quantities of air toxics over time.

Effects of Air Pollution on Human Health

The World Health Organization (WHO) and other international agencies recognize air pollution as a major threat to human health. Numerous scientific studies have linked air pollution to a variety of health problems (Table 12.5.1) including: aggravation of respiratory and cardiovascular diseases; decreased lung function; increased frequency and severity of respiratory symptoms such as difficulty breathing and coughing; increased susceptibility to respiratory infections; effects on the nervous system, including the brain, such as IQ loss and impacts on learning, memory, and behavior; cancer; and premature death. Immediate effects of air pollution may show up after a single exposure or repeated exposures. Other health effects may show up either years after exposure has occurred or only after long or repeated periods of exposure.

Immediate effects of air pollution include irritation of the eyes, nose, and throat, headaches, dizziness, and fatigue. Such immediate effects are usually short-term and treatable. Sometimes the treatment is simply eliminating the person's exposure to the source of the pollution, if it can be identified. Symptoms of some diseases, including asthma, hypersensitivity pneumonitis, and humidifier fever , may also show up soon after exposure to some indoor air pollutants.

Table 12.5.1: Sources and health effects of criteria pollutants

Pollutant	Sources	Health Effects
Ground-level Ozone (O_3)	Secondary pollutant typically formed by chemical reaction of volatile organic compounds (VOCs) and NO_x in the presence of sunlight.	Decreases lung function and causes respiratory symptoms, such as coughing and shortness of breath; aggravates asthma and other lung diseases leading to increased medication use, hospital admissions, emergency department (ED) visits, and premature mortality.
Particulate Matter (PM)	Emitted or formed through chemical reactions; fuel combustion (e.g., burning coal, wood, diesel); industrial processes; agriculture (plowing, field burning); and unpaved roads.	Short-term exposures can aggravate heart or lung diseases leading to respiratory symptoms, increased medication use, hospital admissions, ED visits, and premature mortality; long-term exposures can lead to the development of heart or lung disease and premature mortality.
Lead	Smelters (metal refineries) and other metal industries; combustion of leaded gasoline in piston engine aircraft; waste incinerators; and battery manufacturing.	Damages the developing nervous system, resulting in IQ loss and impacts on learning, memory, and behavior in children. Cardiovascular and renal effects in adults and early effects related to anemia.
Oxides of Nitrogen (NO_x)	Fuel combustion (e.g., electric utilities, industrial boilers, and vehicles) and wood burning.	Aggravate lung diseases leading to respiratory symptoms, hospital admissions, and ED visits; increased susceptibility to respiratory infection.
Carbon Monoxide (CO)	Fuel combustion (especially vehicles), industrial processes, fires, waste combustion, and residential wood burning.	Reduces the amount of oxygen reaching the body's organs and tissues; aggravates heart disease, resulting in chest pain and other symptoms leading to hospital admissions and ED visits.
Sulfur Dioxide (SO_2)	Fuel combustion (especially high-sulfur coal); electric utilities and industrial processes; and natural sources such as volcanoes.	Aggravates asthma and increased respiratory symptoms. Contributes to particle formation with associated health effects.

Source: www.epa.gov

The likelihood of immediate reactions to air pollutants depends on several factors. Age and preexisting medical conditions are two important influences. Some sensitive individuals appear to be at greater risk for air pollution-related health effects, for example, those with pre-existing heart and lung diseases (e.g., heart failure/ischemic heart disease, asthma, emphysema, and chronic bronchitis), diabetics, older adults, and children. In other cases, whether a person reacts to a pollutant depends on individual sensitivity, which varies tremendously from person to person. Some people can become sensitized to biological pollutants after repeated exposures, and it appears that some people can become sensitized to chemical pollutants as well.

Summary

- Air pollution refers to the introduction, into the atmosphere, of substances that have harmful effects on humans, other living organisms, and the environment either as solid particles, liquid droplets or gases.
- Major sources of air pollution are gas emissions from fossil fueled vehicles and their reaction products (CO, NO_x, Ozone) as well as particulate matter, SO_2, and VOCs.

- Examples of toxic air pollutants include benzene, which is found in gasoline; perchloroethylene, which is emitted from some dry cleaning facilities; methylene chloride, which is used as a solvent and paint stripper by a number of industries; and others such as dioxin, asbestos, toluene, and metals such as cadmium, mercury, chromium, and lead compounds.
- Smog is a mixture of air pollutants (sulfur dioxide, nitrogen oxides, ozone, and particulates) that often form over urban areas as a result of fossil fuel combustion. The term was coined from the terms “smoke” and “fog” referring to a brownish haze that pollutes the air, greatly reducing visibility and making it difficult for some people to breathe.
- Numerous scientific studies have linked air pollution to a variety of health problems.

Contributors and Attributions

- Libretext: Introduction to Environmental Science (Zendher et al.)
- TextMap: General CHemistry (Averill and Eldredge)
- Marisa Alviar-Agnew (Sacramento City College)
- Wikipedia

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12.6: Automobile Emissions

Learning Objective

- Identify the different pollutant gases in automobile emissions.

Exhaust gas or flue gas is emitted as a result of the combustion of fuels such as natural gas, gasoline, petrol, biodiesel blends, diesel fuel, fuel oil, or coal. It is a major component of motor vehicle emissions (and from stationary internal combustion engines), which can also include:

- Crankcase blow-by
- Evaporation of unused gasoline

Motor vehicle emissions contribute to air pollution and are a major ingredient in the creation of smog in some large cities. A 2013 study by MIT indicates that 53,000 early deaths occur per year in the United States alone because of vehicle emissions.

Carbon monoxide and nitrogen oxides are the two main pollutant gases from automobile emissions. Ozone is a result of the reaction between nitrogen oxides and volatile organic compounds (VOCs).

Carbon Monoxide

Carbon Monoxide (CO) is a colorless, odorless gas that can be harmful when inhaled in large amounts. CO is released when something is burned. The greatest sources of CO to outdoor air are cars, trucks and other vehicles or machinery that burn fossil fuels. A variety of items in your home such as unvented kerosene and gas space heaters, leaking chimneys and furnaces, and gas stoves also release CO and can affect air quality indoors.

Harmful effects

Breathing air with a high concentration of CO reduces the amount of oxygen that can be transported in the blood stream to critical organs like the heart and brain.

At very high levels, which are possible indoors or in other enclosed environments, CO can cause dizziness, confusion, unconsciousness and death.

Very high levels of CO are not likely to occur outdoors. However, when CO levels are elevated outdoors, they can be of particular concern for people with some types of heart disease. These people already have a reduced ability for getting oxygenated blood to their hearts in situations where the heart needs more oxygen than usual. They are especially vulnerable to the effects of CO when exercising or under increased stress. In these situations, short-term exposure to elevated CO may result in reduced oxygen to the heart accompanied by chest pain also known as angina.

Nitrogen Oxides

Nitrogen dioxide (NO_2) is one of a group of highly reactive gasses known as "oxides of nitrogen," or "nitrogen oxides (NO_x)." Other nitrogen oxides include nitrous acid and nitric acid. NO_2 is a yellowish-brown to reddish-brown foul-smelling gas that is a major contributor to smog and acid rain. Nitrogen oxides result when atmospheric nitrogen and oxygen react at the high temperatures created by combustion engines. Most emissions in the U.S. result from combustion in vehicle engines, electrical utility, and industrial combustion.

NO_2 primarily gets in the air from the burning of fuel. NO_2 forms from emissions from cars, trucks and buses, power plants, and off-road equipment.

Health effects

Breathing air with a high concentration of NO_2 can irritate airways in the human respiratory system. Such exposures over short periods can aggravate respiratory diseases, particularly asthma, leading to respiratory symptoms (such as coughing, wheezing or difficulty breathing), hospital admissions and visits to emergency rooms. Longer exposures to elevated concentrations of NO_2 may contribute to the development of asthma and potentially increase susceptibility to respiratory infections. People with asthma, as well as children and the elderly are generally at greater risk for the health effects of NO_2.

NO_2 along with other NO_x reacts with other chemicals in the air to form both particulate matter and ozone. Both of these are also harmful when inhaled due to effects on the respiratory system.

Environmental effects

NO_2 and other NO_x interact with water, oxygen and other chemicals in the atmosphere to form acid rain. Acid rain harms sensitive ecosystems such as lakes and forests.

The nitrate particles that result from NO_x make the air hazy and difficult to see though. This affects the many national parks that we visit for the view. NO_x in the atmosphere contributes to nutrient pollution in coastal waters.

Ozone

Ground-level ozone (O_3) is a colorless gas with a slightly sweet odor that is not emitted directly into the air, but is created by the interaction of sunlight, heat, oxides of nitrogen (NO_x) and volatile organic compounds (VOCs). Ozone is likely to reach unhealthy levels on hot sunny days in urban environments. Emissions from industrial facilities and electric utilities, motor vehicle exhaust, gasoline vapors, and chemical solvents are some of the major sources of NO_x and VOCs.

Ozone is a gas composed of three atoms of oxygen (O_3). Ozone occurs both in the Earth's upper atmosphere and at ground level. Ozone can be good or bad, depending on where it is found.

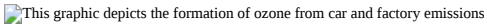
Called stratospheric ozone, good ozone occurs naturally in the upper atmosphere, where it forms a protective layer that shields us from the sun's harmful ultraviolet rays. This beneficial ozone has been partially destroyed by manmade chemicals, causing what is sometimes called a "hole in the ozone." The good news is, this hole is diminishing.

Ozone at ground level is a harmful air pollutant, because of its effects on people and the environment, and it is the main ingredient in “smog."

How does ground-level ozone form?

Tropospheric, or ground level ozone, is not emitted directly into the air, but is created by chemical reactions between oxides of nitrogen (NOx) and volatile organic compounds (VOC). This happens when pollutants emitted by cars, power plants, industrial boilers, refineries, chemical plants, and other sources chemically react in the presence of sunlight.

Ozone is most likely to reach unhealthy levels on hot sunny days in urban environments, but can still reach high levels during colder months. Ozone can also be transported long distances by wind, so even rural areas can experience high ozone levels.


This graphic depicts the formation of ozone from car and factory emissions

Health effects

Ozone in the air we breathe can harm our health especially on hot sunny days when ozone can reach unhealthy levels. People most at risk from breathing air containing ozone include people with asthma, children, older adults, and people who are active outdoors, especially outdoor workers.

Environmental effects

Ozone affects sensitive vegetation and ecosystems, including forests, parks, wildlife refuges and wilderness areas. In particular, ozone harms sensitive vegetation during the growing season.

Summary

- Carbon monoxide and nitrogen oxides are the two main compounds from automobile emissions.
- Ozone but is created by chemical reactions between oxides of nitrogen (NOx) and volatile organic compounds (VOC).
- Different levels of exposure to automobile emissions and ozone can lead to various health problems.

Contributor

- US Environmental Protection Agency
- Marisa Alviar-Agnew (Sacramento City College)

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12.7: Photochemical Smog- Making Haze While the Sun Shines

Learning Objectives

- Describe photochemical smog.
- List different means to address photochemical smog.

Photochemical smog is a type of air pollution due to the reaction of solar radiation with airborne pollutant mixtures of nitrogen oxides (NOx) and volatile organic compounds (hydrocarbons). Smog is a byproduct of modern industrialization. Due to industry and the number of motor vehicles, this is more of a problem in large cities that have a warm, sunny and dry climate.

- **Oxidation**: Photochemical smog is also referred to as oxidizing smog. Oxidation reactions have been defined several ways. In terms of oxygen transfer, oxidation is a gain of oxygen. Oxidation can also be defined as a loss of hydrogen. The most important use of oxidation is described in terms of electron transfer. Oxidation can be described as an increase in oxidation number or loss of electrons. Oxidation numbers represents a distribution of charge. In other words, oxidation numbers represent the charge of the atom if the compound was composed of ions.
- **Reduction**: Reduction can involve the gain of hydrogen or loss of oxygen. Reduction can refer to the gain of electrons, which results in a decrease in oxidation number.

Formation of Photochemical Smog

The different reactions involved in the formation of photochemical smog are given below.

Step 1: People begin driving in the morning, nitrogen is burned or oxidized

$$N_2 + O_2 \rightarrow 2NO$$

- Oxidation number of N_2 is 0. The nitrogen in NO has acquired an oxidation number of +2.

Step 2: After a few hours, NO combines with O_2, in another oxidation reaction

$$2NO + O_2 \rightarrow 2NO_2$$

- The nitrogen in NO has an oxidation number of +2. The nitrogen in NO_2 has an oxidation number of +4.

Step 3: Nitrogen dioxide absorbs light energy, resulting in a reduction reaction

$$NO_2 \rightarrow NO + O$$

- The nitrogen in NO_2 has an oxidation number of +4 and the nitrogen in NO is +2.

Step 4: In sunlight, atomic oxygen combines with oxygen gas to form ozone

$$O + O_2 \rightarrow O_3$$

Step 5: Reaction is temperature and sunlight dependent

$$O_3 + NO \rightleftharpoons NO_2 + O_2$$

Alternative Reactions

NO and NO_2 can also react with the hydrocarbons instead of ozone to form other volatile compounds known as PAN (peroxyacetyl nitrate) as shown in Figure . The accumulation of ozone and volatile organic compounds along with the energy from the sun forms the brown, photochemical smog seen on hot, sunny days. Panoramic view of Santiago covered by a layer of smog on May 10, 2006. The Metropolitan Region of Santiago facing the driest autumn last 28 years due to lack of rainfall, which coupled with poor air circulation, causes an increase in smog.

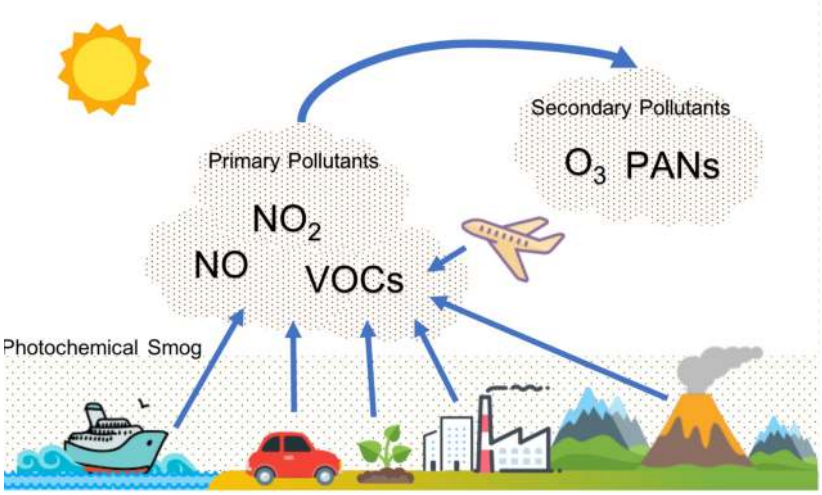


Figure **12.7.1** The photochemical smog formation diagram. Source: Wikipedia

Health Hazards

Because ozone is highly reactive, it has the ability to oxidize and destroy lung tissue. Short term exposures to elevated levels of ozone (above .75 ppm) have been linked to a host of respiratory irritations including coughing, wheezing, substernal soreness, pharyngitis, and dyspnea. Prolonged exposure to the molecule has been proven to cause a permanent reduction in lung function, as well as elevate the risk of developing asthma. Sulfur dioxide is a common component of London smog. Epidemiological studies have linked short term sulfur dioxide exposure to respiratory irritations including coughing, wheezing, and pharyngitis.

Other Harmful Effects of Smog

Plants are harmed by exposure to nitrogen oxides, ozone, and peroxyacetyl nitrate (PAN, see above), all oxidants present in a smoggy atmosphere. PAN is the most harmful of these constituents, damaging younger plant leaves, especially. Ozone exposure causes formation of yellow spots on leaves, a condition called chlorotic stippling. Some plant species, including sword-leaf lettuce, black nightshade, quickweed, and double-fortune tomato, are extremely susceptible to damage by oxidant species in smog and are used as bioindicators of the presence of smog. Costs of crop and orchard damage by smog run into millions of dollars per year in areas prone to this kind of air pollution, such as southern California.

Materials that are adversely affected by smog are generally those that are attacked by oxidants. The best example of such a material is rubber, especially natural rubber, which is attacked by ozone. Indeed, the hardening and cracking of natural rubber has been used as a test for atmospheric ozone.

Visibility-reducing atmospheric aerosol particles are the most common manifestation of the harm done to atmospheric quality by smog. The smog-forming process occurs by the oxidation of organic materials in the atmosphere, and carbon-containing organic materials are the most common constituents of the aerosol particles in an atmosphere afflicted by smog. Conifer trees(pine and cypress) and citrus trees are major contributors to the organic hydrocarbons that are precursors to organic particle formation in smog.

Controlling Photochemical Smog

Every new vehicle sold in the United States must include a catalytic converter to reduce photochemical emissions. Catalytic converters force CO and incompletely combusted hydrocarbons to react with a metal catalyst, typically platinum, to produce CO_2 and H_2O. Additionally, catalytic converters reduce nitrogen oxides from exhaust gases into O_2 and N_2, eliminating the cycle of ozone formation. Many scientists have suggested that pumping gas at night could reduce photochemical ozone formation by limiting the amount of exposure VOCs have with sunlight.

Preventing Smog with Green Chemistry

Smog is basically a chemical problem, which would indicate that it should be amenable to chemical solutions. Indeed, the practice of green chemistry and the application of the principles of industrial ecology can help to reduce smog. This is due in large part to

the fact that a basic premise of green chemistry is to avoid the generation and release of chemical species with the potential to harm the environment. The best way to prevent smog formation is to avoid the release of nitrogen oxides and organic vapors that enable smog to form. At an even more fundamental level, measures can be taken to avoid the use of technologies likely to release such substances, for example, by using alternatives to polluting automobiles for transportation.

The evolution of automotive pollution control devices to reduce smog provides an example of how green chemistry can be used to reduce pollution. The first measures taken to reduce hydrocarbon and nitrogen oxide emissions from automobiles were very much command-and-control and “end-of-pipe” measures. These primitive measures implemented in the early 1970s did reduce emissions, but with a steep penalty in fuel consumption and in driving performance of vehicles. However, over the last three decades, the internal combustion automobile engine has evolved into a highly sophisticated computer-controlled machine that generally performs well, emits few air pollutants, and is highly efficient. (And it would be much more efficient if those drivers who feel that they must drive “sport utility” behemoths would switch to vehicles of a more sensible size.) This change has required an integrated approach involving reformulation of gasoline. The first major change was elimination from gasoline of tetraethyllead, an organometallic compound that poisoned automotive exhaust catalysts (and certainly was not good for people). Gasoline was also reformulated to eliminate excessively volatile hydrocarbons and unsaturated hydrocarbons (those with double bonds between carbon atoms) that are especially reactive in forming photochemical smog.

An even more drastic approach to eliminating smog-forming emissions is the use of electric automobiles that do not burn gasoline. These vehicles certainly do not pollute as they are being driven, but they suffer from the probably unsolvable problem of a very limited range between charges and the need for relatively heavy batteries. However, hybrid automobiles using a small gasoline or diesel engine that provides electricity to drive electric motors propelling the automobile and to recharge relatively smaller batteries can largely remedy the emission and fuel economy problems with automobiles. The internal combustion engine on these vehicles runs only as it is needed to provide power and, in so doing, can run at a relatively uniform speed that provides maximum economy with minimum emissions.

Another approach that is being used on vehicles as large as buses that have convenient and frequent access to refueling stations is the use of fuel cells that can generate electricity directly from the catalytic combination of elemental hydrogen and oxygen, producing only harmless water as a product . There are also catalytic process that can generate hydrogen from liquid fuels, such as methanol, so that vehicles carrying such a fuel can be powered by electricity generated in fuel cells.

Green chemistry can be applied to devices and processes other than automobiles to reduce smog-forming emissions. This is especially true in the area of organic solvents used for parts cleaning and other industrial operations, vapors of which are often released to the atmosphere. The substitution of water with proper additives or even the use of supercritical carbon dioxide fluid can eliminate such emissions.

Summary

- Photochemical smog is a mixture of pollutants that are formed (mostly during the hot summer months) when nitrogen oxides and volatile organic compounds (VOCs) react to sunlight, creating a brown haze above cities.
- Photochemical smog is formed from the reactions of natural and man-made emissions of nitrogen oxides and VOCs.
- Smog is a serious problem in many cities and continues to harm human health and are especially harmful for senior citizens, children, and people with heart and lung conditions such as emphysema, bronchitis, and asthma.
- Catalytic converters in gas powered vehicles help reduce photochemical emissions.
- The practice of green chemistry and the application of the principles of industrial ecology can help to reduce smog.

Contributors and Attributions

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12.8: Acid Rain- Air Pollution Water Pollution

Learning Objective

- Describe acid rain and its effects.

Acid rain is a term referring to a mixture of wet and dry deposition (deposited material) from the atmosphere (Figure **12.8.1**) containing higher than normal amounts of nitric and sulfuric acids. The precursors, or chemical forerunners, of acid rain formation result from both natural sources, such as volcanoes and decaying vegetation, and man-made sources, primarily emissions of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) resulting from fossil fuel combustion. Acid rain occurs when these gases react in the atmosphere with water, oxygen, and other chemicals to form various acidic compounds. The result is a mild solution of sulfuric acid and nitric acid.

$$SO_2 + HOH \rightarrow H_2SO_3 \tag{12.8.1}$$

$$2NO_2 + HOH \rightarrow HNO_2 + HNO_3 \tag{12.8.2}$$

When sulfur dioxide and nitrogen oxides are released from power plants and other sources, *prevailing winds* blow these compounds across state and national borders, sometimes over hundreds of miles.

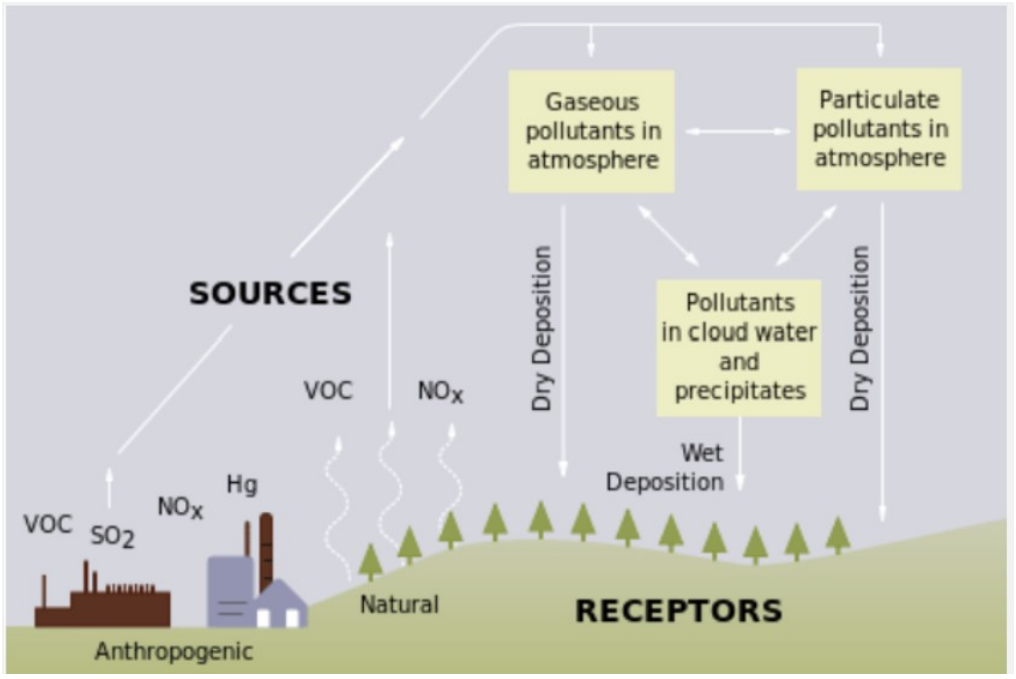


Figure **12.8.1** Processes involved in acid deposition.

Acid rain is measured using a scale called “pH.” The lower a substance’s pH, the more acidic it is. Pure water has a pH of 7.0. However, normal rain is slightly acidic because carbon dioxide (CO_2) dissolves into it forming weak carbonic acid, giving the resulting mixture a pH of approximately 5.6 at typical atmospheric concentrations of CO_2. As of 2000, the most acidic rain falling in the U.S. has a pH of about 4.3.

Effects of Acid Rain

Acid rain causes **acidification** of lakes and streams and contributes to the damage of trees at high elevations (for example, red spruce trees above 2,000 feet) and many sensitive forest soils. In addition, acid rain accelerates the decay of building materials and paints, including irreplaceable buildings, statues, and sculptures that are part of our nation’s cultural heritage. Prior to falling to the earth, sulfur dioxide (SO_2) and nitrogen oxide (NO_x) gases and their particulate matter derivatives—sulfates and nitrates—contribute to visibility degradation and harm public health.

The **ecological** effects of acid rain are most clearly seen in the aquatic, or water, environments, such as streams, lakes, and marshes. Most lakes and streams have a pH between 6 and 8, although some lakes are naturally acidic even without the effects of acid rain. Acid rain primarily affects sensitive bodies of water, which are located in watersheds whose soils have a limited ability to neutralize acidic compounds (called “buffering capacity”). Lakes and streams become acidic (i.e., the pH value goes down) when the water itself and its surrounding soil cannot buffer the acid rain enough to neutralize it. In areas where buffering capacity is low, acid rain releases aluminum from soils into lakes and streams; aluminum is highly toxic to many species of aquatic organisms. Acid rain causes slower growth, injury, or death of forests as shown in Figure **12.8.2**. Of course, acid rain is not the only cause of such conditions. Other factors contribute to the overall stress of these areas, including air pollutants, insects, disease, drought, or very cold weather. In most cases, in fact, the impacts of acid rain on trees are due to the combined effects of acid rain and these other environmental stressors.



Figure **12.8.2**. Acid rain damage to a forest in the Czech Republic.

Acid rain and the dry deposition of acidic particles contribute to the corrosion of **metals**(such as bronze).

The damage that acid rain does to limestone and marble buildings and sculptures is due to a classic acid–base reaction. Marble and limestone both consist of calcium carbonate ($CaCO_3$), a salt derived from the weak acid H_2CO_3. The reaction of a strong acid with a salt of a weak acid goes to completion. Thus we can write the reaction of limestone or marble with dilute sulfuric acid as follows:

$$CaCO_{3(s)} + H_2SO_{4(aq)} \rightarrow CaSO_{4(s)} + H_2O_{(l)} + CO_{2(g)} \tag{12.8.3}$$

Because $CaSO_4$ is sparingly soluble in water, the net result of this reaction is to dissolve the marble or limestone.

These effects significantly reduce the societal value of buildings, bridges, cultural objects (such as statues, monuments, and tombstones), and cars (Figure **12.8.3**).



Figure **12.8.3**. A gargoyle that has been damaged by acid rain.

Sulfates and nitrates that form in the atmosphere from sulfur dioxide (SO_2) and nitrogen oxides (NO_x) emissions contribute to **visibility impairment,** meaning we cannot see as far or as clearly through the air. The pollutants that cause acid rain—sulfur dioxide (SO_2) and nitrogen oxides (NO_x)—damage **human health**. These gases interact in the atmosphere to form fine sulfate and nitrate particles that can be transported long distances by winds and inhaled deep into people's lungs. Fine particles can also penetrate indoors. Many scientific studies have identified a relationship between elevated levels of fine particles and increased illness and premature death from heart and lung disorders, such as asthma and bronchitis.

Summary

- Acid rain is a term referring to a mixture of wet and dry deposition (deposited material) from the atmosphere containing higher than normal amounts of nitric and sulfuric acids.
- Acidic rain water in the soil, streams, lakes, and marshes (and other bodies of water) can be harmful to trees, plants, animals, especially aquatic plants and animals.
- Acid rain and the dry deposition of acidic particles contribute to the corrosion of **metals**(such as bronze) and the deterioration of paint and stone (such as marble and limestone).

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12.9: Indoor Air Pollution

Learning Objectives

- Name the different indoor pollutants and their sources.
- Know the harmful effects of indoor pollutants.

In both developed and developing nations, indoor air pollution poses a greater health risk than outdoor air pollution. According to the World Health Organization (WHO) and other agencies such as the Environmental Protection Agency (EPA), indoor air generally contains higher concentrations of toxic pollutants than outdoor air. Additionally, people generally spend more time indoors than outdoors, hence, the health effects from indoor air pollution in workplaces, schools, and homes are far greater than outdoor. Indoor pollution sources that release gases or particles into the air are the primary cause of indoor air quality problems in homes. Inadequate ventilation can increase indoor pollutant levels by not bringing in enough outdoor air to dilute emissions from indoor sources and by not carrying indoor air pollutants out of the home.

Outdoor air enters and leaves a building by infiltration, natural ventilation, and mechanical ventilation. In infiltration, outdoor air flows into the house through openings, joints, and cracks in walls, floors, and ceilings, and around windows and doors. In natural ventilation, air moves through opened windows and doors. Air movement associated with infiltration and natural ventilation is caused by air temperature differences between indoors and outdoors and by wind. Finally, there are a number of mechanical ventilation devices, from outdoor-vented fans that intermittently remove air from a single room, such as bathrooms and kitchen, to air handling systems that use fans and duct work to continuously remove indoor air and distribute filtered and conditioned outdoor air to strategic points throughout the house. The rate at which outdoor air replaces indoor air is described as the air exchange rate. When there is little infiltration, natural ventilation, or mechanical ventilation, the air exchange rate is low and pollutant levels can increase. High temperature and humidity levels can also increase concentrations of some pollutants.

There are many sources of indoor air pollution in any home (Figure **12.9.1**). These include combustion sources such as oil, gas, kerosene, coal, wood, and tobacco products; building materials and furnishings as diverse as deteriorated, asbestos-containing insulation, wet or damp carpet, and cabinetry or furniture made of certain pressed wood products; products for household cleaning and maintenance, personal care, or hobbies; central heating and cooling systems and humidification devices. Pollutants causing indoor air pollution can also originate from outside sources such as radon, pesticides, and outdoor air pollution. Radon is a naturally occurring radioactive gas produced from the decay of uranium in rock. If a building/home is constructed in an area with uranium containing rock, the gas can seep through the foundations and accumulate in basements. Exposure to radon can cause lung cancer.

The relative importance of any single source depends on how much of a given pollutant it emits and how hazardous those emissions are. In some cases, factors such as how old the source is and whether it is properly maintained are significant. For example, an improperly adjusted gas stove can emit significantly more carbon monoxide than one that is properly adjusted. Some sources, such as building materials, furnishings, and household products like air fresheners, release pollutants more or less continuously. Other sources, related to activities carried out in the home, release pollutants intermittently. These include smoking, the use of unvented or malfunctioning stoves, furnaces, or space heaters, the use of solvents in cleaning and hobby activities, the use of paint strippers in redecorating activities, and the use of cleaning products and pesticides in house-keeping. High pollutant concentrations can remain in the air for long periods after some of these activities.

Risks from indoor air pollution differ between less industrialized and industrialized nations. Indoor pollution has a greater impact in less industrialized nations where many people use cheaper sources of fuel such as wood, charcoal, and crop waste among others for cooking and heating, often with little or no ventilation. The most significant indoor pollutant, therefore, is soot and carbon monoxide. In industrialized nations, the primary indoor air health risks are cigarette smoke and radon.

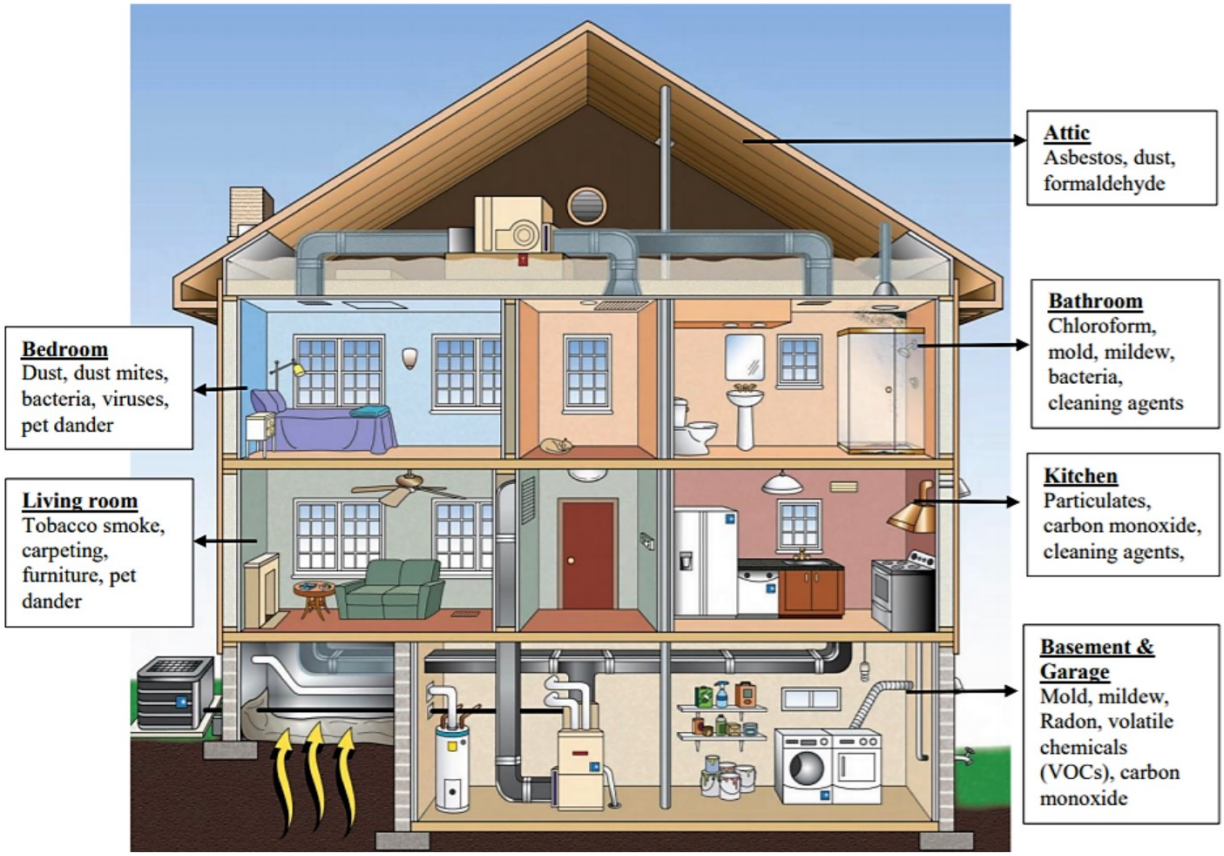


Figure 12.9.1: Sources of indoor air pollution. Image source: EPA http://www.epa.gov/iaq/pdfs/careforyourair.pdf

Combustion Pollutants

Combustion pollutants are gases or particles that come from burning materials. In homes, the major source of combustion pollutants are improperly vented or unvented fuel-burning appliances such as space heaters, wood stoves, gas stoves, water heaters, dryers, and fireplaces. The types and amounts of pollutants produced depends on the type of appliance, how well the appliance is installed, maintained and vented and the kind of fuel it uses. Common combustion pollutants include:

Carbon monoxide (CO) which is a colorless, odorless gas that interferes with the delivery of oxygen throughout the body. Carbon monoxide causes headaches, dizziness, weakness, nausea and even death. Average levels in homes without gas stoves vary from 0.5 to 5 parts per million (ppm). Levels near properly adjusted gas stoves are often 5 to 15 ppm and those near poorly adjusted stoves may be 30 ppm or higher.

Nitrogen dioxide (NO_2) which is a colorless, odorless gas that causes eye, nose and throat irritation, shortness of breath, and an increased risk of respiratory infection. Average level in homes without combustion appliances is about half that of outdoors. In homes with gas stoves, kerosene heaters or un-vented gas space heaters, indoor levels often exceed outdoor levels.

Particulate Matter (PM) which refers to fine particles that forms in smoke when wood or other organic matter burns.

Other pollutants from wood smoke In addition to particle pollution, wood smoke contains several toxic harmful air pollutants including benzene, formaldehyde, acrolein, and polycyclic aromatic hydrocarbons (PAHs).

Secondhand Smoke

Secondhand smoke is a mixture of the smoke given off by the burning of tobacco products, such as cigarettes, cigars or pipes and the smoke exhaled by smokers. Secondhand smoke is also called environmental tobacco smoke (ETS). Exposure to secondhand smoke is sometimes called involuntary or passive smoking. Secondhand smoke, classified by EPA as a Group A carcinogen, contains more than 7,000 substances. Secondhand smoke exposure commonly occurs indoors, particularly in homes and cars.

Secondhand smoke can move between rooms of a home and between apartment units. Opening a window or increasing ventilation in a home or car is not protective from secondhand smoke.

Radon

Radon is a radioactive gas that results from the natural decay of uranium and radiumfound in nearly all rocks and soils. Elevated radon levels have been found in every state. Radon is in the atmosphere and can also be found in ground water. The national average for radon in outdoor air is 0.4 picocuries per liter (pCi/L), while the average for indoor air is 1.3 pCi/L.

Any building can have high levels of radon, including new and old homes, well-sealed and drafty homes, office buildings and schools, and homes with or without basements. Radon gas can get into buildings through cracks in solid floors and walls, construction joints, gaps in suspended floors and around service pipes, cavities inside walls, the water supply and building materials. Testing is the only way to know if your home has elevated radon levels.EPA recommends fixing your home when the radon level is at or above 4 pCi/L.

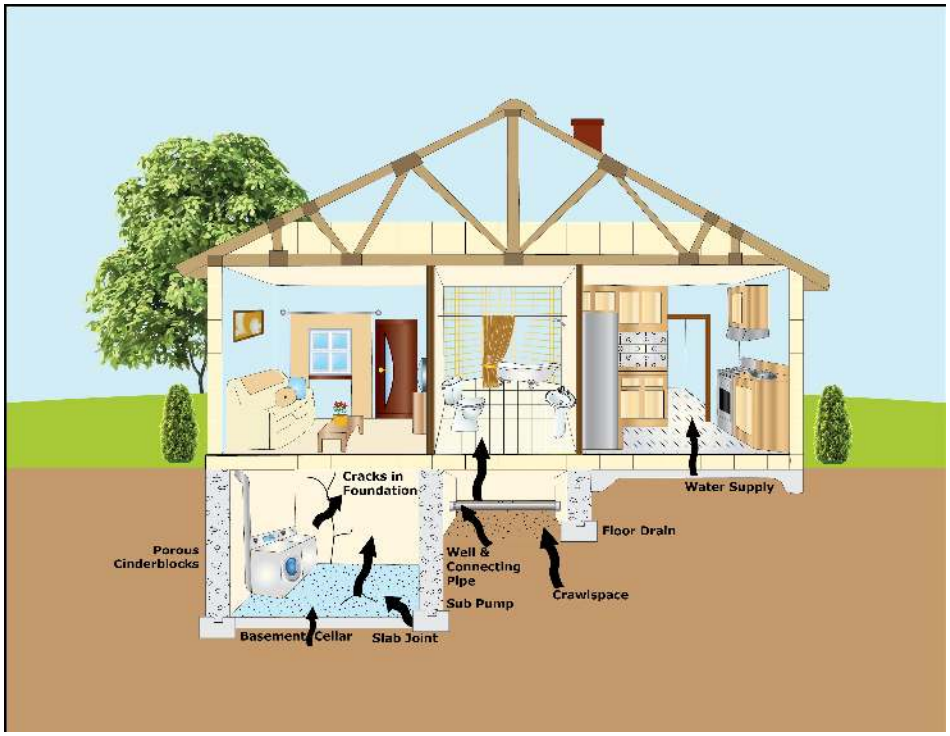


Figure* 12.9.2*: *Sources of Radon. Image source: EPA*https://www.epa.gov/radiation/radionuclide-basics-radon

EPA estimates that about 21,000 lung cancer deaths each year in the U.S. are radon-related. Exposure to radon is the second leading cause of lung cancer after smoking. For most people, radon is the single greatest environmental source of radiation exposure. EPA recommends that all homes and schools be tested for radon. For smokers, the risk of lung cancer is heightened due to the combined effects of radon and smoking.

Other Indoor Pollutants

Molds are usually not a problem indoors, unless mold spores land on a wet or damp spot and begin growing. Molds have the potential to cause health problems. Molds produce allergens (substances that can cause allergic reactions) and irritants. Inhaling or touching mold or mold spores may cause allergic reactions in sensitive individuals. Allergic responses include hay fever-type symptoms, such as sneezing, runny nose, red eyes, and skin rash.

Allergic reactions to mold are common. They can be immediate or delayed. Molds can also cause asthma attacks in people with asthma who are allergic to mold. In addition, mold exposure can irritate the eyes, skin, nose, throat, and lungs of both mold-allergic and non-allergic people. Symptoms other than the allergic and irritant types are not commonly reported as a result of inhaling mold.

Volatile organic compounds (VOCs) are emitted as gases from certain solids or liquids. VOCs include a variety of chemicals, some of which may have short- and long-term adverse health effects. Concentrations of many VOCs are consistently higher indoors (up to ten times higher) than outdoors. VOCs are emitted by a wide array of products numbering in the thousands.

Organic chemicals are widely used as ingredients in household products. Paints, varnishes and wax all contain organic solvents, as do many cleaning, disinfecting, cosmetic, degreasing and hobby products. Fuels are made up of organic chemicals. All of these products can release organic compounds while you are using them, and, to some degree, when they are stored.

EPA's Office of Research and Development's "Total Exposure Assessment Methodology (TEAM) Study" (Volumes I through IV, completed in 1985) found levels of about a dozen common organic pollutants to be 2 to 5 times higher inside homes than outside, regardless of whether the homes were located in rural or highly industrial areas. TEAM studies indicated that while people are using products containing organic chemicals, they can expose themselves and others to very high pollutant levels, and elevated concentrations can persist in the air long after the activity is completed.

VOCs are emitted by a wide array of products used in homes including paints and lacquers, paint strippers, cleaning supplies, varnishes and waxes, pesticides, building materials and furnishings, office equipment, moth repellents, air fresheners, and dry-cleaned clothing. VOCs evaporate into the air when these products are used or sometimes even when they are stored.

Volatile organic compounds irritate the eyes, nose and throat, and cause headaches, nausea, and damage to the liver, kidneys and central nervous system. Some of them can cause cancer.

Asbestos is a mineral fiber that occurs in rock and soil. Because of its fiber strength and heat resistance asbestos has been used in a variety of building construction materials for insulation and as a fire retardant. Asbestos has also been used in a wide range of manufactured goods, mostly in building materials (roofing shingles, ceiling and floor tiles, paper products, and asbestos cement products), friction products (automobile clutch, brake, and transmission parts), heat-resistant fabrics, packaging, gaskets, and coatings.

Asbestos fibers may be released into the air by the disturbance of asbestos-containing material during product use, demolition work, building or home maintenance, repair, and remodeling. In general, exposure may occur only when the asbestos-containing material is disturbed or damaged in some way to release particles and fibers into the air.

Three of the major health effects associated with asbestos exposure are:

· lung cancer

· mesothelioma, a rare form of cancer that is found in the thin lining of the lung, chest and the abdomen and heart

· asbestosis, a serious progressive, long-term, non-cancer disease of the lungs

Improving Your Indoor Air Quality

Take steps to help improve your air quality and reduce your IAQ-related health risks at little or no cost by:

Controlling the sources of pollution: Usually the most effective way to improve indoor air is to eliminate individual sources or reduce their emissions.

Ventilating: Increasing the amount of fresh air brought indoors helps reduce pollutants inside. When weather permits, open windows and doors, or run an air conditioner with the vent control open. Bathroom and kitchen fans that exhaust to the outdoors also increase ventilation and help remove pollutants.

Always ventilate and follow manufacturers' instructions when you use products or appliances that may release pollutants into the indoor air.

Changing filters regularly: Central heaters and air conditioners have filters to trap dust and other pollutants in the air. Make sure to change or clean the filters regularly, following the instructions on the package.

Adjusting humidity: The humidity inside can affect the concentrations of some indoor air pollutants. For example, high humidity keeps the air moist and increases the likelihood of mold.

Keep indoor humidity between 30 and 50 percent. Use a moisture or humidity gauge, available at most hardware stores, to see if the humidity in your home is at a good level. To increase humidity, use a vaporizer or humidifier. To decrease humidity, open the windows if it is not humid outdoors. If it is warm, turn on the air conditioner or adjust the humidity setting on the humid

Get a quick glimpse of some of the most important ways to protect the air in your home by touring the Indoor Air Quality (IAQ) House. Room-by-room, you'll learn about the key pollutants and how to address them.

Interactive Version

https://www.epa.gov/indoor-air-quality-iaq/interactive-tour-indoor-air-quality-demo-house#mainHouse

Text Version

https://www.epa.gov/indoor-air-quality-iaq/text-version-indoor-air-quality-house-tour

Summary

- Indoor pollutants include combustion pollutants (from burning of oil, gas, kerosene, coal, wood, and tobacco products); building materials and furnishings products for household cleaning and maintenance, personal care, or hobbies; central heating and cooling systems and humidification devices.
- Pollutants causing indoor air pollution can also originate from outside sources such as radon, pesticides, and outdoor air pollution.
- Indoor pollutants can cause serious health problems to sensitive groups.
- Several suggestions were provided to improve indoor air quality.

Contributors and Attributions

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12.11: Who Pollutes? Who Pays?

Learning Objectives

- Know the EPA standards for criteria air pollutants.
- Know the sources, health, and environmental effects of criteria air pollutants.

The Clean Air Act, which was last amended in 1990, requires EPA to set National Ambient Air Quality Standards (40 CFR part 50) for pollutants considered harmful to public health and the environment. The Clean Air Act identifies two types of national ambient air quality standards. ***Primary standards*** provide public health protection, including protecting the health of "sensitive" populations such as asthmatics, children, and the elderly. ***Secondary standards*** provide public welfare protection, including protection against decreased visibility and damage to animals, crops, vegetation, and buildings.

The EPA has set National Ambient Air Quality Standards for six principal pollutants, which are called "criteria" air pollutants. Periodically, the standards are reviewed and may be revised. The current standards are listed in Table **12.11.1**. Units of measure for the standards are parts per million (ppm) by volume, parts per billion (ppb) by volume, and micrograms per cubic meter of air ($\mu g/m^3$).

Table **12.11.1** National Ambient Air Quality Standards for Criteria Air Pollutants.

Pollutant [links to historical tables of NAAQS reviews]		Primary/ Secondary	Averaging Time	Level	Form
Carbon Monoxide (CO)		primary	8 hours	9 ppm	Not to be exceeded more than once per year
			1 hour	35 ppm	
Lead (Pb)		primary and secondary	Rolling 3 month average	0.15 µg/m^3 (1)	Not to be exceeded
Nitrogen Dioxide (NO_2)		primary	1 hour	100 ppb	98th percentile of 1-hour daily maximum concentrations, averaged over 3 years
		primary and secondary	1 year	53 ppb (2)	Annual Mean
Ozone (O_3)		primary and secondary	8 hours	0.070 ppm (3)	Annual fourth-highest daily maximum 8-hour concentration, averaged over 3 years
Particle Pollution (PM)	$PM_{2.5}$	primary	1 year	12.0 µg/m^3	annual mean, averaged over 3 years
		secondary	1 year	15.0 µg/m^3	annual mean, averaged over 3 years
		primary and secondary	24 hours	35 µg/m^3	98th percentile, averaged over 3 years
	PM_{10}	primary and secondary	24 hours	150 µg/m^3	Not to be exceeded more than once per year on average over 3 years
Sulfur Dioxide (SO_2)		primary	1 hour	75 ppb (4)	99th percentile of 1-hour daily maximum concentrations, averaged over 3 years
		secondary	3 hours	0.5 ppm	Not to be exceeded more than once per year

(1) In areas designated nonattainment for the Pb standards prior to the promulgation of the current (2008) standards, and for which implementation plans to attain or maintain the current (2008) standards have not been submitted and approved, the previous standards (1.5 µg/m3 as a calendar quarter average) also remain in effect.

(2) The level of the annual NO2 standard is 0.053 ppm. It is shown here in terms of ppb for the purposes of clearer comparison to the 1-hour standard level.

(3) Final rule signed October 1, 2015, and effective December 28, 2015. The previous (2008) O3 standards additionally remain in effect in some areas. Revocation of the previous (2008) O3 standards and transitioning to the current (2015) standards will be addressed in the implementation rule for the current standards.

(4) The previous SO2 standards (0.14 ppm 24-hour and 0.03 ppm annual) will additionally remain in effect in certain areas: (1) any area for which it is not yet 1 year since the effective date of designation under the current (2010) standards, and (2)any area for which an implementation plan providing for attainment of the current (2010) standard has not been submitted and approved and which is designated nonattainment under the previous SO2 standards or is not meeting the requirements of a SIP call under the previous SO2 standards (40 CFR 50.4(3)). A SIP call is an EPA action requiring a state to resubmit all or part of its State Implementation Plan to demonstrate attainment of the required NAAQS.

Table **12.11.2** list the sources and harmful effects of criteria pollutants.

Table **12.11.2** Sources, Health and Environmental Effects of Criteria Pollutants.

Pollutant	Sources	Health Effects	Environmental Effects
Ground-level Ozone (O_3)	Secondary pollutant typically formed by chemical reaction of volatile organic compounds (VOCs) and NO_x in the presence of sunlight.	Decreases lung function and causes respiratory symptoms, such as coughing and shortness of breath; aggravates asthma and other lung diseases leading to increased medication use, hospital admissions, emergency department (ED) visits, and premature mortality.	Ozone affects sensitive vegetation and ecosystems, including forests, parks, wildlife refuges and wilderness areas. In particular, ozone harms sensitive vegetation during the growing season.
Particulate Matter (PM)	Emitted or formed through chemical reactions; fuel combustion (e.g., burning coal, wood, diesel); industrial processes; agriculture (plowing, field burning); and unpaved roads.	Short-term exposures can aggravate heart or lung diseases leading to respiratory symptoms, increased medication use, hospital admissions, ED visits, and premature mortality; long-term exposures can lead to the development of heart or lung disease and premature mortality.	Visibility impairment Fine particles ($PM_{2.5}$) are the main cause of reduced visibility (haze) in parts of the United States, including many of our treasured national parks and wilderness areas. Environmental damage Particles can be carried over long distances by wind and then settle on ground or water. Depending on their chemical composition, the effects of this settling may include: · making lakes and streams acidic · changing the nutrient balance in coastal waters and large river basins · depleting the nutrients in soil · damaging sensitive forests and farm crops · affecting the diversity of ecosystems · contributing to acid rain effects. Materials damage PM can stain and damage stone and other materials, including culturally important objects such as statues and monuments. Some of these effects are related to acid rain effects on materials.
Lead	Smelters (metal refineries) and other metal industries; combustion of leaded gasoline in piston engine aircraft; waste incinerators; and battery manufacturing.	Damages the developing nervous system, resulting in IQ loss and impacts on learning, memory, and behavior in children. Cardiovascular and	Lead is persistent in the environment and can be added to soils and sediments through deposition from sources of lead air pollution. Other sources of lead to ecosystems include

		renal effects in adults and early effects related to anemia.	direct discharge of waste streams to water bodies and mining. Elevated lead in the environment can result in decreased growth and reproductive rates in plants and animals, and neurological effects in vertebrates.
Oxides of Nitrogen (NO_x)	Fuel combustion (e.g., electric utilities, industrial boilers, and vehicles) and wood burning.	Aggravate lung diseases leading to respiratory symptoms, hospital admissions, and ED visits; increased susceptibility to respiratory infection.	NO_2 and other NO_x interact with water, oxygen and other chemicals in the atmosphere to form acid rain. Acid rain harms sensitive ecosystems such as lakes and forests. NO_x in the atmosphere contributes to nutrient pollution in coastal waters.
Carbon Monoxide (CO)	Fuel combustion (especially vehicles), industrial processes, fires, waste combustion, and residential wood burning.	Reduces the amount of oxygen reaching the body's organs and tissues; aggravates heart disease, resulting in chest pain and other symptoms leading to hospital admissions and ED visits.	
Sulfur Dioxide (SO_2)	Fuel combustion (especially high-sulfur coal); electric utilities and industrial processes; and natural sources such as volcanoes.	Aggravates asthma and increased respiratory symptoms. Contributes to particle formation with associated health effects.	At high concentrations, gaseous SOx can harm trees and plants by damaging foliage and decreasing growth. SO_2 and other sulfur oxides can contribute to acid rain which can harm sensitive ecosystems.

Source: www.epa.gov

The likelihood of immediate reactions to air pollutants depends on several factors. Age and preexisting medical conditions are two important influences. Some sensitive individuals appear to be at greater risk for air pollution-related health effects, for example, those with pre-existing heart and lung diseases (e.g., heart failure/ischemic heart disease, asthma, emphysema, and chronic bronchitis), diabetics, older adults, and children. In other cases, whether a person reacts to a pollutant depends on individual sensitivity, which varies tremendously from person to person. Some people can become sensitized to biological pollutants after repeated exposures, and it appears that some people can become sensitized to chemical pollutants as well.

Paying the Price

Pollution has a cost. Manufacturing activities that cause air pollution impose health and clean-up costs on the whole of society, whereas the neighbors of an individual who chooses to fire-proof his home may benefit from a reduced risk of a fire spreading to their own homes. A manufacturing activity that causes air pollution is an example of a negative externality in production. A negative externality in production occurs "when a firm's production reduces the well-being of others who are not compensated by the firm." For example, if a laundry firm exists near a polluting steel manufacturing firm, there will be increased costs for the laundry firm because of the dirt and smoke produced by the steel manufacturing firm. If external costs exist, such as those created by pollution, the manufacturer will choose to produce more of the product than would be produced if the manufacturer were required to pay all associated environmental costs. Because responsibility or consequence for self-directed action lies partly outside

the self, an element of externalization is involved. If there are external benefits, such as in public safety, less of the good may be produced than would be the case if the producer were to receive payment for the external benefits to others. However, goods and services that involve negative externalities in production, such as those that produce pollution, tend to be over-produced and underpriced since the externality is not being priced into the market.

Pollution can also create costs for the firms producing the pollution. Sometimes firms choose, or are forced by regulation, to reduce the amount of pollution that they are producing. The associated costs of doing this are called abatement costs, or marginal abatement costs if measured by each additional unit. In 2005 pollution abatement capital expenditures and operating costs in the US amounted to nearly $27 billion.

Summary

- The EPA has set National Ambient Air Quality Standards for six principal pollutants, which are called "criteria" air pollutants.
- The six criteria pollutants are carbon monoxide, lead, nitrogen dioxide, ozone, particulate matter, and sulfur dioxide.
- The key air pollutants can cause various environmental and health problems that could affect the respiratory, nervous, and cardiovascular systems.

Contributors and Attributions

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CHAPTER OVERVIEW

13: Water

13.1: Water - Some Unique Properties
13.2: Water in Nature
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Thumbnail: Acid mine drainage in the Rio Tinto River. (Public Domain; Carol Stoker @ NASA via Wikipedia).

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13.1: Water - Some Unique Properties

LEARNING OBJECTIVE

Describe the different properties of water as it relates to its polarity and ability to form hydrogen bonds.

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 is a simple molecule consisting of one oxygen atom bonded to two different hydrogen atoms (Figure **13.1.1**). Because of the higher electronegativity of the oxygen atom, the bonds are polar covalent (**polar bonds**). The oxygen atom attracts the shared electrons of the covalent bonds to a significantly greater extent than the hydrogen atoms. As a result, the oxygen atom requires a partial negative charge ($\delta-$), while the hydrogen atoms each acquire a partial positive charge ($\delta+$). The molecule adopts a bent structure because of the two lone pairs of electrons on the oxygen atom. The $\mathrm{H-O-H}$ bond angle is about $105°$, slightly smaller than the ideal $109.5°$ of an sp^3 hybridized atomic orbital.The bent shape of the water molecule is critical because the polar $\mathrm{O-H}$ bonds do not cancel one another and the molecule as a whole is polar.

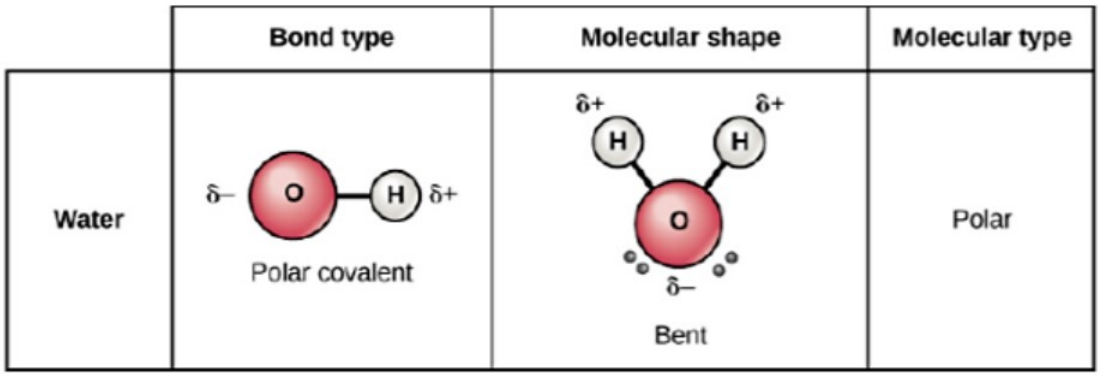


Figure **13.1.1** *Polarity of the water molecule due to the uneven distribution of electrons in its covalent bond. C (From OpenStax Concepts of Biology text)*

Hydrogen Bonds

Due to water's polarity, each water molecule attracts other water molecules as oppositely charged ends of the molecules attract each other. When this happens, a weak interaction occurs between the *positive* hydrogen end from one molecule and the *negative oxygen* end of another molecule. This interaction is called a **hydrogen bond**. This hydrogen bonding contributes to the following water's unique properties.

1. Water is the universal solvent
2. Exists in nature as a solid, liquid, and gas
3. The density of ice is less than liquid water
4. Water has a high heat capacity
5. Water has a high heat of vaporization
6. Water exists as a liquid at room temperature It is important to note here that even we are only focusing on water in this text book, hydrogen bonding also occurs in other substances that have polar molecules.

Density of Water

Liquid water is a fluid. The hydrogen bonds in liquid water constantly break and reform as the water molecules tumble past one another. As water cools, its molecular motion slows and the molecules move gradually closer to one another. The **density** of any

liquid increases as its temperature decreases. For most liquids, this continues as the liquid freezes and the solid state is denser than the liquid state. However, water behaves differently (Table **13.1.1**) . It actually reaches its highest density at about **4°C**.

Table **13.1.1** *Density of Water and Ice*

Temperature (°C)	Density $\left(g/cm^3\right)$
100 (liquid)	0.9584
50	0.9881
25	0.9971
10	0.9997
4	1.0000
0 (liquid)	0.9998
0 (solid)	0.9168

Between **4°C** and **0°C**, the density gradually decreases as the hydrogen bonds begin to form a network characterized by a generally **hexagonal** structure with open spaces in the middle of the hexagons (Figure **13.1.2**).

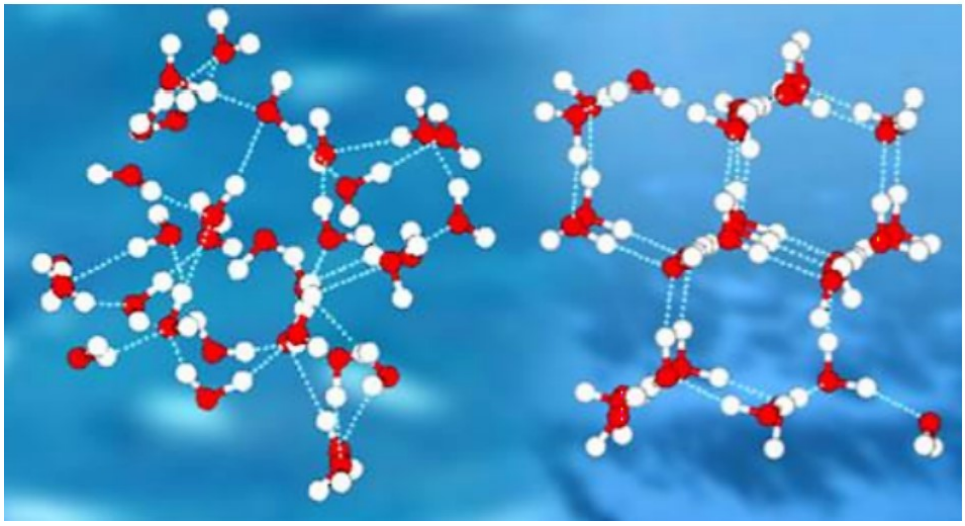


Figure **13.1.2** *Hydrogen bonding makes ice less dense than liquid water. The lattice structure water is more condensed (left structure) than that of ice (right structure). The lattice structure of ice makes it less dense than freely flowing molecules of liquid water, enabling ice to float on liquid water. (Image credit: Lynn Yarris, http://www2.lbl.gov/Science-Articles...ter-solid.html)*

Ice is less dense than liquid water and so it floats. Ponds or lakes begin to freeze at the surface, closer to the cold air. A layer of ice forms, but does not sink as it would if water did not have this unique structure dictated by its shape, polarity, and hydrogen bonding. If the ice were to sink as it froze, entire lakes would freeze solid. Since the ice does not sink, liquid water remains under the ice all winter long. This is important, as fish and other organisms are capable of surviving through winter. Ice is one of only a very few solids that is less dense than its liquid form.

Solvation Ability of Water

Water typically dissolves many ionic compounds and polar molecules. Nonpolar molecules such as those found in grease or oil do not dissolve in water. We will first examine the process that occurs when an ionic compound such as table salt (sodium chloride) dissolves in water.

Water is attracted to the sodium chloride crystal because water is polar and has both a positive and a negative end. The positively charged sodium ions in the crystal attract the oxygen end of the water molecules because they are partially negative. The negatively

charged chloride ions in the crystal attract the hydrogen end of the water molecules because they are partially positive. The action of the polar water molecules takes the crystal lattice apart (see Figure **13.1.3**) .

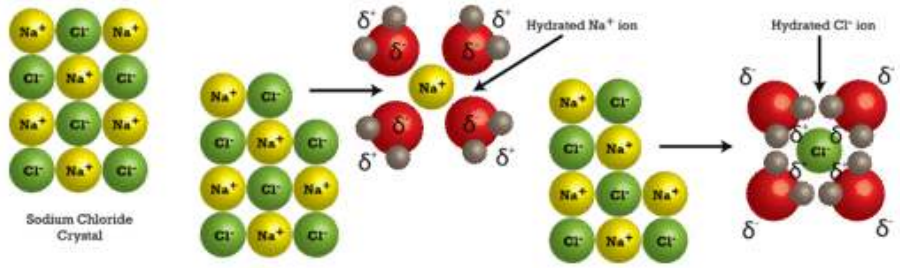


Figure **13.1.3** *The dissolving of sodium chloride in water.*

After coming apart from the crystal, the individual ions are then surrounded by solvent particles in a process called **solvation**. Note that the individual $\mathbf{Na^+}$ ions are surrounded by water molecules with the oxygen atom oriented near the positive ion. Likewise, the chloride ions are surrounded by water molecules with the opposite orientation. **Hydration** is the process of solute particles being surrounded by water molecules arranged in a specific manner. Hydration helps to stabilize aqueous solutions by preventing the positive and negative ions from coming back together and forming a precipitate.

Table sugar is sucrose ($\mathbf{C_{12}H_{22}O_{11}}$) and is an example of a molecular compound. Solid sugar consists of individual sugar molecules held together by intermolecular attractive forces. When water dissolves sugar, it separates the individual sugar molecules by disrupting the attractive forces, but does not break the covalent bonds between the carbon, hydrogen, and oxygen atoms. Dissolved sugar molecules are also hydrated, but without as distinct an orientation to the water molecules as in the case of the ions. The sugar molecules contain many $\mathbf{-OH}$ groups that can form hydrogen bonds with the water molecules, helping form the sucrose solution.

The Amphoteric Nature of Water

Water is amphoteric: it has the ability to act as either an acid or a base in chemical reactions. According to the Brønsted-Lowry definition, an acid is a proton (H^+) donor and a base is a proton acceptor. When reacting with a stronger acid, water acts as a base; when reacting with a stronger base, it acts as an acid. For instance, water receives an H^+ ion from HCl when hydrochloric acid is formed:

$$HCl(acid) + H_2O(base) \rightleftharpoons H_3O^+ + Cl^-$$

In the reaction with ammonia, NH_3, water donates a H^+ ion, and is thus acting as an acid:

$$NH_3(base) + H_2O(acid) \rightleftharpoons NH^+_4 + OH^-$$

High Heat Capacity and Specific Heat of Water

Different substances respond to heat in different ways. If a metal chair sits in the bright sun on a hot day, it may become quite hot to the touch. An equal mass of water in the same sun will not become nearly as hot. Table **13.1.2** list specific heats of various substances compared to water.Water has the highest **specific heat capacity** of any liquid. Water's high heat capacity is a property caused by hydrogen bonding among the water molecules. **Specific heat** is defined as the amount of heat one gram of a substance must absorb or lose to change its temperature by one degree Celsius. For water, this amount is **1 cal/g°C**. The units for specific heat can either be in the SI units of joules per gram per degree ($\mathbf{J/g°C}$) or calories per gram per degree ($\mathbf{cal/g°C}$). This text will use $\mathbf{J/g°C}$ for specific heat.



Figure **13.1.4** *This power plant in West Virginia, like many others, is located next to a large lake so that the water from the lake can be used as a coolant. Cool water from the lake is pumped into the plant, while warmer water is pumped out of the plant and back into the lake.*

It takes water a long time to heat up and a long time to cool down. In fact, the specific heat capacity of water is about five times more than that of sand. This explains why land cools faster than the sea. 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. Water is used as a coolant for machinery because it is able to absorb large quantities of heat (Figure **13.1.4**). Due to its high heat capacity, warm-blooded animals use water to disperse heat more evenly and maintain temperature in their bodies: it acts in a similar manner to a car's cooling system, transporting heat from warm places to cool places, causing the body to maintain a more even temperature.

Table **13.1.2** *Specific Heats of Some Common Substances*

Substance	Specific Heat (J/g°C)
Water (l)	4.18
Water (s)	2.06
Water (g)	1.87
Ammonia (g)	2.09
Ethanol (l)	2.44
Aluminum (s)	0.897
Carbon, graphite (s)	0.709
Copper (s)	0.385
Gold (s)	0.129
Iron (s)	0.449
Lead (s)	0.129
Mercury (l)	0.140
Silver (s)	0.233

High Heat of Vaporization of Water

Water in its liquid form has an unusually high boiling point temperature, a value close to 100°C. As a result of the network of hydrogen bonding present between water molecules, a high input of energy is required to transform one gram of liquid water into water vapor, an energy requirement called the **heat of vaporization.** Water has a heat of vaporization value of **40.65 kJ/mol**. A

considerable amount of heat energy (586 calories) is required to accomplish this change in water. This process occurs on the surface of water. As liquid water heats up, hydrogen bonding makes it difficult to separate the water molecules from each other, which is required for it to enter its gaseous phase (steam). As a result, water acts as a heat sink, or heat reservoir, and requires much more heat to boil than does a liquid such as ethanol (grain alcohol), whose hydrogen bonding with other ethanol molecules is weaker than water's hydrogen bonding.

The fact that hydrogen bonds need to be broken for water to evaporate means that a substantial amount of energy is used in the process. As the water evaporates, energy is taken up by the process, cooling the environment where the evaporation is taking place. In many living organisms, including humans, the evaporation of sweat, which is 90 percent water, allows the organism to cool so that homeostasis of body temperature can be maintained.

Summary

- The polarity of water and its ability to hydrogen bond contributes to its unique properties.
- Ionic solute molecules are hydrated (surrounded by solvent molecules in a specific orientation).
- Ice is less dense than liquid water due to spaces in the intermolecular structure of ice not present in water.
- Heat capacity is the amount of heat required to raise the temperature of an object by **1°C**).
- The specific heat of a substance is the amount of energy required to raise the temperature of 1 gram of the substance by **1°C**.
- The dissociation of liquid water molecules, which changes the substance to a gas, requires a lot of energy.

Contributors and Attributions

-
- Boundless: The Chemical Foundation of Life
- Libretext: Introduction to Environmental Science (Zendher et al.)
- TextMap: Introductory Chemistry (Tro)
- Marisa Alviar-Agnew (Sacramento City College)

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13.2: Water in Nature

Learning Objectives

- Know the distribution of earth's water.
- Describe the water (hydrologic) cycle.
- Know the different natural water contaminants

Water 's influence on the world around us is affected by its unique properties some of which where discussed in the previous section. Without water, life might not be able to exist on Earth, and it certainly would not have the tremendous complexity and diversity that we see.

Distribution of Earth's Water

Earth’s oceans contain 97% of the planet’s water, so just 3% is fresh water, water with low concentrations of salts (Figure **13.2.1**). The majority of the Earth's water can be classified as being **saline** (or salt containing). Most freshwater is trapped as ice in the vast glaciers and ice sheets of Greenland. A storage location for water such as an ocean, glacier, pond, or even the atmosphere is known as a **reservoir**.

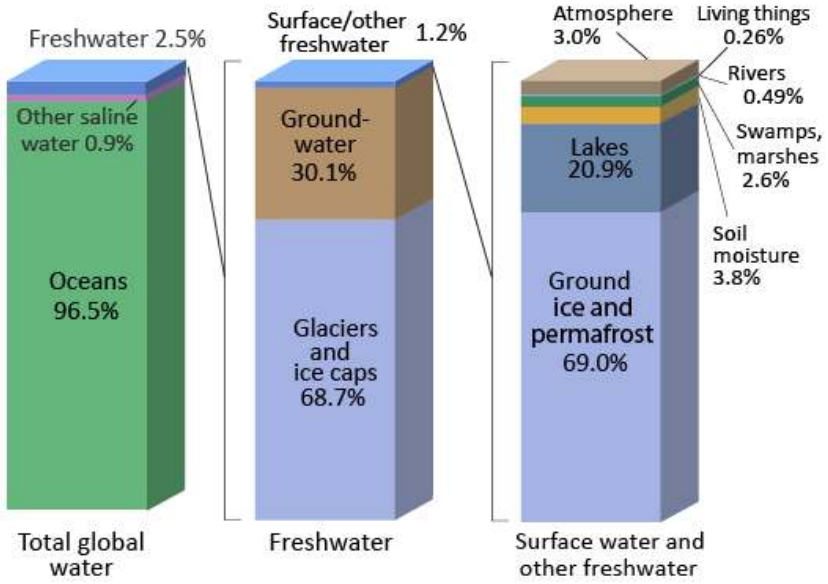


Figure **13.2.1** The distribution of Earth’s water. In the first bar, notice how only 2.5% of Earth's water is freshwater - the amount needed for life to survive. The middle bar shows the breakdown of freshwater. Almost all of it is locked up in ice and in the ground. Only a little more than 1.2% of all freshwater is surface water, which serves most of life's needs.The right bar shows the breakdown of surface freshwater. Source: Igor Shiklomanov's chapter "World Freshwater resources" in Peter H. Gleick (editor), 1993 Water in Crises: A guide to the World's Freshwater Resources. The numbers are rounded.

The Water (Hydrologic) Cycle and Natural Contaminants

Because Earth’s water is present in all three states, it can get into a variety of environments around the planet. The movement of water around Earth’s surface is the **water cycle** (Figure **13.2.2**).

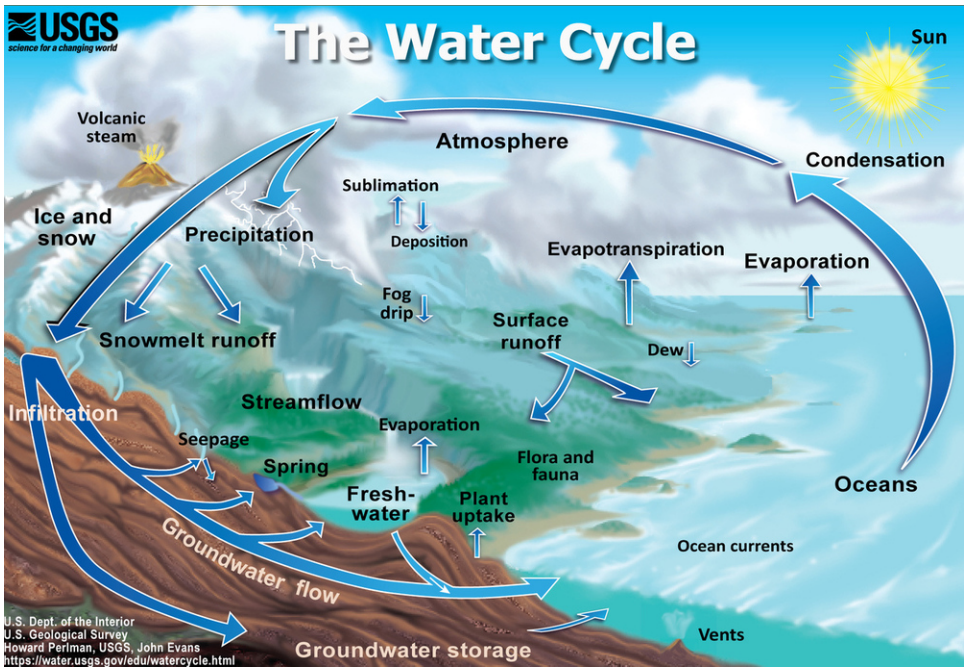


Figure **13.2.2** Because it is a cycle, the water cycle has no beginning and no end. Earth's water is always in movement, and the natural water cycle, also known as the hydrologic cycle, describes the continuous movement of water on, above, and below the surface of the Earth. Water is always changing states between liquid, vapor, and ice, with these processes happening in the blink of an eye and over millions of years.

Water changes from a liquid to a gas by **evaporation** to become water vapor. The Sun's energy can evaporate water from the ocean surface or from lakes, streams, or puddles on land. Only the water molecules evaporate; the salts remain in the ocean or a freshwater reservoir. The water vapor remains in the atmosphere until it undergoes **condensation** and then precipitation. **Precipitation** can be rain, sleet, hail, or snow. At the surface, water or melted water, may eventually evaporate and reenter the atmosphere. A significant amount of water infiltrates into the ground. Water may seep through dirt and rock below the soil through pores infiltrating the ground to go into Earth's groundwater system (Figure Extra close brace or missing open brace). Groundwater enters **aquifers** which are bodies of rock or sediment that store (and yield) large amounts of usable water in their pores. Alternatively, the water may come to the surface through springs or find its way back to the oceans.

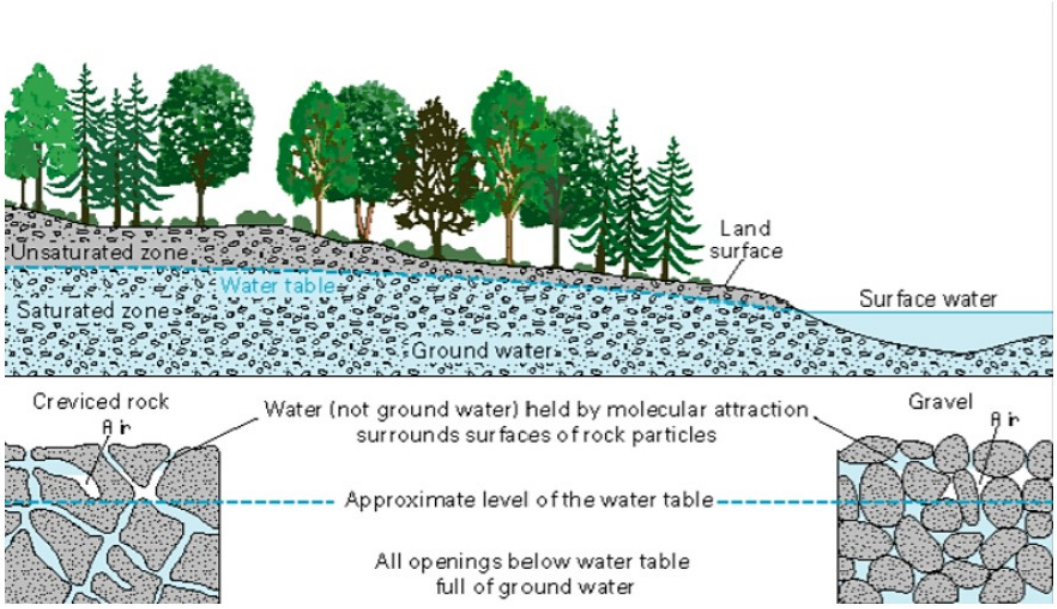


Figure Extra close brace or missing open brace *Model of groundwater system showing the different components of an unconfined groundwater system:* *http://water.usgs.gov/edu/earthgwaquifer.html*

Substances Present in Natural Waters

The amounts of water present in the atmosphere and on land (as surface runoff, lakes and streams) is great enough to make it a significant agent in transporting substances between the lithosphere (the rigid surface of the earth) and the oceans. Water interacts with both the atmosphere and the lithosphere (the rigid surface of the earth) acquiring solutes from each, and thus provides the major chemical link between these two realms. The various transformations undergone by water through the different stages of the hydrologic cycle act to transport both dissolved and particulate substances between different geographic locations.

The Safe Drinking Water Act defines the term "**contaminant**" as meaning any physical, chemical, biological, or radiological substance or matter in water. Therefore, the law defines "contaminant" very broadly as being anything other than water molecules.

Gases

The carbon dioxide in natural water creates an interesting phenomenon. Rainwater is saturated with CO_2, and it dissolves limestones. When CO_2 is lost due to temperature changes or escaping from water drops, the reverse reaction takes place. The solid formed, however, may be a less stable phase called aragonite, which has the same chemical formula as, but a different crystal structure than that of calcite.

The rain dissolves calcium carbonate by the two reactions shown above. The water carries the ions with it, sips through the crack of the rocks. When it reached the ceiling of a cave, the drop dangles there for a long time before fallen. During this time, the carbon dioxide escapes and the pH of the water increases. Calcium carbonate crystals begin to appear. Calcite, aragonite, stalactite, and stalagmite are four common solids found in the formation of caves.

Dissolved Minerals

Table **13.2.1** list the major ions present in seawater. The composition does vary, depending on region, depth, latitude, and water temperature. Waters at the river mouths contain less salt. If the ions are utilized by living organism, its contents vary according to the populations of organisms.

Dust particles and ions present in the air are nucleation center of water drops. Thus, waters from rain and snow also contain such ions: Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, NH_4^{+}. These cations are balanced by anions, HCO_3^{-}, SO_4^{-}, NO_2^{-}, Cl^{-}, and NO_3^{-}. The pH of rain is between 5.5 and 5.6. Rain and snow waters eventually become river or lake waters. When the rain or snow waters fall, they interact with vegetation, top soil, bed rock, river bed and lake bed, dissolving whatever is soluble. Bacteria, algae, and water insects also thrive. Solubilities of inorganic salts are governed by the kinetics and equilibria of dissolution. The most common ions in lake and river waters are the same as those present in rainwater, but at higher concentrations. The pH of these waters depends on the river bed and lake bed. Natural waters contain dissolved minerals. Waters containing Ca^{2+} and Mg^{2+} ions are usually called **hard water**.

Table 1 Major Ions in Seawater (These values, expressed in parts per thousand, are for seawater of 35% salinity).

cations	g/kg	anions	g/kg
Na^{+}	10.77	Cl^{-}	19.354
Mg^{2+}	1.29	SO_4^{2-}	2.712
Ca^{2+}	0.412	Br^{-}	0.087
K^{+}	0.399		
Sr^{2+}	0.0079		
Al^{3+}	0.005		

Note

Although most elements are found in seawater only at trace levels, marine organisms may selectively absorb them and make them more detectable. Iodine, for example, was discovered in marine algae (seaweeds) 14 years before it was found in seawater. Other elements that were not detected in seawater until after they were found in marine organisms include barium,

cobalt, copper, lead, nickel, silver and zinc. Si-32, presumably deriving from cosmic ray bombardment of Ar, has been discovered in marine sponges.

Hard Water

Minerals usually dissolve in natural water bodies such as lakes, rivers, springs, and underground waterways (ground waters). Calcium carbonate, $CaCO_3$, is one of the most common inorganic compounds in the Earth crust. It is the ingredient for both calcite and aragonite. These two minerals have different crystal structures and appearance. This photograph shows crystals of typical Calcite.

Calcium-carbonate minerals dissolve in water, with a solubility product as shown below.

$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-} \quad K_{sp} = 5 \times 10^{-9}$$

From the solubility product, we can (see example 1) evaluate the molar solubility to be 7.1×10^{-5} M or 7.1 mg/L (7.1 ppm of $CaCO_3$ in water). The solubility increases as the pH decrease (increase acidity). This is compounded when the water is saturated with carbon dioxide, CO_2. Saturated CO_2 solution contains carbonic acid, which help the dissolution due to the reaction:

$$H_2O + CO_2 \rightleftharpoons H_2CO_3$$

$$CaCO_3 + H_2CO_3 \rightleftharpoons Ca^{2+} + 2HCO_3^-$$

Because of these reactions, some natural waters contain more than 300 ppm calcium carbonates or its equivalents.

The composition of the ocean has attracted the attention of some of the more famous names in science, including Robert Boyle, Antoine Lavoisier and Edmund Halley. Their early investigations tended to be difficult to reproduce, owing to the different conditions under which they crystallized the various salts. As many as 54 salts, double salts and hydrated salts can be obtained by evaporating seawater to dryness. At least 73 elements are now known to be present in seawater.

Organic Matter

Most of the organic carbon in seawater is present as dissolved material, with only about 1-2% in particulates. The total organic carbon content ranges between 0.5 mg/L in deep water to 1.5 mg/L near the surface. There is still considerable disagreement about the composition of the dissolved organic matter; much of it appears to be of high molecular weight, and may be polymeric. Substances qualitatively similar to the humic acids found in soils can be isolated. The greenish color that is often associated with coastal waters is due to a mixture of fluorescent, high molecular weight substances of undetermined composition known as *"Gelbstoffe"*. It is likely that the significance of the organic fraction of seawater may be much greater than its low abundance would suggest. For one thing, many of these substances are lipid-like and tend to adsorb onto surfaces. It has been shown that any particle entering the ocean is quickly coated with an organic surface film that may influence the rate and extent of its dissolution or decomposition. Certain inorganic ions may be strongly complexed by humic-like substances. The surface of the ocean is mostly covered with an organic film, only a few molecular layers thick. This is believed to consist of hydrocarbons, lipids, and the like, but glycoproteins and proteoglycans have been reported. If this film is carefully removed from a container of seawater, it will quickly be reconstituted. How significant this film is in its effects on gas exchange with the atmosphere is not known.

Summary

- The water (hydrologic) cycle describes the continuous movement of water on, above and below the surface of the Earth. The water moves from one reservoir to another, such as from river to ocean, or from the ocean to the atmosphere, by the physical processes of evaporation, condensation, precipitation, infiltration, surface runoff, and subsurface flow. In doing so, the water goes through different forms: liquid, solid (ice) and capor.
- Different substances that can be found in natural waters include dissolved minerals, dissolved gases, and organic matter.

Contributors and Attributions

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- Marisa Alviar-Agnew (Sacramento City College)
- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook

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13.3: Chemical and Biological Contamination

Learning Objective

- Describe the impact of human activities on water quality.

The global water crisis also involves water pollution. For water to be useful for drinking and irrigation, it must not be polluted beyond certain thresholds. According to the World Health Organization, in 2008 approximately 880 million people in the world (or 13% of world population) did not have access to safe drinking water. At the same time, about 2.6 billion people (or 40% of world population) lived without improved sanitation, which is defined as having access to a public sewage system, septic tank, or even a simple pit latrine. Each year approximately 1.7 million people die from diarrheal diseases associated with unsafe drinking water, inadequate sanitation, and poor hygiene. Almost all of these deaths are in developing countries, and around 90% of them occur among children under the age of 5 (Figure 1). Compounding the water crisis is the issue of social justice; poor people more commonly lack clean water and sanitation than wealthy people in similar areas. Globally, improving water safety, sanitation, and hygiene could prevent up to 9% of all disease and 6% of all deaths.

In addition to the global waterborne disease crisis, chemical pollution from agriculture, industry, cities, and mining threatens global water quality. In Gallup public polls conducted over the past decade Americans consistently put water pollution and water supply as the top environmental concerns over issues such as air pollution, deforestation, species extinction, and global warming.

Water pollution is the contamination of water by an excess amount of a substance that can cause harm to human beings and/or the ecosystem. The level of water pollution depends on the abundance of the pollutant, the ecological impact of the pollutant, and the use of the water. Pollutants are derived from biological, chemical, or physical processes. Although natural processes such as volcanic eruptions or evaporation sometimes can cause water pollution, most pollution is derived from human, land-based activities. Water pollutants can move through different water reservoirs, as the water carrying them progresses through stages of the water cycle.

Pollutants enter water supplies from **point sources**, which are readily identifiable and relatively small locations, or **nonpoint sources**, which are large and more diffuse areas (Figure 13.3.1) . Point sources of pollution include animal factory farms that raise a large number and high density of livestock such as cows, pigs, and chickens. Also, pipes included are pipes from a factories or sewage treatment plants. Combined sewer systems that have a single set of underground pipes to collect both sewage and storm water runoff from streets for wastewater treatment can be major point sources of pollutants. During heavy rain, storm water runoff may exceed sewer capacity, causing it to back up and spilling untreated sewage directly into surface waters.

picture6



Figure 13.3.1 *Point source and non point source pollution. The Image taken from: https://theskyguys.ca/2017/02/water-...e-great-lakes/ (I took this pic from a site that I don't think is cc). and (CC BY-SA 2.0; N Chadwick).*

This section and the next will focus on how human activities affect water quality.

Too Much Organic Matter Means Too Little Oxygen

Oxygen-demanding waste is an extremely important pollutant to ecosystems. Most surface water in contact with the atmosphere has a small amount of dissolved oxygen, which is needed by aquatic organisms for cellular respiration. Bacteria decompose dead organic matter and remove dissolved oxygen (O_2) according to the following reaction:

$$\text{organic matter} + O_2 \rightarrow CO_2 + H_2O$$

Too much decaying organic matter in water is a pollutant because it removes oxygen from water, which can kill fish, shellfish, and aquatic insects. The amount of oxygen used by **aerobic** (in the presence of oxygen) bacterial decomposition of organic matter is called **biochemical oxygen demand** (BOD). The major source of dead organic matter in many natural waters is sewage; grass and leaves are smaller sources. An unpolluted water body with respect to BOD is a turbulent river that flows through a natural forest. Turbulence continually brings water in contact with the atmosphere where the O_2 content is restored. The dissolved oxygen content in such a river ranges from 10 to 14 ppm O_2, BOD is low, and clean-water fish such as trout. A polluted water body with respect to oxygen is a stagnant deep lake in an urban setting with a combined sewer system. This system favors a high input of dead organic carbon from sewage overflows and limited chance for water circulation and contact with the atmosphere. In such a lake, the dissolved O_2 content is ≤5 ppm O_2, BOD is high, and low O_2-tolerant fish, such as carp and catfish dominate.

Excessive plant nutrients, particularly nitrogen (N) and phosphorous (P), are pollutants closely related to oxygen-demanding waste. Aquatic plants require about 15 nutrients for growth, most of which are plentiful in water. N and P are called **limiting nutrients**, however, because they usually are present in water at low concentrations and therefore restrict the total amount of plant growth. This explains why N and P are major ingredients in most fertilizer. High concentrations of N and P from human sources (mostly agricultural and urban runoff including fertilizer, sewage, and phosphorus-based detergent) can cause cultural **eutrophication**, which leads to the rapid growth of aquatic producers, particularly algae. Thick mats of floating algae or rooted plants lead to a form of water pollution that damages the ecosystem by clogging fish gills and blocking sunlight. A small percentage of algal species produce toxins that can kill animals, including humans. Exponential growths of these algae are called **harmful algal blooms**. When the prolific algal layer dies, it becomes oxygen-demanding waste, which can create very low O_2 concentrations in the water (< 2 ppm O_2), a condition called **hypoxia.** This results in a **dead zone** because it causes death from asphyxiation to organisms that are unable to leave that environment. An estimated 50% of lakes in North America, Europe, and Asia are negatively impacted by cultural eutrophication. In addition, the size and number of marine hypoxic zones have grown dramatically over the past 50 years including a very large dead zone located offshore Louisiana in the Gulf of Mexico. Cultural eutrophication and hypoxia are difficult to combat, because they are caused primarily by nonpoint source pollution, which is difficult to regulate, and N and P, which are difficult to remove from wastewater.

Eutrophication is an increase in the concentration of chemical nutrients in an ecosystem to an extent that increases the primary productivity of the ecosystem. Depending on the degree of eutrophication, subsequent negative environmental effects such as anoxia (oxygen depletion) and severe reductions in water quality may occur, affecting fish and other animal populations.

Chemical Pollution from Waste

Since the 1990s, water contamination by pharmaceuticals has been an environmental issue of concern. In addition, it is important to note that many public health professionals in the United States began writing reports of pharmaceutical contamination in waterways in the 1970s." Most pharmaceuticals are deposited in the environment through human consumption and excretion, and are often filtered ineffectively by municipal sewage treatment plants which are not designed to manage them (Figure **13.3.2**) . Once in the water, they can have diverse, subtle effects on organisms, although research is still limited. Pharmaceuticals may also be deposited in the environment through improper disposal, runoff from sludge fertilizer and reclaimed wastewater irrigation, and leaky sewer pipes. In 2009, an investigative report by Associated Press concluded that U.S. manufacturers had legally released 271 million pounds of compounds used as drugs into the environment, 92% of which was the industrial chemicals phenol and hydrogen peroxide, which are also used as antiseptics. It could not distinguish between drugs released by manufacturers as opposed to the pharmaceutical industry. It also found that an estimated 250 million pounds of pharmaceuticals and contaminated packaging were discarded by hospitals and long-term care facilities.



Figure 13.3.2 Illicit drugs such as ecstasy (above) can be found in waterways. (Public Domain; Willy turner via Wikipedia)

The use of pharmaceuticals and personal care products (PPCPs) is on the rise with an estimated increase from 2 billion to 3.9 billion annual prescriptions between 1999 and 2009 in the United States alone. Figure 13.3.3 illustrates how PPCPs enter into the environment through individual human activity and as residues from manufacturing, agribusiness, veterinary use, and hospital and community use. In Europe, the input of pharmaceutical residues via domestic waste water is estimated to be around 80% whereas 20% is coming from hospitals. Individuals may add PPCPs to the environment through waste excretion and bathing as well as by directly disposing of unused medications to septic tanks, sewers, or trash. Because PPCPs tend to dissolve relatively easily and do not evaporate at normal temperatures, they often end up in soil and water bodies.

Some PPCPs are broken down or processed easily by a human or animal body and/or degrade quickly in the environment . However, others do not break down or degrade easily. The likelihood or ease with which an individual substance will break down depends on its chemical makeup and the metabolic pathway of the compound.

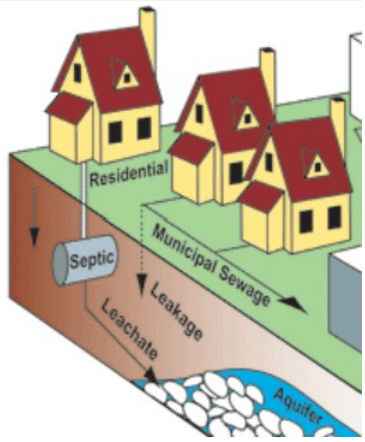


Figure 13.3.3 Methods of PPCP entry into the environment from residential homes via septic and sewage systems.[11]

While the full effects of most PPCPs on the environment are not understood, there is concern about the potential they have for harm because they may act unpredictably when mixed with other chemicals from the environment or concentrate in the food chain. Additionally, some PPCPs are active at very low concentrations, and are often released continuously in large or widespread quantities.

Because of the high solubility of most PPCPs, aquatic organisms are especially vulnerable to their effects. The increased presence of estrogen and other synthetic hormones in waste water due to birth control and hormonal therapies has been linked to increased feminization of exposed fish and other aquatic organisms. The chemicals within these PPCP products could either affect the feminization or masculinization of different fishes, therefore affecting their reproductive rates.

The major route for pharmaceutical residues to reach the aquatic environment is most probably by excretion from patients undergoing pharma treatment. Since many pharmaceutical substances are not metabolized in the body they may be excreted in biologically active form, usually via the urine. Furthermore, many pharmaceutical substances are not fully taken up from the

intestine (following oral administration in patients) into their blood stream. The fraction not taken up into the blood stream will remain in the gut and eventually be excreted via the faeces. Hence, both urine and faeces from treated patients contain pharmaceutical residues. Between 30 and 90% of the orally administered dose is generally excreted as active substance in the urine.

An additional source to environmental pollution with pharmaceuticals is improper disposal of unused or expired drug residues. In European countries take-back systems for such residues are usually in place (although not always utilized to full extent) while in e.g. the US only voluntary initiatives on a local basis exist. Though most of the waste goes to incineration and people are asked to throw unused or expired pharmaceuticals into the household waste investigations in Germany showed that up to 24% of liquid pharmaceuticals and 7% of tablets or ointments are disposed always or at least “rarely” via the toilet or sink.

Proper destruction of pharma residues should yield rest products without any pharmaceutical or ecotoxic activity. Furthermore, the residues should not act as components in the environmental formation of new such products. Incineration at a high temperature (>1000 degrees Celsius) is considered to fulfill the requirements, but even following such incineration residual ashes from the incineration should be properly taken care of.

Pharmaceuticals used in veterinary medicine, or as additives to animal food, pose a different problem, since they are excreted into soil or possibly open surface waters. It is well known that such excretions may affect terrestrial organisms directly, leading to extinction of exposed species (e.g. dung-beetles). Lipid-soluble pharma residues from veterinary use may bind strongly to soil particles, with little tendency to leak out to ground water or to local surface waters. More water-soluble residues may be washed out with rain or melting snow and reach both ground water and surface water streams.

Water Borne Diseases

Waterborne diseases are conditions caused by pathogenic micro-organisms that are transmitted in water. These diseases can be spread while bathing, washing, drinking water, or by eating food exposed to contaminated water. While diarrhea and vomiting are the most commonly reported symptoms of waterborne illness, other symptoms can include skin, ear, respiratory, or eye problems. Waterborne diseases are impacted by a country's economy and also impact the economy by being costly to deal with.

Microorganisms causing diseases that characteristically are waterborne prominently include protozoa and bacteria, many of which are intestinal parasites, or invade the tissues or circulatory system through walls of the digestive tract. Various other waterborne diseases are caused by viruses. (In spite of philosophical difficulties associated with defining viruses as "organisms", it is practical and convenient to regard them as microorganisms in this connection.)

Yet other important classes of water-borne diseases are caused by metazoan parasites. Typical examples include certain Nematoda, that is to say "roundworms". As an example of water-borne Nematode infections, one important waterborne nematode disease is Dracunculiasis. It is acquired by swallowing water in which certain copepoda occur that act as vectors for the Nematoda. Anyone swallowing a copepod that happens to be infected with Nematode larvae in the genus Dracunculus, becomes liable to infection. The larvae cause guinea worm disease.

Another class of waterborne metazoan pathogens are certain members of the Schistosomatidae, a family of blood flukes. They usually infect victims that make skin contact with the water. Blood flukes are pathogens that cause Schistosomiasis of various forms, more or less seriously affecting hundreds of millions of people worldwide.



***Video* 13.3.1** *The Coalition for Global Community Health is working within existing social structures in Belén, Iquitos, Peru to uphold the human rights of the community members. We speak directly with community members in an open forum to learn about their needs, desires, and ideas for creating an opportunity to change their communities for the better*

The table below shows water-borne diseases that can result from viruses, bacteria, and parasites. In some cases, vaccines are available. When eating, drinking, or swimming, it is important to be aware of how you could be affected by these pathogens. Sanitation of drinking water with chlorine-based compounds reduces the power of these pathogens. In addition, proper handling of foods and beverages could reduce your risk of developing one or more of the following health problems.

Table **13.3.1** Pathogens That Cause Waterborne Illnesses.

Pathogen Name	Pathogen Type	Source	Health problem	Prevention/Treatment
Giardia	Parasite	Fecal contamination and uncooked food	Vomiting, diarrhea, and cramps	Medication afterward
Cryptosporidium	Parasite	Fecal contamination	Vomiting, diarrhea, fever, and cramps	Medication afterward
Typhoid	Bacteria	Fecal contamination	High fever, stomach pains, headache, and rash	Vaccination/Antibiotics
E. coli	Bacteria	Fecal contamination	Diarrhea and cramps	Fluids
Legionella	Bacteria	Found naturally in heated water	Causes Legionnaires (a type of pneumonia)	Medications afterward
Cholera	Bacteria	Related to fecal contamination or undercooked or raw shellfish	Diarrhea	Vaccine/Rehydration, antibiotics, and Zinc
Hepatitis A	Virus	Contaminated food and water	Vomiting, dark urine, and yellowing of the eyes.	Vaccination/Fluids
Polio	Virus	Fecal contamination	Flu symptoms, paralysis	Vaccination

(Figure **13.3.4**) shows how a person might contract Giardiasis from *giardia*, a parasite. This particular pathogen can live in a body up to six months. Once detected through a stool sample, a patient can be prescribed specific antibiotics like Flagyl to treat the infection. Unfortunately, there is no vaccine for preventing Giardiasis.

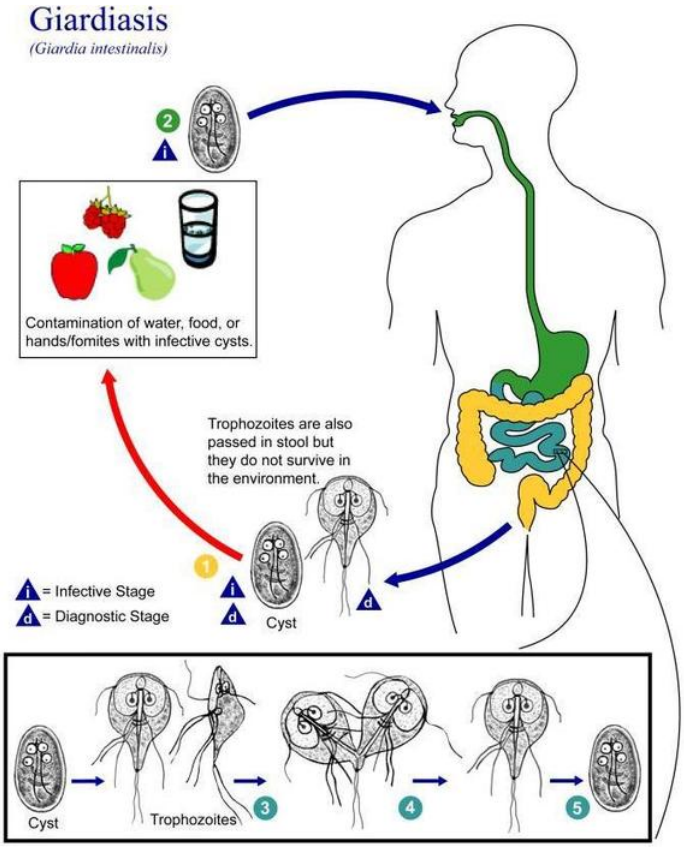


Figure **13.3.4** The life cycle of Giardia.



Acidic Waters

Water can become contaminated at any part of the water cycle. Air pollution can affect water vapor and water liquid. Combustion sources like vehicles and power plants generate compounds like NO_xs, SO_xs, CO, CO_2, and other various inorganic and organic volatile organic compounds (VOC) species (Table **13.3.2**). Some of these compounds can become soluble in water. This could affect pH (or acidity) level of water surface water. Normally, the pH of water is a neutral value (or pH= 7). When NO_xs, SO_xs, CO, CO_2 enter the water cycle, then the pH level is lowered below 7.0. If these gases are absorbed in rain clouds, then acid rain results. Specific acids involved in acid rain are **sulfuric, nitric,** and **carbonic**. This environmental problem affects living organisms and building materials. Acid solutions can corrode metals and make them soluble as well.

Table **13.3.2**: Source of Water Contamination (Due to Acid Rain) in the United States

Combustion products	Sources
CO_2 and CO	Combustion of any material (any fuel or tree)
NO_X (NO_2 and NO_3)	High-temperature combustion of any fuel (gas, diesel, or coal), a product of lightning
SO_x (SO_2 and SO_3)	Combustion of sulfur-based fuels (diesel and coal), volcanic release
VOC (volatile organic compound)	Combustion of any carbon-based fuel (gas, diesel, or coal), fumes from paints or solvents

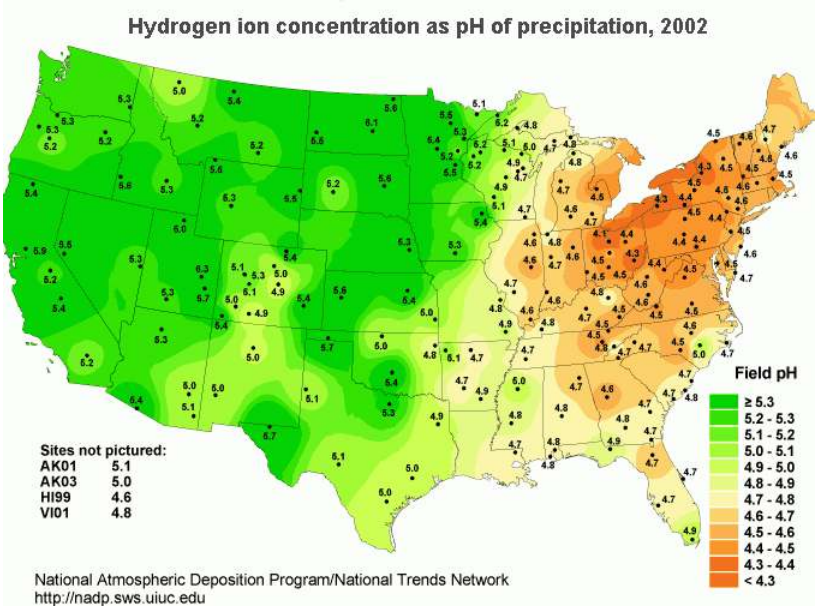


Figure **13.3.5**: pH of rainwater over the continental United States.

In the United States, the northeast has the most problems with acid rain. Concentrated populations that use electrical energy and vehicles contribute greatly to the pH reduction of rainwater. Reducing gaseous output requires capping combustion sources (vehicles and power plants). Acidity in rain is measured by collecting samples of rain and measuring its pH. To find the distribution of rain acidity, weather conditions are monitored and rain samples are collected at sites all over the country (Figure **13.3.5**). The areas of greatest acidity (lowest pH values) are located in the Northeastern United States. This pattern of high acidity is caused by a large number of cities, the dense population, and the concentration of power and industrial plants in the Northeast. In addition, the prevailing wind direction brings storms and pollution to the Northeast from the Midwest, and dust from the soil and rocks in the Northeastern United States is less likely to neutralize acidity in the rain.

Summary

- Water pollution is the contamination of water by an excess amount of a substance that can cause harm to human beings and/or the ecosystem.
- Pollutants enter water supplies from **point sources**, which are readily identifiable and relatively small locations, or **nonpoint sources**, which are large and more diffuse areas
- Organic matter as well as phosphates and nitrates from human and farm animal waste support the growth of algae and microorganisms, including bacteria.
- Eutrophication is an increase in the concentration of chemical nutrients in an ecosystem to an extent that increases the primary productivity of the ecosystem. Depending on the degree of eutrophication, subsequent negative environmental effects such as anoxia (oxygen depletion) and severe reductions in water quality may occur, affecting fish and other animal populations.
- Acid rain (formed as a consequence of air pollution) could affect building materials and living organisms on land and various bodies of water.

Contributors and Attributions

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13.4: Groundwater Contamination to Tainted Tap Water

Learning Objective

- Define groundwater contamination.
- List other groundwater contaminants and their sources.

Ground water contamination (also called groundwater pollution) occurs when pollutants are released to the ground and make their way down into groundwater. This type of water pollution can also occur naturally due to the presence of a minor and unwanted constituent, contaminant or impurity in the groundwater, in which case it is more likely referred to as contamination rather than pollution.

How Does Groundwater Become Contaminated?

The pollutant often creates a contaminant plume within an aquifer. Movement of water and dispersion within the aquifer spreads the pollutant over a wider area. Its advancing boundary, often called a plume edge, can intersect with groundwater wells or daylight into surface water such as seeps and springs, making the water supplies unsafe for humans and wildlife. The movement of the plume, called a plume front, may be analyzed through a hydrological transport model or groundwater model. Analysis of groundwater pollution may focus on soil characteristics and site geology, hydrogeology, hydrology, and the nature of the contaminants.

Pollution can occur from on-site sanitation systems, landfills, effluent from wastewater treatment plants, leaking sewers, petrol filling stations or from over application of fertilizers in agriculture. Pollution (or contamination) can also occur from naturally occurring contaminants, such as arsenic or fluoride. Using polluted groundwater causes hazards to public health through poisoning or the spread of disease.

Different mechanisms have influence on the transport of pollutants, e.g. diffusion, adsorption, precipitation, decay, in the groundwater. The interaction of groundwater contamination with surface waters is analyzed by use of hydrology transport models.

Pollutant types

Contaminants found in groundwater cover a broad range of physical, inorganic chemical, organic chemical, bacteriological, and radioactive parameters. Principally, many of the same pollutants that play a role in surface water pollution may also be found in polluted groundwater, although their respective importance may differ.

Arsenic and fluoride

Arsenic and fluoride have been recognized by the World Health Organization (WHO) as the most serious inorganic contaminants in drinking-water on a worldwide basis.

Inorganic arsenic is the most common type of arsenic in soil and water. The metalloid arsenic can occur naturally in groundwater, as seen most frequently in Asia, including in China, India and Bangladesh. In the Ganges Plain of northern India and Bangladesh severe contamination of groundwater by naturally occurring arsenic affects 25% of water wells in the shallower of two regional aquifers. Groundwater in these areas is also contaminated by the use of arsenic-based pesticides.

Arsenic in groundwater can also be present where there are mining operations or mine waste dumps that will leach arsenic.

Natural fluoride in groundwater is of growing concern as deeper groundwater is being used, "with more than 200 million people at risk of drinking water with elevated concentrations." Fluoride can especially be released from acidic volcanic rocks and dispersed volcanic ash when water hardness is low. High levels of fluoride in groundwater is a serious problem in the Argentinean Pampas, Chile, Mexico, India, Pakistan, the East African Rift, and some volcanic islands (Tenerife)

In areas that have naturally occurring high levels of fluoride in groundwater which is used for drinking water, both dental and skeletal fluorosis can be prevalent and severe.

Pathogens

Waterborne diseases can be spread via a groundwater well which is contaminated with fecal pathogens from pit latrines

The lack of proper sanitation measures, as well as improperly placed wells, can lead to drinking water contaminated with pathogens carried in feces and urine. Such fecal-oral transmitted diseases include typhoid, cholera and diarrhea. Of the four pathogen types that are present in feces (bacteria, viruses, protozoa, and helminths or helminth eggs), the first three can be commonly found in polluted groundwater, whereas the relatively large helminth eggs are usually filtered out by the soil matrix.

Deep, confined aquifers are usually considered the safest source of drinking water with respect to pathogens. Pathogens from treated or untreated wastewater can contaminate certain, especially shallow, aquifers.

Nitrate

Nitrate is the most common chemical contaminant in the world's groundwater and aquifers. In some low-income countries, nitrate levels in groundwater are extremely high, causing significant health problems. It is also stable (it does not degrade) under high oxygen conditions.

Nitrate levels above 10 mg/L (10 ppm) in groundwater can cause "blue baby syndrome" (acquired methemoglobinemia). Drinking water quality standards in the European Union stipulate less than 50 mg/L for nitrate in drinking water.

However, the linkages between nitrates in drinking water and blue baby syndrome have been disputed in other studies. The syndrome outbreaks might be due to other factors than elevated nitrate concentrations in drinking water.

Elevated nitrate levels in groundwater can be caused by on-site sanitation, sewage sludge disposal and agricultural activities. It can therefore have an urban or agricultural origin.

Organic compounds

Volatile organic compounds (VOCs) are a dangerous contaminant of groundwater. They are generally introduced to the environment through careless industrial practices. Many of these compounds were not known to be harmful until the late 1960s and it was some time before regular testing of groundwater identified these substances in drinking water sources.

Primary VOC pollutants found in groundwater include aromatic hydrocarbons such as BTEX compounds (benzene, toluene, ethylbenzene and xylenes), and chlorinated solvents including tetrachloroethylene (PCE), trichloroethylene (TCE), and vinyl chloride (VC). BTEX are important components of gasoline. PCE and TCE are industrial solvents historically used in dry cleaning processes and as a metal degreaser, respectively.

Other organic pollutants present in groundwater and derived from industrial operations are the polycyclic aromatic hydrocarbons (PAHs). Due to its molecular weight, Naphthalene is the most soluble and mobile PAH found in groundwater, whereas benzo(a)pyrene is the most toxic one. PAHs are generally produced as byproducts by incomplete combustion of organic matter.

Organic pollutants can also be found in groundwater as insecticides and herbicides. As many other synthetic organic compounds, most pesticides have very complex molecular structures. This complexity determines the water solubility, adsorption capacity, and mobility of pesticides in the groundwater system. Thus, some types of pesticides are more mobile than others so they can more easily reach a drinking-water source.

Metals

Several trace metals occur naturally in certain rock formations and can enter in the environment from natural processes such as weathering. However, industrial activities such as mining, metallurgy, solid waste disposal, paint and enamel works, etc. can lead to elevated concentrations of toxic metals including lead, cadmium and chromium. These contaminants have the potential to make their way into groundwater.

The migration of metals (and metalloids) in groundwater will be affected by several factors, in particular by chemical reactions which determine the partitioning of contaminants among different phases and species. Thus, the mobility of metals primarily depends on the pH and redox state of groundwater.

Pharmaceuticals

Trace amounts of pharmaceuticals from treated wastewater infiltrating into the aquifer are among emerging ground-water contaminants being studied throughout the United States. Popular pharmaceuticals such as antibiotics, anti-inflammatories, antidepressants, decongestants, tranquilizers, etc. are normally found in treated wastewater. This wastewater is discharged from the treatment facility, and often makes its way into the aquifer or source of surface water used for drinking water.

Trace amounts of pharmaceuticals in both groundwater and surface water are far below what is considered dangerous or of concern in most areas, but it could be an increasing problem as population grows and more reclaimed wastewater is utilized for municipal water supplies.

Others

Other organic pollutants include a range of organohalides and other chemical compounds, petroleum hydrocarbons, various chemical compounds found in personal hygiene and cosmetic products, drug pollution involving pharmaceutical drugs and their metabolites. Inorganic pollutants might include other nutrients such as ammonia and phosphate, and radionuclides such as uranium (U) or radon (Rn) naturally present in some geological formations. Saltwater intrusion is also an example of natural contamination, but is very often intensified by human activities.

Groundwater pollution is a worldwide issue. A study of the groundwater quality of the principal aquifers of the United States conducted between 1991 and 2004, showed that 23% of domestic wells had contaminants at levels greater than human-health benchmarks. Another study suggested that the major groundwater pollution problems in Africa, considering the order of importance are: (1) nitrate pollution, (2) pathogenic agents, (3) organic pollution, (4) salinization, and (5) acid mine drainage.

Potential Health and Other Effects of Groundwater Contaminants

The United States Geological Survey provides an extensive list of groundwater contaminants with their potential health and other effects.

https://www.epa.gov/sites/production/files/2015-08/documents/mgwc-gwc1.pdf

Summary

- Ground water contamination (also called groundwater pollution) occurs when pollutants are released to the ground and make their way down into groundwater.
- Contaminants found in groundwater cover a broad range of physical, inorganic chemical, organic chemical, bacteriological, and radioactive parameters.
- The United States Geological Survey developed an extensive list of groundwater contaminants with their potential health and other effects.

Contributors and Attributions

- Marisa Alviar-Agnew (Sacramento City College)
- Wikipedia
- US Geological Survey (USGS)

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13.5: Making Water Fit to Drink

Learning Objectives

- Know the primary standards for various contaminants in drinking water.
- Describe the importance of the different steps in water treatment.

Public Water Systems Fast Facts from US CDC

- Of the approximately 155,693 public water systems in the United States, 52,110 (33.5%) are community systems and 103,583 (66.5%) are noncommunity systems, including 84,744 transient systems and 18,839 nontransient systems [1].
- Over 286 million Americans get their tap water from a community water system [1].
- 8% of U.S. community water systems provide water to 82% of the U.S. population through large municipal water systems [1].
- Although the majority of community water systems (78%) are supplied by ground water, more people (68%) are supplied year-round by community water systems that use surface water .

  Note: EPA. Factoids: drinking water and ground water statistics for 2007. March 2008, April 2008.

Safe Drinking Water Act

Up until 1974, public drinking water supplies in the United States were monitored and regulated by state and local authorities. Lists of contaminants with their various concentrations could vary from state to state. As the chemical industry grew, these same state agencies noted the increased presence of existing and new organic chemicals in public water systems. In order to standardize drinking water across the country, the Environmental Protection Agency (EPA) enacted the Safe Water Drinking Act of 1974.



Figure **13.5.1**: AFGE members and environmental activists participated in an event at the Washington, D.C. EPA headquarters to thank EPA workers for their work. (CC BY 2.0; AFGE).

The 1974 act enabled the EPA to monitor and regulate public water systems that serve over 25 people. Implementation and enforcement of drinking water standards would still be performed by each state. Regarding drinking water sources (surface and ground), the EPA and state agencies protect and monitor these as well. Levels of contaminants would be defined using the concentration terms Maximum Contaminant Level (MCL) and Treatment Technique (TT)

National Primary Standards for Drinking Water

The first set of drinking water standards included only 22 chemicals and/or pathogens. EPA established two major types of contaminants: primary and secondary. The first of these types (primary) contaminants are substances (examples could include Hg, As, and U) that can be toxic in small amounts. On the other hand, secondary contaminants are less toxic species (Fe and Zn) and would include cosmetic issues (color, taste, and odor) of drinking water.

All primary contaminants have enforceable concentration values. For the majority of these pollutants, EPA lists concentration limits by using the term **Maximum Contaminant Level (MCL)**. If a water supplier exceeds a given MCL for a toxin, then fines and penalties could by imposed by the EPA. A few pathogens (Giardia Lamblia and Legionella) use Treatment Technique (TT) notation rather than numerical MCL concentrations. Water that contains any amount of these pathogens must be sanitized immediately with a standardized EPA procedure.

A detailed list of acceptable levels of different contaminants by EPA classification can be found on the the link below.

https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations

The complete table of standards is given below.

https://www.epa.gov/sites/production/files/2016-06/documents/npwdr_complete_table.pdf

Table **13.5.1**

***Table* 13.5.1** *Standards for Various Contaminants in Drinking Water.*

Contaminant	MCLG[1](mg/L)[2]	MCL or TT[1](mg/L)[2]	Potential Health Effects from Long-Term Exposure Above the MCL (unless specified as short-term)	Sources of Contaminant in Drinking Water
Microorganisms-*Cryptosporidium*	zero	TT[3]	Gastrointestinal illness (such as diarrhea, vomiting, and cramps)	Human and animal fecal waste
Microorganisms-*Giardia lamblia*	zero	TT	Gastrointestinal illness (such as diarrhea, vomiting, and cramps)	Human and animal fecal waste
Microorganisms-Total Coliforms (including fecal coliform and *E. Coli*)	zero	5.0%	Not a health threat in itself; it is used to indicate whether other potentially harmful bacteria may be present[5]	Coliforms are naturally present in the environment; as well as feces; fecal coliforms and *E. coli* only come from human and animal fecal waste.
Viruses (enteric)	zero	TT	Gastrointestinal illness (such as diarrhea, vomiting, and cramps)	Human and animal fecal waste
Inorganic Chemicals-Antimony	0.006	0.006	Increase in blood cholesterol; decrease in blood sugar	Discharge from petroleum refineries; fire retardants; ceramics; electronics; solder
Inorganic Chemicals-Chromium (total)	0.1	0.1	Allergic dermatitis	Discharge from steel and pulp mills; erosion of natural deposits
Inorganic Chemicals-Nitrate (measured as Nitrogen)	10	10	Infants below the age of six months who drink water containing nitrate in excess of the MCL could become seriously ill and, if untreated, may die. Symptoms include shortness of breath and blue-baby syndrome.	Runoff from fertilizer use; leaking from septic tanks, sewage; erosion of natural deposits
Organic Chemicals-Benzene	zero	0.005	Anemia; decrease in blood platelets; increased risk of cancer	Discharge from factories; leaching from gas storage tanks and landfills
Organic Chemicals-Carbon tetrachloride	zero	0.005	Liver problems; increased risk of cancer	Discharge from chemical plants and other industrial activities
Organic Chemicals-Styrene	0.1	0.1	Liver, kidney, or circulatory system problems	Discharge from rubber and plastic factories; leaching from landfills

Radionuclides Alpha particles	none ---------- zero	15 picocuries per Liter (pCi/L)	Increased risk of cancer	Erosion of natural deposits of certain minerals that are radioactive and may emit a form of radiation known as alpha radiation

Notes

[1]Definitions:

- Maximum Contaminant Level Goal (MCLG) - The level of a contaminant in drinking water below which there is no known or expected risk to health. MCLGs allow for a margin of safety and are non-enforceable public health goals.
- Maximum Contaminant Level (MCL) - The highest level of a contaminant that is allowed in drinking water. MCLs are set as close to MCLGs as feasible using the best available treatment technology and taking cost into consideration. MCLs are enforceable standards.
- Maximum Residual Disinfectant Level Goal (MRDLG) - The level of a drinking water disinfectant below which there is no known or expected risk to health. MRDLGs do not reflect the benefits of the use of disinfectants to control microbial contaminants.
- Treatment Technique (TT) - A required process intended to reduce the level of a contaminant in drinking water.
- Maximum Residual Disinfectant Level (MRDL) - The highest level of a disinfectant allowed in drinking water. There is convincing evidence that addition of a disinfectant is necessary for control of microbial contaminants.

[2] Units are in milligrams per liter (mg/L) unless otherwise noted. Milligrams per liter are equivalent to parts per million (PPM).

Calculations of Parts per Million and Parts per Billion

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, contaminants, 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.

ppm and ppb

In aqueous solutions, 1 ppm is essentially equal to 1 mg/L, and 1 ppb is equivalent to 1 µg/L.

$$1 \text{ ppm} = \frac{1 \text{ mg Solute}}{1 \text{ L Solution}}$$

$$1 \text{ ppb} = \frac{1 \ \mu\text{g Solute}}{1 \text{ L Solution}}$$

Amendment SDWA of 1986

This change to the Safe Drinking Water Act established MCLGs and increased the total of regulated contaminants to 83. The EPA would also install more monitoring devices to detect organic contaminants. Research was done to detect pathogens more effectively to reduce disease. Lastly, public notifications from water systems to the consumers would be made announced if severe water issues occurred.

Amendment of SDWA of 1996

This particular legislation provided more protection and assessment of water sources (lakes, river, streams). In addition, water companies were required to provide consumers with a water quality report. States could seek federal money for upgrading their water quality processes. Cost benefit analysis would be done to determine risk and reward of lowering the concentration of a contaminant. For small regulated water companies, more financial and technical assistance would be offered to help them maintain drinking water standards.

Water Treatment (US CDC)

Drinking water supplies in the United States are among the safest in the world. However, even in the U.S., drinking water sources can become contaminated, causing sickness and disease from waterborne germs, such as *Cryptosporidium*, *E. coli*, Hepatitis A, *Giardia intestinalis*, and other pathogens.

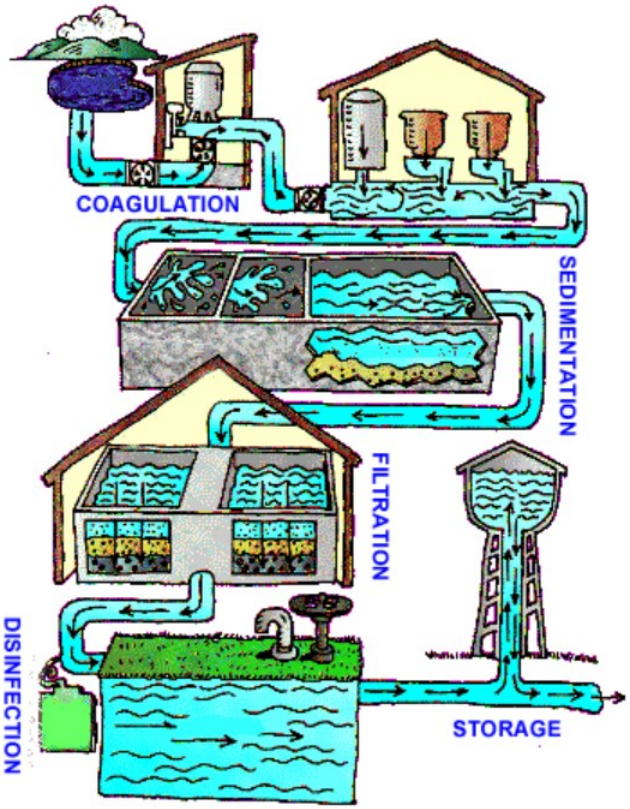


Figure **13.5.1** The common steps in water treatment. Source: US EPA

Drinking water sources are subject to contamination and require appropriate treatment to remove disease-causing agents. Public drinking water systems use various methods of water treatment to provide safe drinking water for their communities. Today, the most common steps in water treatment (Figure **13.5.1**) used by community water systems (mainly surface water treatment) include:

Coagulation and Flocculation

Coagulation and flocculation are often the first steps in water treatment. Chemicals with a positive charge are added to the water. The positive charge of these chemicals neutralizes the negative charge of dirt and other dissolved particles in the water. When this

occurs, the particles bind with the chemicals and form larger particles, called floc. Historically, dirty water is cleaned by treating with alum, $Al_2(SO_4)_3 \cdot 12\ H_2O$, and lime, $Ca(OH)_2$. These electrolytes cause the pH of the water to change due to the following reactions:

$$Al_2(SO_4)_3.12\ H_2O, \rightarrow Al^{3+}(aq) + 3\ SO_4^{2-}(aq) + 12\ H_2O$$
$$SO_4^{2-}(aq) + H_2O \rightarrow HSO_4^-(aq) + OH^- \text{ (causing pH change)}$$
$$Ca(OH)_2 \rightarrow Ca^{2+}(aq) + 2\ OH^- \text{ (causing pH change)}$$

The slightly basic water causes $Al(OH)_3$, $Fe(OH)_3$ and $Fe(OH)_2$ to precipitate, bringing the small particulates with them and the water becomes clear. Some records have been found that Egyptians and Romans used these techniques as early as 2000 BC.

Suspension of iron oxide particulates and humic organic matter in water gives water the yellow muddy appearance. Both iron oxide particulates and organic matter can be removed from coagulation and flocculation. The description given here is oversimplified, and many more techniques have been applied in the treatment of water. Coagulation is a major application of lime in the treatment of wastewater.

Other salts such as iron sulfates $Fe_2(SO_4)_3$ and $FeSO_4$, chromium sulfate $Cr_2(SO_4)_3$, and some special polymers are also useful. Other ions such as sodium, chloride, calcium, magnesium, and potassium also affect the coagulation process. So do temperature, pH, and concentration.

Disposal of coagulation sludge is a concern, however.

Sedimentation

During sedimentation, floc settles to the bottom of the water supply, due to its weight. This settling process is called sedimentation. The floc particles are then removed from the bottom of the basins.

Aeration

Bringing air into intimate contact with water for the purpose of exchanging certain components between the two phases is called **aeration**. Oxygenation is one of the purposes of aeration. Others are removal of volatile organic substances, hydrogen sulfide, ammonia, and volatile organic compounds

Filtration

Once the floc has settled to the bottom of the water supply, the clear water on top will pass through filters of varying compositions (sand, gravel, and charcoal) and pore sizes, in order to remove dissolved particles, such as dust, parasites, bacteria, viruses, and chemicals.

Treatment with Chlorine and/or Chloramine

Most communities use either chlorine or chloramines. Some communities switch back and forth between chlorine and chloramines at different times of the year or for other operational reasons. Less commonly, utilities use other disinfectants, such as chlorine dioxide. Some water systems that use water from a groundwater source (like community wells) do not have to add a disinfectant at all.

Ozone Disinfection

Ozone disinfection, or ozonation, is an unstable molecule which readily gives up one atom of oxygen providing a powerful oxidizing agent which is toxic to most waterborne organisms. It is a very strong, broad spectrum disinfectant that is widely used in Europe and in a few municipalities in the United States and Canada. It is an effective method to inactivate harmful protozoa that form cysts. It also works well against almost all other pathogens. Ozone is made by passing oxygen through ultraviolet light or a "cold" electrical discharge. To use ozone as a disinfectant, it must be created on-site and added to the water by bubble contact. Some of the advantages of ozone include the production of fewer dangerous by-products and the absence of taste and odor problems (in comparison to). No residual ozone is left in the water. In the absence of a residual disinfectant in the water, chlorine or chloramine may be added throughout a distribution system to remove any potential pathogens in the distribution piping.

Ultraviolet Disinfection

Ultraviolet disinfection of water is a purely physical, chemical-free process. Even parasites such as Cryptosporidium or Giardia, which are extremely resistant to chemical disinfectants, are efficiently reduced. UV can also be used to remove chlorine and chloramine species from water; this process is called photolysis, and requires a higher dose than normal disinfection. The dead microorganisms are not removed from the water. UV disinfection does not remove dissolved organics, inorganic compounds or particles in the water. The world's largest water disinfection plant treats drinking water for New York city. The Catskill-Delaware Water Ultraviolet Disinfection Facility, commissioned on 8 October 2013, incorporates a total of 56 energy-efficient UV reactors treating up to 2.2 billion US gallons (8,300,000 m^3) a day.

Ultraviolet can also be combined with ozone or hydrogen peroxide to produce hydroxyl radicals to break down trace contaminants through an advanced oxidation process.

Fluoridation (US CDC)

The mineral fluoride occurs naturally on earth and is released from rocks into the soil, water, and air. All water contains some fluoride. Usually, the fluoride level in water is not enough to prevent tooth decay; however, some groundwater and natural springs can have naturally high levels of fluoride.

Fluoride has been proven to protect teeth from decay. Bacteria in the mouth produce acid when a person eats sugary foods. This acid eats away minerals from the tooth’s surface, making the tooth weaker and increasing the chance of developing cavities. Fluoride helps to rebuild and strengthen the tooth’s surface, or enamel. Water fluoridation prevents tooth decay by providing frequent and consistent contact with low levels of fluoride. By keeping the tooth strong and solid, fluoride stops cavities from forming and can even rebuild the tooth’s surface.

Community water fluoridation is the process of adjusting the amount of fluoride found in water to achieve optimal prevention of tooth decay.

Although other fluoride-containing products, such as toothpaste, mouth rinses, and dietary supplements are available and contribute to the prevention and control of tooth decay, community water fluoridation has been identified as the most cost-effective method of delivering fluoride to all, reducing tooth decay by 25% in children and adults.[1]

Benefits: Strong Teeth (US CDC)

Fluoride benefits children and adults throughout their lives. For children younger than age 8, fluoride helps strengthen the adult (permanent) teeth that are developing under the gums. For adults, drinking water with fluoride supports tooth enamel, keeping teeth strong and healthy. The health benefits of fluoride include having:

- Fewer cavities.
- Less severe cavities.
- Less need for fillings and removing teeth.
- Less pain and suffering because of tooth decay.

Fluoride in the Water Today

In 2012, more than 210 million people, or 75% of the US population, were served by community water systems that contain enough fluoride to protect their teeth.[5] However, approximately 100 million Americans still do not have access to water with fluoride. Because it is so beneficial, the United States has a national goal for 80% of Americans to have water with enough fluoride to prevent tooth decay by 2020.



https://www.youtube.com/watch?v=0_ZcCqqpS2o&feature=youtu.be

Summary

- The Safe Drinking Water Act (SDWA) (originally passed by Congress in 1974) protects public health by regulating the nation's public drinking water supply.
- The different steps in water treatment include floculation, sedimentation, filtration, aeration, and disinfection or combinations thereof. Fluoride is also added to municipal water systems for prevention of tooth decay.

Contributors and Attributions

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- Marisa Alviar-Agnew (Sacramento City College)
- US EPA
- Center for Disease Control (CDC)
- Wikipedia

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13.6: Wastewater Treatment

Learning Objectives

- Explain the major steps in wastewater treatment.
- List the different uses of reclaimed water.

Wastewater and sewage is treated in three phases: primary (solid removal), secondary (bacterial decomposition), and tertiary (extra filtration).

Sewage is generated by residential and industrial establishments. It includes household waste liquid from toilets, baths, showers, kitchens, sinks, and so forth that is disposed of via sewers. In many areas, sewage also includes liquid waste from industry and commerce. The separation and draining of household waste into greywater and blackwater is becoming more common in the developed world. Greywater is water generated from domestic activities such as laundry, dishwashing, and bathing, and can be reused more readily. Blackwater comes from toilets and contains human waste.

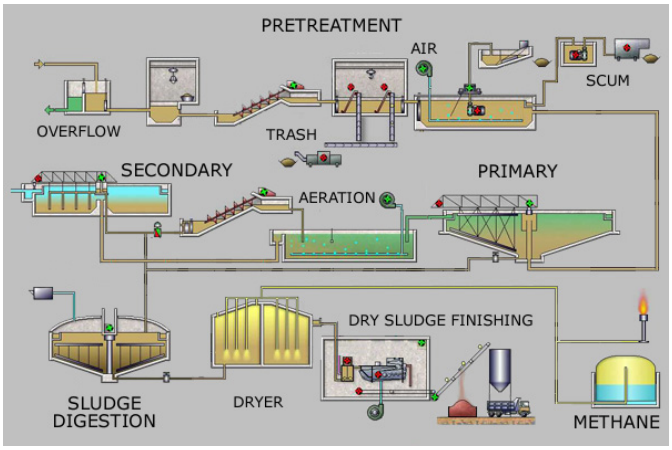


***Figure* 13.6.1 Diagram of Sewage Treatment Process**: Sewage passes through primary, secondary, and tertiary treatment.

Primary Treatment

In primary treatment, sewage is stored in a basin where solids (sludge) can settle to the bottom and oil and lighter substances can rise to the top. These layers are then removed and then the remaining liquid can be sent to secondary treatment. Sewage sludge is treated in a separate process called sludge digestion.

Secondary Treatment

Secondary treatment removes dissolved and suspended biological matter, often using microorganisms in a controlled environment. Most secondary treatment systems use aerobic bacteria, which consume the organic components of the sewage (sugar, fat, and so on). Some systems use fixed film systems, where the bacteria grow on filters, and the water passes through them. Suspended growth systems use “activated” sludge, where decomposing bacteria are mixed directly into the sewage. Because oxygen is critical to bacterial growth, the sewage is often mixed with air to facilitate decomposition.

Tertiary Treatment

Tertiary treatment (sometimes called “effluent polishing”) is used to further clean water when it is being discharged into a sensitive ecosystem.

Several methods can be used to further disinfect and purify sewage beyond primary and secondary treatment.

Sand filtration, where water is passed through a sand filter, can be used to remove particulate matter.

Wastewater may still have high levels of nutrients such as nitrogen and phosphorus. These can disrupt the nutrient balance of aquatic ecosystems and cause algae blooms and excessive weed growth. Phosphorus can be removed biologically in a process

called **enhanced biological phosphorus removal**. In this process, specific bacteria, called polyphosphate accumulate organisms that store phosphate in their tissue. When the biomass accumulated in these bacteria is separated from the treated water, these biosolids have a high fertilizer value. Nitrogen can also be removed using nitrifying bacteria.

Lagooning is another method for removing nutrients and waste from sewage. Water is stored in a lagoon and native plants, bacteria, algae, and small zooplankton filter nutrients and small particles from the water.

Treatment by activated carbon is mostly due to adsorption or absorption. When a chemical species is adhered to the surface of a solid, it is an **adsorption**. When partial chemical bonds are formed between adsorbed species or when the absorbate got into the channels of the solids, we call it **absorption**. However, these two terms are often used to mean the same, because to distinguish one from type from the other is very difficult.

Application of activated charcoal for the removal of undesirable order and taste in drinking water has been recognized at the dawn of civilization. Using bone char and charred vegetation, gravel, and sand for the filtration of water for domestic application has been practised for thousands of years. Charcoal absorbs many substances, ranging from colored organic particulates to inorganic metal ions. Charcoal has been used to remove the colour of raw sugar from various sources.

Filtration is the process of removing solids from a fluid by passing it through a porous medium. Coarse, medium, and fine porous media have been used depending on the requirement. The filter media are artificial membranes, nets, sand filter, and high technological filter systems. The choice of filters depends on the required filtering speed and the *cleanness* requirement. The flow required for filtration can be achieved using gravity or pressure. In pressure filtration, one side of the filter medium is at higher pressure than that of the other so that the filter plane has a pressure drop. Some portion of this filter type must be enclosed in a container.

When a compartment containing a dilute solution is connected to another compartment containing a concentrated solution by a semipermeable membrane, water molecules move from the dilute solution to concentrated solution. This phenomenon is called **osmosis**. By applying pressure in the higher concentration solution, water molecules migrate from a high concentration solution to a low concentration solution through a semipermeable membrane. This method is called **reverse osmosis water filter system**. In this technique, the membrane must be able to tolerate the high pressure, and prevent solute molecules to pass through. This technology certainly works, and it has been used to convert salt (ocean or sea) water into fresh water. With this technique, the water with higher concentration is discharged. Thus, this technology is costly in regions where the water cost is high.

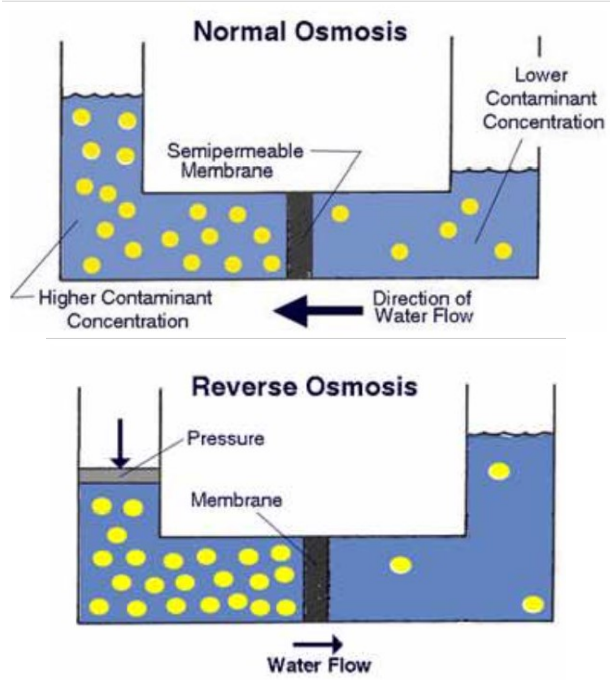


Figure **13.6.2** Comparison of normal osmosis and reverse osmosis. Source: PurePro.

Sludge Digestion

Sewage sludge scraped off the bottom of the settling tank during primary treatment is treated separately from wastewater. Sludge can be disposed of in several ways. First, it can be digested using bacteria; bacterial digestion can sometimes produce methane biogas, which can be used to generate electricity. Sludge can also be incinerated, or condensed, heated to disinfect it, and reused as fertilizer.



Uses of Reclaimed Wastewater

Water reclamation (also called **wastewater reuse**) is the process of converting wastewater into water that can be reused for other purposes. Reuse may include irrigation of gardens and agricultural fields or replenishing surface water and groundwater (i.e., groundwater recharge). Reused water may also be directed toward fulfilling certain needs in residences (e.g. toilet flushing), businesses, and industry, and could even be treated to reach drinking water standards. This last option is called either "direct potable reuse" or "indirect potable" reuse, depending on the approach used.

Reclaiming water for reuse applications instead of using freshwater supplies can be a water-saving measure. When used water is eventually discharged back into natural water sources, it can still have benefits to ecosystems, improving streamflow, nourishing plant life and recharging aquifers, as part of the natural water cycle.

Wastewater reuse is a long-established practice used for irrigation, especially in arid countries. Reusing wastewater as part of sustainable water management allows water to remain as an alternative water source for human activities. This can reduce scarcity and alleviate pressures on groundwater and other natural water bodies. Another potentially positive aspect is the nutrient content in the wastewater, which might reduce the need of other fertilizers.

Drawbacks or risks often mentioned include the content of potentially harmful substances such as bacteria, heavy metals or organic pollutants (including pharmaceuticals, personal care products and pesticides). Irrigation with wastewater can have both positive and negative effects on soil and plants, depending on the composition of the wastewater and on the soil or plant characteristics.

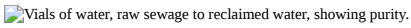


Figure **13.6.3** *The Sequence of reclamation from left: raw sewage, plant effluent, and finally reclaimed water (after several treatment steps). (Credit: Wikipedia)*

Most of the uses of water reclamation are non potable uses such as washing cars, flushing toilets, cooling water for power plants, concrete mixing, artificial lakes, irrigation for golf courses and public parks, and for hydraulic fracturing. Where applicable, systems run a dual piping system to keep the recycled water separate from the potable water.

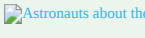
The main reclaimed water applications in the world are shown below:

Table **13.6.1** Uses of Reclaimed Water

Categories of use	Uses
Urban uses	Irrigation of public parks, sporting facilities, private gardens, roadsides; Street cleaning; Fire protection systems; Vehicle washing; Toilet flushing; Air conditioners; Dust control.
Agricultural uses	Food crops not commercially processed; Food crops commercially processed; Pasture for milking animals; Fodder; Fibre; Seed crops; Ornamental flowers; Orchards; Hydroponic culture; Aquaculture; Greenhouses; Viticulture.
Industrial uses	Processing water; Cooling water; Recirculating cooling towers; Washdown water; Washing aggregate; Making concrete; Soil compaction; Dust control.
Recreational uses	Golf course irrigation; Recreational impoundments with/without public access (e.g. fishing, boating, bathing); Aesthetic impoundments without public access; Snowmaking.
Environmental uses	Aquifer recharge; Wetlands; Marshes; Stream augmentation; Wildlife habitat; Silviculture.
Potable uses	Aquifer recharge for drinking water use; Augmentation of surface drinking water supplies; Treatment until drinking water quality.

Astronauts and Reclaimed Urine

If it's good enough for astronauts...



Astronauts aboard the International Space Station drink reclaimed urine. (Credit: NASA)

In outer space, as on the International Space Station, water is at a premium and not a drop is to be wasted. Astronauts aboard the station must drink recycled water. Water from humidity in the air is condensed and used as drinking water, but American astronauts also drink recycled urine! You can imagine the urine, which is of course almost all water, would go through a rigorous purification process, but this just shows if the need exists, that the same water can serve valuable purposes over and over again.

Summary

- Wastewater treatment is a process used to remove from or and convert it into an that can be returned to the with minimum impact on the environment, or directly reused.
- In a wastewater treatment plant wastewater or sewage undergo primary,secondary, as well as tertiary treatments depending on the end use.
- Most of the uses of water reclamation are non potable uses such as washing cars, flushing toilets, cooling water for power plants, concrete mixing, artificial lakes, irrigation for golf courses and public parks, and for hydraulic fracturing

Contributors and Attributions

- Libretexts: Microbioloy (Boundless)
- USGS
- Chung (Peter) Chieh (Professor Emeritus, Chemistry @ University of Waterloo)
- Marisa Alviar-Agnew (Sacramento City College)
- Wikipedia

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13.7: Water Who Uses It and How Much?

Learning Objective

- List the end uses of water in residential and non residential areas.

Water in Daily Life

Residential water use (also called domestic use, household use, or tap water use) includes all indoor and outdoor uses of drinking quality water at single-family and multifamily dwellings. These uses include a number of defined purposes (or water end uses) such as flushing toilets, washing clothes and dishes, showering and bathing, drinking, food preparation, watering lawns and gardens, and maintaining swimming pools. Some of these end uses are detectable (and measurable) while others are more difficult to gauge.

Indoor water use includes water flows through fixtures and appliances inside the house. Because the distribution of indoor use in the sample of homes measured is positively skewed, a more appropriate measure of central tendency is the median, which is about 125 gphd (gallons per household per day) or 472 lphd, liters per household per day). Toilet flushing is the largest indoor use of water, followed by flows through kitchen and bathroom faucets, showers, clothes washers, leaks, bathtubs, other/miscellaneous uses, and dishwashers. Since the late 1990s, total indoor use has decreased by 22 percent, primarily due to the improved water efficiency of clothes washers and toilets, among other low-flow fixtures.

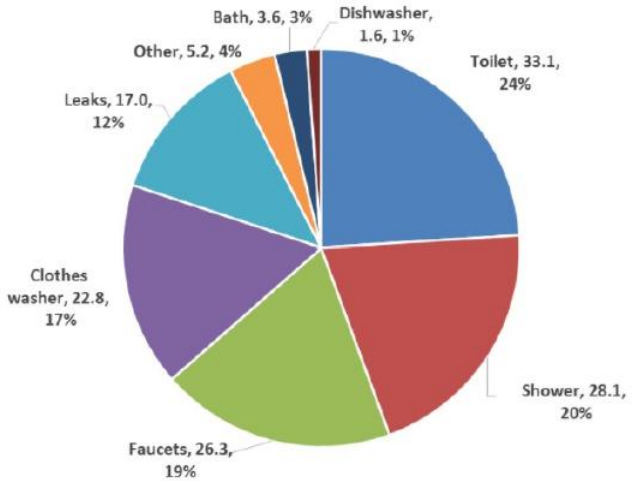


Figure **13.7.1** End uses of water for households in the U.S.in gallons per household per day and percent of indoor use.

The outdoor residential water use includes landscape irrigation, filling and back washing swimming pools, water used through outdoor faucets (hose bibs) for washing pavement and cars, and other outdoor uses. Annual outdoor use in North American cities differs by climatic region and ranged from 13,000 gallons in Waterloo, Canada to 120,400 gallons in Scottsdale, Arizona. The average outdoor use across 9 sampled cities in the Water Research Foundation study was 50,500 gallons per household per year or 138 gallons per day (524 liters per day). Nearly 17 percent of homes irrigate their landscapes in excess of theoretical irrigation requirement. If excess irrigation could be eliminated, the average outdoor use would drop by 8,200 gallons per house, or by 16 percent.

Commercial, Industrial, Agricultural & Electricity Water Use

It’s easy to forget that we also use water in ways we don't see every day (Figure **13.7.2**). Water is used to grow our food, manufacture our favorite goods, and keep our businesses running smoothly. We also use a significant amount of water to meet the nation's energy needs.US Freshwater Withdrawals Chart

***Figure* 13.7.2** *U.S. freshwater withdrawals.*

Water Footprint

A **water footprint** shows the extent of water use in relation to consumption by people. The water footprint of an individual, community or business is defined as the total volume of fresh water used to produce the goods and services consumed by the individual or community or produced by the business. Water use is measured in water volume consumed (evaporated) and/or polluted per unit of time. A water footprint can be calculated for any well-defined group of consumers (e.g., an individual, family, village, city, province, state or nation) or producers (e.g., a public organization, private enterprise or economic sector), for a single process (such as growing rice) or for any product or service.

Traditionally, water use has been approached from the production side, by quantifying the following three columns of water use: water withdrawals in the agricultural, industrial, and domestic sector. While this does provide valuable data, it is a limited way of looking at water use in a globalized world, in which products are not always consumed in their country of origin. International trade of agricultural and industrial products in effect creates a global flow of virtual water, or *embodied water* (akin to the concept of embodied energy).

In 2002, the water footprint concept was introduced in order to have a consumption-based indicator of water use, that could provide useful information in addition to the traditional production-sector-based indicators of water use. It is analogous to the ecological footprint concept introduced in the 1990s. The water footprint is a geographically explicit indicator, not only showing volumes of water use and pollution, but also the locations. Thus, it gives a grasp on how economic choices and processes influence the availability of adequate water resources and other ecological realities across the globe (and vice versa).

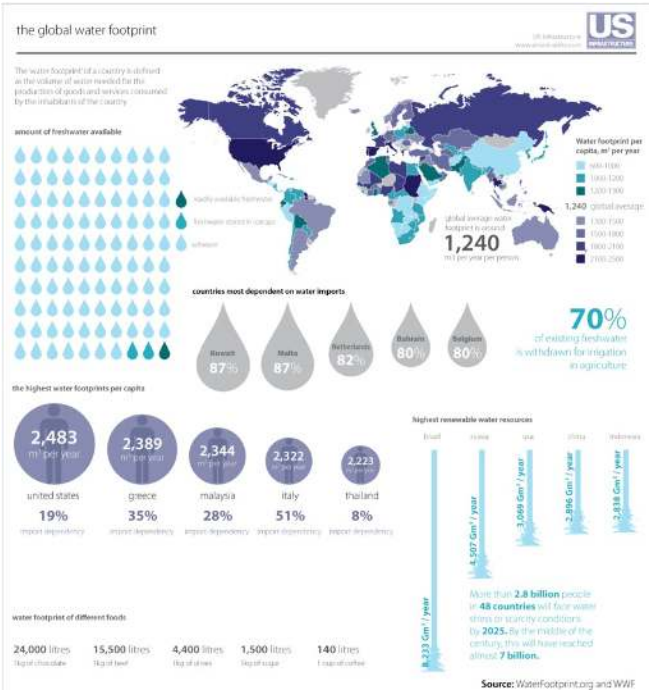


Figure **13.7.3** *The global water footprint.*

The water footprint of a product is the total volume of freshwater used to produce the product, summed over the various steps of the production chain. The water footprints involved in various diets vary greatly, and much of the variation tends to be associated with levels of meat consumption. The following table gives examples of estimated global average water footprints of popular agricultural products.

Table **13.7.3** *Global average water footprints of some agricultural products.*

Product	Global average water footprint, L/kg
almonds, shelled	16,194
beef	15,415
chocolate	17,196
cotton lint	9,114
lettuce	238
milk	1,021
olive oil	14,430
tomatoes, fresh	214
tomatoes, dried	4,275
vanilla beans	126,505
wheat bread	1,608

(For more product water footprints: see the Product Gallery of the Water Footprint Network)

Summary

- The average American family daily indoor water use is approximately 125 gallons per household per day.
- The water footprint is a geographically explicit indicator, not only showing volumes of water use and pollution, but also the locations.

Contributors and Attributions

- Marisa Alviar-Agnew (Sacramento City College)
- Wikipedia

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CHAPTER OVERVIEW

14: Earth

14.1: Spaceship Earth- Structure and Composition

14.2: Silicates and the Shapes of Things

14.3: Metals and Ores

14.4: Earth's Dwindling Resources

Thumbnail: Nutrient pollution caused by Surface runoff of soil and fertilizer during a rain storm. (Public Domain; Lynn Betts via Wikipedia).

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14.1: Spaceship Earth- Structure and Composition

Learning Objective

- Describe the chemical composition and structure of Earth.

The layers found inside Earth are divided by composition into core, mantle, and crust or by mechanical properties into lithosphere and asthenosphere. Scientists use information from earthquakes and computer modeling to learn about Earth's interior.

THE EARTH'S LAYERS

The layers scientists recognize are pictured in Figure **14.1.1**.

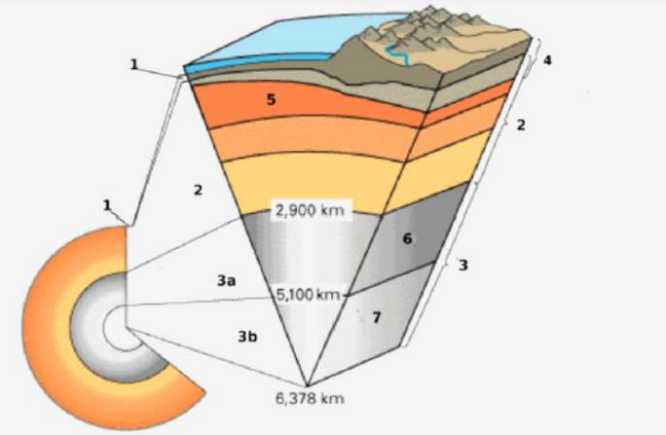


Figure **14.1.1** *A cross section of Earth showing the following layers: (1) crust (2) mantle (3a) outer core (3b) inner core (4) lithosphere (5) asthenosphere (6) outer core (7) inner core.*

Core, mantle, and crust are divisions based on chemical composition:

Crust: The Earth's surface is the crust. Generally speaking, the crust is predominately silicon oxide and aluminum oxide. Continental crust is thicker and less dense than oceanic crust. Earth's crust varies in thickness from less than 5 km (under mid-ocean spreading ridges) to more than 70 km (beneath the highest mountain range).

Mantle: The next layer down chemically is the mantle. The mantle has an ultramafic composition – it contains more iron, magnesium, less aluminum and somewhat less silicon than the crust. The mantle is roughly 2,900 km thick. In terms of volume, the mantle is the largest of earth's three chemical layers.

Core:The final layer is the core, which is mostly iron and nickel. The core is about 3,500 km thick.

Table **14.1.1** summarizes the chemical layers of the earth.

Table **14.1.1** *Chemical Layers of Earth.*

Crust	Mantle	Core
composition: high Si, Al, & O	*composition:* moderate Si, high Mg & Fe	*composition:* Fe & Ni
thickness: 5 to 70 km	*thickness:* 2,900 km	*thickness:* 3,500 km

Table **14.1.2** provides the elemental composition of the Earth's crust.

Table **14.1.2** The Elements of Earth's Crust. Source: Wikipedia

Most Abundant Elements of Earth's Crust	Approximate % by weight
O	46.6
Si	27.7
Al	8.1
Fe	5.0
Ca	3.6
Na	2.8
K	2.6
Mg	1.5

Lithosphere and asthenosphere are divisions based on mechanical properties:

1. The lithosphere is composed of both the crust and the portion of the upper mantle that behaves as a brittle, rigid solid.
2. The asthenosphere is partially molten upper mantle material that behaves plastically and can flow.

Compositional and Mechanical Layers of the Earth

https://www.khanacademy.org/science/cosmology-and-astronomy/earth-history-topic/plate-techtonics/v/compositional-and-mechanical-layers-of-the-earth

***Video* 14.1.1** *A comparison of the compositional and mechanical layers of the earth.*

Crust and Lithosphere

Earth's outer surface is its crust; a cold, thin, brittle outer shell made of rock. The crust is very thin, relative to the radius of the planet. There are two very different types of crust, each with its own distinctive physical and chemical properties, which are summarized in Table **14.1.3**.

Table **14.1.3** *The Physical and Chemical Properties of Oceanic and Continental Crust.*

Crust	Thickness	Density	Composition	Rock types
Oceanic	5-12 km (3-8 mi)	3.0 g/cm^3	Mafic	Basalt and gabbro
Continental	Avg. 35 km (22 mi)	2.7 g/cm^3	Felsic	All types

Oceanic crust is composed of mafic magma that erupts on the seafloor to create basalt lava flows or cools deeper down to create the intrusive igneous rock gabbro (Figure **14.1.2**).



Figure **14.1.2** Gabbro

Sediments, primarily muds and the shells of tiny sea creatures, coat the sea floor. Sediment is thickest near the shore where it comes off the continents in rivers and on wind currents.

Continental crust is made up of many different types of igneous, metamorphic, and sedimentary rocks. The average composition is granite, which is much less dense than the mafic rocks of the oceanic crust (Figure **14.1.3**). Because it is thick and has relatively low density, continental crust rises higher on the mantle than oceanic crust, which sinks into the mantle to form basins. When filled with water, these basins form the planet's oceans.

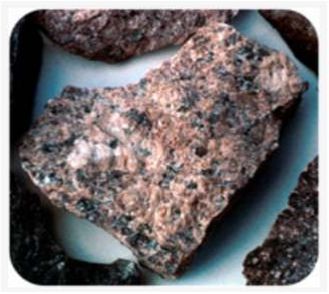


Figure **14.1.3** *The granite from Missouri is more than 1 billion years old.*

The **lithosphere** is the outermost mechanical layer, which behaves as a brittle, rigid solid. The lithosphere is about 100 kilometers thick. Look at Figure **14.1.1**. Can you find where the crust and the lithosphere are located? How are they different from each other?

The definition of the lithosphere is based on how earth materials behave, so it includes the crust and the uppermost mantle, which are both brittle. Since it is rigid and brittle, when stresses act on the lithosphere, it breaks. This is what we experience as an earthquake.

Mantle

The two most important things about the mantle are: (1) it is made of solid rock, and (2) it is hot. Scientists know that the mantle is made of rock based on evidence from seismic waves, heat flow, and meteorites.

The properties fit the ultramafic rock peridotite, which is made of the iron- and magnesium-rich silicate minerals (Figure **14.1.4**). Peridotite is rarely found at Earth's surface.

Scientists know that the mantle is extremely hot because of the heat flowing outward from it and because of its physical properties.



Figure **14.1.4** *Peridotite is formed of crystals of olivine (green) and pyroxene (black).*

Core

At the planet's center lies a dense metallic core. Scientists know that the core is metal because:

1. The density of Earth's surface layers is much less than the overall density of the planet, as calculated from the planet's rotation. If the surface layers are less dense than average, then the interior must be denser than average. Calculations indicate that the core is about 85% iron metal with nickel metal making up much of the remaining 15%.
2. Metallic meteorites are thought to be representative of the core. The 85% iron/15% nickel calculation above is also seen in metallic meteorites (Figure **14.1.5**).



Figure **14.1.5** *An iron meteorite is the closest thing to the Earth's core that we can hold in our hands.*

If Earth's core were not metal, the planet would not have a magnetic field. Metals such as iron are magnetic, but rock, which makes up the mantle and crust, is not.

Summary

- The core, mantle, and crust are divisions of Earth based on chemical composition.
- The lithosphere and asthenosphere are divisions of Earth based on mechanical properties.
- The three most abundant elements of Earth's crust are oxygen (46.6% by weight), silicon (27.7%), and aluminum (8.1%).

Contributors

Libretext: Fundamentals of Geology (Schulte)

Marisa Alviar-Agnew (Sacramento City College)

Wikipedia

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14.2: Silicates and the Shapes of Things

Learning Objective

- Describe different types of silicate based minerals.

The silicates are the largest, the most interesting and the most complicated class of minerals than any other minerals. Approximately 30% of all minerals are silicates and some geologists estimate that 90% of the Earth's crust is made up of silicates, SiO_4^{4-} based material. Thus, oxygen and silicon are the two most abundant elements in the earth's crust.

The building block of all of these minerals is the **silica tetrahedron**, a combination of four oxygen atoms and one silicon atom. As we've seen, it's called a tetrahedron because planes drawn through the oxygen atoms form a shape with 4 surfaces (Figure **14.2.1**). Since the silicon ion has a charge of 4 and each of the four oxygen ions has a charge of −2, the silica tetrahedron has a net charge of −4.

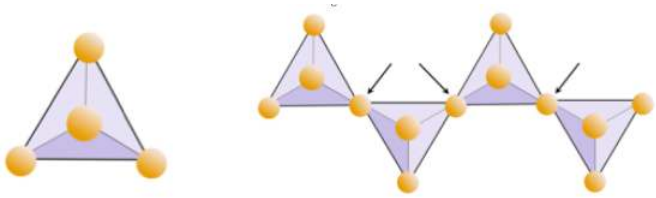
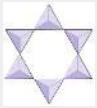
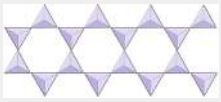
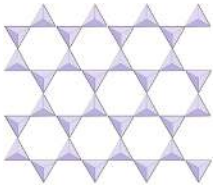


Figure **14.2.1** *A single silica tetrahedron (left) with four oxygen ions per silicon ion (SiO_4). Part of a single chain of tetrahedra (right), where the oxygen atoms at the adjoining corners are shared between two tetrahedra (arrows). For a very long chain the resulting ratio of silicon to oxygen is 1 to 3 (SiO_3).*

In silicate minerals, these tetrahedra are arranged and linked together in a variety of ways, from single units to complex frameworks (Table **14.2.1**).

Table **14.2.1** *Silicate Mineral Configurations (The triangles represent silica tetrahedra).*

Tetrahedron Configuration Picture	Tetrahedron Configuration Name	Example Minerals
	Isolated (nesosilicates)	Olivine, garnet, zircon, kyanite
	Pairs (sorosilicates)	Epidote, zoisite
	Rings (cyclosilicates)	Tourmaline
	Single chains (inosilicates)	Pyroxenes, wollastonite
	Double chains (inosilicates)	Amphiboles
	Sheets (phyllosilicates)	Micas, clay minerals, serpentine, chlorite
3-dimensional structure	Framework (tectosilicates)	Feldspars, quartz, zeolite

In the extreme case, the tetrahedra are arranged in a regular, orderly fashion forming a three-dimensional network. **Quartz** is such a structure (Figure **14.2.2**), and its formula is SiO_2. If silica in the molten state is cooled very slowly it crystallizes at the freezing point. But if molten silica is cooled more rapidly, the resulting solid is a disorderly arrangement which is called **glass**, often also called *quartz*.

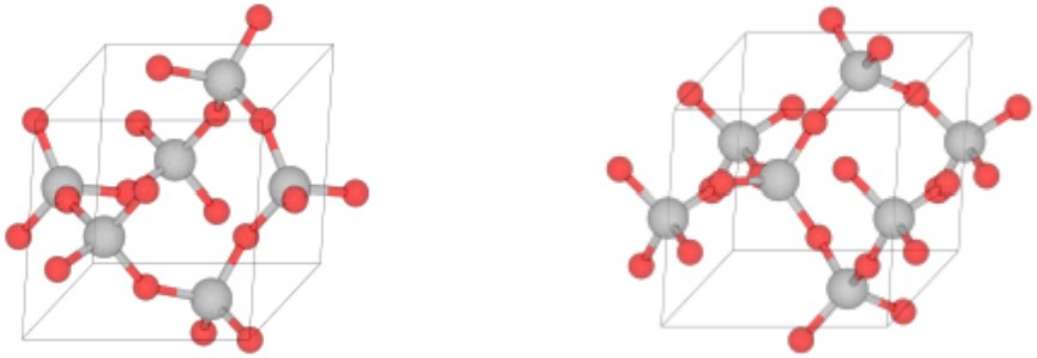


Figure **14.2.2** Crystal structure of alpha (left) and beta (right) quartz. The red balls are oxygen and gray are silicon.

Note:

Silicates are extremely important materials, both natural (such as granite, gravel, and garnet) and artificial (such as Portland cement, ceramics, glass, and waterglass), for all sorts of technological and artistic activities. Source: Wikipedia

Glasses

Glass is a non-crystalline, often transparent amorphous solid, that has widespread practical, technological, and decorative use in, for example, window panes, tableware, optics, and optoelectronics. The most familiar, and historically the oldest, types of manufactured glass are "silicate glasses" based on the chemical compound silica (silicon dioxide, or quartz), the primary constituent of sand. The term *glass*, in popular usage, is often used to refer only to this type of material, which is familiar from use as window glass and glass bottles. Of the many silica-based glasses that exist, ordinary glazing and container glass is formed from a specific type called soda-lime glass, composed of approximately 75% silicon dioxide (SiO_2), sodium oxide (Na_2O) from sodium carbonate (Na_2CO_3), calcium oxide (CaO), also called lime, and several minor additives.

Table **14.2.2** list the more common types of silicate glasses and their ingredients, properties, and applications. Figure **14.2.3** are examples of silicate glasses.

Table **14.2.2** *Common Types of Silicate Glasses.*

Type and Properties	Key Ingredients	Applications
Fused quartz has very low thermal expansion and excellent resistance to thermal shock, being able to survive immersion in water while red hot, resists high temperatures (1000–1500 °C) and chemical weathering, and is very hard.	Chemically pure silica (silicon dioxide)	Used for high-temperature applications such as furnace tubes, lighting tubes, melting crucibles, etc.
Soda-lime-silica glass is transparent, easily formed, and most suitable for window glass and tableware.[68] However, it has a high thermal expansion and poor resistance to heat.	(Na_2O) + lime (CaO) + magnesia (MgO) + alumina (Al_2O_3) account for over 75% of manufactured glass, containing about 70 to 74% silica by weight	Typically used for windows, bottles, light bulbs, and jars.[
Sodium borosilicate glasses have fairly low coefficients of thermal expansion (7740 Pyrex CTE is 3.25×10^{-6}/°C[69] as compared to about 9×10^{-6}/°C for a typical soda-lime glass[70]). They are, therefore, less subject to stress caused by thermal expansion and thus less vulnerable to cracking from thermal shock.	5–13% boron trioxide (B_2O_3)	Commonly used for e.g. labware (e.g. Pyrex, Duran), household cookware, and sealed beam car head lamps.[
Lead-oxide glass, crystal glass, lead glass has high density which results in a high electron density, and hence high refractive index, making the look of glassware more brilliant and causing noticeably more specular reflection and increased optical dispersion.[61][72] Lead glass has a high elasticity, making the glassware more workable and giving rise to a clear "ring" sound when struck.	silica + lead oxide (PbO) + potassium oxide (K_2O) + soda (Na_2O) + zinc oxide (ZnO) + alumina	Used for tableware, art objects, optical glass.
Aluminosilicate glass tends to be more difficult to melt and shape compared to borosilicate compositions, but has excellent thermal resistance and durability.	alumina and silica	Extensively used for fiberglass, used for making glass-reinforced plastics (boats, fishing rods, etc.), top-of-stove cookware, and halogen bulb glass.
Germanium-oxide glass is an extremely clear glass. Light loses only 5% of its intensity through 1 km of glass fiber.	alumina + germanium dioxide (GeO_2).	Used for fiber-optic waveguides in communication networks.
Colored glass is clear glass with oxides added .	Different oxide additives produce the different colors in glass: turquoise (copper(II) oxide),[121] purple (manganese dioxide), red (cadmium sulfide), blue (cobalt oxide) and green (Iron(II) oxide and chromium(III) oxide).	Used for tableware and decorative glassware.



a. b. c.

***Figure* 14.2.3** *Examples of silicate glasses: a. Pyrex measuring cup, b. red glass bottle with yellow glass overlay, and c. four-color Roman glass bowl, manufactured circa 1st century B.C..*

Asbestos

Asbestos is the name applied to six naturally occurring minerals that are mined from the earth. The different types of asbestos are:

- Amosite
- Chrysotile
- Tremolite
- ActinoliteUnlink
- Anthophyllite
- Crocidolite

Of these six, three are used more commonly. **Chrysotile** (white) is the most common, but it is not unusual to encounter**. Amosite** (brown / off-white), or **Crocidolite** (blue) as well. Asbestos are noncombustable fibrous material, and they have been used for terminal insulation material, brake linings, construction material, and filters. When mixed with cement, it reinforce the mechanical strength of concrete. It decomposes due to loss of water, and forms forsterite and silica at high temperature.

Ceramics

A **ceramic** is a solid material comprising an inorganic compound of metal, non-metal or ionic and covalent bonds. Common examples are earthenware, porcelain, and brick.

Varying crystallinity and electron composition in the ionic and covalent bonds cause most ceramic materials to be good thermal and electrical insulators (extensively researched in ceramic engineering). With such a large range of possible options for the composition/structure of a ceramic (e.g. nearly all of the elements, nearly all types of bonding, and all levels of crystallinity), the breadth of the subject is vast, and identifiable attributes (e.g. hardness, toughness, electrical conductivity, etc.) are difficult to specify for the group as a whole. General properties such as high melting temperature, high hardness, poor conductivity, high moduli of elasticity, chemical resistance and low ductility are the norm,[1] with known exceptions to each of these rules (e.g. piezoelectric ceramics, glass transition temperature, superconductive ceramics, etc.).

Cement and Concrete

A **cement** is a binder, a substance used for construction that sets, hardens, and adheres to other materials to bind them together. Cement is seldom used on its own, but rather to bind sand and gravel (aggregate) together. Cement mixed with fine aggregate produces mortar for masonry, or with sand and gravel, produces concrete. Cement is the most widely used material in existence and is only behind water as the planet's most-consumed resource.[1]

Cements used in construction are usually inorganic, often lime or calcium silicate based.

Concrete is a composite material composed of fine and coarse aggregate bonded together with a fluid cement (cement paste) that hardens over time—most frequently in the past a lime-based cement binder, such as lime putty, but sometimes with other hydraulic cements, such as a calcium aluminate cement or with Portland cement to form **Portland cement concrete** (for its visual resemblance to Portland stone).[2][3] Many other non-cementitious types of concrete exist with different methods of binding

aggregate together, including asphalt concrete with a bitumen binder, which is frequently used for road surfaces, and polymer concretes that use polymers as a binder.

Summary

- The silicates are the largest, the most interesting and the most complicated class of minerals than any other minerals. Approximately 90% of the Earth's crust is made up of silicates, SiO_4^{4-} based material.
- Silicates are extremely important materials, both natural (such as granite, gravel, and garnet) and artificial (such as Portland cement, ceramics, glass, and waterglass), for all sorts of technological and artistic activities

Contributors and Attributions

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- Wikipedia

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14.3: Metals and Ores

Learning Objectives

- Identify important metals and describe their extraction from their main ores.
- List different metals, their uses, and their alloys.
- Describe the environmental impact of metal production.

Most metals are found as types of rock in the Earth's crust. These ores contain sufficient minerals with important elements including metals that can be economically extracted from the rock. Metal ores are generally oxides, sulfides, silicates (Table **14.3.1**) or "native" metals (such as native copper) that are not commonly concentrated in the Earth's crust, or "noble" metals (not usually forming compounds) such as gold (Figure **14.3.1**). The ores must be processed to extract the metals of interest from the waste rock and from the ore minerals.



Figure **14.3.1**: Three Common Ores. (left) Iron ore, (middle) Manganese ore – psilomelane, and (right) Lead ore – galena and anglesite.

Alloys

An **alloy** is a mixture composed of two or more elements, at least one of which is a metal. You are probably familiar with some alloys of copper (such as brass and bronze) and iron (steel) . Alloys can be one of two general types. In one type, called a **substitutional alloy**, the various atoms simply replace each other in the crystal structure. In another type, called an **interstitial alloy**, the smaller atoms such as carbon fit in between the larger atoms in the crystal packing arrangement.

Steels are a very important class of alloys. The many types of steels are primarily composed of iron, with various amounts of the elements carbon, chromium, manganese, nickel, molybdenum, and boron. Steels are widely used in building construction because of their strength, hardness, and resistance to corrosion. Most large modern structures like skyscrapers and stadiums are supported by a steel skeleton (see figure below).



Figure **14.3.2**: The Willis Tower (formerly called the Sears Tower) in Chicago was once the tallest building in the world and is still the tallest in the Western Hemisphere. The use of steel columns makes it possible to build taller, stronger, and lighter buildings.

Copper,Brass, and Bronze

Copper is a chemical element with the symbol **Cu** (from Latin:) and atomic number 29. It is a soft, malleable, and ductile metal with very high thermal and electrical conductivity. A freshly exposed surface of pure copper has a pinkish-orange color. Copper is used as a conductor of heat and electricity and as a building material.

Copper is one of the few metals that can occur in nature in a directly usable metallic form (native metals). This led to very early human use in several regions, from c. 8000 BC. Thousands of years later, it was the first metal to be smelted from sulfide ores, c.

5000 BC, the first metal to be cast into a shape in a mold, c. 4000 BC and the first metal to be purposefully alloyed with another metal, tin, to create bronze, c. 3500 BC.

Most commercial ores are sulfides, especially chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4) and, to a lesser extent, covellite (CuS) and chalcocite (Cu_2S).

Cu_2S, is converted into oxides:

$$2\ Cu_2S + 3\ O_2 \rightarrow 2\ Cu_2O + 2\ SO_2$$

The cuprous oxide is then converted to copper upon heating:

$$2\ Cu_2O \rightarrow 4\ Cu + O_2$$

Copper is a constituent of various metal alloys, such as sterling silver used in jewelry, cupronickel used to make marine hardware and coins, and constantan used in strain gauges and thermocouples for temperature measurement. Bronze, an alloy of copper and tin has been in use since ancient times. The Bronze Age saw the increased use of metals rather than stone for weapons, tools, and decorative objects. Brass, an alloy of copper and zinc, is widely used in musical instruments like the trumpet and trombone. Alloys are commonly used in manufactured items because the properties of these metal mixtures are often superior to a pure metal. Bronze is harder than copper and more easily cast. Brass is very malleable and its acoustic properties make it useful for musical instruments (Figure **14.3.1**).



Figure **14.3.3** A bronze helmet and a trumpet made of brass. Copper alloys are widely used in the production of coinage; seen here are two examples - post-1964 American dimes, which are composed of the alloy cupronickel and a pre-1968 Canadian dime, which is composed of an alloy of 80 percent silver and 20 percent copper. (Source: Wikipedia)

Iron and Steel

The early application of iron to the manufacture of tools and weapons was possible because of the wide distribution of iron ores and the ease with which iron compounds in the ores could be reduced by carbon. Iron ore is reduced with coke in a blast furnace (Figure **14.3.1**). The blast furnace is loaded with iron ores, usually hematite Fe_2O_3 or magnetite Fe_3O_4, together with coke (coal that has been separately baked to remove volatile components). Air pre-heated to 900 °C is blown through the mixture, in sufficient amount to turn the carbon into carbon monoxide:

$$2\ C + O_2 \rightarrow 2\ CO$$

This reaction raises the temperature to about 2000 °C The carbon monoxide reduces the iron ore to metallic iron[112]

$$Fe_2O_3 + 3\ CO \rightarrow 2\ Fe + 3\ CO_2$$

Some iron in the high-temperature lower region of the furnace reacts directly with the coke:[112]

$$2\ Fe_2O_3 + 3\ C \rightarrow 4\ Fe + 3\ CO_2$$

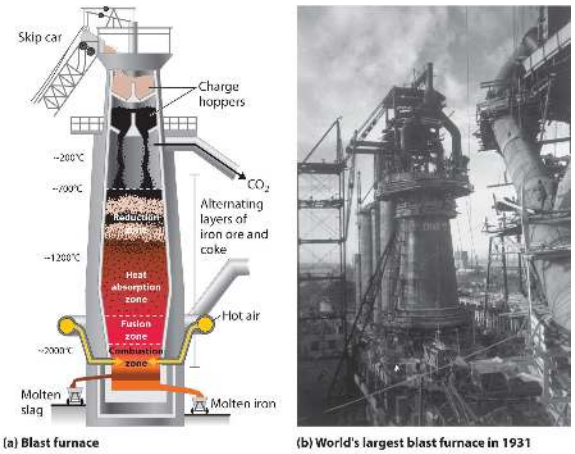


Figure 14.3.4: A Blast Furnace for Converting Iron Oxides to Iron Metal. (a) The furnace is charged with alternating layers of iron ore (largely Fe2O3) and a mixture of coke (C) and limestone (CaCO3). (b) This blast furnace in Magnitogorsk, Russia, was the largest in the world when it was built in 1931.

Much of the iron produced is refined and converted into steel. Steel is made from iron by removing impurities and adding substances such as manganese, chromium, nickel, tungsten, molybdenum, and vanadium to produce alloys with properties that make the material suitable for specific uses. Most steels also contain small but definite percentages of carbon (0.04%–2.5%). However, a large part of the carbon contained in iron must be removed in the manufacture of steel; otherwise, the excess carbon would make the iron brittle. However, there is not just one substance called steel - they are a family of alloys of iron with carbon or various metals.

Impurities in the iron from the Blast Furnace include carbon, sulfur, phosphorus and silicon, which have to be removed.

- **Removal of sulfur**: Sulfur has to be removed first in a separate process. Magnesium powder is blown through the molten iron and the sulfur reacts with it to form magnesium sulfide. This forms a slag on top of the iron and can be removed.

$$Mg + S \rightarrow MgS \tag{14.3.1}$$

- **Removal of carbon:** The still impure molten iron is mixed with scrap iron (from recycling) and oxygen is blown on to the mixture. The oxygen reacts with the remaining impurities to form various oxides. The carbon forms carbon monoxide. Since this is a gas it removes itself from the iron! This carbon monoxide can be cleaned and used as a fuel gas.
- **Removal of other elements:** Elements like phosphorus and silicon react with the oxygen to form acidic oxides. These are removed using quicklime (calcium oxide) which is added to the furnace during the oxygen blow. They react to form compounds such as calcium silicate or calcium phosphate which form a slag on top of the iron.

Cast iron has already been mentioned above. This section deals with the types of iron and steel which are produced as a result of the steel-making process.

- Wrought iron: If all the carbon is removed from the iron to give high purity iron, it is known as wrought iron. Wrought iron is quite soft and easily worked and has little structural strength. It was once used to make decorative gates and railings, but these days mild steel is normally used instead.
- Mild steel: Mild steel is iron containing up to about 0.25% of carbon. The presence of the carbon makes the steel stronger and harder than pure iron. The higher the percentage of carbon, the harder the steel becomes. Mild steel is used for lots of things - nails, wire, car bodies, ship building, girders and bridges amongst others.
- High carbon steel: High carbon steel contains up to about 1.5% of carbon. The presence of the extra carbon makes it very hard, but it also makes it more brittle. High carbon steel is used for cutting tools

and masonry nails (nails designed to be driven into concrete blocks or brickwork without bending). High carbon steel tends to fracture rather than bend if mistreated.

- Special steels: These are iron alloyed with other metals (Table **14.3.1**).

Table **14.3.1** *Special Steels*

	Iron mixed with	Special properties	Uses include
stainless steel	chromium and nickel	resists corrosion	cutlery, cooking utensils, kitchen sinks, industrial equipment for food and drink processing
titanium steel	titanium	withstands high temperatures	gas turbines, spacecraft
manganese steel	manganese	very hard	rock-breaking machinery, some railway track (e.g. points), military helmets

Steelmaking Animation



Video **14.3.1** The process of steelmaking.

Aluminum

Aluminum is too high in the electrochemical series (reactivity series) to extract it from its ore using carbon reduction. The temperatures needed are too high to be economic. Instead, it is extracted by electrolysis. The ore is first converted into pure aluminum oxide by the Bayer Process, and this is then electrolyzed in solution in molten cryolite - another aluminum compound. The aluminum oxide has too high a melting point to electrolyse on its own. The usual aluminum ore is bauxite. Bauxite is essentially an impure aluminum oxide. The major impurities include iron oxides, silicon dioxide and titanium dioxide.

Crushed bauxite is treated with moderately concentrated sodium hydroxide solution. The concentration, temperature and pressure used depend on the source of the bauxite and exactly what form of aluminum oxide it contains. Temperatures are typically from 140°C to 240°C; pressures can be up to about 35 atmospheres. With hot concentrated sodium hydroxide solution, aluminum oxide reacts to give a solution of sodium tetrahydroxoaluminate.

$$Al_2O_3 + 2NaOH + 3H_2O \longrightarrow 2NaAl(OH)_4$$

The sodium tetrahydroxoaluminate solution is cooled, and "seeded" with some previously produced aluminum hydroxide. This provides something for the new aluminum hydroxide to precipitate around.

$$NaAl(OH)_4 \longrightarrow Al(OH)_3 + NaOH$$

Aluminum oxide (sometimes known as alumina) is made by heating the aluminum hydroxide to a temperature of about 1100 - 1200°C.

$$2Al(OH)_3 \longrightarrow Al_2O_3 + 3H_2O$$

The aluminum oxide is electrolyzed in solution in molten cryolite, Na_3AlF_6. Cryolite is another aluminum ore, but is rare and expensive, and most is now made chemically.

Uses of Aluminum

Aluminum is usually alloyed with other elements such as silicon, copper or magnesium. Pure aluminum isn't very strong, and alloying it adds to it strength. Aluminum is especially useful because it

- has a low density;
- is strong when alloyed;
- is a good conductor of electricity;
- has a good appearance;
- resists corrosion because of the strong thin layer of aluminum oxide on its surface. This layer can be strengthened further by anodizing the aluminum.

Anodizing essentially involves etching the aluminum with sodium hydroxide solution to remove the existing oxide layer, and then making the aluminum article the anode in an electrolysis of dilute sulfuric acid. The oxygen given of at the anode reacts with the aluminum surface, to build up a film of oxide up to about 0.02 mm thick. As well as increasing the corrosion resistance of the aluminum, this film is porous at this stage and will also take up dyes. (It is further treated to make it completely non-porous afterwards.) That means that you can make aluminum articles with the colour built into the surface.

Some uses include:

Aluminum is used for	because
aircraft	light, strong, resists corrosion
other transport such as ships' superstructures, container vehicle bodies, tube trains (metro trains)	light, strong, resists corrosion
overhead power cables (with a steel core to strengthen them)	light, resists corrosion, good conductor of electricity
saucepans	light, resists corrosion, good appearance, good conductor of heat

Recycling

Aluminum is an infinitely recyclable material, and it takes up to 95 percent less energy to recycle it than to produce primary aluminum, which also limits emissions, including greenhouse gases. Today, about 75 percent of all aluminum produced in history, nearly a billion tons, is still in use.[6]

The recycling of aluminum generally produces significant cost savings over the production of new aluminum, even when the cost of collection, separation and recycling are taken into account.[7] Over the long term, even larger national savings are made when the reduction in the capital costs associated with landfills, mines, and international shipping of raw aluminum are considered.

Environmental Impact of Steel and Aluminum Production

The impact of steel and aluminum production on the environment can be traced back from the mining of the ores to the production of the final commercial products (i.e. steel and aluminum). The main sources of emissions during the different phases of manufacture include the products of combustion such as nitrous oxide, carbon dioxide, carbon monoxide, and sulfur dioxide and fugitive dust from the operation of equipment. The effect of the different emissions on air quality (i.e. smog formation, greenhouse effect, acid rain etc.) will be discussed in more detail in Chapter 13.

Sulfuric acid is created when water and oxygen interact with sulfur bearing minerals and chemicals in rocks. Many metals become mobile as water becomes more acidic and at high concentrations these metals become toxic to most life forms. There is also

production of enormous amounts of wastewater contaminants, hazardous wastes, and solid wastes.

Summary

- Metal ores contain sufficient minerals with important elements including metals that can be economically extracted from the rock. The ores must be processed to extract the metals of interest from the waste rock and from the ore minerals.
- Alloys are mixtures of materials, at least one of which is a metal.
- Bronze alloys were widely used in weapons.
- Brass alloys have long been employed in musical instruments.
- Steel alloys are strong and durable.
- Aluminum alloys are widely used due to its durability, resistance to corrosion, and good conductivity.

Contributors and Attributions

-
- TextMap: General Chemistry: General Chemistry (Petrucci et al.)
- Marisa Alviar-Agnew (Sacramento City College)
- Wikipedia

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14.4: Earth's Dwindling Resources

Learning Objectives

- Describe the composition and classification of solid waste.
- List the 3R's of Garbage and its benefits.

Land Pollution: Solid Wastes

Municipal solid waste (**MSW**), commonly known as **trash** or **garbage** in the United States and **rubbish** in Britain, is a waste type consisting of everyday items that are discarded by the public. "Garbage" can also refer specifically to food waste, as in a garbage disposal; the two are sometimes collected separately. In the European Union, the semantic definition is 'mixed municipal waste,' given waste code 20 03 01 in the European Waste Catalog. Although the waste may originate from a number of sources that has nothing to do with a municipality, the traditional role of municipalities in collecting and managing these kinds of waste have produced the particular etymology 'municipal.'

The composition of municipal solid waste varies greatly from municipality to municipality,[1] and it changes significantly with time. In municipalities which have a well developed waste recycling system, the waste stream mainly consists of intractable wastes such as plastic film and non-recyclable packaging materials. At the start of the 20th century, the majority of domestic waste (53%) in the UK consisted of coal ash from open fires.[2] In developed areas without significant recycling activity it predominantly includes food wastes, market wastes, yard wastes, plastic containers and product packaging materials, and other miscellaneous solid wastes from residential, commercial, institutional, and industrial sources.[3] Most definitions of municipal solid waste do not include industrial wastes, agricultural wastes, medical waste, radioactive waste or sewage sludge.[4] Waste collection is performed by the municipality within a given area. The term *residual waste* relates to waste left from household sources containing materials that have not been separated out or sent for processing.[5] Waste can be classified in several ways but the following list represents a typical classification:

- Biodegradable waste: food and kitchen waste, green waste, paper (most can be recycled, although some difficult to compost plant material may be excluded[6])
- Recyclable materials: paper, cardboard, glass, bottles, jars, tin cans, aluminum cans, aluminium foil, metals, certain plastics, textiles, clothing, tires, batteries, etc.
- Inert waste: construction and demolition waste, dirt, rocks, debris
- Electrical and electronic waste (WEEE) - electrical appliances, light bulbs, washing machines, TVs, computers, screens, mobile phones, alarm clocks, watches, etc.
- Composite wastes: waste clothing, Tetra Pack food and drink cartons, waste plastics such as toys and plastic garden furniture
- Hazardous waste including most paints, chemicals, tires, batteries, light bulbs, electrical appliances, fluorescent lamps, aerosol spray cans, and fertilizers
- Toxic waste including pesticides, herbicides, and fungicides
- Biomedical waste, expired pharmaceutical drugs, etc.

For example, typical municipal solid waste in China is composed of 55.9% food residue, 8.5% paper, 11.2% plastics, 3.2% textiles, 2.9% wood waste, 0.8% rubber, and 18.4% non-combustibles. The breakdown of municipal waste by material is shown below (Figure **14.4.1**).

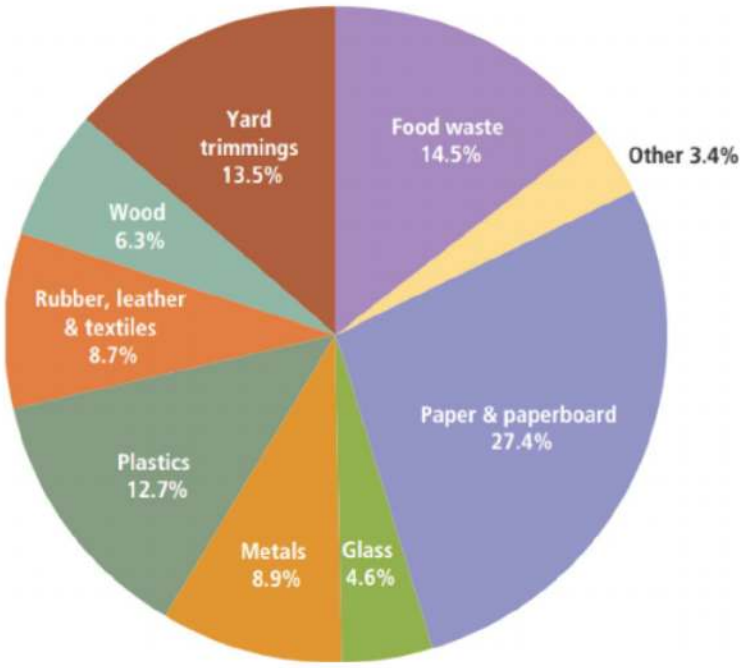


Figure **14.4.1** Total municipal waste generation by material. Source: US EPA

The Three R's of Garbage: Reduce, Reuse and Recyle

Reducing and Reusing Basics

The most effective way to reduce waste is to not create it in the first place. Making a new product requires a lot of materials and energy - raw materials must be extracted from the earth, and the product must be fabricated then transported to wherever it will be sold. As a result, reduction and reuse are the most effective ways you can save natural resources, protect the environment and save money.

Benefits of Reducing and Reusing

- Prevents pollution caused by reducing the need to harvest new raw materials
- Saves energy
- Reduces greenhouse gas emissions that contribute to global climate change
- Helps sustain the environment for future generations
- Saves money
- Reduces the amount of waste that will need to be recycled or sent to landfills and incinerators
- Allows products to be used to their fullest extent

Ideas on How to Reduce and Reuse

- Buy used. You can find everything from clothes to building materials at specialized reuse centers and consignment shops. Often, used items are less expensive and just as good as new.
- Look for products that use less packaging. When manufacturers make their products with less packaging, they use less raw material. This reduces waste and costs. These extra savings can be passed along to the consumer. Buying in bulk, for example, can reduce packaging and save money.
- Buy reusable over disposable items. Look for items that can be reused; the little things can add up. For example, you can bring your own silverware and cup to work, rather than using disposable items.

- Maintain and repair products, like clothing, tires and appliances, so that they won't have to be thrown out and replaced as frequently.
- Borrow, rent or share items that are used infrequently, like party decorations, tools or furniture.

Recycling Basics

Recycling is the process of collecting and processing materials that would otherwise be thrown away as trash and turning them into new products. Recycling can benefit your community and the environment.

Benefits of Recycling

- Reduces the amount of waste sent to landfills and incinerators
- Conserves natural resources such as timber, water and minerals
- Increases economic security by tapping a domestic source of materials
- Prevents pollution by reducing the need to collect new raw materials
- Saves energy
- Supports American manufacturing and conserves valuable resources
- Helps create jobs in the recycling and manufacturing industries in the United States

Recycling Creates Jobs

EPA released significant findings on the economic benefits of the recycling industry with an update to the national Recycling Economic Information (REI) Study in 2016. This study analyzes the numbers of jobs, wages and tax revenues attributed to recycling. The study found that in a single year, recycling and reuse activities in the United States accounted for:

- 757,000 jobs
- $36.6 billion in wages; and
- $6.7 billion in tax revenues.

This equates to 1.57 jobs, $76,000 in wages, and $14,101 in tax revenues for every 1,000 tons of materials recycled.

Summary

- Municipal solid waste (MSW), (i.e. trash or garbage in the United States and rubbish in Britain), is a type of waste consisting of everyday items that are discarded by the public.
- Most definitions of municipal solid waste do not include industrial wastes, agricultural wastes, medical waste, radioactive waste or sewage sludge.
- Typical classification of waste includes biodegradable wastes, recyclable materials, inert waste, electrical and electronic waste, composite wastes, hazardous wastes, toxic waste, and biomedical wastes.
- Reducing, reusing, and recycling solid wastes reduces the amount of waste in landfills and incinerators and promotes safer and cleaner environment.

Contributors and Attributions

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Wikipedia

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CHAPTER OVERVIEW

15: Energy

15.1: Our Sun, a Giant Nuclear Power Plant
15.2: Power- People, Horses, and Fossils
15.3: Coal - The Carbon Rock of Ages
15.4: Natural Gas and Petroleum
15.5: Convenient Energy
15.6: Renewable Energy Sources

It takes energy to launch a spaceship into space. If it takes 1 energy unit to warm 0.25 g of water by 1°C, then it takes over 15,100 energy units to put that 0.25 g of water into earth orbit. The most powerful engines designed to lift rockets into space were part of the Saturn V rocket, that was built by the National Aeronautics and Space Administration (NASA). The rocket had three stages, with the first stage having the capability of launching about 3.5 million kg of mass. About 2.3 million kg was the actual fuel for the first stage; rockets in space have the unpleasant task of having to take their own chemicals with them to provide thrust.



Fig. 7.1.1: Saturn V SA-513 lifts off to boost the Skylab Orbital Workshop into Earth orbit. It takes a lot of energy to launch a rocket into space. The Saturn V rocket used five of the most powerful engines ever built to take its initial step into orbit. (Public Domain; NASA)

Having to carry its own fuel puts a lot of mass burden on an engine in space. This is why NASA is developing other types of engines to minimize fuel mass. An ion thruster uses xenon atoms that have had at least one electron removed from their atoms. The resulting ions can be accelerated by electric fields, causing a thrust. Because xenon atoms are very large for atoms, the thrusting efficiency is high even though the actual thrust is low. Because of this, ion engines are useful only in space.

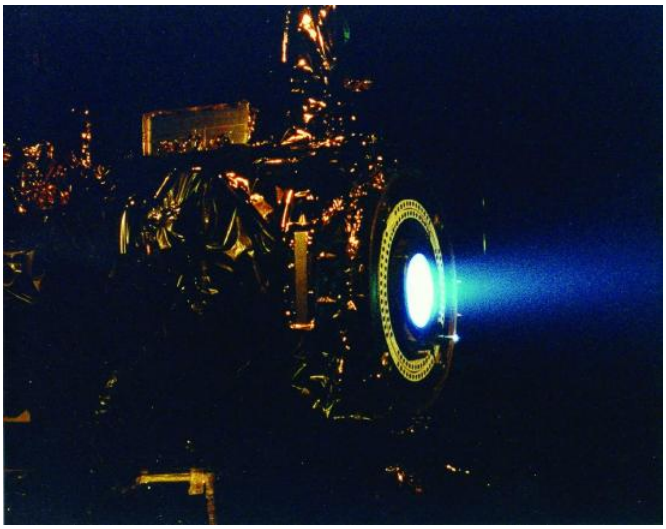


Fig. 7.1.2: An Ion Thruster. Ion drives have low thrust but high efficiency. They have already been used on several space missions, including NASA's *Deep Space 1* spacecraft and Japan's *Hayabusa* asteroid sampling probe. Source: Photo courtesy of NASA, commons.wikimedia.org/wiki/File:Ion_Engine_Test_Firing_-_GPN-2000-000482.jpg.

Energy is a very important quantity in science and the world around us. Although most of our energy ultimately comes from the sun, much of the energy we use on a daily basis is rooted in chemical reactions. The gasoline in your car, the electricity in your house, the food in your diet-all provide substances for chemical reactions to provide energy (gasoline, food) or are produced from chemical reactions (electricity, about 50% of which is generated by burning coal). As such, it is only natural that the study of chemistry involves energy.

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15.1: Our Sun, a Giant Nuclear Power Plant

Learning Objectives

- Define energy and distinguish between kinetic and potential enregy.
- Describe photosynthesis
- Perform calculations involving power and energy.

The Sun currently fuses about 600 million tons of hydrogen into helium every second, converting 4 million tons of matter into energy every second as a result. Sunlight at the top of Earth's atmosphere is composed (by total energy) of about 50% infrared light, 40% visible light, and 10% ultraviolet light.[46] The atmosphere in particular filters out over 70% of solar ultraviolet, especially at the shorter wavelengths.[47] Solar ultraviolet radiation ionizes Earth's dayside upper atmosphere, creating the electrically conducting ionosphere.[48]The energy of sunlight supports almost all life[c] on Earth by photosynthesis,[37] and drives Earth's climate and weather.

Energy can be defined as the capacity to supply heat or do work. One type of work (*w*) is the process of causing matter to move against an opposing force. For example, we do work when we inflate a bicycle tire—we move matter (the air in the pump) against the opposing force of the air surrounding the tire. Energy is measured in SI units, in joules (J). The Joule (= 1 Newton-meter) is a very small unit, however it is equivalent to the amount of work of lifting a small apple (98 grams) vertically up one meter. In terms of heat,

$$1\ \text{cal} = 4.184\ \text{J}$$

The rate of work done or energy transfer is called **power**, and its unit is **watt**.

$$1\ \text{watt} = 1\ \text{J/s}$$

Your calculator may consume some milliwatt, and a computer consumes about 100 watt, as does a 100-W light bulb. The **kilowatt (kW)** is equal to one thousand (10^3) watts. This unit is typically used to express the output power of engines and the power of electric motors, tools, machines, and heaters. It is also a common unit used to express the electromagnetic power output of broadcast radio and television transmitters. Different examples of power are given in Table **15.1.1**.

One kilowatt is approximately equal to 1.34 horsepower. A small electric heater with one heating element can use 1.0 kilowatt. The average electric power consumption of a household in the United States is about one kilowatt.

Table **15.1.1** Power in Kilowatts of Various Objects or Phenomenon.

Object or Phenomenon	Power in kilowatts (kW)
Supernova (at peak)	5×10^{34}
Milky Way galaxy	10^{34}
Crab Nebula pulsar	10^{25}
The Sun	4×10^{23}
Volcanic eruption (maximum)	4×10^{12}
Lightning bolt	2×10^{9}
Nuclear power plant (total electric and heat transfer)	3×10^{6}
Aircraft carrier (total useful and heat transfer)	10^{5}
Dragster (total useful and heat transfer)	2×10^{3}
Car (total useful and heat transfer)	8×10^{1}
Football player (total useful and heat transfer)	5
Clothes dryer	4
Typical incandescent light bulb (total useful and heat transfer) (60W)	0.06
Electric clock	0.003
Pocket calculator	10^{-6}

✔ Example 15.1.1 Power and Energy Conversion

Calculate the electrical energy, in joules (J) , that is used by a 20W LED bulb that was left "on" for 3.0 hours.

Solution

1. Since 1 W = 1 J/s then 20W = 20 J/s.
2. Convert 3 h to s.
3. Calculate the amount in J for 10,800 s.

? Exercise 15.1.1

Calculate the electrical energy, in joules (J) , that is used by a 100W incandescent bulb that was left "on" for 2 hours.

Answer

720,000 J

Energy and the Life-Support System

Photosynthesis is essential to all life on earth; both plants and animals depend on it. It is the only biological process that can capture energy that originates in outer space (sunlight) and convert it into chemical compounds (carbohydrates) that every organism uses to power its metabolism. In brief, the energy of sunlight is captured and used to energize electrons, which are then stored in the covalent bonds of sugar molecules. How long lasting and stable are those covalent bonds? The energy extracted today by the burning of coal and petroleum products represents sunlight energy captured and stored by photosynthesis almost 200 million years ago.

Photosynthesis is a multi-step process that requires sunlight, carbon dioxide (which is low in energy), and water as substrates (Figure 15.1.1). After the process is complete, it releases oxygen and produces simple carbohydrate molecules (which are high in energy) that can subsequently be converted into glucose, sucrose, or any of dozens of other sugar molecules. These sugar molecules contain energy and the energized carbon that all living things need to survive.

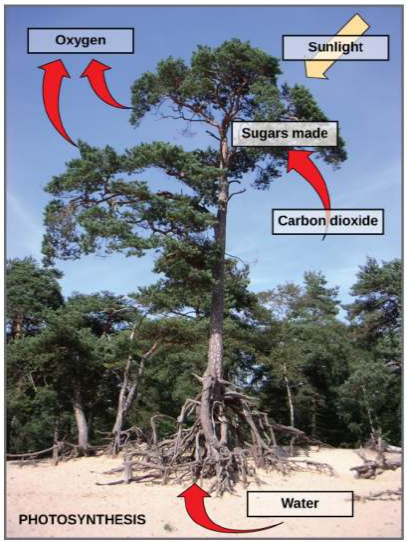


Figure 15.1.1 Photosynthesis uses solar energy , carbon dioxide, and water to produce energy-storing carbohydrates. Oxygen is generated as a waste product of photosynthesis.

The chemical equation for photosynthesis is given in Figure 15.1.2. Although the equation looks simple, the many steps that take place during photosynthesis are actually quite complex. In reality, the process takes place in many steps involving intermediate reactants and products.

Photosynthesis Equation						
Carbon dioxide	+	Water	SUNLIGHT →	Sugar	+	Oxygen
$6CO_2$		$6H_2O$		$C_6H_{12}O_6$		$6O_2$

Figure 15.1.2 The basic equation for photosynthesis.

Kinetic and Potential Energy

Like matter, energy comes in different types. One scheme classifies energy into two types: **potential energy**, the energy an object has because of its relative position, composition, or condition, and **kinetic energy**, the energy that an object possesses because of its motion. Water at the top of a waterfall or dam has potential energy because of its position; when it flows downward through generators, it has kinetic energy that can be used to do work and produce electricity in a hydroelectric plant (Figure 15.1.3). A battery has potential energy because the chemicals within it can produce electricity that can do work.



(a) (b)

Figure **15.1.3** *The (a) Water that is higher in elevation, for example, at the top of Victoria Falls, has a higher potential energy than water at a lower elevation. As the water falls, some of its potential energy is converted into kinetic energy. (b) If the water flows through generators at the bottom of a dam, such as the Hoover Dam shown here, its kinetic energy is converted into electrical energy. (credit a: modification of work by Steve Jurvetson; credit b: modification of work by "curimedia"/Wikimedia commons).*

Potential energy is not only associated with the location of matter, but also with the structure of matter. Even a spring on the ground has potential energy if it is compressed; so does a rubber band that is pulled taut. On a molecular level, the bonds that hold the atoms of molecules together exist in a particular structure that has potential energy. The fact that energy can be released by the breakdown of certain chemical bonds implies that those bonds have potential energy. In fact, there is potential energy stored within the bonds of all the food molecules we eat, which is harnessed for use. The type of potential energy that exists within chemical bonds, and is released when those bonds are broken, is called **chemical energy**. Chemical energy is responsible for providing living cells with energy from food. The release of energy occurs when the molecular bonds within food molecules are broken.

Summary

- Energy can be defined as the capacity to supply heat or do work and is measured in SI units, in joules (J)
- Photosynthesis is essential to all life on earth and it is the only biological process that can capture energy that originates in outer space (sunlight) and convert it into chemical compounds (carbohydrates) that every organism uses to power its metabolism.
- Energy comes in two fundamentally different forms – kinetic energy and potential energy.
- Kinetic energy is the energy of motion.
- Potential energy is stored energy that depends on the position of an object relative to another object.

Contributors and Attributions

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15.2: Power- People, Horses, and Fossils

Learning Objective

- Describe the different fossil fuels.

Fossil fuels is the term given to energy sources with a high **hydrocarbon** content (see Chapter 1 for a review of hydrocarbon molecules) found in the Earth's crust that formed in the geologic past and can be burned to release their energy. They were formed from prehistoric plants and animals that lived hundreds of millions of years ago (100 – 500 million years ago). When these ancient living organisms died they were quickly buried and subjected to immense pressure from overlying earth materials including layers of mud, rock, sand, and sometimes surface water bodies such as oceans and lakes.

During the millions of years that passed, the dead plants and animals slowly decomposed in **anaerobic** (very low to no oxygen) conditions and their chemical energy became concentrated. The organic compounds that once made up tissues of these organisms were chemically changed under high pressures and temperatures. While some fossil fuels may be in the process of formation today, the amount of time required for usable quantities to form is measured in millions of years, so these fuels will never be available for us. Thus for all practical purposes we consider fossil fuels to be finite and **non-renewable**.

Fossil Fuel Types and Formation

There are three main types of fossil fuels – natural gas, oil, and coal – and the specific type formed depends on the combination of organic matter that was present, how long it was buried and what temperature and pressure conditions existed when they were decomposing. **Oil** and **natural gas** were created from organisms that lived in water and were buried under ocean or river sediments. Long after the great prehistoric seas and rivers vanished, heat, pressure, and bacteria combined to compress and transform the organic material under layers of silt or shale rock (Figure **15.2.1**). In most areas, a thick liquid called oil formed first, but in deeper, hot regions underground, the transformation process continued until natural gas was formed. Over time, some of this oil and natural gas began working its way upward through the earth's crust until they ran into rock formations called "**caprocks**" that are dense enough to prevent them from seeping to the surface. It is from under these caprocks that most oil and natural gas is retrieved today.

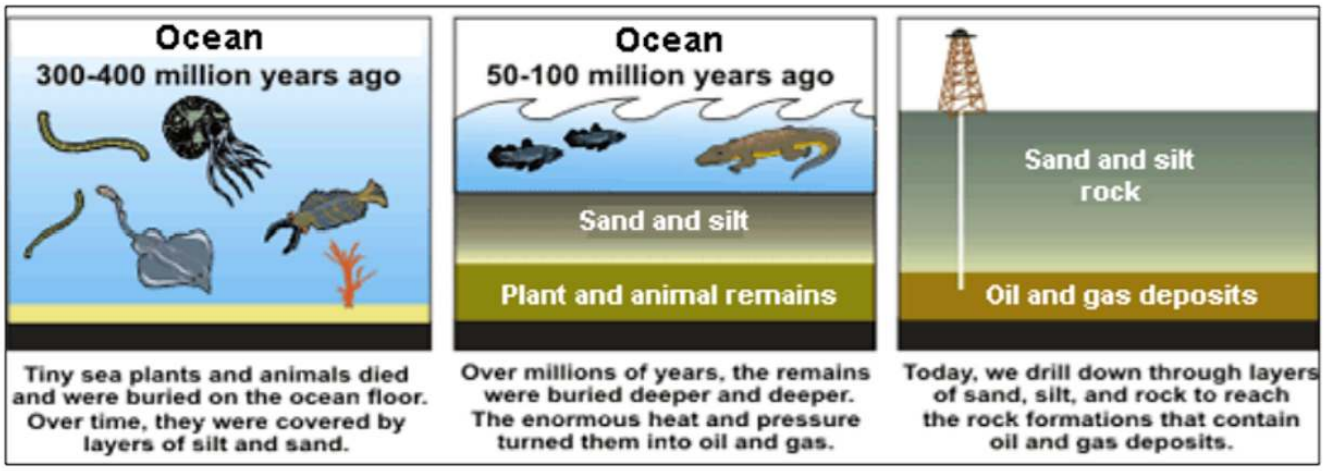


***Figure* 15.2.1** *Oil and natural gas (petroleum) formation. Source: U.S. Energy Information Administration. http://www.eia.gov/energyexplained/i...tural_gas_home*

Coal is a fossil fuel that formed from the remains of trees, ferns, and other plants that lived 300 to 400 million years ago (Figure **15.2.2**). In some areas, such as portions of what is now the eastern United States, coal was formed from swamps covered by sea water. The sea water contained a large amount of sulfur, and as the seas dried up, the sulfur was left behind in the coal. Scientists are working on ways to take the sulfur out of coal because when coal burns, the sulfur is released in to the atmosphere as an air pollutant (see Chapter 6). Some coal deposits, however, were formed from freshwater swamps which had very little sulfur in them. These coal deposits, located largely in the western part of the United States, have much less sulfur in them.

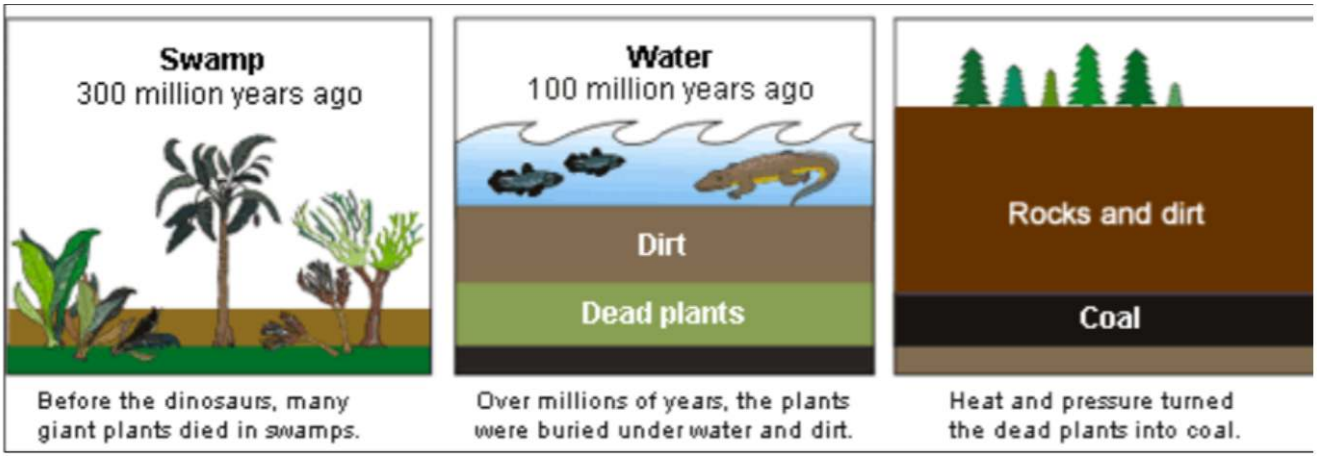


***Figure* 15.2.2** *The process of coal formation. Source: U.S. Energy Information Administration.*

Consumption and Production

Historically, human prosperity has been directly correlated with energy use. The health and vitality of world societies critically depends on energy, most of which comes from fossil fuels (Figure **15.2.3**). Energy resources, however, are unevenly distributed throughout the world, and so are the consumption rates. Developed regions generally consume far more energy than the developing regions. For example, the United States has only about 5% of the world's population but constitutes over 20% of the world's energy consumption. Additionally, developing countries devote a larger proportion of energy consumption to subsistence activities such as growing and preparing food, and heating homes. Industrialized nations rely more on mechanized equipment and technology and, therefore, a greater proportion of their energy consumption goes to transportation and industry.

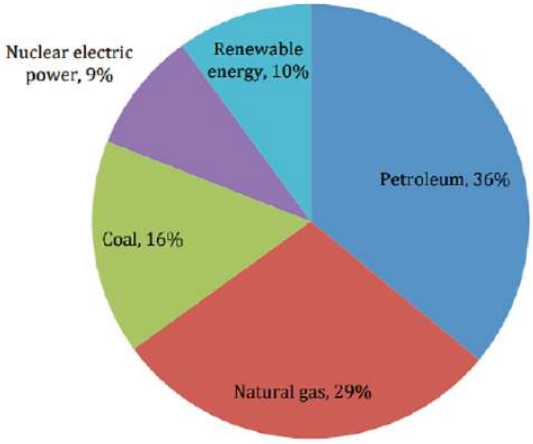


Figure **15.2.3** U.S. primary energy consumption by source (all sectors), 2015, showing that about 80 % of our energy consumption comes from fossil fuels. Data from U.S. Energy Information Administration, April 2016.

Fossil fuels can be utilized without being converted or transformed to another form of energy, this is referred to as **primary energy** consumption. In their primary form, fossil fuels can be used for transportation, heating and cooking, or used to generate electricity. The use of **electricity** is a form of **secondary energy** consumption. Transforming fossil fuel energy into electricity allows for easier transportation over long distances and application to a variety of uses. Additionally, as shown in Figure **15.2.4**, there are four major sectors that consume energy: 1) The industrial sector which includes facilities and equipment used for manufacturing, agriculture, mining, and construction; 2) The transportation sector includes vehicles that transport people or goods including cars, trucks, buses, motorcycles, trains, aircraft, boats, barges, and ships; 3) The residential sector consists of homes and apartments; 4) The commercial sector includes offices, malls, stores, schools, hospitals, hotels, warehouses, restaurants, places of worship, and more. Each of these sectors also consumes electricity produced by the electric power sector.

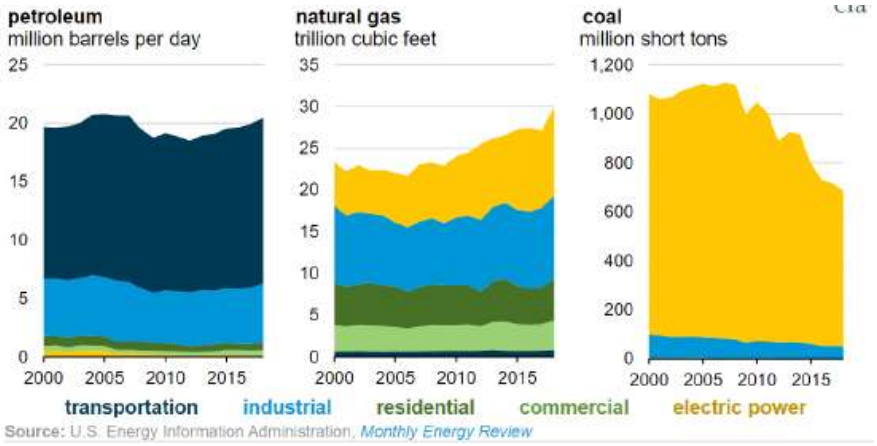


Figure **15.2.4** *U.S. fossil fuel energy consumption by major sector (2000-2018). Source : U.S. Energy Information Administration, April 2019.*

In 2019, U.S. energy production exceeded U.S. energy consumption on an annual basis for the first time since 1957. The United States produced 101.0 quads of energy and consumed 100.2 quads. After record high energy production and consumption in 2018, U.S. energy production grew 5.7% and energy consumption decreased by 0.9% in 2019.

Fossil fuels—petroleum, natural gas, and coal—accounted for about 80% of total U.S. primary energy production in 2019 see Figure **15.2.5**.

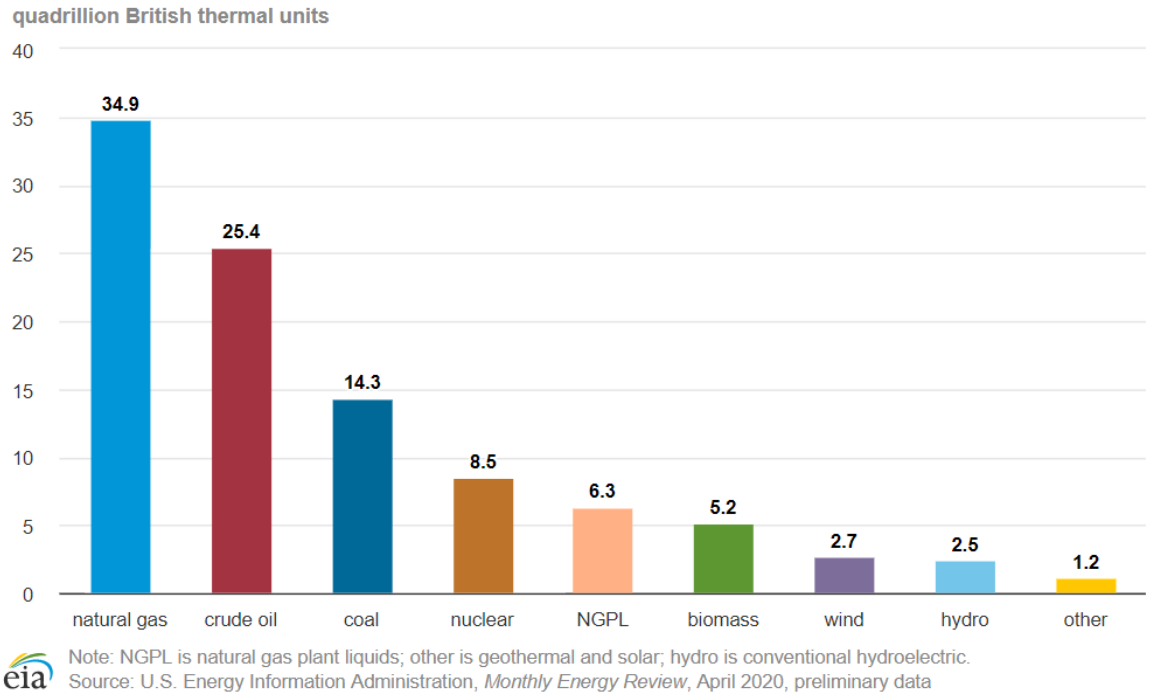


Figure **15.2.5** *U.S. primary energy production by major source, 2019.*

Summary

- Fossil fuels are energy sources from the Earth's crust (that formed in the geologic past) with a high hydrocarbon content and can be burned to release their energy.
- The three main types of fossil fuels that were discussed are natural gas, oil, and coal.

Contributors and Attributions

- U.S. Energy Information Administration
- Libretext: Introduction to Environmental Science (Zendher et al.)

- Marisa Alviar-Agnew (Sacramento City College)

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15.3: Coal - The Carbon Rock of Ages

Learning Objectives

- Describe coal and its processing.
- List the products of coal burning that promotes pollution.

Coal is a complex solid material derived primarily from plants that died and were buried hundreds of millions of years ago and were subsequently subjected to high temperatures and pressures. It is a combustible black or brownish-black sedimentary rock with a high amount of carbon and hydrocarbons. Coal is classified into four main types, or ranks depending on the types and amounts of carbon present and on the amount of heat energy the coal can produce, including anthracite, bituminous, subbituminous, and lignite (highest to lowest ranked, pictured in *Figure* **15.3.1**.

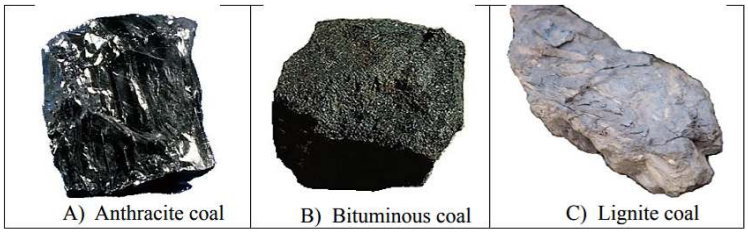


Figure **15.3.1** Different types of coal. Images obtained from Wikimedia Commons.

There are four distinct classes of coal (Table **15.3.1**); their hydrogen and oxygen contents depend on the length of time the coal has been buried and the pressures and temperatures to which it has been subjected. The most abundant form in the United States is bituminous coal, which has a high sulfur content becauseof the presence of small particles of pyrite (FeS_2). The combustion of coal releases the sulfur in FeS_2 as SO_2, which is a major contributor to acid rain.

Table **15.3.1** *Properties of Different Types of Coal.*

Type	% Carbon	Hydrogen:Carbon Mole Ratio	% Oxygen	% Sulfur	US Deposits
anthracite	92	0.5	3	1	Pennsylvania, New York
bituminous	80	0.6	8	5	Appalachia, Midwest, Utah
subbituminous	77	0.9	16	1	Rocky Mountains
lignite	71	1.0	23	1	Montana

Peat, a precursor to coal, is the partially decayed remains of plants that grow in swampy areas. It is removed from the ground in the form of soggy bricks of mud that will not burn until they have been dried. If a peat bog were buried under many layers of sediment for a few million years, the peat could eventually be compressed and heated enough to become lignite, the lowest grade of coal; given enough time and heat, lignite would eventually become anthracite, a much better fuel.

For us to use the potential energy stored in coal, it first must be mined from the ground. This process in itself uses a great deal of resources and has its own environmental impacts. Coal then typically undergoes processing to make it suitable for use in **coal-fire power plants**. Finally, the processed coal is burned in these power plants, and the kinetic energy released from its combustion is harnessed for electricity generation or other purposes. Figure **15.3.2** below is a schematic diagram showing a typical layout of a coal-fire power plant. You can also watch a short video of a virtual tour of a coal power plant at the URL provided below.

Power Plant Virtual Tour

***Video* 15.3.1** *Coal-Fueled Power Plant Virtual Tour Video*

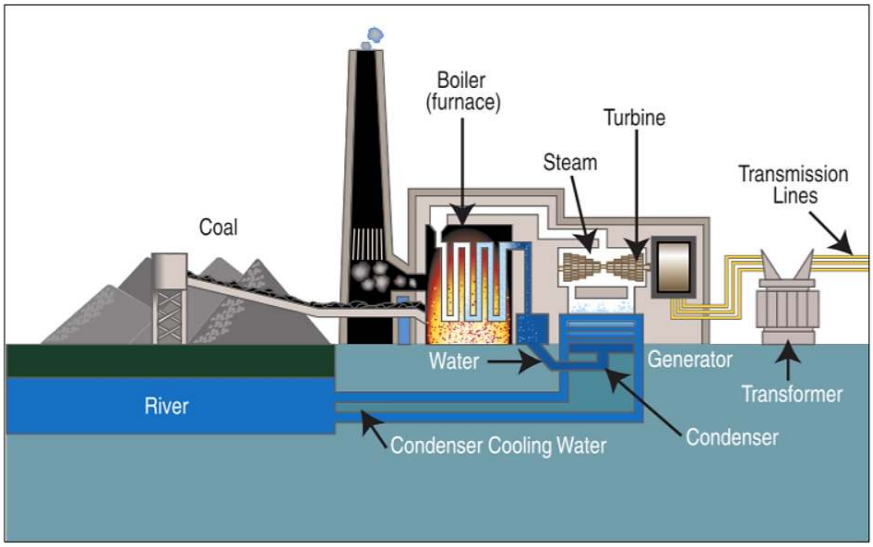


Figure **15.3.2** Diagram of a typical steam-cycle coal power plant (proceeding from left to right). Image by US Tennessee Valley Authority – Public domain. www.tva.com

The Global Carbon Cycle

Figure **15.3.3** illustrates the global carbon cycle, the distribution and flow of carbon on Earth. Normally, the fate of atmospheric CO_2 is to either (1) dissolve in the oceans and eventually precipitate as carbonate rocks or (2) be taken up by plants. The rate of uptake of CO_2 by the ocean is limited by its surface area and the rate at which gases dissolve, which are approximately constant. The rate of uptake of CO_2 by plants, representing about 60 billion metric tons of carbon per year, partly depends on how much of Earth's surface is covered by vegetation. Unfortunately, the rapid deforestation for agriculture is reducing the overall amount of vegetation, and about 60 billion metric tons of carbon are released annually as CO_2 from animal respiration and plant decay. The amount of carbon released as CO_2 every year by fossil fuel combustion is estimated to be about 5.5 billion metric tons. The net result is a system that is slightly out of balance, experiencing a slow but steady increase in atmospheric CO_2 levels. As a result, average CO_2 levels have increased by about 30% since 1850.

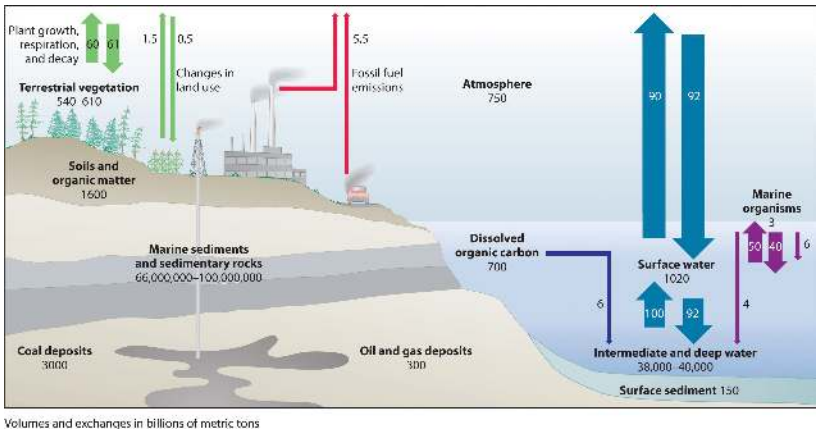


Figure **15.3.3** The global carbon cycle.

Most of Earth's carbon is found in the crust, where it is stored as calcium and magnesium carbonate in sedimentary rocks. The oceans also contain a large reservoir of carbon, primarily as the bicarbonate ion (HCO_3^-). Green plants consume about 60 billion metric tons of carbon per year as CO_2 during photosynthesis, and about the same amount of carbon is released as CO_2 annually from animal and plant respiration and decay. The combustion of fossil fuels releases about 5.5 billion metric tons of carbon per year as CO_2.

Pollution from Coal Burning

In the United States and most of the world, most of the coal consumed is used as a fuel to generate electricity. Burning coal produces emissions such as **sulfur dioxide** (SO_2) and **nitrogen oxides** (NO_x) that are associated with acid rain (more on this in chapter 6). **Carbon dioxide** (CO_2), another emission resulting from burning coal, is a major greenhouse gas that is associated with global warming (see Chapter 13). Burning of coal is classified as incomplete combustion, since the reaction of carbon (in coal) with oxygen produces carbon monoxide and/or carbon (soot) in addition to carbon dioxide.

Burning coal produces emissions that also impact human health. Emissions such as sulfur dioxide (SO_2), nitrogen oxides (NO_x) and particulates contribute to respiratory illnesses. Particulates also contribute to a condition among coal miners and other coal workers known as coal workers' pneumoconiosis (CWP) or black lung disease, which results from long exposure to coal dust. Inhaled coal dust progressively builds up in the lungs and is unable to be removed by the body; this leads to inflammation, fibrosis, and in worse cases, tissue death (necrosis).

Coal is the largest source of **mercury** and also a source of other **heavy metals**, many of which have been linked to both neurological and developmental problems in humans and other animals. Mercury concentrations in the air usually are low and of little direct concern. However, when mercury enters water, either directly or through deposition from the air, biological processes transform it into **methylmercury**, a highly toxic chemical that accumulates in fish and the animals (including humans) that eat fish.

Reducing the Environmental Impacts of Coal Use

Regulations such as the **Clean Air Act** and the **Clean Water Act** require industries to reduce pollutants released into the air and water. Below are some actions that have been taken to reduce the negative impacts of coal on human and environmental health:

• **Clean coal technology**: Industry has found several ways to reduce sulfur, NO_x, and other impurities from coal before burning.

• Coal consumers have shifted toward greater use of low sulfur coal.

• Power plants use **scrubbers**, to clean SO_2, NO_x, particulate matter, and mercury from the smoke before it leaves their smokestacks. In addition, industry and the U.S. government have cooperated to develop technologies that make coal more energy-efficient so less needs to be burned.

• Research is underway to address emissions of carbon dioxide from coal combustion. **Carbon capture & sequestration** separates CO_2 from emissions sources and recovers it in a concentrated stream. The CO_2 can then be sequestered, which puts CO_2 into storage, possibly underground, where it will remain permanently.

• Reuse and recycling can also reduce coal's environmental impact. Land that was previously used for coal mining can be reclaimed and used for airports, landfills, and golf courses. Waste products captured by scrubbers can be used to produce products like cement and synthetic gypsum for wallboard.

Summary

- Coal is a complex solid material derived primarily from plants that died and were buried hundreds of millions of years ago and were subsequently subjected to high temperatures and pressures.
- Coal is classified into four main types, depending on the types and amounts of carbon present and on the amount of heat energy the coal can produce, including anthracite, bituminous, subbituminous, and lignite.
- The processing of coal is described as well as the environmental and health impacts of its use.
- Research is underway and various approaches are implemented (clean coal technology, use of low sulfur coal, use of scrubbers etc.) to reduce the environmental impacts of coal use.

Contributors and Attributions

Libretext: Introduction to Environmental Science (Zendher et al.)

Libretext: General Chemistry (Petrucci et al.)

Anne Marie Helmenstine, Ph.D. "What Is a Combustion Reaction?" *ThoughtCo*, www.thoughtco.com/combustion-reactions-604030.

- Marisa Alviar-Agnew (Sacramento City College)

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15.4: Natural Gas and Petroleum

Learning Objectives

- Describe the nature and processing of natural gas, petroleum, and gasoline.
- List different alternative fuels.

Crude oil is frequently found in reservoirs along with natural gas. In the past, natural gas was either burned or allowed to escape into the atmosphere. Now, technology has been developed to capture the natural gas and either reinject it into the well or compress it into **liquid natural gas** (LNG).

Natural Gas

Natural gas is predominately composed of methane (CH_4). Some of the gases that are produced along with methane, such as butane and propane (by-products), are separated and cleaned at a gas processing plant. The by-products, once removed, are used in a number of ways. For example, propane can be used for cooking on gas grills. Natural gas withdrawn from a well may contain liquid hydrocarbons and non-hydrocarbon gases. This is called "wet" natural gas. The natural gas is separated from these components near the site of the well or at a processing plant. The gas is then considered "dry" and is sent through pipelines to a local distribution company, and, ultimately, to the consumer.

Most of the natural gas consumed in the United States is produced in the United States. Some is imported from Canada and shipped to the United States in pipelines. A small amount of natural gas is shipped to the United States as LNG.

Fracking for Gas

Conventional natural gas is found in permeable reservoirs, typically composed of sandstone or limestone, where extraction is relatively straightforward because the gas generally flows freely. Unconventional gas is found in rocks with extremely low permeability, which makes extracting it much more difficult. Such gas is extracted by employing so-called “unconventional” techniques such as hydraulic fracturing (fracking), which has been in use since the late 1940s. In recent decades, fracking technology has greatly improved, and its use has been expanded. The process of fracking for gas is very similar to that of fracking for oil, and the environmental impacts are similar also.

Petroleum

Petroleum Oil is currently the most widely used fossil fuel and accounts for about one third of global energy consumption. Unlike coal, which is primarily used as a fuel for electricity generation, oil is primarily used as a fuel for **transportation**. Oil is also used to manufacture plastics and other synthetic compounds ubiquitous to our everyday life. **Crude** (unprocessed) oil varies greatly in appearance depending on its composition. It is usually black or dark brown (although it may be yellowish, reddish, or even greenish). In the reservoir it is usually found in association with natural gas, which being lighter forms a gas cap over the oil.

Oil is made up of hydrocarbons which are molecules that contain hydrogen and carbon in various lengths and structures, from straight chains to branching chains to rings. Hydrocarbons contain a lot of energy and many of the things derived from crude oil like gasoline, diesel fuel, paraffin wax and so on take advantage of this energy.

Extraction

Oil is mainly obtained by drilling either on land (**onshore**) or in the ocean (**offshore**). Early offshore drilling was generally limited to areas where the water was less than 300 feet deep. Oil and natural gas drilling rigs now operate in water as deep as two miles. Offshore oil producers are required to take precautions to prevent pollution, spills, and significant changes to the ocean environment. Offshore rigs are designed to withstand hurricanes. Offshore production is much more expensive than land-based production. When offshore oil wells are no longer productive enough to be economical, they are sealed and abandoned according to applicable regulations.

Processing and Refining

When extracted, crude oil consists of many types of hydrocarbons as well as some unwanted substances such as sulfur, nitrogen, oxygen, dissolved metals, and water all mixed together. Unprocessed crude oil is therefore, not generally useful in industrial applications and must first be separated into different useable products at a **refinery** (Figure 15.4.1). All refineries perform three basic steps: separation, conversion, and treatment in the processing and refining of crude oil.



Figure 15.4.1 *Tesoro Corporation Oil Refinery in Anacortes, Washington. Photo by Walter Siegmund.* commons.wikimedia.org/wiki/O...nery_31904.JPG

During **separation**, the various products (hydrocarbons) are separated in to different components (called *fractions*), by taking advantage of the differences in boiling temperature of the components. This process is called *fractional distillation* and involves heating up the crude, letting it vaporize and then condensing the vapor. The lightest components have the lowest boiling temperature and rise to the top while the heaviest which also have the highest boiling temperature remain at the bottom.

Conversion is the chemical processing in which some of the fractions are transformed in to other products, for example, a refinery can turn diesel fuel into gasoline depending on the demand for gasoline. Conversion can involve breaking larger hydrocarbon chains into smaller ones (cracking), combining smaller chains into larger ones (unification) or rearranging the molecules to created desired products (alteration).

Treatment is done to the fractions to remove impurities such as sulfur, nitrogen and water among others. Refineries also combine the various fractions (processed and unprocessed) into mixtures to make desired products. For example, different mixtures of hydrocarbon chains can create gasolines with different octane ratings, with and without additives, lubricating oils of various weights and grades (e.g., WD-40, 10W-40, 5W-30, etc.), heating oil and many others. The products are stored on-site until they can be delivered to various markets such as gas stations, airports and chemical plants.

A 42 U.S. gallon barrel of crude oil yields about 45 gallons of petroleum products because of refinery processing gain. This increase in volume is similar to what happens to popcorn when it is popped. Gasoline makes up the largest fraction of all petroleum products obtained (Figure 15.4.2). Other products include diesel fuel and heating oil, jet fuel, petrochemical feedstocks, waxes, lubricating oils, and asphalt.

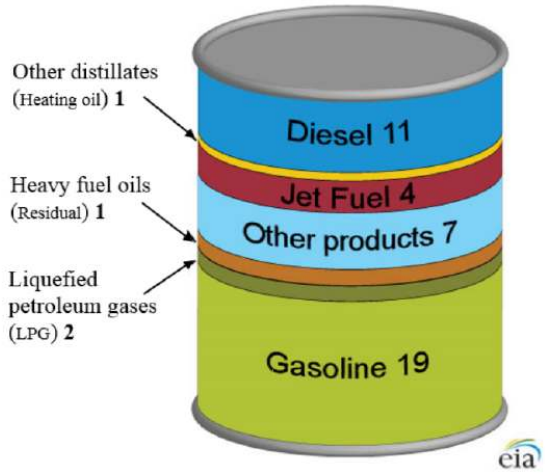


Figure **15.4.2** Main products (measured in gallons) made from a barrel of crude oil, 2013. Source: U.S. Energy information administration http://www.eia.gov/energyexplained/i...?page=oil_home

Fracking for oil

Hydraulic fracturing, informally referred to as "fracking," is an oil well development process that typically involves injecting water, sand, and chemicals under high pressure into a bedrock formation via the well. This process is intended to create new fractures in the rock as well as increase the size, extent, and connectivity of existing fractures. Hydraulic fracturing is a well-stimulation technique used commonly in low-permeability rocks like tight sandstone, shale, and some coal beds to increase oil flow to a well from petroleum-bearing rock formations.

There are concerns regarding the potential contamination of fresh groundwater resources from oil and gas extraction wells that use hydraulic fracturing; either from the petroleum resource being produced or from the chemicals introduced in the fracturing process. Fracking fluid flowback – the fluid pumped out of the well and separated from oil and gas – not only contains the chemical additives used in the drilling process but also contains heavy metals, radioactive materials, **volatile organic compounds** (VOCs) and hazardous air pollutants such as benzene, toluene, ethylbenzene and xylene. In some cases, this contaminated water is sent to water treatment plants that are not equipped to deal with some of these classes of contamination.

Gasoline

Petroleum is converted to useful products such as gasoline in three steps: distillation, cracking, and reforming. Part (a) in Figure \(\PageIndex{3}\) shows a cutaway drawing of a column used in the petroleum industry for separating the components of crude oil. The petroleum is heated to approximately 400°C (750°F), at which temperature it has become a mixture of liquid and vapor. This mixture, called the feedstock, is introduced into the refining tower. The most volatile components (those with the lowest boiling points) condense at the top of the column where it is cooler, while the less volatile components condense nearer the bottom. Some materials are so nonvolatile that they collect at the bottom without evaporating at all. Thus the composition of the liquid condensing at each level is different. These different fractions, each of which usually consists of a mixture of compounds with similar numbers of carbon atoms, are drawn off separately. Part (b) Figure \(\PageIndex{3}\) shows the typical fractions collected at refineries, the number of carbon atoms they contain, their boiling points, and their ultimate uses. These products range from gases used in natural and bottled gas to liquids used in fuels and lubricants to gummy solids used as tar on roads and roofs.

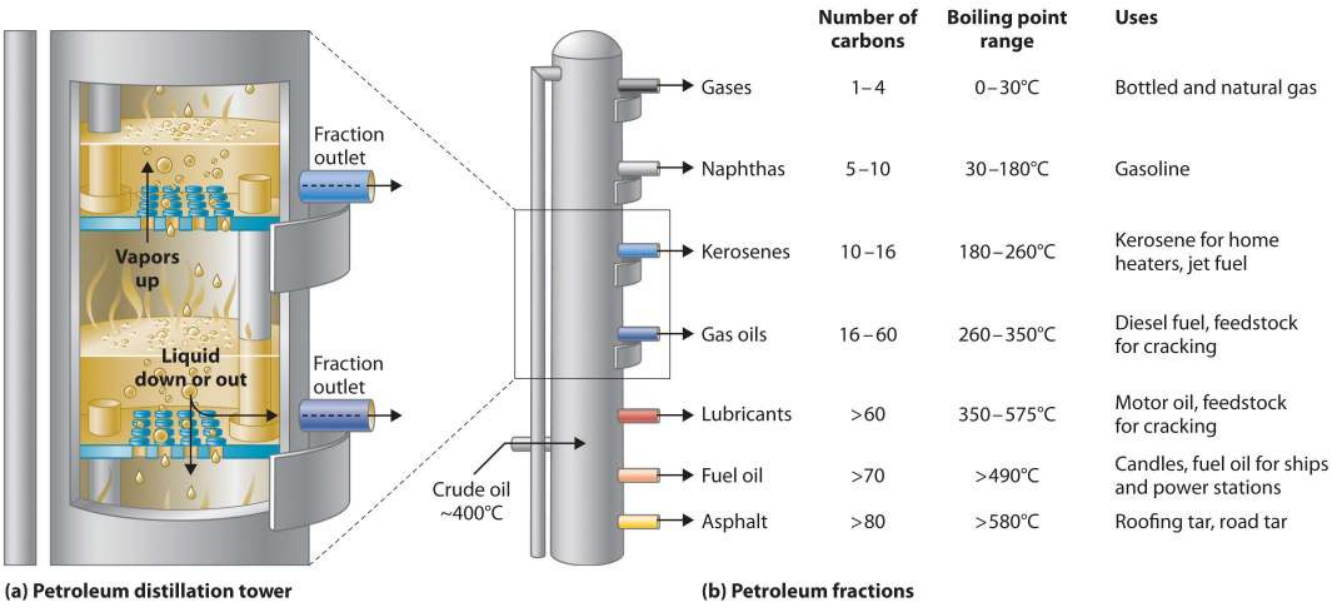


***Figure* 15.4.3** *The Distillation of Petroleum. (a) This is a diagram of a distillation column used for separating petroleum fractions. (b) Petroleum fractions condense at different temperatures, depending on the number of carbon atoms in the molecules, and are drawn off from the column. The most volatile components (those with the lowest boiling points) condense at the top of the column, and the least volatile (those with the highest boiling points) condense at the bottom.*

Octane Ratings of Gasolines

The quality of a fuel is indicated by its octane rating, which is a measure of its ability to burn in a combustion engine without knocking or pinging. Knocking and pinging signal premature combustion (Figure **15.4.4**) which can be caused either by an engine malfunction or by a fuel that burns too fast. In either case, the gasoline-air mixture detonates at the wrong point in the engine cycle, which reduces the power output and can damage valves, pistons, bearings, and other engine components. The various gasoline formulations are designed to provide the mix of hydrocarbons least likely to cause knocking or pinging in a given type of engine performing at a particular level.

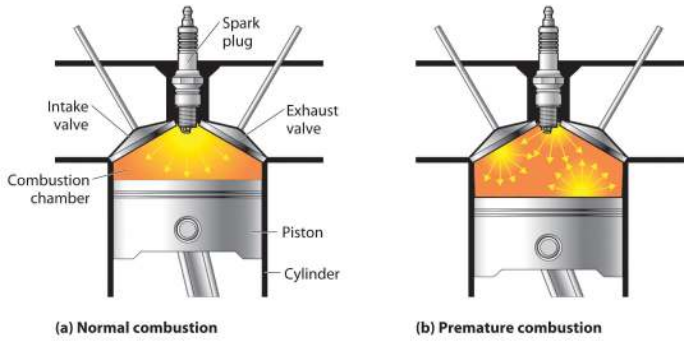


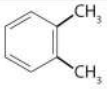
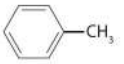
Figure **15.4.4** *The Burning of Gasoline in an Internal Combustion Engine. (a) Normally, fuel is ignited by the spark plug, and combustion spreads uniformly outward. (b) Gasoline with an octane rating that is too low for the engine can ignite prematurely, resulting in uneven burning that causes knocking and pinging.*

The octane scale was established in 1927 using a standard test engine and two pure compounds: n-heptane and isooctane (2,2,4-trimethylpentane). n-Heptane, which causes a great deal of knocking on combustion, was assigned an octane rating of 0, whereas isooctane, a very smooth-burning fuel, was assigned an octane rating of 100. Chemists assign octane ratings to different blends of gasoline by burning a sample of each in a test engine and comparing the observed knocking with the amount of knocking caused by specific mixtures of n-heptane and isooctane. For example, the octane rating of a blend of 89% isooctane and 11% n-heptane is simply the average of the octane ratings of the components weighted by the relative amounts of each in the blend. Converting percentages to decimals, we obtain the octane rating of the mixture:

$$0.89(100) + 0.11(0) = 89 \tag{3.8.1}$$

As given in Table \(\PageIndex{1}\, many compounds that are now available have octane ratings greater than 100, which means they are better fuels than pure isooctane. In addition, antiknock agents, also called octane enhancers, have been developed. One of the most widely used for many years was tetraethyllead [$(C_2H_5)_4Pb$], which at approximately 3 g/gal gives a 10–15-point increase in octane rating. Since 1975, however, lead compounds have been phased out as gasoline additives because they are highly toxic. Other enhancers, such as methyl t-butyl ether (MTBE), have been developed to take their place. They combine a high octane rating with minimal corrosion to engine and fuel system parts. Unfortunately, when gasoline containing MTBE leaks from underground storage tanks, the result has been contamination of the groundwater in some locations, resulting in limitations or outright bans on the use of MTBE in certain areas. As a result, the use of alternative octane enhancers such as ethanol, which can be obtained from renewable resources such as corn, sugar cane, and, eventually, corn stalks and grasses, is increasing.

***Table* 15.4.1** *The Octane Ratings of Some Hydrocarbons and Common Additives.*

Name	Condensed Structural Formula	Octane Rating	Name	Condensed Structural Formula	Octane Rating
n-heptane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	0	*o*-xylene		107
n-hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$	25	ethanol	CH_3CH_2OH	108
n-pentane	$CH_3CH_2CH_2CH_2CH_3$	62	*t*-butyl alcohol	$(CH_3)_3COH$	113
isooctane	$(CH_3)_3CCH_2CH(CH_3)_2$	100	*p*-xylene		116
benzene		106	methyl *t*-butyl ether	$H_3COC(CH_3)_3$	116
methanol	CH_3OH	107	toluene		118

Alternative Fuels

Alternative means to power vehicles is a hot topic in environmental chemistry. Hybrid vehicles, ethanol, biodiesel (Figure **15.4.5**), natural gas, and hydrogen fuel cells are all options for powering vehicles that reduce the environmental impact of greenhouse gases in the environment. The main concern for these alternative fuels is their efficiency vs. cost when compared to fossil fuels. Table **15.4.2** shows the chemical structure for several fuels, as well as the energy content of each.



Figure **15.4.5***Biofuel station (SECO)*

Table **15.4.2** Energy Content of Fuels*.

	Gasoline	No. 2 Diesel	Biodiesel	Ethanol	Hydrogen	Liquefied Natural Gas (LNG)	Liquefied Petroleum Gas
Chemical Structure	C4 to C12	C8 to C25	Methyl esters of C12 to C22 fatty acids	CH_3CH_2OH	H_2	CH_4	C_3H_8 (majority) and C4H10 (minority)
Energy Content (Higher Heat Value)	124,340 Btu/gal (g)	137,380 Btu/gal (g)	127,960 Btu/gal for B100 (g)	84,530 Btu/gal for E100 (g)	61,013 Btu/lb (g)	84,820 Btu/gal (g)	91,410 Btu/gal (g
Energy Contained in Various Alternative Fuels as Compared to One Gallon of Gasoline	100%	113%	103%	77%	100%	64%	73%

*Table created at: http://www.afdc.energy.gov/afdc/fuels/properties.html

Ethanol

Ethanol can be used in varying percent grades by vehicles. Gasohol is 10% ethanol, produces less carbon emissions than typical gasoline, but decreases the miles per gallon (MPG) of the vehicle slightly. E85 is up to 85% ethanol, can be less expensive depending upon where you live, but lowers the MPG up to 30% compared to typical gasoline. Let's look at the bond enthalpy change for the burning of fossil fuels vs. the burning of E85 to understand the drop in MPG.

Summary

- The extraction and processing of natural gas (mainly methane) and petroleum oil were discussed.
- Petroleum is converted to useful products such as gasoline by distillation, cracking, and reforming.
- Alternative means to power vehicles and reduce the effect of greenhouse gases in the environment include hybrid vehicles, ethanol, biodiesel , natural gas, and hydrogen fuel cells.

Contributors and Attributions

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- US Department of Energy. Alternative Fuels. Retrieved 6/13/2012 from: http://www.fueleconomy.gov/feg/current.shtml
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15.5: Convenient Energy

Learning Objective

- Describe the gasification and liquefaction of coal and the interest in its conversion.

Oil and natural gas resources are limited. Current estimates suggest that the known reserves of petroleum will be exhausted in about 60 years, and supplies of natural gas are estimated to run out in about 120 years. Coal, on the other hand, is relatively abundant, making up more than 90% of the world's fossil fuel reserves. As a solid, coal is much more difficult to mine and ship than petroleum (a liquid) or natural gas.

Coal Gasification and Liquefaction

A great deal of current research focuses on developing methods to convert coal to gaseous fuels (*coal* gasification) or liquid fuels (coal liquefaction). In the most common approach to coal gasification, coal reacts with steam to produce a mixture of CO and H_2 known as synthesis gas, or syngas:Because coal is 70%–90% carbon by mass, it is approximated as C in Equation 15.5.1.

$$\mathrm{C_{(s)} + H_2O_{(g)} \rightarrow CO_{(g)} + H_{2(g)} \quad \Delta H = 131\ kJ} \tag{15.5.1}$$

Converting coal to syngas removes any sulfur present and produces a clean-burning mixture of gases.

Syngas is also used as a reactant to produce methane and methanol. A promising approach is to convert coal directly to methane through a series of reactions:

$$\begin{aligned}
&\mathrm{2C(s) + 2H_2O(g) \rightarrow \cancel{2CO(g)} + \cancel{2H_2(g)} \quad \Delta H_1 = 262\ kJ}\\
&\mathrm{\cancel{CO(g)} + \cancel{H_2O(g)} \rightarrow CO_2(g) + \cancel{H_2(g)} \quad \Delta H_2 = -41\ kJ}\\
&\mathrm{\cancel{CO(g)} + \cancel{3H_2(g)} \rightarrow CH_4(g) + \cancel{H_2O(g)} \quad \Delta H_3 = -206\ kJ}\\
\hline
&\mathrm{Overall:\ 2C(s) + 2H_2O(g) \rightarrow CH_4(g) + CO_2(g) \quad \Delta H_{comb} = 15\ kJ}
\end{aligned}$$

Burning a small amount of coal or methane provides the energy consumed by these reactions. Unfortunately, methane produced by this process is currently significantly more expensive than natural gas. As supplies of natural gas become depleted, however, this coal-based process may well become competitive in cost.

Similarly, the techniques available for converting coal to liquid fuels are not yet economically competitive with the production of liquid fuels from petroleum. Current approaches to coal liquefaction use a catalyst to break the complex network structure of coal into more manageable fragments. The products are then treated with hydrogen (from syngas or other sources) under high pressure to produce a liquid more like petroleum. Subsequent distillation, cracking, and reforming can be used to create products similar to those obtained from petroleum. The total yield of liquid fuels is about 5.5 bbl of crude liquid per ton of coal (1 bbl is 42 gal or 160 L). Although the economics of coal liquefaction are currently even less attractive than for coal gasification, liquid fuels based on coal are likely to become economically competitive as supplies of petroleum are consumed.

Summary

- There is great interest in developing methods to convert coal to gaseous fuels (coal gasification) or liquid fuels (coal liquefaction) as it is more convenient to mine and transport gas and liquid fuels.
- Converting coal to syngas (synthesis gas) removes any sulfur present and produces a clean-burning mixture of gases.

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15.6: Renewable Energy Sources

Learning Objectives

- Describe the different renewable energy sources.
- List any impacts it may have on the environment.

Energy sources that are more or less continuously made available in a time frame useful to people are called **renewable energy.** Renewable energy sources are often considered alternative sources because, in general, most industrialized countries do not rely on them as their main energy source. Instead, they tend to rely on the conventional energy sources such as fossil fuels or nuclear power that are non-renewable. Because of the energy crisis in the United States during the 1970s, dwindling supplies of fossil fuels and hazards associated with nuclear power, use of renewable energy sources such as solar energy, hydroelectric, wind, biomass, and geothermal has grown. Renewable energy comes from the sun (considered an "unlimited" supply) or other sources that can theoretically be renewed at least as quickly as they are consumed. If used at a sustainable rate, these sources will be available for consumption for thousands of years or longer. Renewable alternatives derive from wind, water, solar or biomass (Figure 15.6.1). Note that wind, water and biomass energy sources are indirect sources of solar energy. One limitation currently associated with most forms of renewable energy is that the energy is not concentrated and not easily portable.



Figure 15.6.1 A variety of voltage sources (clockwise from top left): the Brazos Wind Farm in Fluvanna, Texas (credit: Leaflet, Wikimedia Commons); the Krasnoyarsk Dam in Russia (credit: Alex Polezhaev); a solar farm (credit: U.S. Department of Energy); and a group of nickel metal hydride batteries (credit: Tiaa Monto). The voltage output of each depends on its construction and load, and equals emf only if there is no load.

Energy is an important ingredient in all phases of society. We live in a very interdependent world, and access to adequate and reliable energy resources is crucial for economic growth and for maintaining the quality of our lives. The principal energy resources used in the world are shown in Figure 15.6.2. With the rapid growth of electricity generation, renewables—including solar, wind, and hydroelectric power—are the fastest-growing energy source between 2018 and 2050, surpassing petroleum and other liquids to become the most used energy source in the Reference case. Worldwide renewable energy consumption increases by 3.1% per year between 2018 and 2050, compared with 0.6% annual growth in petroleum and other liquids, 0.4% growth in coal, and 1.1% annual growth in natural gas consumption.

Global natural gas consumption increases more than 40% between 2018 and 2050, and total consumption reaches nearly 200 quadrillion Btu by 2050. In addition to the natural gas used in electricity generation, natural gas consumption increases in the industrial sector. Chemical and primary metals manufacturing, as well as oil and natural gas extraction, account for most of the growing industrial demand.

Global liquid fuels consumption increases more than 20% between 2018 and 2050, and total consumption reaches more than 240 quadrillion Btu in 2050. Demand in OECD (Organisation for Economic Cooperation and Development) countries remains relatively stable during the projection period, but non-OECD demand increases by about 45%.

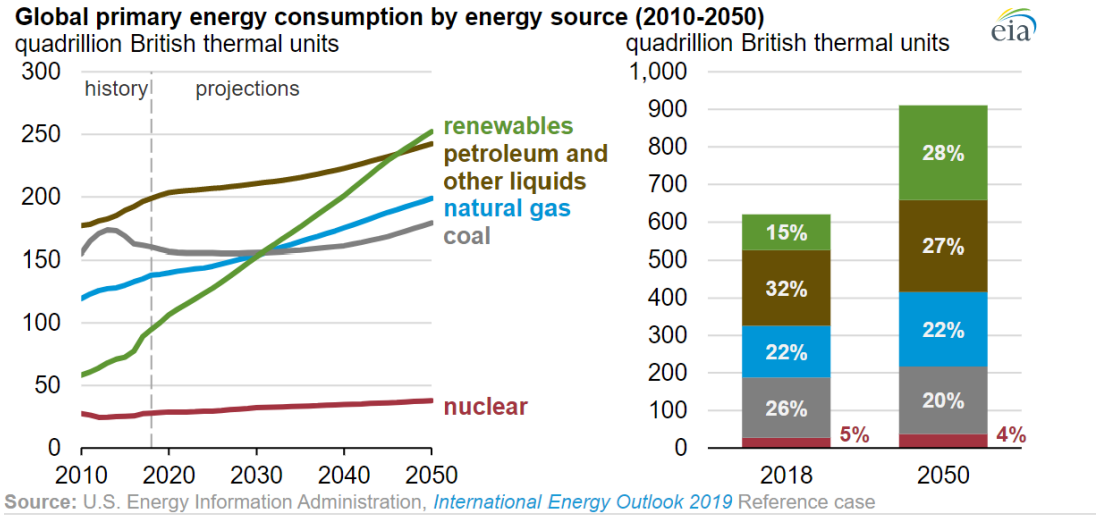


Figure **15.6.2**: Global primary energy consumption by energy source (2010-2050)

Why Use Renewable Energy Sources?

Majority of renewable energy sources including solar, wind, water, and biomass can be directly or indirectly attributed to the sun. The fact that the sun will continue burning for another 4-5 billion years makes it inexhaustible as an energy source for human civilization. With appropriate technology, renewable energy sources allow for local, decentralized control over power. Homes, businesses, and isolated communities can use sources such as solar to produce electricity without being near a power plant or being connected to a grid. This eliminates problems such as spills associated with extraction and transportation of fossil fuels that is needed in order to supply these fossil fuels to those areas that are lacking. Most renewable energy sources do not pollute the air with greenhouse gas emissions and other air pollutants associated with fossil fuels. This is especially important in combating climate change.

Solar Energy

Solar energy is the ultimate energy source driving life on earth and many human activities. Though only one billionth of the energy that leaves the sun (Figure **15.6.3**) actually reaches the earth's surface, this is more than enough to meet the world's energy requirement. In fact, all other sources of energy, renewable and non-renewable, are actually stored forms of solar energy. The process of directly converting solar energy to heat or electricity is considered a renewable energy source. Solar energy represents an essentially unlimited supply of energy as the sun will long outlast human civilization on earth. The difficulties lie in harnessing the energy. Solar energy has been used for centuries to heat homes and water, and modern technology (photovoltaic cells) has provided a way to produce electricity from sunlight. There are two basic forms of solar energy collectors are passive and active.

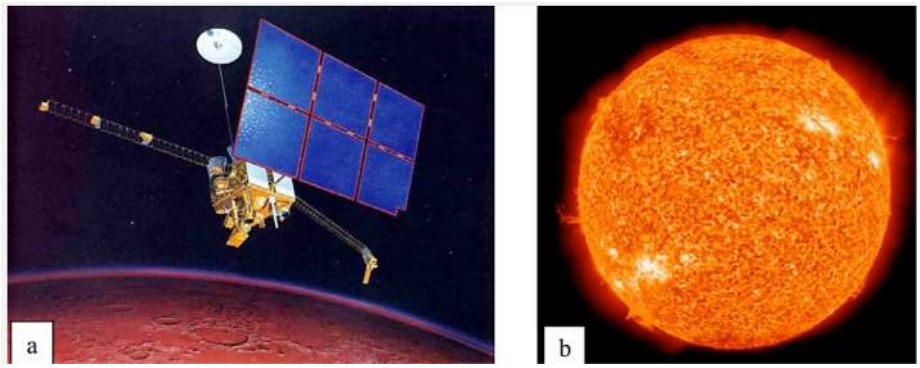


Figure **15.6.3**: a) Mars Observer in Mars Orbit showing the solar panel. (Picture: Wikimedia Commons www.jpl.nasa.gov/images/space...t1-browse.jpg,). b) The Sun photographed at 304 angstroms by the Atmospheric Imaging Assembly (AIA 304) of NASA's Solar Dynamics Observatory (SDO). This is a false-color image of the Sun observed in the extreme ultraviolet region of the spectrum. sdo.gsfc.nasa.gov/assets/img/..._4096_0304.jpg, NASA/SDO (AIA)

Solar photovoltaic (PV) devices, or solar cells, change sunlight directly into electricity. PV uses semiconducting materials such as silicon to produce electricity from sunlight: when light hits the cells, the material produces free electrons that migrate across the cell, creating an electric current. Small PV cells can power calculators, watches, and other small electronic devices. Arrangements of many solar cells in PV panels and arrangements of multiple PV panels in PV arrays can produce electricity for an entire house or building (Figure 15.6.4a). Some PV power plants have large arrays that cover many acres to produce electricity for thousands of homes.

Hundreds of thousands of houses and buildings around the world have PV systems on their roofs. Many multi-megawatt PV power plants have also been built. Covering 4% of the world's desert areas with photovoltaics could supply the equivalent of all of the world's electricity. The Gobi Desert alone could supply almost all of the world's total electricity demand.

Solar thermal power plants, like the one in Figure 15.6.4b use concentrating solar collector systems to collect and concentrate sunlight to produce the high temperature heat needed to generate electricity.

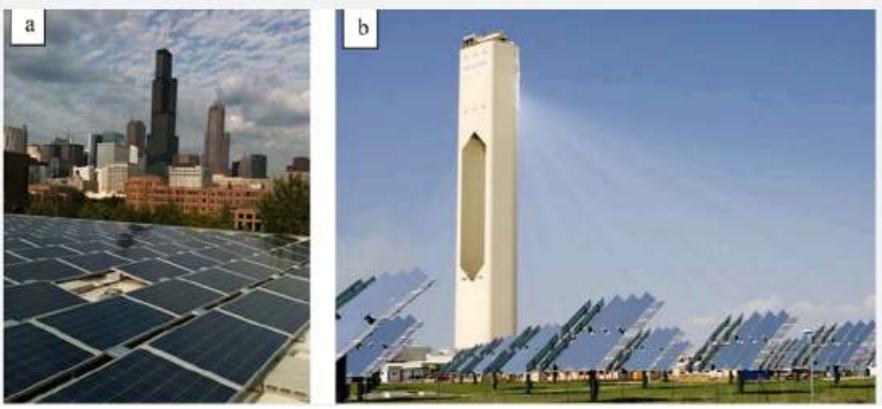


Figure 15.6.4 a) Rooftop Solar Installations on Douglas Hall at the University of Illinois at Chicago has no effect on land resources, while producing electricity with zero emissions. Source: Office of Sustainability. b) Solucar PS10 solar power tower in Andalusia, Spain, is a solar thermal power plant that generates electricity commercially. (Photo by Afloresm Solucar PS10 CC BY 2.0)

Solar power has minimal impact on the environment, depending on where it is placed. The manufacturing of photovoltaic (PV) cells generates some hazardous waste from the chemicals and solvents used in processing. Often solar arrays are placed on roofs of buildings or over parking lots or integrated into construction in other ways. However, large systems may be placed on land and particularly in deserts where those fragile ecosystems could be damaged if care is not taken. Some solar thermal systems use potentially hazardous fluids (to transfer heat) that require proper handling and disposal. Concentrated solar systems may need to be cleaned regularly with water, which is also needed for cooling the turbine-generator. Using water from underground wells may affect the ecosystem in some arid locations.

Biomass Energy

Biomass energy is from the energy stored in materials of biological origin such as plants and animals. Biomass energy is the oldest energy source used by humans. Until the Industrial Revolution prompted a shift to fossil fuels in the mid-18th century, biomass energy was the world's dominant fuel source. Currently, about 12 percent of the world's energy comes from biomass. Biomass is most frequently used as a fuel source in many developing nations, but with the decline of fossil fuel availability and the increase in fossil fuel prices, biomass is increasingly being used as a fuel source even in developed nations.

Direct combustion of solid biomass. The most common source for direct combustion is wood, but energy can also be generated by burning animal manure (dung), herbaceous plant material (non-wood), peat (partially decomposed plant and animal tissues), or converted biomass such as charcoal (wood that has been partially burned to produce a coal-like substance). Using wood and charcoal made from wood, for heating and cooking can replace fossil fuels and may result in lower CO_2 emissions. If wood is harvested from forests or woodlots that have to be thinned or from urban trees that fall down or needed be cut down anyway, then using it for biomass does not impact those ecosystems.

Biomass is also being used on a larger scale, where small power plants are powered by biomass such as woodchips (Figure 15.6.5). For instance, Central State Hospital, Milledgeville, GA has a woodchip burning plant that was the most advanced system available for its time and operating today. Colgate University in Hamilton, New York, has had a wood-burning boiler since the mid-1980's

that processes about 20,000 tons of locally and sustainably harvested wood chips, the equivalent of 1.17 million gallons (4.43 million liters) of fuel oil, avoiding 13,757 tons of emissions, and saving the university over $1.8 million in heating costs. The University's steam-generating wood-burning facility now satisfies more than 75 percent of the campus's heat and domestic hot water needs. For more information about this, click here Colgate University.



Figure 15.6.5 A biomass (woodchip) power plant in Germany. Image from Wikimedia Public Domain.

Gaseous Biomass. Organic material can be converted to methane, the main component of natural gas, by anaerobic decomposition or fermentation, a process that utilizes anaerobic bacteria. Methane is a relatively clean fuel that burns efficiently. It can be generated from any kind of organic waste such as municipal sewage and garbage, livestock manure, kitchen, and garden scraps. In fact, municipal landfills are active sites of methane production contributing annually to methane in the atmosphere and to global warming. This gas can and is currently being captured by numerous landfills around the United States that burn it to generate electricity at power plants or supply it to homes for heating.

Liquid Biofuels. Biofuels are transportation fuels produced from plant sources and used to power vehicles. The most common ones are ethanol and biodiesel.

- **Ethanol**, also known as ethyl alcohol or grain alcohol, is produced by fermenting crops such as corn, sugarcane, and other crops and then mixed with conventional gasoline. As an additive, ethanol lowers reliance on conventional oil and increases the combustion efficiency of gasoline, reducing pollutant emissions.
- **Biodiesel** which is essentially vegetable oil, can also be derived from a wide range of plant sources, including rapeseed, sunflowers, and soybeans, and can be used in most conventional diesel engines. Biodiesel can also be made from used vegetable oil and has been produced on a very local basis. Because it burns more cleanly than its petroleum-based counterpart, biodiesel can reduce pollution from heavy-duty vehicles such as trucks and buses. Compared to petroleum diesel, biodiesel combustion produces less sulfur oxides, particulate matter, carbon monoxide, and unburned and other hydrocarbons, but more nitrogen oxide.

Environmental Impacts of Biomass Energy

A major challenge of biomass is determining if it is really a more sustainable option. The energy content of some biomass energy sources may not be as high as fossil fuels so more must be burned to generate the same energy. It often takes energy to make energy and biomass is one example where the processing to make it may not be offset by the energy it produces. If traditional monoculture crops like corn or soybeans are used, they require major quantities of fossil fuel to manufacture fertilizer, run farm machines, and ship the fuel to markets, so these biofuels do not always offer significant net energy savings over gasoline and diesel fuel. In such instances, biofuels may not be carbon-neutral because the process of producing the biofuels results in more CO_2 added to the atmosphere than that removed by the growing crops.

Burning biomass directly (wood, manure, etc.) produces high particulate material pollution (see chapter 13 on Air Pollution), produces CO_2 and deprives the soil of nutrients it normally would have received from the decomposition of the organic matter. Each type of biomass energy source, therefore, must be evaluated for its full life-cycle impact in order to determine if it is really advancing sustainability and reducing environmental impacts.

Hydrogen: Light and Powerful

Hydrogen gas may be an important clean fuel of the future. Hydrogen is considered an energy carrier, like electricity and batteries, it carries energy that can be converted for use later. Hydrogen gas does not tend to exist freely but rather hydrogen atoms bind to other atoms and molecules becoming incorporated in everything from water to organic compounds. Therefore, to obtain hydrogen gas for fuel, energy is needed to force these substances to release their hydrogen atoms. One such procedure is known as **electrolysis** in which an electric current is passed through water to decompose the water molecule into oxygen and hydrogen (Figure 15.6.6). Hydrogen can also be produced from hydrocarbons such as natural gas and coal, fermentation of plant waste material, and using algae.

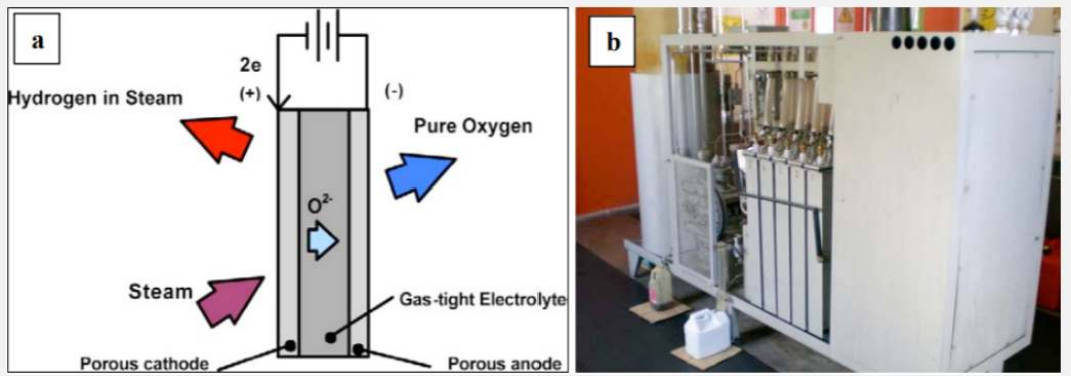


***Figure* 15.6.6** *a) An electric current passed through water resulting in the separation of hydrogen atoms from oxygen to produce the hydrogen fuel. b) An electrolyser used in the production of hydrogen by CambridgeBayWeather. After production the hydrogen is used to inflate weather balloons to which a radiosonde is attached. The oxygen produced is vented to the outside.*

Fuel cells are highly efficient power plants that produce electricity using hydrogen fuel in a chemical reaction that is a reverse of the electrolysis process that produced the hydrogen fuel (Figure 15.6.7). Energy is released by an exothermic electrochemical reaction that combines hydrogen and oxygen ions through an electrolyte material to generate electricity and heat. Experimental fuel cells that can power automobiles have been developed (Figure 15.6.2).



Figure 15.6.7 The electrochemical processes showing how hydrogen fuel is combined with oxygen generating heat energy along with water as a waste product. Some vehicles that use the fuel cell include buses (photo is a hydrogen fuel bus on Tower Bridge London, photo by Sludge G.), cars (The Toyota Fine N car based on fuel cell technology, photo by Chris 73, CC BY-SA 3.0) and motorcycles (Suzuki Burgman Fuel Cell cutaway model shown here, Photo by Mario CC BY-SA 3.0).

Challenges of Hydrogen

Currently, the infrastructure for using hydrogen fuel is lacking and converting a nation such as the United States to hydrogen would require massive and costly development of facilities to produce, store, transport, and provide the fuel. The environmental impact of hydrogen production itself depends on the source of material used to supply the hydrogen. For example, biomass and fossil fuel sources result in carbon-based emissions. Some research suggests that leakage of hydrogen from its production, transport, and use could potentially deplete stratospheric ozone. Research into this is still ongoing.

Other Renewable Sources

Wind Power

Wind is a renewable energy source that uses the power of moving air to generate electricity. Wind turbines use blades to collect the wind's kinetic energy. Wind flows over the blades creating lift (similar to the effect on airplane wings), which causes the blades to turn. The blades are connected to a drive shaft that turns an electric generator, which produces electricity (Figure **15.6.8**). Wind turbines are becoming a more prominent sight across the United States, even in regions that are considered to have less wind potential. Wind turbines (often called windmills) do not release emissions that pollute the air or water (with rare exceptions), and they do not require water for cooling. The U.S. wind industry had 40,181 MW of wind power capacity installed at the end of 2010, with 5,116 MW installed in 2010 alone, providing more than 20 % of installed wind power around the globe. According to the American Wind Energy Association, over 35 % of all new electrical generating capacity in the United States since 2006 was due to wind, surpassed only by natural gas.

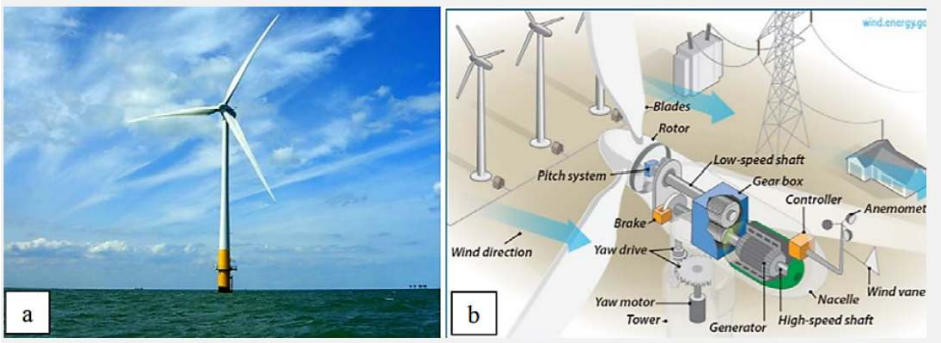


Figure **15.6.8** a) This wind turbine in the Thames Estuary in the UK is an example of induction at work, (credit: Phault, Flickr). Wind pushes the blades of the turbine, spinning a shaft attached to magnets, see image b for parts. The magnets spin around a conductive coil, inducing an electric current in the coil, and eventually feeding the electrical grid.

Most windmills generate about 1kW of electricity, which is only practical for decentralized power generation. California has about 17,000 windmills with a capacity of about 1,400 MW. This is about 80% of all windmills in the U.S. In West Europe windmill generators are quite common. Since a wind turbine has a small physical footprint relative to the amount of electricity it produces, many wind farms are located on crop, pasture, forest land, or coastal areas. They contribute to economic sustainability by providing extra income to farmers and ranchers, allowing them to stay in business and keep their property from being developed for other uses. For example, energy can be produced by installing wind turbines in the Appalachian Mountains of the United States instead of engaging in mountain top removal for coal mining.

Offshore wind turbines on lakes or the ocean may have smaller environmental impacts than turbines on land. Wind turbines do have a few environmental challenges. There are aesthetic concerns to some people when they see them on the landscape. A few wind turbines have caught on fire, and some have leaked lubricating fluids, though this is relatively rare. Some people do not like the sound that wind turbine blades make. Turbines have been found to cause bird and bat deaths particularly if they are located along their migratory path. This is of particular concern if these are threatened or endangered species. There are ways to mitigate that impact and it is currently being researched. There are some small impacts from the construction of wind projects or farms, such as the construction of service roads, the production of the turbines themselves, and the concrete for the foundations. However, overall life cycle analysis has found that turbines make much more energy than the amount used to make and install them.

Geothermal Energy

Geothermal energy uses heat from the Earth's internal geologic processes in order to produce electricity or provide heating. The subsurface temperature of the Earth provides an endless energy resource. One source of geothermal energy is steam. Groundwater percolates down through cracks in the subsurface rocks until it reaches rocks heated by underlying magma, and the heat converts the water to steam. Sometimes this steam makes its way back to the surface in the form of a geyser or hot spring. Wells can be dug to tap the steam reservoir and bring it to the surface, to drive generating turbines and produce electricity (Figure **15.6.9**a). Hot water can be circulated to heat buildings. Regions near tectonic plate boundaries have the best potential for geothermal activity.

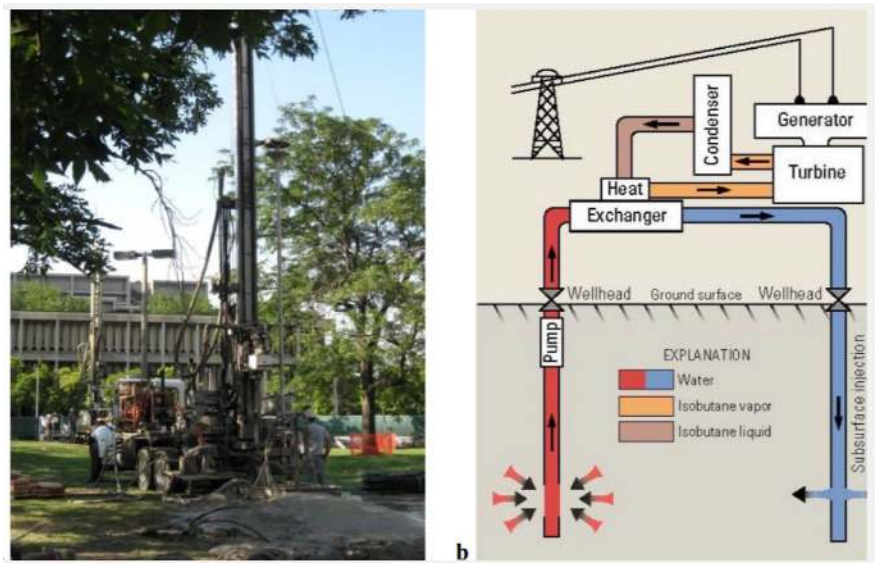


Figure **15.6.9** a) Installing a Geothermal Pipe System Drilling to install geothermal ground source pipe system. Source: Office of Sustainability. b) Electricity generation at a moderate-temperature hydrothermal system. The geothermal water is used to boil a second fluid (isobutane in this example) whose vapor then drives a turbine generator. The wastewater is injected back into the subsurface. Source: USGS.

The environmental impact of geothermal energy depends on how it is being used. Direct use and heating applications have almost no negative impact on the environment. Geothermally heated water can release dissolved gases, including carbon dioxide, methane, ammonia and hydrogen sulfide, although these are usually in very small quantities when compared to those released from fossil fuel plants. In addition, geothermal plants use scrubber systems to clean the air of hydrogen sulfide that is naturally found in the steam and hot water. They emit 97 % less acid rain-causing sulfur compounds than are emitted by fossil fuel plants.

Hydroelectric Power (Hydropower)

This is the second largest source of renewable energy used, next to biomass energy. The majority of hydropower currently comes from dams built across a river to block the flow of river water. The water stored behind the dam contains potential energy and when released, the potential energy is converted to kinetic energy as the water rushes down. This energy is used to turn blades of turbines and causing a generator to generate electricity. Electricity generated in the powerhouse of a dam is transmitted to the electric grid by transmission lines while the water flows into the riverbed below the dam and continues down river. An alternative approach considered less disruptive involves diverting a portion of the river's water through a pipe or channel and passed through a powerhouse to generate electricity and returned to the river. Another approach involves pumping water from a lower reservoir to a higher reservoir and then allowed to flow downhill through a turbine, generating electricity. This approach, however, requires energy input to pump the water. Figure **15.6.10** show a hydroelectric facility (a) and also illustrates the generation of electricity (b).

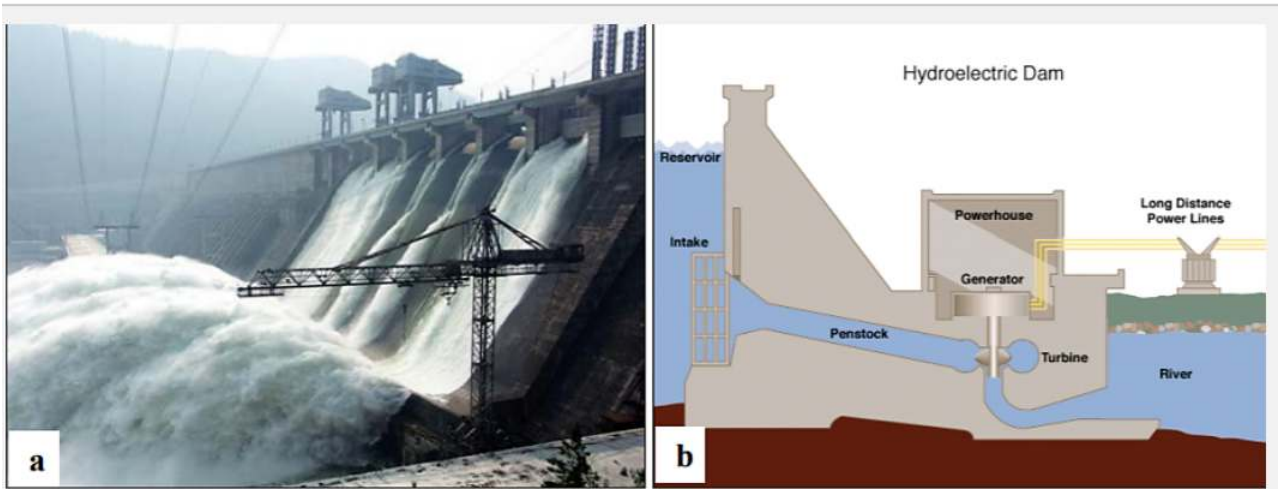


Figure **15.6.10** a) Hydroelectric facility (credit: Denis Belevich, Wikimedia Commons); b) An illustration showing how water is funneled through a portion of the dam to rotate turbines and generate electricity. (Image from Wikimedia, public domain).

Hydropower (hydro-electric) is considered a clean and renewable source of energy since it does not directly produce emissions of air pollutants and the source of power is regenerated. However, hydropower dams, reservoirs, and the operation of generators can have serious environmental impacts. A dam that is used to create a reservoir or to divert water to a run-ofriver hydropower plant can obstruct migration of fish to their upstream spawning areas in areas where salmon must travel upstream to spawn, such as along the Columbia River in Washington and Oregon. Hydro turbines kill and injure some of the fish that pass through the turbine although there are ways to reduce that effect. This problem can be partially alleviated by using 'fish ladders' that help the salmon get up the dams.

A reservoir and operation of the dam can affect the natural water habitat due to changes in water temperatures, chemistry, flow characteristics, and silt loads, all of which can lead to significant changes in the ecology and physical characteristics of the river upstream and downstream.

Potential of Tidal Power

Tidal power involves placing turbines in zones of the ocean with significant tides and currents, and using the power of flowing water to turn the blades of a turbine to generate electricity. Ocean power systems are still being researched and currently still experimental. For example, the Bay of Fundy, which has a 15 m tide, a dam constructed across the estuary would let water enter on the incoming tide, then release the water through turbines at low tide. The energy potential is great http://www.ialtenergy.com/tidal-power-news.html , and so is the environmental cost. Tapping tidal energy resources involves building major dams on inlets and estuaries that are prized for other purposes, so few tidal energy facilities have been developed. Harnessing waves and currents on a significant scale will involve designing turbine structures that are large, inexpensive, and can operate for long periods under the physical stresses and corrosive forces of ocean environments. Though proposed, a tidal power plant has not been constructed at Fundy. There is a 240,000 kW tidal plant at La Rance, France.

Summary

- Renewable sources of energy are derived from wind, water, solar or biomass.
- One limitation currently associated with most forms of renewable energy is that the energy is not concentrated and not easily portable.
- There is a projected increase from 15% (2018) to 28% of global renewable energy consumption.

Contributor

US Energy Information Administration

Libretext: Introduction to Environmental Science (Zendher et al.)

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CHAPTER OVERVIEW

16: Nuclear Chemistry

16.1: Nuclear Equations
16.2: Penetrating Power of Radiation
16.3: Half-Life and Radioisotopic Dating
16.4: Natural Radioactivity
16.5: Artificial Transmutation
16.6: Uses of Radioisotopes
16.7: Energy from the Nucleus
16.8: Nuclear Energy
16.9: Uses and Consequences of Nuclear Energy
16.10: Nuclear Bombs

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16.1: Nuclear Equations

Learning Objectives

- Identify common particles and energies involved in nuclear reactions.
- Write and balance nuclear equations.

Changes of nuclei that result in changes in their atomic numbers, mass numbers, or energy states are nuclear reactions. To describe a nuclear reaction, we use an equation that identifies the nuclides involved in the reaction, their mass numbers and atomic numbers, and the other particles involved in the reaction.

Types of Particles in Nuclear Reactions

Many entities can be involved in nuclear reactions. The most common are protons, neutrons, alpha particles, beta particles, positrons, and gamma rays, as shown in Table **16.1.1**.

Table **16.1.1** A Summary of the Names, Symbols, Representations, and Descriptions of the Most Common Particles in Nuclear Reactions.

Name	Symbol(s)	Representation	Description
Alpha particle	^4_2He or $^4_2\alpha$		(High-energy) helium nuclei consisting of two protons and two neutrons
Beta particle	$^0_{-1}\text{e}$ or $^0_{-1}\beta$		(High-energy) electrons
Positron	$^0_{+1}\text{e}$ or $^0_{+1}\beta$		Particles with the same mass as an electron but with 1 unit of positive charge
Proton	^1_1H or ^1_1p		Nuclei of hydrogen atoms
Neutron	^1_0n		Particles with a mass approximately equal to that of a proton but with no charge
Gamma ray	γ		Very high-energy electromagnetic radiation

Balancing Nuclear Reactions

A balanced chemical reaction equation reflects the fact that during a chemical reaction, bonds break and form, and atoms are rearranged, but the total numbers of atoms of each element are conserved and do not change. A balanced nuclear reaction equation indicates that there is a rearrangement during a nuclear reaction, but of subatomic particles rather than atoms. Nuclear reactions also follow conservation laws, and they are balanced in two ways:

1. The sum of the mass numbers of the reactants equals the sum of the mass numbers of the products.
2. The sum of the charges of the reactants equals the sum of the charges of the products.

If the atomic number and the mass number of all but one of the particles in a nuclear reaction are known, we can identify the particle by balancing the reaction. For instance, we could determine that $^{17}_8\text{O}$ is a product of the nuclear reaction of $^{14}_7\text{N}$ and ^4_2He if we knew that a proton, ^1_1H, was one of the two products. Example **16.1.1** shows how we can identify a nuclide by balancing the nuclear reaction.

Nuclear Decay Processes

Radioactive decay involves the emission of a particle and/or energy as one atom changes into another. In most instances, the atom changes its identity to become a new element. There are four different types of emissions that occur.

Alpha Emission

Alpha (α) decay involves the release of helium ions from the nucleus of an atom. This ion consists of two protons and two neutrons and has a $2+$ charge. Release of an α-particle produces a new atom that has an atomic number two less than the original atom and an atomic weight that is four less. A typical alpha decay reaction is the conversion of uranium-238 to thorium:

$$^{238}_{92}\text{U} \rightarrow {}^{234}_{90}\text{Th} + {}^{4}_{2}\alpha^{+}$$

We see a decrease of two in the atomic number (uranium to thorium) and a decrease of four in the atomic weight (238 to 234). Usually the emission is not written with atomic number and weight indicated since it is a common particle whose properties should be memorized. Quite often the alpha emission is accompanied by gamma (γ) radiation, a form of energy release. Many of the largest elements in the periodic table are alpha-emitters.

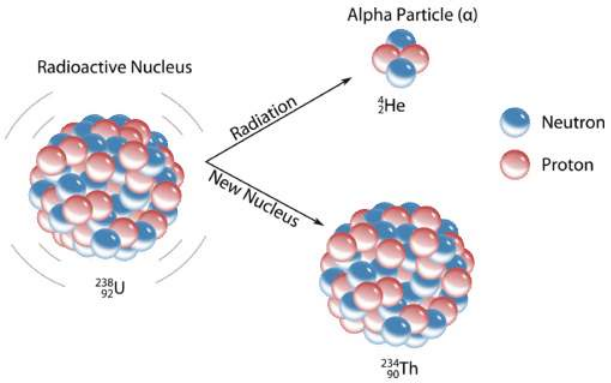


Figure **16.1.1** *Emission of an alpha particle from the nucleus.*

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,

$$^{238}_{92}\text{U}$$

is the parent isotope, and

$$^{234}_{90}\text{Th}$$

is the daughter isotope. When one element changes into another in this manner, it undergoes **radioactive decay**.

Example 16.1.1

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

$$^{222}_{86}\text{Rn}$$

We represent the alpha particle as

$$^{4}_{2}\text{He}$$

Use subtraction (222 − 4 = 218 and 86 − 2 = 84) to identify the daughter isotope as polonium:

$$^{222}_{86}\text{Rn} \rightarrow {}^{4}_{2}\text{He} + {}^{218}_{84}\text{Th}$$

Exercise 16.1.1

Write the nuclear equation that represents radioactive decay of polonium-208 by alpha particle emission and identify the daughter isotope.

Answer

$$^{208}_{80}\text{Po} \rightarrow {}^{4}_{2}\text{He} + {}^{204}_{82}\text{Pb}$$

$$^{204}_{82}\text{Pb}$$

Beta Emission

Beta (β) **decay** is a more complicated process. Unlike the α-emission, which simply expels a particle, the β-emission involves the transformation of a neutron in the nucleus to a proton and an electron. The electron is then ejected from the nucleus. In the process,the atomic number increases by one while the atomic weight stays the same. As is the case with α-emissions, β-emissions are often accompanied by γ-radiation.

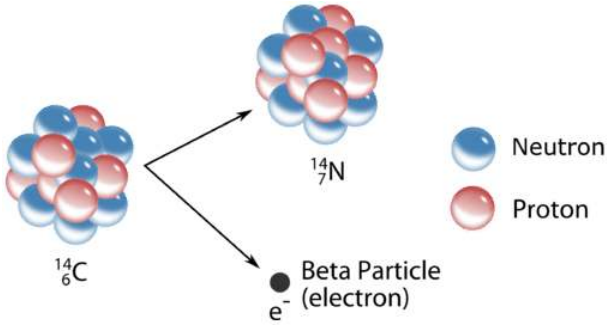


Figure **16.1.2** *Beta emission.*

A typical beta decay process involves carbon-14, often used in radioactive dating techniques. The reaction forms nitrogen-14 and an electron:

$$^{14}_{6}\text{C} \rightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}\text{e}$$

Again, the beta emission is usually simply indicated by the Greek letter β; memorization of the process is necessary in order to follow nuclear calculations in which the Greek letter β appears without further notation.

Example 16.1.2

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 $^{4}_{2}\text{He}$

while one of the products is $^{0}_{-1}\text{e}$

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 carbon-12.

? Exercise 16.1.2

Write the nuclear equation that represents the radioactive decay of rubidium-87 by beta particle emission and identify the daughter isotope.

Answer

$$^{87}_{37}\text{Rb} \rightarrow {}^{87}_{38}\text{Sr} + {}^{0}_{-1}\text{e}$$

$^{87}_{38}\text{Sr}$

Gamma Emission

Gamma (γ) radiation is simply energy. It may be released by itself or more commonly in association with other radiation events. There is no change of atomic number of atomic weight in a simple γ-emission. Often, an isotope may produce γ-radiation as a result of a transition in a metastable isotope. This type of isotope may just "settle", with a shifting of particles in the nucleus. The composition of the atom is not altered, but the nucleus could be considered more "comfortable" after the shift. This shift increases the stability of the isotope from the energetically unstable (or "metastable") isotope to a more stable form of the nucleus. Gamma (γ) emission can occur virtually instantaneously, as it does in the alpha decay of uranium-238 to thorium-234, where the asterisk denotes an excited state:

$$^{238}_{92}\text{U} \rightarrow \underset{\substack{\text{excited}\\ \text{nuclear}\\ \text{state}}}{^{234}_{90}\text{Th}^{*}} + {}^{4}_{2}\alpha \xrightarrow{\text{relaxation}} {}^{234}_{90}\text{Th} + {}^{0}_{0}\gamma \tag{16.1.1}$$

If we disregard the decay event that created the excited nucleus, then

$$^{234}_{88}\text{Th}^{*} \rightarrow {}^{234}_{88}\text{Th} + {}^{0}_{0}\gamma \tag{16.1.2}$$

or more generally,

$$^{A}_{Z}\text{X}^{*} \rightarrow {}^{A}_{Z}\text{X} + {}^{0}_{0}\gamma \tag{16.1.3}$$

Gamma emission can also occur after a significant delay. For example, technetium-99*m* has a half-life of about 6 hours before emitting a γ ray to form technetium-99 (the *m* is for metastable). Because γ rays are energy, their emission does not affect either the mass number or the atomic number of the daughter nuclide. Gamma-ray emission is therefore the only kind of radiation that does not necessarily involve the conversion of one element to another, although it is almost always observed in conjunction with some other nuclear decay reaction.

Positron Emission

A **positron** is a positive electron (a form of antimatter). This rare type of emission occurs when a proton is converted to a neutron and a positron in the nucleus, with ejection of the positron. The atomic number will decrease by one while the atomic weight does not change. A positron is often designated by β^{+}.

Carbon-11 emits a positron to become boron-11:

$$^{11}_{6}\text{C} \rightarrow {}^{11}_{5}\text{B} + {}^{0}_{+1}\beta$$

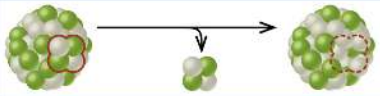
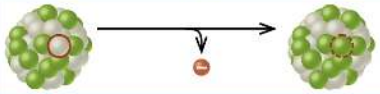
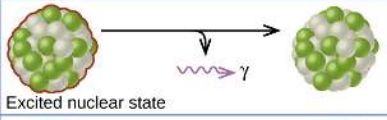
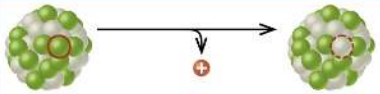
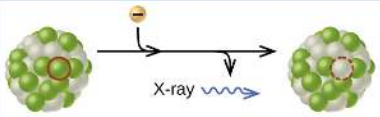
Electron Capture

An alternate way for a nuclide to increase its neutron to proton ratio is by a phenomenon called electron capture. In electron capture, an electron from an inner orbital is captured by the nucleus of the atom and combined with a proton to form a neutron. For example, silver-106 undergoes electron capture to become palladium-106.

$$^{106}_{47}\text{Ag} + {}^{0}_{-1}\text{e} \rightarrow {}^{106}_{46}\text{Pd}$$

Note that the overall result of electron capture is identical to positron emission. The atomic number decreases by one while the mass number remains the same.

Table **16.1.2** Different Types of Decay and Changes in Atomic and Mass Numbers.

Type	Nuclear equation	Representation	Change in mass/atomic numbers
Alpha decay	${}^{A}_{Z}X \rightarrow {}^{4}_{2}He + {}^{A-4}_{Z-2}Y$		A: decrease by 4 Z: decrease by 2
Beta decay	${}^{A}_{Z}X \rightarrow {}^{0}_{-1}e + {}^{A}_{Z+1}Y$		A: unchanged Z: increase by 1
Gamma decay	${}^{A}_{Z}X \rightarrow {}^{0}_{0}\gamma + {}^{A}_{Z}Y$		A: unchanged Z: unchanged
Positron emission	${}^{A}_{Z}X \rightarrow {}^{0}_{+1}e + {}^{A}_{Y-1}Y$		A: unchanged Z: decrease by 1
Electron capture	${}^{A}_{Z}X + {}^{0}_{-1}e \rightarrow {}^{A}_{Y-1}Y$		A: unchanged Z: decrease by 1

Following are the equations of several nuclear reactions that have important roles in the history of nuclear chemistry:

- The first naturally occurring unstable element that was isolated, polonium, was discovered by the Polish scientist Marie Curie and her husband Pierre in 1898. It decays, emitting α particles:

$$^{212}_{84}\text{Po} \longrightarrow {}^{208}_{82}\text{Pb} + {}^{4}_{2}\text{He}$$

- The first nuclide to be prepared by artificial means was an isotope of oxygen, ^{17}O. It was made by Ernest Rutherford in 1919 by bombarding nitrogen atoms with α particles:

$$^{14}_{7}\text{N} + {}^{4}_{2}\alpha \longrightarrow {}^{17}_{8}\text{O} + {}^{1}_{1}\text{H}$$

- James Chadwick discovered the neutron in 1932, as a previously unknown neutral particle produced along with ^{12}C by the nuclear reaction between ^{9}Be and ^{4}He:

$$^{9}_{4}\text{Be} + {}^{4}_{2}\text{He} \longrightarrow {}^{12}_{6}\text{C} + {}^{1}_{0}\text{n}$$

- The first element to be prepared that does not occur naturally on the earth, technetium, was created by bombardment of molybdenum by deuterons (heavy hydrogen, $^{2}_{1}\text{H}$), by Emilio Segre and Carlo Perrier in 1937:

$$^{2}_{1}\text{H} + {}^{97}_{42}\text{Mo} \longrightarrow 2{}^{1}_{0}\text{n} + {}^{97}_{43}\text{Tc}$$

- The first controlled nuclear chain reaction was carried out in a reactor at the University of Chicago in 1942. One of the many reactions involved was:

$$^{235}_{92}\text{U} + {}^{1}_{0}\text{n} \longrightarrow {}^{87}_{35}\text{Br} + {}^{146}_{57}\text{La} + 3{}^{1}_{0}\text{n}$$

Summary

- Nuclei can undergo reactions that change their number of protons, number of neutrons, or energy state.
- Many different particles can be involved in nuclear reactions. The most common are protons, neutrons, positrons (which are positively charged electrons), electrons, alpha (α) particles (which are high-energy helium nuclei), beta (β) particles (which are high-energy electrons), and gamma (γ) rays (which compose high-energy electromagnetic radiation).
- As with chemical reactions, nuclear reactions are always balanced. When a nuclear reaction occurs, the total mass (number) and the total charge remain unchanged.

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- Marisa Alviar-Agnew (Sacramento City College)

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16.2: Penetrating Power of Radiation

Learning Objective

- Compare qualitatively the ionizing and penetration power of alpha particles (α), beta particles (β), and gamma rays (γ).

With all the radiation from natural and man-made sources, we should quite reasonably be concerned about how all the radiation might affect our health. The damage to living systems is done by radioactive emissions when the particles or rays strike tissue, cells, or molecules and alter them. These interactions can alter molecular structure and function; cells no longer carry out their proper function and molecules, such as DNA, no longer carry the appropriate information. Large amounts of radiation are very dangerous, even deadly. In most cases, radiation will damage a single (or very small number) of cells by breaking the cell wall or otherwise preventing a cell from reproducing.

The ability of radiation to damage molecules is analyzed in terms of what is called **ionizing power**. When a radiation particle interacts with atoms, the interaction can cause the atom to lose electrons and thus become ionized. The greater the likelihood that damage will occur by an interaction is the ionizing power of the radiation.

Much of the threat from radiation is involved with the ease or difficulty of protecting oneself from the particles. How thick of wall do you need to hide behind to be safe? The ability of each type of radiation to pass through matter is expressed in terms of **penetration power.** The more material the radiation can pass through, the greater the penetration power and the more dangerous they are. In general, the greater mass present the greater the ionizing power and the lower the penetration power.

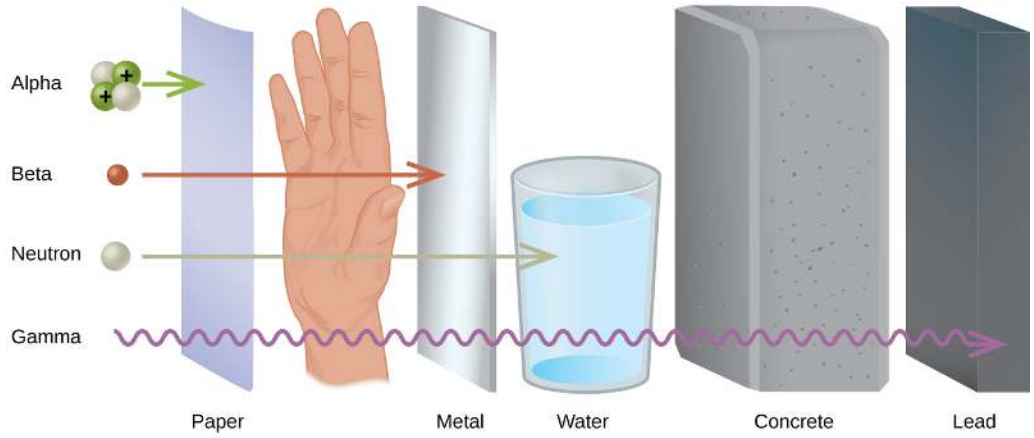


Figure **16.2.1**: The ability of different types of radiation to pass through material is shown. From least to most penetrating, they are alpha < beta < neutron < gamma. (CC BY-SA 4.0; OpenStax).

Comparing only the three common types of ionizing radiation, **alpha particles** have the greatest mass. Because of the large mass of the alpha particle, it has the highest ionizing power and the greatest ability to damage tissue. That same large size of alpha particles, however, makes them less able to penetrate matter. Alpha particles have the least penetration power and can be stopped by a thick sheet of paper or even a layer of clothes. They are also stopped by the outer layer of dead skin on people. This may seem to remove the threat from alpha particles but only from external sources. In a situation like a nuclear explosion or some sort of nuclear accident where radioactive emitters are spread around in the environment, the emitters can be inhaled or taken in with food or water and once the alpha emitter is inside you, you have no protection at all.

Beta particles are much smaller than alpha particles and therefore, have much less ionizing power (less ability to damage tissue), but their small size gives them much greater penetration power. Most resources say that beta particles can be stopped by a one-quarter inch thick sheet of aluminum. Once again, however, the greatest danger occurs when the beta emitting source gets inside of you.

Gamma rays are not particles but a high energy form of electromagnetic radiation (like x-rays except more powerful). Gamma rays are energy that has no mass or charge. Gamma rays have tremendous penetration power and require several inches of dense material (like lead) to shield them. Gamma rays may pass all the way through a human body without striking anything. They are considered to have the least ionizing power and the greatest penetration power.

A comparison of Alpha particles, beta particles and gamma rays is given in Table **16.2.1**.

Table **16.2.1** Comparison of Penetrating Power,Ionizing Power and Shielding of Alpha and Beta Particles, and Gamma Rays.

Particle	Symbol	Mass	Penetrating Power	Ionizing Power	Shielding
Alpha	α	4amu	Very Low	Very High	Paper Skin
Beta	β	$1/2000\text{amu}$	Intermediate	Intermediate	Aluminum
Gamma	γ	0 (energy only)	Very High	Very Low	2 inches lead

The safest amount of radiation to the human body is zero. It isn't possible to be exposed to no ionizing radiation so the next best goal is to be exposed to as little as possible. The two best ways to minimize exposure is to limit time of exposure and to increase distance from the source.

Summary

- Types of radiation differ in their ability to penetrate material and damage tissue, with alpha particles the least penetrating but potentially most damaging and gamma rays the most penetrating.
- The two best ways to minimize exposure is to limit time of exposure and to increase distance from the source.

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16.3: Half-Life and Radioisotopic Dating

Learning Objectives

- Define *half-life*.
- Determine the amount of radioactive substance remaining after a given number of half-lives.
- Define a radioactive decay series.

Whether or not a given isotope is radioactive is a characteristic of that particular isotope. Some isotopes are stable indefinitely, while others are radioactive and decay through a characteristic form of emission. As time passes, less and less of the radioactive isotope will be present, and the level of radioactivity decreases. An interesting and useful aspect of radioactive decay is **half life**. which is the amount of time it takes for one-half of a radioactive isotope to decay. The half-life of a specific radioactive isotope is constant; it is unaffected by conditions and is independent of the initial amount of that isotope.

For example, cobalt-60, an isotope that emits gamma rays used to treat cancer, has a half-life of 5.27 years (Figure **16.3.1**). In a given cobalt-60 source, since half of the $^{60}_{27}\text{Co}$ nuclei decay every 5.27 years, both the amount of material and the intensity of the radiation emitted is cut in half every 5.27 years. (Note that for a given substance, the intensity of radiation that it produces is directly proportional to the rate of decay of the substance and the amount of the substance.) This is as expected for a process following first-order kinetics. Thus, a cobalt-60 source that is used for cancer treatment must be replaced regularly to continue to be effective.

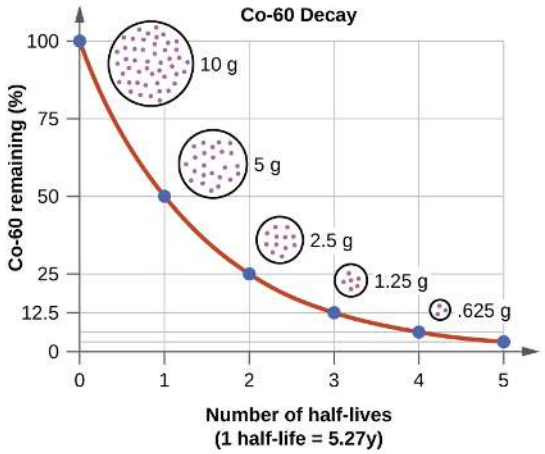


Figure **16.3.1** For cobalt-60, which has a half-life of 5.27 years, 50% remains after 5.27 years (one half-life), 25% remains after 10.54 years (two half-lives), 12.5% remains after 15.81 years (three half-lives), and so on.

We can determine the amount of a radioactive isotope remaining after a given number half-lives by using the following expression:

$$\textit{amount remaining} = \textit{initial amount} \times \left(\frac{1}{2}\right)^{n}$$

where n is the number of half-lives. This expression works even if the number of half-lives is not a whole number.

Example 16.3.1:

The half-life of fluorine-20 is 11.0 s. If a sample initially contains 5.00 g of fluorine-20, how much remains after 44.0 s?

Solution

If we compare the time that has passed to the isotope's half-life, we note that 44.0 s is exactly 4 half-lives, so using the previous expression, $n = 4$. Substituting and solving results in the following:

$$amount\ remaining = 5.00g \times \left(\frac{1}{2}\right)^4$$
$$amount\ remaining = 5.00g \times \left(\frac{1}{16}\right)$$
$$amount\ remaining = 0.313g$$

Less than one-third of a gram of fluorine-20 remains.

? Exercise 16.3.1

The half-life of titanium-44 is 60.0 y. A sample of titanium contains 0.600 g of titanium-44. How much remains after 240.0 y?

Answer

0.0375 g

✓ Example 16.3.2

If there are 60 grams of **Np**-240 present, how much **Np**-240 will remain after 4 hours? (**Np**-240 has a half-life of 1 hour)

Solution

Np-240 with a half life of only 1 hour.

Amount of Np-240 present	Amount of time passed
60 g	0 (this is the amount before any time has passed)
30 g	1 hour (1 half-life)
15 g	2 hours (2 half-lives)
7.5 g	3 hours
3.75 g	4 hours

After 4 hours, only **3.75 g** of our original **60 g** sample would remain the radioactive isotope **Np**-240.

✓ Exercise 16.3.2

A sample of **Ac**-225 originally contained 80 grams and after 50 days only 2.55 grams of the original **Ac**-225 remain. What is the half life of **Ac**-225?

Answer

10 days.

The half-lives of many radioactive isotopes have been determined and they have been found to range from extremely long half-lives of 10 billion years to extremely short half-lives of fractions of a second. For example: the half-life of $^{209}_{83}\mathbf{Bi}$ is 1.9×10^{19} years; $^{239}_{94}\mathbf{Ra}$ is 24,000 years; $^{222}_{86}\mathbf{Rn}$ is 3.82 days; and element-111 (Rg for roentgenium) is 1.5×10^{-3} seconds. The table below illustrates half-lives for several selected elements.

Table **16.3.1**: Table of Selected Half-lives

Element	Mass Number (A)	Half-life	Element	Mass Number (A)	Half Life
Uranium	238	4.5 Billion years	Californium	251	800 years
Neptunium	240	1 hour	Nobelium	254	3 seconds
Plutonium	243	5 hours	Carbon	14	5730 years
Americium	245	25 minutes	Carbon	16	740 milliseconds

Uranium Decay Series

The naturally occurring radioactive isotopes of the heaviest elements fall into chains of successive disintegrations, or decays, and all the species in one chain constitute a radioactive family, or radioactive decay series. Three of these series include most of the naturally radioactive elements of the periodic table. They are the uranium series, the actinide series, and the thorium series. (Figure **16.3.2**). In all three series, the end-product is a stable isotope of lead.

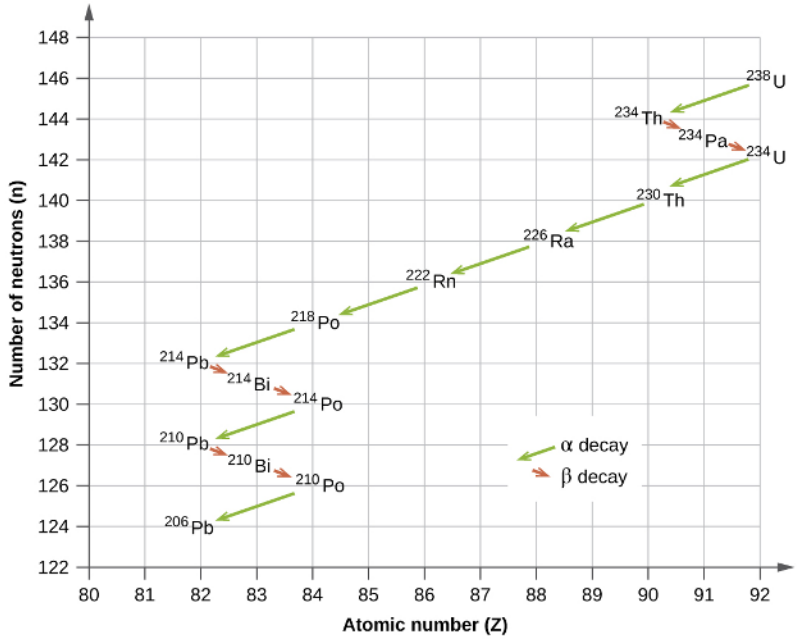


Figure **16.3.2** Uranium-238 undergoes a radioactive decay series consisting of 14 separate steps before producing stable lead-206. This series consists of eight α decays and six β decays.

Radioactive Dating

Radioactive dating *is a process by which the approximate age of an object is determined through the use of certain radioactive nuclides*. For example, carbon-14 has a half-life of 5,730 years and is used to measure the age of organic material. The ratio of carbon-14 to carbon-12 in living things remains constant while the organism is alive because fresh carbon-14 is entering the organism whenever it consumes nutrients. When the organism dies, this consumption stops, and no new carbon-14 is added to the organism. As time goes by, the ratio of carbon-14 to carbon-12 in the organism gradually declines, because carbon-14 radioactively decays while carbon-12 is stable. Analysis of this ratio allows archaeologists to estimate the age of organisms that were alive many thousands of years ago. For example, with the half-life of $^{14}_{6}C$ being 5730 years, if the $^{14}_{6}C:\ ^{12}_{6}C$ ratio in a wooden object found in an archaeological dig is half what it is in a living tree, this indicates that the wooden object is 5730 years old.

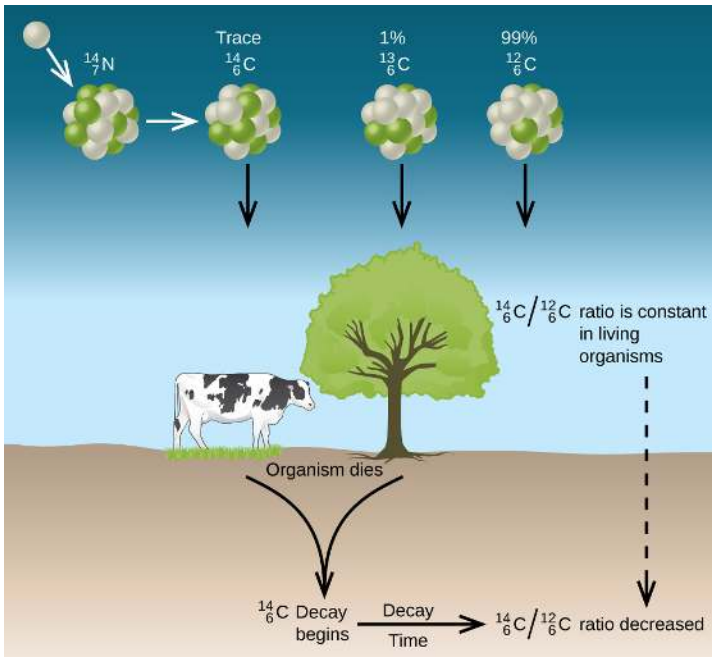


Figure **16.3.3**: Along with stable carbon-12, radioactive carbon-14 is taken in by plants and animals, and remains at a constant level within them while they are alive. After death, the C-14 decays and the C-14:C-12 ratio in the remains decreases. Comparing this ratio to the C-14:C-12 ratio in living organisms allows us to determine how long ago the organism lived (and died). (CC-BY 4.0; OpenStax).

C-14 dating does have limitations. For example, a sample can be C-14 dating if it is approximately 100 to 50,000 years old. Before or after this range, there is too little of the isotope to be detected. Substances must have obtained C-14 from the atmosphere. For this reason, aquatic samples cannot be effectively C-14 dated. Lastly, accuracy of C-14 dating has been affected by atmosphere nuclear weapons testing. Fission bombs ignite to produce more C-14 artificially. Samples tested during and after this period must be checked against another method of dating (isotopic or tree rings).

To calculate the age of a substance using isotopic dating, use the equation below:

$$\text{how old (time)} = n \times t_{1/2}$$

where n is the number of half-lives and $t_{1/2}$ is the half-life (in time).

Example 16.3.3

How long will it take for 18.0 grams of Ra-226 to decay to leave a total of 2.25 grams? Ra-226 has a half-life of 1600 years.

Solution

18.0g ⇒ 9.0g ⇒ 4.5g ⇒ 2.25g, this is three half-lives

$$\text{how old (time)} = 3 \times 1600\,years$$

This decay process takes 4800 years to occur.

Willard Libby

A National Historic Chemical Landmark -American Chemical Society

Dedicated at the University of Chicago on October 10, 2016.

In 1946, Willard Libby proposed an innovative method for dating organic materials by measuring their content of carbon-14, a newly discovered radioactive isotope of carbon. Known as radiocarbon dating, this method provides objective age estimates for carbon-based objects that originated from living organisms. The “radiocarbon revolution” made possible by Libby’s discovery



greatly benefited the fields of archaeology and geology by allowing practitioners to develop more precise historical chronologies across geography and cultures.

Willard F. Libby (right), the physical chemist who conceived of radiocarbon dating, with graduate student Ernest Anderson.

University of Chicago Photographic Archive, apf1-03868, Special Collections Research Center, University of Chicago Library.

Go to Link below for more details

www.acs.org/content/acs/en/education/whatischemistry/landmarks/radiocarbon-dating.html



Libby's anti-coincidence counter. The circular arrangement of Geiger counters (center) detected radiation in samples while the thick metal shields on all sides were designed to reduce background radiation.
University of Chicago Photographic Archive, apf1-03874, Special Collections Research Center, University of Chicago Library.

Radioactive Dating Using Nuclides Other than Carbon-14

Radioactive dating can also use other radioactive nuclides with longer half-lives to date older events. An ingenious application of half-life studies established a new science of determining ages of materials by half-life calculations. For geological dating, the decay of **U**-238 can be used. The half-life of **U**-238 is 4.5×10^9 years. The end product of the decay of **U**-238 is **Pb**-206. After one half-life, a 1.00 gram sample of uranium will have decayed to 0.50 grams of **U**-238 and 0.43 grams of **Pb**-206. By comparing the amount of **U**-238 to the amount of **Pb**-206 in a sample of uranium mineral, the age of the mineral can be estimated. Present day estimates for the age of the Earth's crust from this method is at 4 billion years. This radioactivity approach can be used to detecting fake wine vintages too.

Isotopes with shorter half-lives are used to date more recent samples. For example, tritium ($t_{1/2}$ =12.3 years) can date samples within an age range of 1-100 years. Chemists and geologists use tritium dating to determine the age of water (ocean and fresh). In addition, tritium dating can be useful in determining the age of wines and brandies.

K-40 decays by positron emission and electron capture to form Ar-40 with a half-life of 1.25 billion years. If a rock sample is crushed and the amount of Ar-40 gas that escapes is measured, determination of the Ar-40:K-40 ratio yields the age of the rock. Other methods, such as rubidium-strontium dating (Rb-87 decays into Sr-87 with a half-life of 48.8 billion years), operate on the same principle. To estimate the lower limit for the earth’s age, scientists determine the age of various rocks and minerals, making the assumption that the earth is older than the oldest rocks and minerals in its crust. As of 2014, the oldest known rocks on earth are the Jack Hills zircons from Australia, found by uranium-lead dating to be almost 4.4 billion years old.

Summary

- 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 determined using the following expression:

$$\textit{amount remaining} = \textit{initial amount} \times \left(\frac{1}{2}\right)^n$$

  where *n* is the number of half-lives.

- **C**-14 dating procedures have been used to determine the age of organic artifacts. Its half-life is approximately 5700 years.

Contributors and Attributions

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-
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- Elizabeth R. Gordon (Furman University)
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16.4: Natural Radioactivity

Learning Objectives

- Know the different sources of background radiation.
- Describe the biological impact of ionizing radiation
- List common sources of radiation exposure in the US.

Background Radiation

We are all exposed to a small amount of radiation in our daily lives. This **background radiation** comes from naturally occurring sources and from human-produced radiation. Exposure to x-rays and nuclear medicine isotopes, ground sources, and cosmic radiation account for almost half of the background exposure of the average American. Radon gas, formed from the decay of uranium and thorium isotopes, is responsible for a little over half the total amount of background radiation. See the table below for background sources.

***Table* 16.4.1** *Sources of Background Radiation*

radon	54%
consumer products	3%
nuclear medicine	4%
cosmic radiation	8%
terrestrial	8%
internal	11%
x-rays	11%
other	1%

The Problem of Radon

For many people, one of the largest sources of exposure to radiation is from radon gas (Rn-222). Radon-222 is an α emitter with a half–life of 3.82 days. It is one of the products of the radioactive decay series of U-238, which is found in trace amounts in soil and rocks. The radon gas that is produced slowly escapes from the ground and gradually seeps into homes and other structures above. Since it is about eight times more dense than air, radon gas accumulates in basements and lower floors, and slowly diffuses throughout buildings (Figure **16.4.1**).

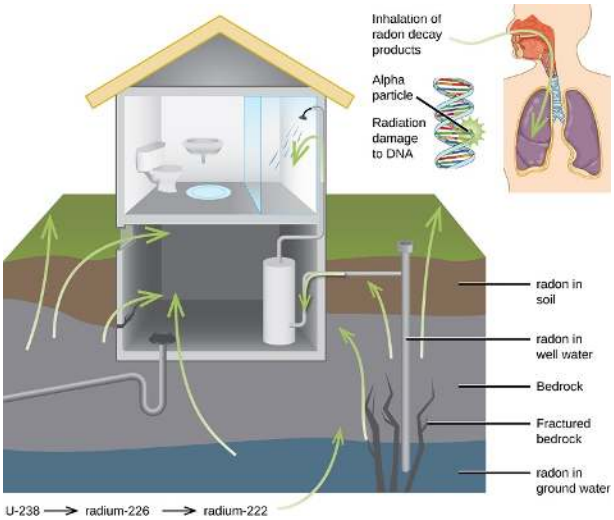


Figure **16.4.1**: Radon-222 seeps into houses and other buildings from rocks that contain uranium-238, a radon emitter. The radon enters through cracks in concrete foundations and basement floors, stone or porous cinderblock foundations, and openings for water and gas pipes.

Radon is found in buildings across the country, with amounts depending on where you live. The average concentration of radon inside houses in the US (1.25 pCi/L) is about three times the levels found in outside air, and about one in six houses have radon levels high enough that remediation efforts to reduce the radon concentration are recommended. Exposure to radon increases one's risk of getting cancer (especially lung cancer), and high radon levels can be as bad for health as smoking a carton of cigarettes a day. Radon is the number one cause of lung cancer in nonsmokers and the second leading cause of lung cancer overall. Radon exposure is believed to cause over 20,000 deaths in the US per year.

Measuring Radiation Exposure

Several different devices are used to detect and measure radiation, including Geiger counters, scintillation counters (scintillators), and radiation dosimeters (Figure **16.4.2**). Probably the best-known radiation instrument, the Geiger counter (also called the Geiger-Müller counter) detects and measures radiation. Radiation causes the ionization of the gas in a Geiger-Müller tube. The rate of ionization is proportional to the amount of radiation. A scintillation counter contains a scintillator—a material that emits light (luminesces) when excited by ionizing radiation—and a sensor that converts the light into an electric signal. Radiation dosimeters also measure ionizing radiation and are often used to determine personal radiation exposure. Commonly used types are electronic, film badge, thermoluminescent, and quartz fiber dosimeters.

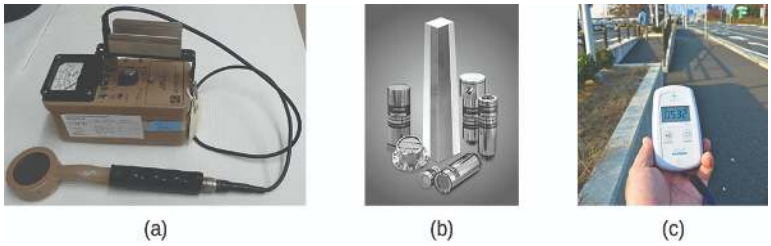


Figure **16.4.2**: Devices such as (a) Geiger counters, (b) scintillators, and (c) dosimeters can be used to measure radiation. (credit c: modification of work by "osaMu"/Wikimedia commons).

Radiation Damage to Cells

The increased use of radioisotopes has led to increased concerns over the effects of these materials on biological systems (such as humans). All radioactive nuclides emit high-energy particles or electromagnetic waves. When this radiation encounters living cells, it can cause heating, break chemical bonds, or ionize molecules. The most serious biological damage results when these radioactive emissions fragment or ionize molecules. For example, alpha and beta particles emitted from nuclear decay reactions possess much higher energies than ordinary chemical bond energies. When these particles strike and penetrate matter, they produce ions and molecular fragments that are extremely reactive. The damage this does to biomolecules in living organisms can cause serious

malfunctions in normal cell processes, taxing the organism's repair mechanisms and possibly causing illness or even death (Figure **16.4.3**).

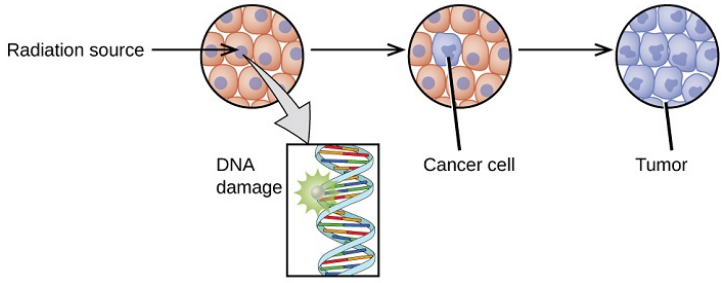


Figure **16.4.3**: Radiation can harm biological systems by damaging the DNA of cells. If this damage is not properly repaired, the cells may divide in an uncontrolled manner and cause cancer.

Radiation can harm either the whole body (somatic damage) or eggs and sperm (genetic damage). Its effects are more pronounced in cells that reproduce rapidly, such as the stomach lining, hair follicles, bone marrow, and embryos. This is why patients undergoing radiation therapy often feel nauseous or sick to their stomach, lose hair, have bone aches, and so on, and why particular care must be taken when undergoing radiation therapy during pregnancy.

Ionizing vs. Nonionizing Radiation

There is a large difference in the magnitude of the biological effects of nonionizing radiation (for example, light and microwaves) and ionizing radiation, emissions energetic enough to knock electrons out of molecules (for example, α and β particles, γ rays, X-rays, and high-energy ultraviolet radiation) (Figure **16.4.4**).

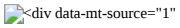


Figure **16.4.4**: Lower frequency, lower-energy electromagnetic radiation is nonionizing, and higher frequency, higher-energy electromagnetic radiation is ionizing.

Energy absorbed from nonionizing radiation speeds up the movement of atoms and molecules, which is equivalent to heating the sample. Although biological systems are sensitive to heat (as we might know from touching a hot stove or spending a day at the beach in the sun), a large amount of nonionizing radiation is necessary before dangerous levels are reached. Ionizing radiation, however, may cause much more severe damage by breaking bonds or removing electrons in biological molecules, disrupting their structure and function. The damage can also be done indirectly, by first ionizing H_2O (the most abundant molecule in living organisms), which forms a H_2O^+ ion that reacts with water, forming a hydronium ion and a hydroxyl radical:

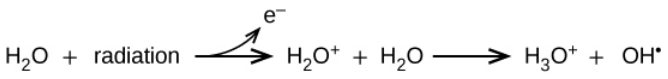


Figure **16.4.5**.

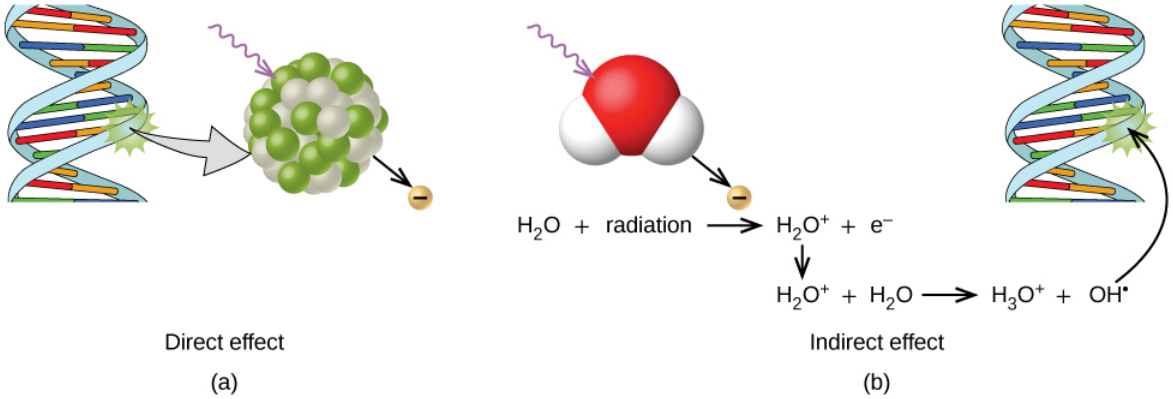


Figure **16.4.5**: Ionizing radiation can (a) directly damage a biomolecule by ionizing it or breaking its bonds, or (b) create an H_2O^+ ion, which reacts with H_2O to form a hydroxyl radical, which in turn reacts with the biomolecule, causing damage indirectly.

The effects of radiation depend on the type, energy, and location of the radiation source, and the length of exposure. As shown in Figure **16.4.6**, the average person is exposed to background radiation, including cosmic rays from the sun and radon from uranium in the ground; radiation from medical exposure, including CAT scans, radioisotope tests, X-rays, and so on; and small amounts of radiation from other human activities, such as airplane flights (which are bombarded by increased numbers of cosmic rays in the upper atmosphere), radioactivity from consumer products, and a variety of radionuclides that enter our bodies when we breathe (for example, carbon-14) or through the food chain (for example, potassium-40, strontium-90, and iodine-131).

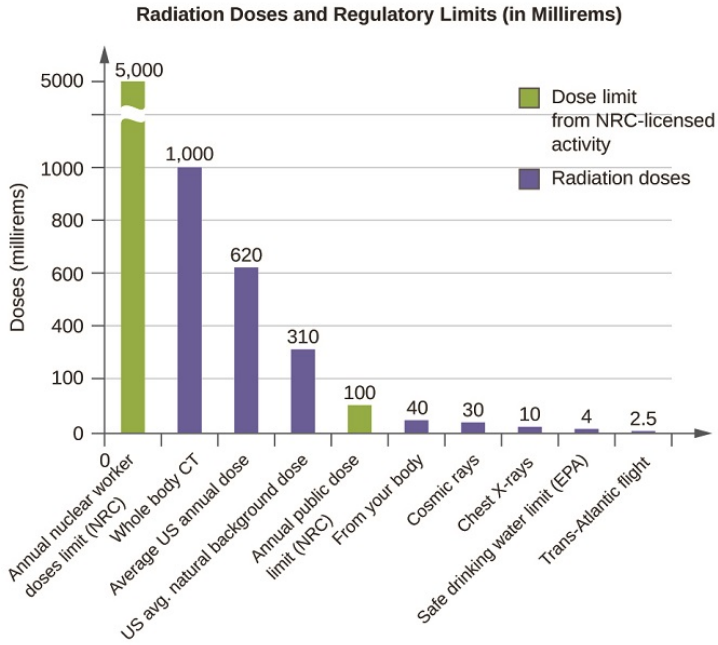


Figure **16.4.6** The total annual radiation exposure for a person in the US is about 620 mrem. The various sources and their relative amounts are shown in this bar graph. (source: U.S. Nuclear Regulatory Commission).

A short-term, sudden dose of a large amount of radiation can cause a wide range of health effects, from changes in blood chemistry to death. Short-term exposure to tens of rems of radiation will likely cause very noticeable symptoms or illness; a dose of about 500 rems is estimated to have a 50% probability of causing the death of the victim within 30 days of exposure. Exposure to radioactive emissions has a cumulative effect on the body during a person's lifetime, which is another reason why it is important to avoid any unnecessary exposure to radiation. Health effects of short-term exposure to radiation are shown in Table **16.4.2**.

Table **16.4.2** Health Effects of Radiation

Exposure (rem)	Health Effect	Time to Onset (without treatment)
5–10	changes in blood chemistry	—
50	nausea	hours
55	fatigue	—
70	vomiting	—
75	hair loss	2–3 weeks
90	diarrhea	—
100	hemorrhage	—
400	possible death	within 2 months
1000	destruction of intestinal lining	—
	internal bleeding	—
	death	1–2 weeks
2000	damage to central nervous system	—
	loss of consciousness;	minutes
	death	hours to days

It is impossible to avoid some exposure to ionizing radiation. We are constantly exposed to background radiation from a variety of natural sources, including cosmic radiation, rocks, medical procedures, consumer products, and even our own atoms. We can minimize our exposure by blocking or shielding the radiation, moving farther from the source, and limiting the time of exposure.

Summary

- Background radiation is defined and different sources of background radiation are listed.
- We are constantly exposed to radiation from a variety of naturally occurring and human-produced sources.
- Various devices, including Geiger counters, scintillators, and dosimeters, are used to detect and measure radiation, and monitor radiation exposure.
- Ionizing radiation is the most harmful because it can ionize molecules or break chemical bonds, which damages the molecule and causes malfunctions in cell processes. It can also create reactive hydroxyl radicals that damage biological molecules and disrupt physiological processes.

Contributors and Attributions

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16.5: Artificial Transmutation

Learning Objective

- Describe the synthesis of transuranium nuclides.

After the discovery of radioactivity, the field of nuclear chemistry was created and developed rapidly during the early twentieth century. A slew of new discoveries in the 1930s and 1940s, along with World War II, combined to usher in the Nuclear Age in the mid-twentieth century. Science learned how to create new substances, and certain isotopes of certain elements were found to possess the capacity to produce unprecedented amounts of energy, with the potential to cause tremendous damage during war, as well as produce enormous amounts of power for society's needs during peace.

Synthesis of Nuclides

Nuclear transmutation is the conversion of one nuclide into another. It can occur by the radioactive decay of a nucleus, or the reaction of a nucleus with another particle. The first manmade nucleus was produced in Ernest Rutherford's laboratory in 1919 by a transmutation reaction, the bombardment of one type of nuclei with other nuclei or with neutrons. Rutherford bombarded nitrogen atoms with high-speed α particles from a natural radioactive isotope of radium and observed protons resulting from the reaction:

$$^{14}_{7}\mathrm{N} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{H}$$

The $^{17}_{8}\mathrm{O}$ and $^{1}_{1}\mathrm{H}$ nuclei that are produced are stable, so no further (nuclear) changes occur.

To reach the kinetic energies necessary to produce transmutation reactions, devices called particle accelerators are used. These devices use magnetic and electric fields to increase the speeds of nuclear particles. In all accelerators, the particles move in a vacuum to avoid collisions with gas molecules. When neutrons are required for transmutation reactions, they are usually obtained from radioactive decay reactions or from various nuclear reactions occurring in nuclear reactors. The Chemistry in Everyday Life feature that follows discusses a famous particle accelerator that made worldwide news.

CERN Particle Accelerator

Located near Geneva, the CERN ("Conseil Européen pour la Recherche Nucléaire," or European Council for Nuclear Research) Laboratory is the world's premier center for the investigations of the fundamental particles that make up matter. It contains the 27-kilometer (17 mile) long, circular Large Hadron Collider (LHC), the largest particle accelerator in the world (Figure **16.5.1**). In the LHC, particles are boosted to high energies and are then made to collide with each other or with stationary targets at nearly the speed of light. Superconducting electromagnets are used to produce a strong magnetic field that guides the particles around the ring. Specialized, purpose-built detectors observe and record the results of these collisions, which are then analyzed by CERN scientists using powerful computers.



Figure **16.5.1**: A small section of the LHC is shown with workers traveling along it. (credit: Christophe Delaere)

In 2012, CERN announced that experiments at the LHC showed the first observations of the Higgs boson, an elementary particle that helps explain the origin of mass in fundamental particles. This long-anticipated discovery made worldwide news

and resulted in the awarding of the 2013 Nobel Prize in Physics to François Englert and Peter Higgs, who had predicted the existence of this particle almost 50 years previously.

Prior to 1940, the heaviest-known element was uranium, whose atomic number is 92. Now, many artificial elements have been synthesized and isolated, including several on such a large scale that they have had a profound effect on society. One of these—element 93, neptunium (Np)—was first made in 1940 by McMillan and Abelson by bombarding uranium-238 with neutrons. The reaction creates unstable uranium-239, with a half-life of 23.5 minutes, which then decays into neptunium-239. Neptunium-239 is also radioactive, with a half-life of 2.36 days, and it decays into plutonium-239. The nuclear reactions are:

$$^{238}_{92}\text{U} + {}^{1}_{0}\text{n} \longrightarrow {}^{239}_{92}\text{U} \tag{16.5.1}$$

$$^{239}_{92}\text{U} \longrightarrow {}^{239}_{93}\text{Np} + {}^{0}_{-1}\text{e} \quad t_{\frac{1}{2}} \quad \text{half-life} = 23.5\ \text{min} \tag{16.5.2}$$

$$^{239}_{93}\text{Np} \longrightarrow {}^{239}_{94}\text{Pu} + {}^{0}_{-1}\text{e} \quad t_{\frac{1}{2}} \quad \text{half-life} = 2.36\ \text{days} \tag{16.5.3}$$

Plutonium is now mostly formed in nuclear reactors as a byproduct during the decay of uranium. Some of the neutrons that are released during U-235 decay combine with U-238 nuclei to form uranium-239; this undergoes β decay to form neptunium-239, which in turn undergoes β decay to form plutonium-239 as illustrated in the preceding three equations. It is possible to summarize these equations as:

$$^{238}_{92}\text{U} + {}^{1}_{0}\text{n} \longrightarrow {}^{239}_{92}\text{U} \xrightarrow{\beta^-} {}^{239}_{93}\text{Np} \xrightarrow{\beta^-} {}^{239}_{94}\text{Pu}$$

Heavier isotopes of plutonium—Pu-240, Pu-241, and Pu-242—are also produced when lighter plutonium nuclei capture neutrons. Some of this highly radioactive plutonium is used to produce military weapons, and the rest presents a serious storage problem because they have half-lives from thousands to hundreds of thousands of years.

Although they have not been prepared in the same quantity as plutonium, many other synthetic nuclei have been produced. Nuclear medicine has developed from the ability to convert atoms of one type into other types of atoms. Radioactive isotopes of several dozen elements are currently used for medical applications. The radiation produced by their decay is used to image or treat various organs or portions of the body, among other uses.

The elements beyond element 92 (uranium) are called transuranium elements. As of this writing, 22 transuranium elements have been produced and officially recognized by IUPAC; several other elements have formation claims that are waiting for approval. Some of these elements are shown in Table **16.5.1**.

Table **16.5.1** Preparation of Some of the Transuranium Elements

Name	Symbol	Atomic Number	Reaction
americium	Am	95	$^{239}_{94}\text{Pu} + {}^{1}_{0}\text{n} \longrightarrow {}^{240}_{95}\text{Am} + {}^{0}_{-1}\text{e}$
curium	Cm	96	$^{239}_{94}\text{Pu} + {}^{4}_{2}\text{He} \longrightarrow {}^{242}_{96}\text{Cm} + {}^{1}_{0}\text{n}$
californium	Cf	98	$^{242}_{96}\text{Cm} + {}^{4}_{2}\text{He} \longrightarrow {}^{245}_{98}\text{Cf} + {}^{1}_{0}\text{n}$
einsteinium	Es	99	$^{238}_{92}\text{U} + 15\,{}^{1}_{0}\text{n} \longrightarrow {}^{253}_{99}\text{Es} + 7\,{}^{0}_{-1}\text{e}$
mendelevium	Md	101	$^{253}_{99}\text{Es} + {}^{4}_{2}\text{He} \longrightarrow {}^{256}_{101}\text{Md} + {}^{1}_{0}\text{n}$
nobelium	No	102	$^{246}_{96}\text{Cm} + {}^{12}_{6}\text{C} \longrightarrow {}^{254}_{102}\text{No} + 4\,{}^{1}_{0}\text{n}$
rutherfordium	Rf	104	$^{249}_{98}\text{Cf} + {}^{12}_{6}\text{C} \longrightarrow {}^{257}_{104}\text{Rf} + 4\,{}^{1}_{0}\text{n}$
seaborgium	Sg	106	$^{206}_{82}\text{Pb} + {}^{54}_{24}\text{Cr} \longrightarrow {}^{257}_{106}\text{Sg} + 3\,{}^{1}_{0}\text{n}$ $^{249}_{98}\text{Cf} + {}^{18}_{8}\text{O} \longrightarrow {}^{263}_{106}\text{Sg} + 4\,{}^{1}_{0}\text{n}$
meitnerium	Mt	107	$^{209}_{83}\text{Bi} + {}^{58}_{26}\text{Fe} \longrightarrow {}^{266}_{109}\text{Mt} + {}^{1}_{0}\text{n}$

Summary

- It is possible to produce new atoms by bombarding other atoms with nuclei or high-speed particles.
- The products of transmutation reactions can be stable or radioactive.

- A number of artificial elements, including technetium, astatine, and the transuranium elements, have been produced in this way.

Contributors and Attributions

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16.6: Uses of Radioisotopes

Learning Objectives

- Understand how radiation is used in agriculture and various industries.
- Understand the difference between diagnostic and therapeutic radiation.

Radioactive isotopes have the same chemical properties as stable isotopes of the same element, but they emit radiation, which can be detected. If we replace one (or more) atom(s) with radioisotope(s) in a compound, we can track them by monitoring their radioactive emissions. This type of compound is called a radioactive tracer (or radioactive label). Radioisotopes are used to follow the paths of biochemical reactions or to determine how a substance is distributed within an organism.

Radioisotopes in Industry and Agriculture

Radioisotopes (radioactive isotopes or radionuclides or radioactive nulcides) are used in two major ways: either for their radiation alone (irradiation, nuclear batteries) or for the combination of chemical properties and their radiation (tracers, biopharmaceuticals).

Tracer Applications

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 (H-3)**-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 is a radioactive isotope of hydrogen.)

Tracers are used in diverse ways to study the mechanisms of chemical reactions in plants and animals. These include labeling fertilizers in studies of nutrient uptake by plants and crop growth, investigations of digestive and milk-producing processes in cows, and studies on the growth and metabolism of animals and plants.

For example, the radioisotope **C-14** was used to elucidate the details of how photosynthesis occurs. The overall reaction is:

$$6\,CO_2(g) + 6\,H_2O(l) \longrightarrow C_6H_{12}O_6(s) + 6\,O_2(g),$$

but the process is much more complex, proceeding through a series of steps in which various organic compounds are produced. In studies of the pathway of this reaction, plants were exposed to CO_2 containing a high concentration of $^{14}_{6}C$. At regular intervals, the plants were analyzed to determine which organic compounds contained carbon-14 and how much of each compound was present. From the time sequence in which the compounds appeared and the amount of each present at given time intervals, scientists learned more about the pathway of the reaction.

Phosphorus-32 is used in plant sciences for tracking a plant's uptake of fertilizer from the roots to the leaves. The phosphorus-32-labelled fertilizer is given to the plant hydroponically or via water in the soil and the usage of the phosphorus can be mapped from the emitted beta radiation. The information gathered by mapping the fertilizer uptake show how the plant takes up and uses the phosphorus from fertilizer.

Irradiation of Food and Mail

Co-60 (gamma source) and x-rays are use to irradiate many foods in the United States. Ionizing radiation can be used to kill food borne illnesses like salmonella and e coli. Irradiating food can also prolong shelf-life, delay ripening, and destroy insects. In addition, gamma/x-ray can sterilize foods making refrigeration unnecessary. Often, sterilized food is served to hospital patients who have impaired immune systems.

In the United States, irradiation of food is regulated by the FDA (Food and Drug Administration). Foods that have been irradiated must display the symbol called the radura on their packaging. Some foods that could display this symbol are: meats (beef, pork, chicken), shrimp, lobster, fruits, vegetables, shellfish, and spices. Contrary to the belief of some people, irradiation of food *does not* make the food itself radioactive.



Figure **16.6.1** The preservation of strawberries with Ionizing Radiation.

In the fall of 2001, anthrax laced letters *(*Figure **16.6.2**) were sent to various new agencies and two United States senators. Anthrax is an infectious disease caused by bacteria. It exists naturally in some soils and can be isolated in a laboratory.

Figure **16.6.2** Anthrax-laced letter that was sent to Senator Tom Daschle. Image taken from: https://upload.wikimedia.org/wikiped...hle_letter.jpg

To combat this form of bioterrorism, the United States Postal Service(USPS)and the Federal Bureau of Investigation (FBI) installed x-ray generators to irradiate suspicious looking mail sent to some governmental facilities. X-rays will kill the majority of this bacteria and some viruses as well. Once irradiated, mail (packages and letters) might change in color, texture, and smell. This ionizing radiation chemically alters the composition of the mail's paper component. The x-rays do not leave the mail radioactive.

Smoke Detectors

Americium-241, an α emitter with a half-life of 458 years, is used in tiny amounts in ionization-type smoke detectors (Figure **16.6.3**). The α emissions from Am-241 ionize the air between two electrode plates in the ionizing chamber. A battery supplies a potential that causes movement of the ions, thus creating a small electric current. When smoke enters the chamber, the movement of the ions is impeded, reducing the conductivity of the air. This causes a marked drop in the current, triggering an alarm.

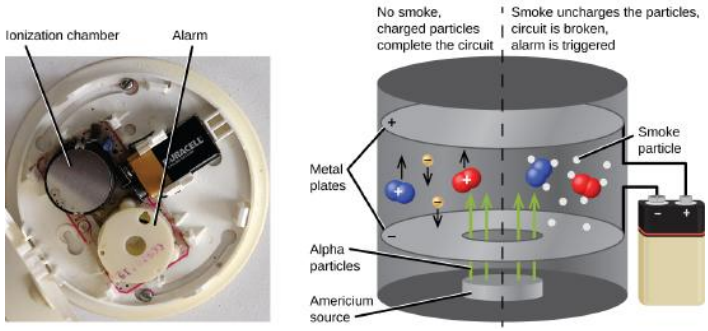


Figure **16.6.3** Inside a smoke detector, Am-241 emits α particles that ionize the air, creating a small electric current. During a fire, smoke particles impede the flow of ions, reducing the current and triggering an alarm. (credit a: modification of work by "Muffet"/Wikimedia Commons)

Other Applications

Commercial applications of radioactive materials are equally diverse . They include determining the thickness of films, paper, and thin metal sheets by exploiting the penetration power of various types of radiation(Figure **16.6.4**). Flaws in metals used for structural purposes can be detected using high-energy gamma rays from cobalt-60 in a fashion similar to the way X-rays are used to examine the human body. In one form of pest control, flies are controlled by sterilizing male flies with γ radiation so that females breeding with them do not produce offspring.

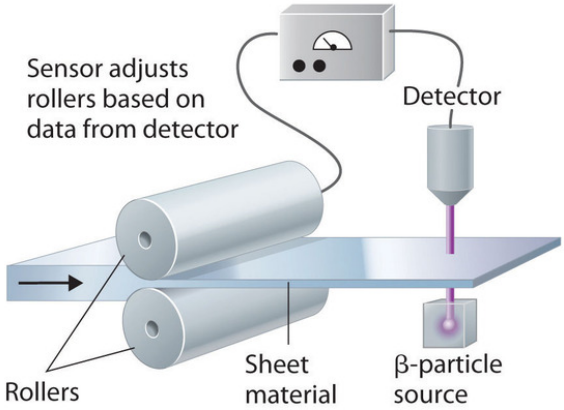


Figure **16.6.4** Using radiation to control the thickness of a material. Because the amount of radiation absorbed by a material is proportional to its thickness, radiation can be used to control the thickness of plastic film, tin foil, or paper. As shown, a beta emitter is placed on one side of the material being produced and a detector on the other. An increase in the amount of radiation that reaches the detector indicates a decrease in the thickness of the material and vice versa. The output of the detector can thus be used to control the thickness of the material.

Radioisotopes in Medicine

Radioactive tracers are also used in many medical applications, including both diagnosis and treatment. They are used to measure engine wear, analyze the geological formation around oil wells, and much more.

Radioisotopes have revolutionized medical practice, where they are used extensively. Over 10 million nuclear medicine procedures and more than 100 million nuclear medicine tests are performed annually in the United States.

Diagnostic Medical Applications

Diagnostic medical applications involve testing for a disease or condition. In nuclear medicine, this could involve using PET scans, or isotopic studies. The radiation involved for each of these types of tools will vary in mrem or mSv amounts.

PET Scanning

Positron Emission Tomography or PET scan is a type of nuclear medicine imaging. Depending on the area of the body being imaged, a radioactive isotope is either injected into a vein, swallowed by mouth, or inhaled as a gas. When the radioisotope is collected in the appropriate area of the body, the gamma ray emissions are detected by a PET scanner (often called a gamma camera) which works together with a computer to generate special pictures, providing details on both the structure and function of various organs. Watch this informational video on how this technique works.

PET Scan



***Video* 16.6.1** *PET scans: What to expect.*

PET scans are used to:

- Detect cancer
- Determine the amount of cancer spread
- Assess the effectiveness of treatment plans
- Determine blood flow to the heart muscle
- Determine the effects of a heart attack
- Evaluate brain abnormalities such as tumors and memory disorders
- Map brain and heart function

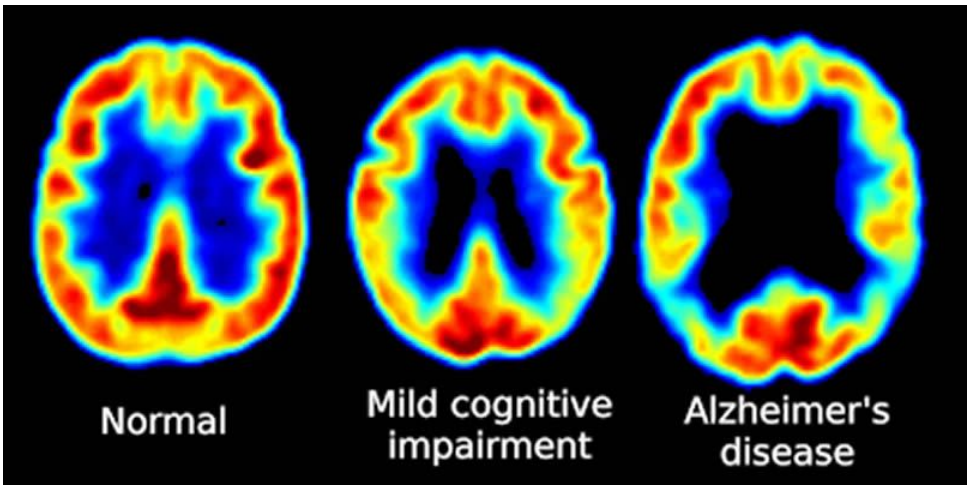


Figure **16.6.5** Mild cognitive impairment (MCI) is a state between normal ageing and dementia, where someone's mind is functioning less well than would be expected for their age. This image is for illustrative purposes only. (Public Domain; Center For Functional Imaging, Lawrence Berkeley National Laboratory. Alzheimer's Disease Neuroimaging Initiative (ADNI).

PET Scanning, is used to image the physiological aspects of the body rather than the anatomy (Figures **16.6.5** and **16.6.6**). It images the function of the body rather than the form, such as where tagged molecules go and how they are used. For instance, if you were to image the brain of a deceased person, nothing would show up on a PET scan opposed to a CAT scan, as the brain is no longer functional. Pet Scanning is very useful in imaging tumors, which can be done when patients are injected with certain tracers. Often times PET scanners are used in collaboration with CAT scanners to create a composite image that shows both the function and form

of the body. The animation below is a whole-body PET scan using the radioisotope of ^{18}F ($t_{1/2}$ = 110 min). Using this tracer, doctors can determine if cancer has metastasized by looking at the metabolic activity of glucose.

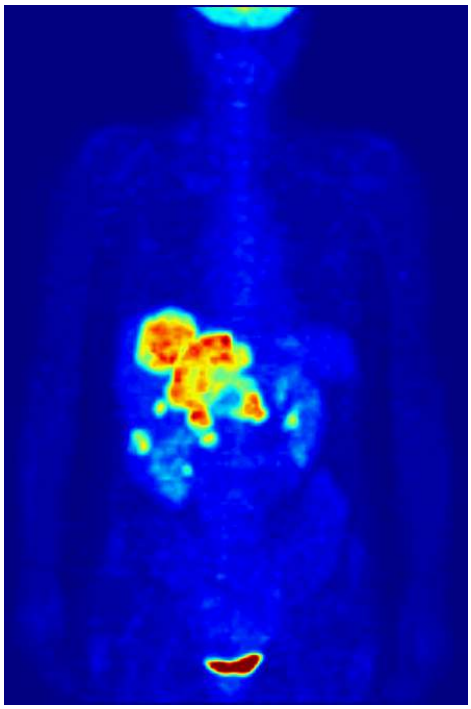


Figure **16.6.6** A whole body analysis by a PET scan. (Public Domain; Jens Maus, http://jens-maus.de/)

Other Isotopic Tests

Radioisotopes have revolutionized medical practice, where they are used extensively. Over 10 million nuclear medicine procedures and more than 100 million nuclear medicine tests are performed annually in the United States. Four typical examples of radioactive tracers used in medicine are technetium-99 ($^{99}_{43}Tc$), thallium-201 ($^{201}_{81}Tl$), iodine-131 ($^{131}_{53}I$), and sodium-24 ($^{24}_{11}Na$). Damaged tissues in the heart, liver, and lungs absorb certain compounds of technetium-99 preferentially. After it is injected, the location of the technetium compound, and hence the damaged tissue, can be determined by detecting the γ rays emitted by the Tc-99 isotope. Thallium-201 (Figure **16.6.7**) becomes concentrated in healthy heart tissue, so the two isotopes, Tc-99 and Tl-201, are used together to study heart tissue. Iodine-131 concentrates in the thyroid gland, the liver, and some parts of the brain. It can therefore be used to monitor goiter and treat thyroid conditions, such as Grave's disease, as well as liver and brain tumors. Salt solutions containing compounds of sodium-24 are injected into the bloodstream to help locate obstructions to the flow of blood.



Figure **16.6.7** Administering thallium-201 to a patient and subsequently performing a stress test offer medical professionals an opportunity to visually analyze heart function and blood flow. (credit: modification of work by "Blue0ctane"/Wikimedia Commons)

Small doses of **I**-131 (too small to kill cells) are used for purposes of imaging the thyroid. Once the iodine is concentrated in the thyroid, the patient lays down on a sheet of film and the radiation from the **I**-131 makes a picture of the thyroid on the film. The half-life of iodine-131 is approximately 8 days so after a few weeks, virtually all of the radioactive iodine is out of the patient's system. During that time, they are advised that they will set off radiation detectors in airports and will need to get special permission to fly on commercial flights.

Some isotopes that are used to diagnose diseases are shown in Table **16.6.1**. All of these nuclear isotopes release one form of ionizing radiation (either/add particle or ray). In addition, each isotopic application would involve a specific amount of mrem/mSv radiation.

Table **16.6.1** Selected Radioisotopes Used in Diagnostic Nuclear Medicine

Symbol-mass	Half-Life ($t_{1/2}$)	Application
Xe-133	5.27 days	Lung imaging
H-3	12.26 years	Analyzing total body water
Tl-201	73 hours	Stress tests for heart problems
Fe-59	44.5 days	Detection of anemia
Gd-153	242 days	Analyzing bone density
Cr-51	27.8 days	Determining blood volume
C-11	20.4 minutes	Brain scans
Tc-99m	6.0 hours	Heart, lung, kidney, bone marrow, brain, or bone marrow imaging
Pu-238	86 years	Powering pacemakers
I-131	8.0 days	Imaging Thyroid

The “m” in Tc-99m stands for “metastable,” indicating that this is an unstable, high-energy state of Tc-99. Metastable isotopes emit γ radiation to rid themselves of excess energy and become (more) stable.

Keep in mind that x-rays, CT scans, PET scans, and isotopic studies involve ionizing radiation. In contrast, MRI (magnetic resonance imaging) and ultrasounds do not utilize ionizing forms of radiation.

Therapeutic Radiation

There are many techniques used to treat cancer. Surgery can be used to remove cancerous tumors inside or on the body. With chemotherapy, ingested or injected chemicals are used to kill rapidly dividing cells (cancerous and noncancerous). Other cancer treatment methods include immunotherapy, stem cell replacement, hormone therapy, and targeted therapy.

Radiation therapy and Chemotherapy: Two different treatment procedures

Patients diagnosed with cancer might be required to do chemotherapy or radiation therapy. Sometimes, both of these methods are used for a patient. In this picture, a female patient is receiving chemotherapy through an IV. She is participating in cooling therapy while receiving her treatment. By placing her hands and feet in cooling devices, this will lower her chances of losing her finger and toenails. Cold cap therapy is also now available for chemotherapy patients. Wearing this type of device could enable a patient to keep his/her hair during chemotherapy.



Figure **16.6.8** *(CC BY 2.0; Jenny Mealing).*

Current therapeutic radiation applications involve the use of gamma, x-rays, or protons. Recently, some research facilities are investigating the use of alpha and beta tagged molecules to kill cancer cells. These radioisotopes will first locate a cancer related molecule on a tumor cell. Then, the alpha or beta tagged species will inject its radiation into the tumor. Sr-89 (beta emitter) and Ra-223 (alpha emitter) have been used in clinical research trials of certain types of bone cancers.

Radiation Therapy is used as a treatment to control malignant cells within cancer patients. Oncologists (specialists that deal with cancer) utilize radiation frequently to help slow or cure the spread of cancer within individuals. Radiation is specifically applied to malignant tumors in order to shrink them in size. Medical professionals, mainly radiation oncologists, administer a variety of dosages to patient, contingent to the patients current health, as well as other treatments such as chemotherapy, success of surgery, etc.

External Beam Therapy (Photon and Proton Therapy)

External Beam Therapy (EBT) is a method of delivering a high energy beam of radiation to the precise location of a patient's tumor. These beams can destroy cancer cells and with careful planning, NOT kill surrounding cells. The concept is to have several beams of radiation, each of which is sub-lethal, enter the body from different directions. The only place in the body where the beam would be lethal is at the point where all the beams intersect. Before the EBT process, the patient is three-dimensionally mapped using CT scans and x-rays. The patient receives small tattoos to allow the therapist to line up the beams exactly. Alignment lasers are used to precisely locate the target. The radiation beam is usually generated with a linear accelerator. The video below illustrates the basic preparation and administration of external beam therapy.

Radiation Therapy



***Video* 16.6.2** *Targeting cancer - Radiation therapy treatment process.*

Photon EBT utilizes either x-ray or gamma rays. An x-ray source would require a linear accelerator to produce high energy electrons. In contrast, a gamma source incorporates a radioactive isotope (like Co-60). Keep in mind both of these technologies use ionizing radiation. As a result, cancer patients must be monitored throughout their life to ensure they do not develop other cancers, like leukemia. EBT is used to treat the following diseases as well as others:

- Breast cancer
- Colorectal cancer
- Head and neck cancer
- Lung cancer
- Prostate cancer

The majority of radiation patients receive photon EBT. The smaller size of this machine makes this therapy an option for all sizes of hospitals and cancer treatment centers. Photon EBT equipment costs approximately three million dollars. The size and the price of this technology enables smaller facilities to keep their patients closer to home during treatment

Another method of radiation treatment involving protons is not as commonly used in the United States. **Photon therapy** requires a cyclotron to generate proton beams (recall, a proton is an ionized H-1 isotope). Unlike x-ray or gamma rays (photon therapy), protons are extremely heavy.

At this time, research facilities are working on miniaturizing proton generators. An ideal technology would reduce the cost from hundreds of millions of dollars to about twenty to thirty million per device. This would make proton therapy more available and convenient for patients.



***Video*16.6.3** *Proton therapy versus radiation therapy*

There are many advantages to choosing proton therapy over photon therapy. Unlike photon radiation, proton beams will only penetrate to the depth of the tumor and not pass through the entire body. This reduces the overall toxicity dose. In addition, fewer treatments are required for proton therapy patients than photon therapy.Unfortunately, proton therapy is more expensive than photon therapy and less common. Once approved by a facility and medical insurance, a patient may have to move temporarily to a larger city to receive treatment. Some forms of cancer have never been clinically treated with proton therapy (namely, breast cancer). Patients desiring proton therapy might not be able to receive type of therapy due to lack of research.

Brachtherapy

Brachytherapy involves placing ionizing pellets(seeds) or rods directly at the tumor. Photons (in the form of x-ray or gamma ray) are produced inside the body and will penetrate throughout this particular area localizing the radiation. Pellets are surgically implanted while rods can be temporarily inserted to produce radiation internally. With pellets/seeds, the patient will remain radioactive as long as these devices remain inside the body. People undergoing this type of radiotherapy need to be aware of their constant emission of radiation. Radiation that is administered through rods connected to a photon device will disperse energy immediately and not leave the patient radioactive.

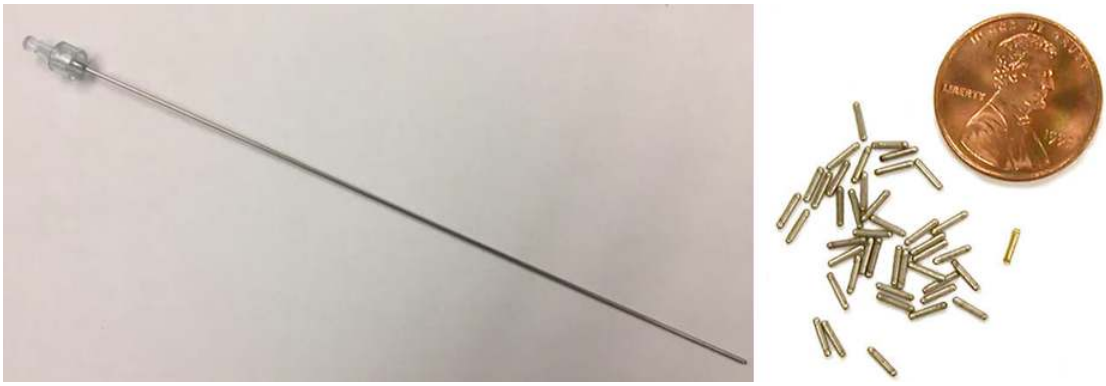


Figure **16.6.9** The picture on the left shows a brachytherapy rod. This device would be connected to a gamma source and connected inside a human body. The second images shows radioactive pellets or seeds that can be surgically implanted near a tumor. Note how small the pellets are when compared to an American penny. Image taken from: https://c1.staticflickr.com/8/7254/7...74d83b7058.jpg

Brachytherapy is widely used in the treatment of cancers involving reproductive organs. Because the radiation is isolated internally, patients are less likely to experience side effects when receiving this type of treatment. Cancers that have been treated with brachytherapy are shown below:

- Prostate
- Breast
- Esophageal
- Lung
- Uterine
- Anal/Rectal
- Sarcomas
- Head and neck

Table **16.6.2** list commonly used radionuclides for brachtherapy.

Table **16.6.2** Commonly Used Radiation Sources (radionuclides) for Brachytherapy.

Radionuclide	Type	Half-life
Cesium-131 (^{131}Cs)	Electron Capture, ε	9.7 days
Cesium-137 (^{137}Cs)	β^-- particles, γ-rays	30.17 years
Cobalt-60 (^{60}Co)	β^-- particles, γ-rays	5.26 years
Iridium-192 (^{192}Ir)	γ-rays	73.8 days
Iodine-125 (^{125}I)	Electron Capture, ε	59.6 days
Palladium-103 (^{103}Pd)	Electron Capture, ε	17.0 days
Ruthenium-106 (^{106}Ru)	β^-- particles	1.02 years
Radium-226 (^{226}Ra)	β^-- particles	1599 years

Side Effects of Radiation Therapy

Patients receiving radiation therapy can experience a variety of side effects. For example, sterility could occur if reproductive organs are irradiated. Skin that has been irradiated can appear dry and feel itchy. Some patients will loose sensation in the irradiated area. Radiation can affect the production of white and red blood cells. A reduction of white blood cells results in immunity disorders. Red blood cell lose causes anemia. Gastrointestinal issues such as diarrhea and nausea are common during radiation therapy. Some patients will lose hair as well. Lastly, dry mouth and tooth decay are prevalent during radiation treatments.

Medications are available to alleviate symptoms of radiation therapy. Narcotics can be prescribed to help alleviate intense pain. Prescription medications like zofran (Figure **16.6.10**) and phenergan can help with nausea. Special mouthwashes have been formulated to reduce dry mouth and cavities.

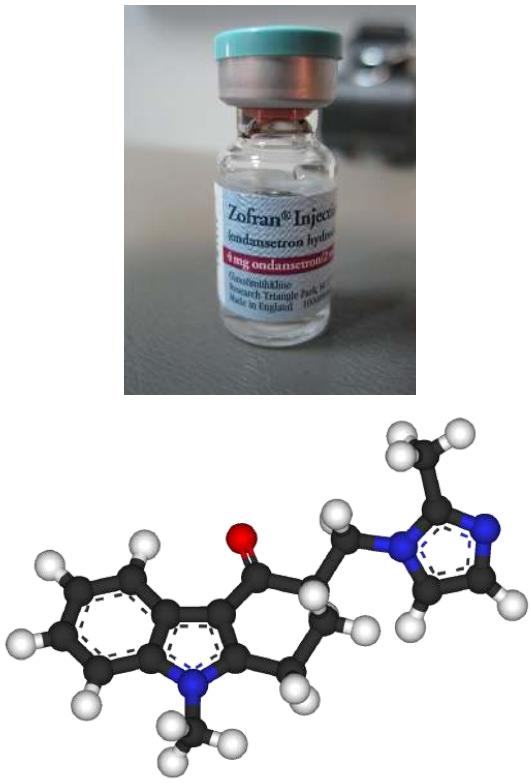


Figure **16.6.10**(left) *Zofran is a medication used to prevent nausea and vomiting caused by cancer chemotherapy, radiation therapy, or surgery. (right) A vial of Zofran 4 mg containing ondansetron for intravenous injection. This medicine is a controlled substance and is used for nausea. Images used with permision (left: Public domain; Fvasconcellos and right: CC BY 3.0; Intropin)*

Hair loss is a side effect of radiation, but only locally

Radiation therapy can cause hair loss, but hair is only lost in the area being treated. For instance, radiation to your head may cause you to lose some or all the hair on your head (even eyebrows and lashes), but if you get treatment to your hip, you won't lose the hair on your head.

Summary

- Compounds known as radioactive tracers can be used to follow reactions, track the distribution of a substance, diagnose and treat medical conditions, and much more.
- Other radioactive substances are helpful for controlling pests, visualizing structures, providing fire warnings, and for many other applications.
- Hundreds of millions of nuclear medicine tests and procedures, using a wide variety of radioisotopes with relatively short half-lives, are performed every year in the US.
- Radiation therapy uses high-energy radiation to kill cancer cells by damaging their DNA. The radiation used for this treatment may be delivered externally or internally.

Contributors and Attributions

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16.7: Energy from the Nucleus

Learning Objectives

- Explain where nuclear energy comes from.
- Describe the difference between fission and fusion.
- Know key examples of nuclear fission and nuclear fusion.

A combination of radiochemistry and radiation chemistry is used to study nuclear reactions such as fission and fusion. Some early evidence for nuclear fission was the formation of a short-lived radioisotope of barium which was isolated from neutron irradiated uranium (^{139}Ba, with a half-life of 83 minutes and ^{140}Ba, with a half-life of 12.8 days, are major fission products of uranium). **Nuclear fission** is the splitting of an atomic nucleus. In nuclear weapons and reactors, neutrons hit unstable nuclei to form smaller atoms. **Nuclear Fusion** is the bringing together of two atomic nuclei to form a larger atom. Figure 16.7.1 illustrates the difference between nuclear fission and nuclear fusion.

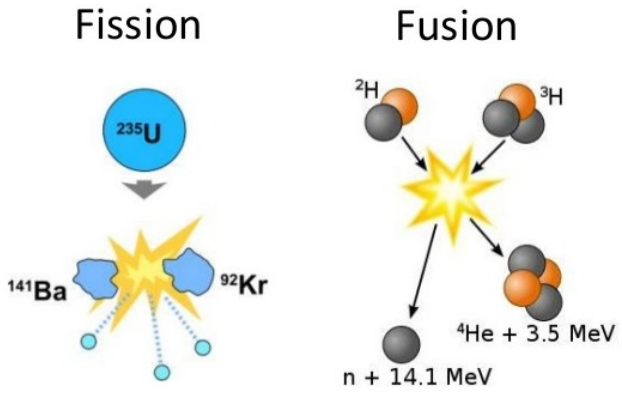


Figure **16.7.1** Nuclear fission occurs with one large nuclear is split into two or more smaller nuclei (left) . Nuclear fusion happens when two small nuclei combine to make a larger nucleus (right) .

Einstein and the Equivalence of Mass and Energy

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 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 equation, in which the molar mass of each species is indicated to four decimal places:

$$^{235}_{235.0439}\text{U} \rightarrow ^{139}_{138.9088}\text{Ba} + ^{94}_{93.9343}\text{Kr} + ^{2^1}_{2\times1.0087}\text{n}$$

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:

$$E = mc^2$$

where c is the speed of light, or

$$c = 3.00 \times 10^8\, m/s$$

In the course of the chemical reaction for uranium, the mass difference is converted to energy, which is given off by the reaction:

$$E = (-0.0001834\, kg)(3.00 \times 10^8\, m/s)^2 = -1.65 \times 10^{13} J = -1.65 \times 10^{10} kJ$$

(For the units to work out, mass must be expressed in units of kilograms.) That is, 16.5 billion kJ of energy is 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 650kJ/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:

$$^{235}\mathrm{U} + {}^{1}\mathrm{n} \rightarrow {}^{139}\mathrm{Ba} + {}^{94}\mathrm{Kr} + 3{}^{1}\mathrm{n}$$

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. (Artificial or induced radioactivity, in which neutrons are injected into a sample of matter that subsequently cause fission, was first demonstrated in 1934 by Irène Joliot-Curie and Frédéric Joliot, the daughter and son-in-law of Marie Curie.)

Binding Energy

The forces that bind nucleons together in an atomic nucleus are much greater than those that bind an electron to an atom through electrostatic attraction. This is evident by the relative sizes of the atomic nucleus and the atom (10^{-15} and 10^{-10}m, respectively). The energy required to pry a nucleon from the nucleus is therefore much larger than that required to remove (or ionize) an electron in an atom. In general, all nuclear changes involve large amounts of energy per particle undergoing the reaction. This has numerous practical applications.

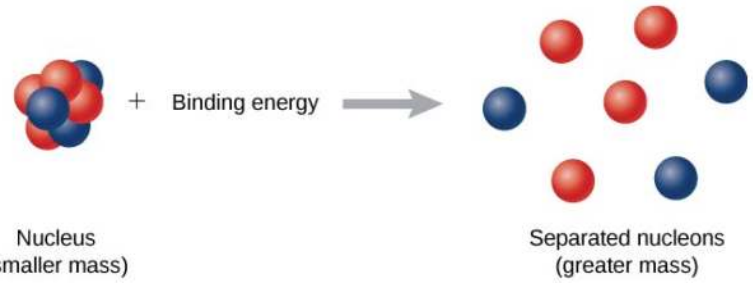


Figure **16.7.2***The binding energy is the energy required to break a nucleus into its constituent protons and neutrons. A system of separated nucleons has a greater mass than a system of bound nucleons.*

As shown in figure **16.7.2**, energy is put into the system to break apart the nucleus. The amount of energy required is called the total **binding energy** (BE), E_b. The binding energy is equal to the amount of energy released in forming the nucleus, and is therefore given by

$$E_b = (\Delta m)c^2. \tag{16.7.1}$$

In nuclear physics, one of the most important experimental quantities is the *binding energy per nucleon (BEN)*, which is defined by

$$BEN = \frac{E_b}{A} \tag{16.7.2}$$

This quantity is the average energy required to remove an individual nucleon (proton or neutron) from a nucleus—analogous to the ionization energy of an electron in an atom. If the BEN is relatively large, the nucleus is relatively stable. BEN values are estimated from nuclear scattering experiments.

Figure **16.7.3** shows the relative binding energies for various isotopes. Of these elements, fission requires heavy, unstable nuclei. This means selected atoms would have low binding energies and would have large atomic masses. Nuclei that are larger than Fe-56 may undergo fission. Uranium-238 and uranium-235 both have lower binding energies with heavy masses-.

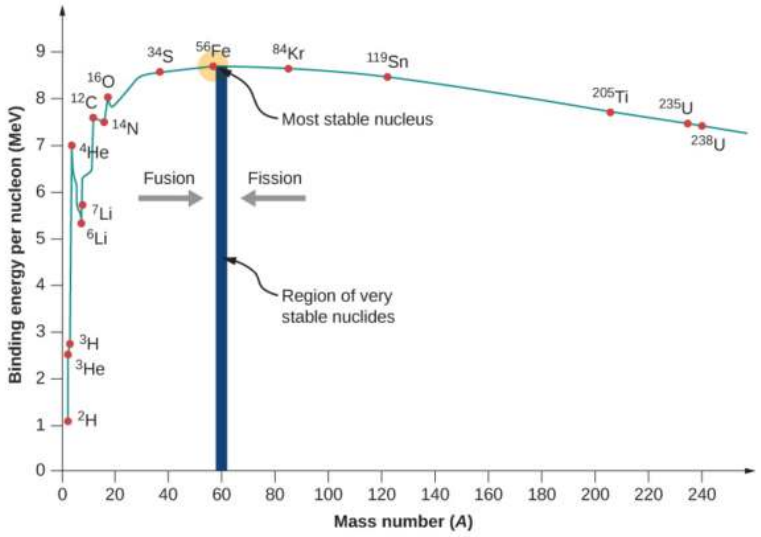


Figure **16.7.3** In this graph of binding energy per nucleon for stable nuclei, the BEN is greatest for nuclei with a mass near ^{56}Fe. Therefore, fusion of nuclei with mass numbers much less than that of Fe, and fission of nuclei with mass numbers greater than that of Fe, are exothermic processes. (CC BY. OpenStax).

These two isotopes would be suitable for splitting based on these requirements. Of these two isotopes, only uranium-235 is readily fissionable. This is due to odd neutron count contributing to additional instability. Another fissionable isotope not shown in Figure **16.7.3** is plutonium-239. This is a synthetic isotope produced by transmutation and decay reactions. Like uranium-235, it has low binding energy, high mass, and an odd number of neutrons. U-235 and Pu-239 are used in atomic bombs (fission based) and nuclear reactors.

Positively charged centers of atoms make nuclear fusion extremely difficult. For this reason, smaller atoms are suitable for fusion reactions. In addition, these particular isotopes need to have low binding energies in order to undergo fusion. Atoms that possess these two qualities are H-2 and H-3. For fusion to occur, extreme temperatures are required to fuse these deuterium and tritium together.

As we will see, the BEN-versus-*A* graph implies that nuclei divided or combined release an enormous amount of energy. This is the basis for a wide range of phenomena, from the production of electricity at a nuclear power plant to sunlight.

Nuclear Fission

In both fission and fusion, large amounts of energy are given off in the form of heat, light, and gamma radiation. Italian physicist, Enrico Fermi, performed the first fission reaction in 1934. He was unaware that he had split a uranium atom into two smaller nuclei. Nuclear fission of heavy elements was discovered on December 17, 1938 by German Otto Hahn and his assistant Fritz Strassmann, and explained theoretically in January 1939 by Lise Meitner (Figure **16.7.4**) and her nephew Otto Robert Frisch. Frisch named the process "fission" by analogy with biological fission of living cells.

Figure **16.7.4** *Austrian physicist, Lise Meitner of U-238.*

Image take from: https://upload.wikimedia.org/wikiped...ner12crop2.J

Since then, fission has been observed in many other isotopes, including most actinide isotopes that have an odd number of neutrons. A typical nuclear fission reaction is shown in Figure **16.7.5**.

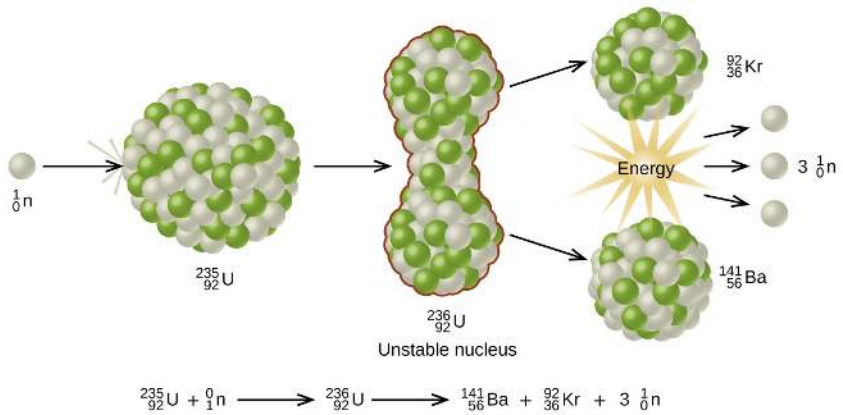


Figure **16.7.5** When a slow neutron hits a fissionable U-235 nucleus, it is absorbed and forms an unstable U-236 nucleus. The U-236 nucleus then rapidly breaks apart into two smaller nuclei (in this case, Ba-141 and Kr-92) along with several neutrons (usually two or three), and releases a very large amount of energy.

Among the products of Meitner, Hahn, and Strassman's fission reaction were barium, krypton, lanthanum, and cerium, all of which have nuclei that are more stable than uranium-235. Since then, hundreds of different isotopes have been observed among the products of fissionable substances.

Fission has been used in nuclear weapons and powers all nuclear reactors. Approximately fifty-five countries worldwide possess fission technology in the form of research or energy reactors. Less than ten of these countries have fission weapons.

A tremendous amount of energy is produced by the fission of heavy elements. For instance, when one mole of U-235 undergoes fission, the products weigh about 0.2 grams less than the reactants; this "lost" mass is converted into a very large amount of energy, about 1.8×10^{10} kJ per mole of U-235. Nuclear fission reactions produce incredibly large amounts of energy compared to chemical reactions. The fission of 1 kilogram of uranium-235, for example, produces about 2.5 million times as much energy as is produced by burning 1 kilogram of coal.

Nuclear Chain Reaction

As described earlier, when undergoing fission U-235 produces two "medium-sized" nuclei, and two or three neutrons. These neutrons may then cause the fission of other uranium-235 atoms, which in turn provide more neutrons that can cause fission of even more nuclei, and so on. If this occurs, we have a nuclear chain reaction (Figure **16.7.6**). On the other hand, if too many neutrons escape the bulk material without interacting with a nucleus, then no chain reaction will occur.

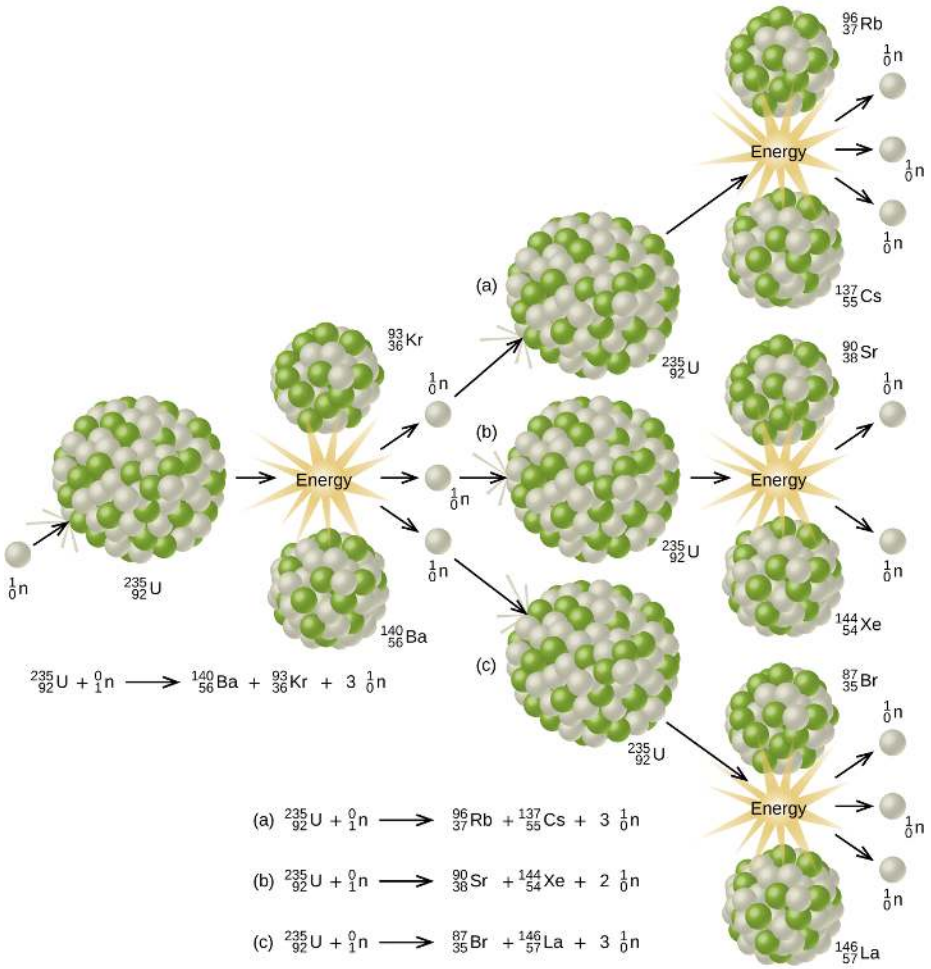


Figure **16.7.6** The fission of a large nucleus, such as U-235, produces two or three neutrons, each of which is capable of causing fission of another nucleus by the reactions shown. If this process continues, a nuclear chain reaction occurs.

Material that can sustain a nuclear fission chain reaction is said to be fissile or fissionable. (Technically, fissile material can undergo fission with neutrons of any energy, whereas fissionable material requires high-energy neutrons.) Nuclear fission becomes self-sustaining when the number of neutrons produced by fission equals or exceeds the number of neutrons absorbed by splitting nuclei plus the number that escape into the surroundings. The amount of a fissionable material that will support a self-sustaining chain reaction is a critical mass. An amount of fissionable material that cannot sustain a chain reaction is a subcritical mass. An amount of material in which there is an increasing rate of fission is known as a supercritical mass. The critical mass depends on the type of material: its purity, the temperature, the shape of the sample, and how the neutron reactions are controlled (Figure 16.7.7).

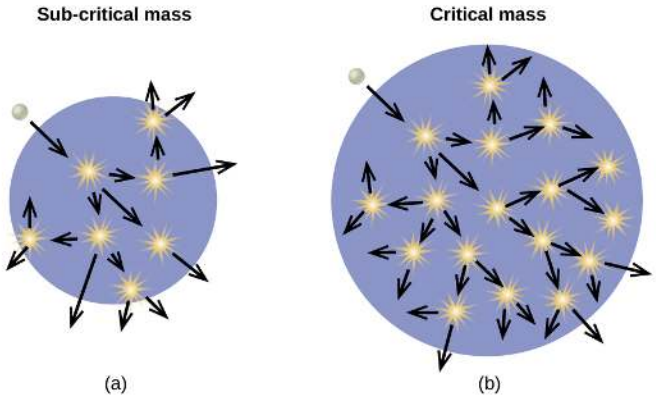


Figure **16.7.7** (a) In a subcritical mass, the fissile material is too small and allows too many neutrons to escape the material, so a chain reaction does not occur. (b) In a critical mass, a large enough number of neutrons in the fissile material induce fission to create a chain reaction.

Thermonuclear Reactions

Thermonuclear fusion is a way to achieve nuclear fusion by using extremely high temperatures. There are two forms of thermonuclear fusion: *uncontrolled*, in which the resulting energy is released in an uncontrolled manner, as it is in thermonuclear weapons ("hydrogen bombs") and in most stars; and *controlled*, where the fusion reactions take place in an environment allowing some or all of the energy released to be harnessed for constructive purposes. The discussion below is limited to the fusion process that powers the sun and the stars.

The prime energy producer in the sun is the fusion of hydrogen to form helium, which occurs at a solar-core temperature of 14 million kelvin. The net result is the fusion of four protons into one alpha particle, with the release of two positrons, two neutrinos (which changes two of the protons into neutrons), and energy (Figure **16.7.8**).

This is a net reaction of a more complicated series of events:

$$4\,{}^{1}_{1}\mathrm{H} \longrightarrow {}^{4}_{2}\mathrm{He} + 2\,{}^{1}_{0}\mathrm{n}$$

A helium nucleus has a mass that is 0.7% less than that of four hydrogen nuclei; this lost mass is converted into energy during the fusion. This reaction produces about 3.6×10^{11} kJ of energy per mole of ${}^{4}_{2}\mathrm{He}$ produced. This is somewhat larger than the energy produced by the nuclear fission of one mole of U-235 (1.8×10^{10} kJ), and over 3 million times larger than the energy produced by the (chemical) combustion of one mole of octane (5471 kJ).

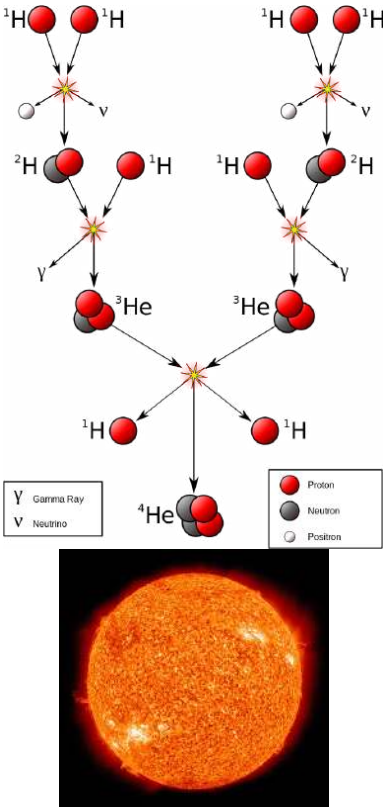


Figure **16.7.8** Nuclear fusion producing helium (left). The Sun is a main-sequence star, and thus generates its energy by nuclear fusion of hydrogen nuclei into helium (right).

Summary

- 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.
- The continues process whereby neutrons produced from the initial fission of a large nucleus like U-235 cause further fission of another nucleus.
- In a critical mass, a large enough number of neutrons in the fissile material induce fission to create a chain reaction.
- The most important fusion process in nature is the one that powers the stars. The net result is the fusion of four protons into one alpha particle, with the release of two positrons, two neutrinos (which changes two of the protons into neutrons), and energy

Contributors and Attributions

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- TextMap: Beginning Chemistry (Ball et al.)
- Marisa Alviar-Agnew (Sacramento City College)
- Wikipedia

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16.8: Nuclear Energy

Learning Objective

- List the benefits and problems with nuclear energy.

Nuclear power is the use of nuclear reactions that release nuclear energy to generate heat, which most frequently is then used in steam turbines to produce electricity in a nuclear power plant. Nuclear power can be obtained from nuclear fission, nuclear decay and nuclear fusion reactions. Presently, the vast majority of electricity from nuclear power is produced by nuclear fission of uranium and plutonium. Nuclear decay processes are used in niche applications such as radioisotope thermoelectric generators. Generating electricity from fusion power remains at the focus of international research.

Civilian nuclear power supplied 2,563 terawatt hours (TWh) of electricity in 2018, equivalent to about 10% of global electricity generation, and was the second largest low-carbon power source after hydroelectricity. As of December 2019, there are 443 civilian fission reactors in the world, with a combined electrical capacity of 395 gigawatt (GW). There are also 56 nuclear power reactors under construction and 109 reactors planned, with a combined capacity of 60 GW and 120 GW, respectively. The United States has the largest fleet of nuclear reactors, generating over 800 TWh zero-emissions electricity per year with an average capacity factor of 92%. Most reactors under construction are generation III reactors in Asia.

Nuclear power has one of the lowest levels of fatalities per unit of energy generated compared to other energy sources. Coal, petroleum, natural gas and hydroelectricity each have caused more fatalities per unit of energy due to air pollution and accidents. [10] Since its commercialization in the 1970s, nuclear power has prevented about 1.84 million air pollution-related deaths and the emission of about 64 billion tonnes of carbon dioxide equivalent that would have otherwise resulted from the burning of fossil fuels.

There is a debate about nuclear power. Proponents, such as the World Nuclear Association and Environmentalists for Nuclear Energy, contend that nuclear power is safe and it reduces carbon emissions. Nuclear power opponents, such as Greenpeace and NIRS, contend that nuclear power poses many threats to people and the environment.

There are over thirty countries that use nuclear power to generate electricity (see Table **16.8.1**. There were about 450 nuclear power reactors worldwide, producing close to 400,000 MW (MegaWatts) of electrical capacity. Commercial nuclear reactors can be found in North and South America, Europe, Africa, and Asia. The United States has the most reactors of any other countries. There are around ninety-eight reactors in the United States that provide around twenty percent of the electrical energy in the United States. Other countries, like France, employ around sixty nuclear reactors to produce 70% of their electrical power.

Table **16.8.1**: Nuclear Share of Electricity Generation and Number of Operated Reactors in 2019. Source: International Atomic Energy Agency (IAEA)

Country	Number of Operated Reactors	Total Net Electrical Capacity [MW]	Nuclear Electricity Supplied [GW.h]	Nuclear Share [%]
UNITED STATES OF AMERICA	98	99648	809358.57	19.7
UNITED KINGDOM	15	8923	51032.09	15.6
UKRAINE	15	13107	78144.26	53.9
SWITZERLAND	5	3333	25369.65	23.9
SWEDEN	8	8592	64428.86	34.0
SPAIN	7	7121	55856.07	21.4
SOUTH AFRICA	2	1860	13602.57	6.7
SLOVENIA	1	688	5532.98	37.0
SLOVAKIA	4	1814	14282.25	53.9
RUSSIA	39	28448	195535.15	19.7
ROMANIA	2	1300	10368.21	18.5
PAKISTAN	5	1318	9065.80	6.6
NETHERLANDS	1	482	3700.71	3.2
MEXICO	2	1552	10880.73	4.5
KOREA, REPUBLIC OF	25	23833	138809.35	26.2
JAPAN	38	36476	65681.92	7.5
IRAN, ISLAMIC REPUBLIC OF	1	915	5865.73	1.8
INDIA	22	6255	40740.49	3.2
HUNGARY	4	1902	15414.83	49.2
FRANCE	58	63130	382402.75	70.6
FINLAND	4	2794	22914.88	34.7
CZECH REPUBLIC	6	3932	28581.12	35.2
CHINA	48	45518	330122.19	4.9
CANADA	19	13554	94853.85	14.9
BULGARIA	2	2006	15868.88	37.5
BRAZIL	2	1884	15224.11	2.7
BELGIUM	7	5930	41421.66	47.6
ARMENIA	1	375	2028.96	27.8
ARGENTINA	3	1641	7926.96	5.9
Total	449	392779	2586163.02	N

Nuclear Power Plants

After fabrication, fuel assemblies are transported to nuclear power plants where they are used as a source of energy for generating electricity. They are stored onsite until they are needed by the reactor operators. At this stage, the uranium is only mildly radioactive, and essentially all radiation is contained within the metal tubes. When needed, the fuel is loaded into a reactor core (Figure **16.8.2**). Typically, about one third of the reactor core (40 to 90 fuel assemblies) is changed out every 12 to 24 months.

The most common type of reactors are the **pressurized water reactors** (PWR) (Figure 16.8.2) in which water is pumped through the reactor core and heated by the fission process. The water is kept under high pressure inside the reactor so it does not boil. The heated water from the reactor passes through tubes inside the steam generator where the heat is transferred to water flowing around the tubes in the steam generator. The water in the steam generator boils and turns to steam. The steam is piped to the turbines. The force of the expanding steam drives the turbines, which spin a magnet in coil of wire – the generator– to produce electricity.

After passing through the turbines, the steam is converted back to water by circulating it around tubes carrying cooling water in the condenser. The condensed steam – now water – is returned to the steam generators to repeat the cycle.

The three water systems (condenser, steam generator, and reactor) are separate from each other and are not permitted to mix. Water in the reactor is radioactive and is contained within the containment structure whereas water in the steam generator and condenser is nonradioactive.

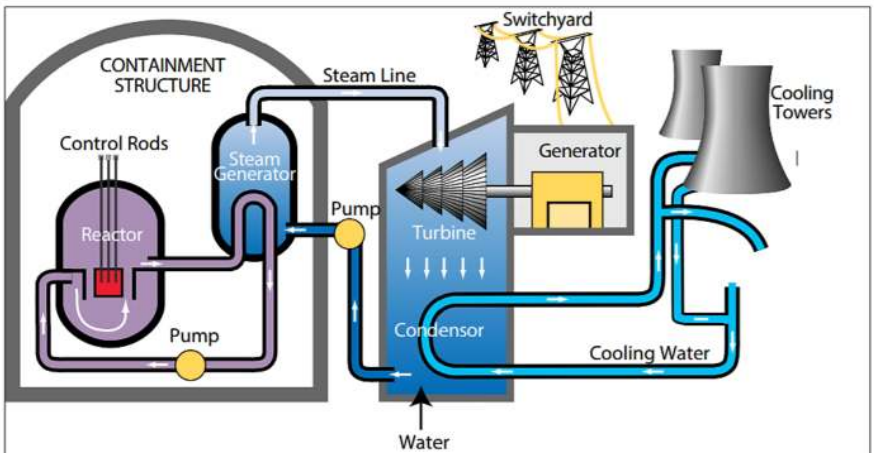


Figure **16.8.1**: A schematic diagram of a pressurized water reactor (PWR), the most common type of nuclear reactor. (Public Domain; Tennessee Valley Authority)

The Nuclear Advantage: Minimal Air Pollution

By using fission, nuclear power plants generate electricity without emitting air pollutants like those emitted by fossil fuel-fired power plants. This means that financial costs related to chronic health problems caused by air pollutants such as particulate material, carbon monoxide, nitrogen oxides and ozone among others are significantly reduced. In addition nuclear reactors do not produce carbon dioxide while operating which means that nuclear energy does not contribute to the global warming problem.

Another benefit of nuclear energy over fossil fuels especially coal is that uranium generates far more power per unit weight or volume. This means that less of it needs to be mined and consequently the damage to the landscapes is less especially when compared to the damage that results from coal mining such as mountaintop removal.

Problems with Nuclear Power

The main environmental concern related to nuclear power is the creation of radioactive wastes such as uranium mill tailings, spent (used) reactor fuel, and other radioactive wastes. These materials can remain radioactive and dangerous to human health for thousands of years. Radioactive wastes are classified as low-level and high-level. By volume, most of the waste related to the nuclear power industry has a relatively low-level of radioactivity. Uranium mill tailings contain the radioactive element radium, which decays to produce **radon**, a radioactive gas. Most uranium mill tailings are placed near the processing facility or mill where they come from. Uranium mill tailings are covered with a barrier of material such as clay to prevent radon from escaping into the atmosphere, and they are then covered by a layer of soil, rocks, or other materials to prevent erosion of the sealing barrier.

The other types of low-level radioactive waste are the tools, protective clothing, wiping cloths, and other disposable items that get contaminated with small amounts of radioactive dust or particles at nuclear fuel processing facilities and power plants. These materials are subject to special regulations that govern their handling, storage, and disposal so they will not come in contact with the outside environment.

High-level radioactive waste consists of spent nuclear reactor fuel (i.e., fuel that is no longer useful for producing electricity). The spent reactor fuel is in a solid form consisting of small fuel pellets in long metal tubes called rods. Spent reactor fuel assemblies are initially stored in specially designed pools of water, where the water cools the fuel and acts as a radiation shield. Spent reactor fuel assemblies can also be stored in specially designed dry storage containers. An increasing number of reactor operators now store their older spent fuel in dry storage facilities using special outdoor concrete or steel containers with air cooling. There is currently no permanent disposal facility in the United States for high-level nuclear waste.

When a nuclear reactor stops operating, it must be **decommissioned**. This involves safely removing the reactor and all equipment that has become radioactive from service and reducing radioactivity to a level that permits other uses of the property. The U.S. Nuclear Regulatory Commission has strict rules governing nuclear power plant decommissioning that involve cleanup of radioactively contaminated plant systems and structures, and removal of the radioactive fuel.

The processes for mining and refining uranium ore and making reactor fuel require large amounts of energy. Nuclear power plants have large amounts of metal and concrete, which also require large amounts of energy to manufacture. If fossil fuels are used for mining and refining uranium ore or in constructing the nuclear plant, then the emissions from burning those fuels could be associated with the electricity that nuclear power plants generate.

Nuclear Accidents

A **nuclear meltdown**, or uncontrolled nuclear reaction in a nuclear reactor, can potentially result in widespread contamination of air and water. Some serious nuclear and radiation accidents have occurred worldwide. The most severe accident was the Chernobyl accident of 1986 in the then Soviet Union (now Ukraine) which killed 31 people directly and sickened or caused cancer in thousands more. The Fukushima Daiichi nuclear disaster (2011) in Japan was caused by a 9.0 magnitude earthquake that shut down power supply and a tsunami that flooded the plant's emergency power supply. This resulted in the release of radioactivity although it did not directly result in any deaths at the time of the disaster. Another nuclear accident was the Three Mile Island accident (1979) in Pennsylvania, USA. This accident resulted in a near disastrous core meltdown that was due to a combination of human error and mechanical failure but did not result in any deaths and no cancers or otherwise have been found in follow up studies of this accident. While there are potentially devastating consequences to a nuclear meltdown, the likelihood of one occurring is extremely small. After every meltdown, including the 2011 Fukushima Daiichi disaster, new international regulations were put in place to prevent such an event from occurring again.

Breeder Reactors: Making More Fuel Than They Burn

Because $^{235}_{92}\mathrm{U}$ is only 0.7 percent of naturally occurring uranium, its supply is fairly limited and could well only last for about 50 years of full-scale use. The other 99 percent of the uranium can also be utilized if it is first converted into plutonium by neutron bombardment:

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{239}_{94}\mathrm{Pu} + 2\,{}^{0}_{-1}\mathrm{e}$$

$^{239}_{94}\mathrm{Pu}$ is also fissionable, and so it could be used in a nuclear reactor as well as $^{235}_{92}\mathrm{U}$.

The production of plutonium can be carried out in a breeder reactor which not only produces energy like other reactors but is designed to allow some of the fast neutrons to bombard the $^{235}_{92}\mathrm{U}$, producing plutonium at the same time. More fuel is then produced than is consumed.

Breeder reactors present additional safety hazards to those already outlined. They operate at higher temperatures and use very reactive liquid metals such as sodium in their cooling systems, and so the possibility of a serious accident is higher. In addition the large quantities of plutonium which would be produced in a breeder economy would have to be carefully safeguarded. Plutonium is an α emitter and is very dangerous if taken internally. Its half-life is 24,000 years, and so it will remain in the environment for a long time if dispersed. Moreover, $^{239}_{94}\mathrm{Pu}$ can be separated chemically (not by the much more expensive gaseous diffusion used to

concentrate $^{235}_{92}\text{U}$ from fission products and used to make bombs. Such a material will obviously be attractive to terrorist groups, as well as to countries which are not currently capable of producing their own atomic weapons.

Today many nations are considering an expanded role for nuclear power in their energy portfolios. This expansion is driven by concerns about global warming, growth in energy demand, and relative costs of alternative energy sources. In 2008, 435 nuclear reactors in 30 countries provided 16% of the world's electricity. In January 2009, 43 reactors were under construction in 11 countries, with several hundred more projected to come on line globally by 2030.

Nuclear Fusion

The most important fusion process in nature is the one that powers stars. The fusion of hydrogen and helium, which is the primary energy producer in the sun has been discussed in Chapter 11. This section briefly discusses harnessing energy from nuclear fusion to generate electricity.

The fusion reaction of great interest is known as deuterium–tritium fusion (D–T fusion) wherein a deuterium atom and a tritium atom fuse to produce helium-4 (Figure **16.8.3**).

$$^{2}_{1}\text{H} + {}^{3}_{1}\text{H} \rightarrow {}^{4}_{2}\text{He} + {}^{1}_{0}\text{n} \tag{21.6.13}$$

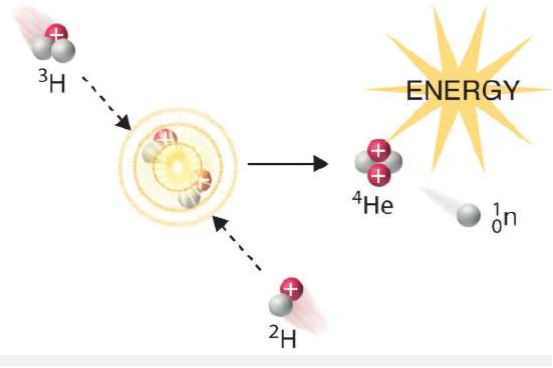


Figure **16.8.2**: Nuclear fusion. The fusion of ^{3}H and ^{2}H produces ^{4}He and a neutron and releases an enormous amount of energy.

Fusion power has the potential to provide sufficient energy to satisfy mounting demand, and to do so sustainably, with a relatively small impact on the environment. Nuclear fusion has many potential attractions. Firstly, its hydrogen isotope fuels are relatively abundant – one of the necessary isotopes, deuterium, can be extracted from seawater, while the other fuel, tritium, would be bred from a lithium blanket using neutrons produced in the fusion reaction itself. Furthermore, a fusion reactor would produce virtually no CO_2 or atmospheric pollutants, and its radioactive waste products would mostly be very short-lived compared to those produced by conventional nuclear reactors (fission reactors).

Useful fusion reactions require very high temperatures for their initiation—about 15,000,000 K or more. At these temperatures, all molecules dissociate into atoms, and the atoms ionize, forming plasma. These conditions occur in an extremely large number of locations throughout the universe—stars are powered by fusion. Humans have already figured out how to create temperatures high enough to achieve fusion on a large scale in thermonuclear weapons. A thermonuclear weapon such as a hydrogen bomb contains a nuclear fission bomb that, when exploded, gives off enough energy to produce the extremely high temperatures necessary for fusion to occur.

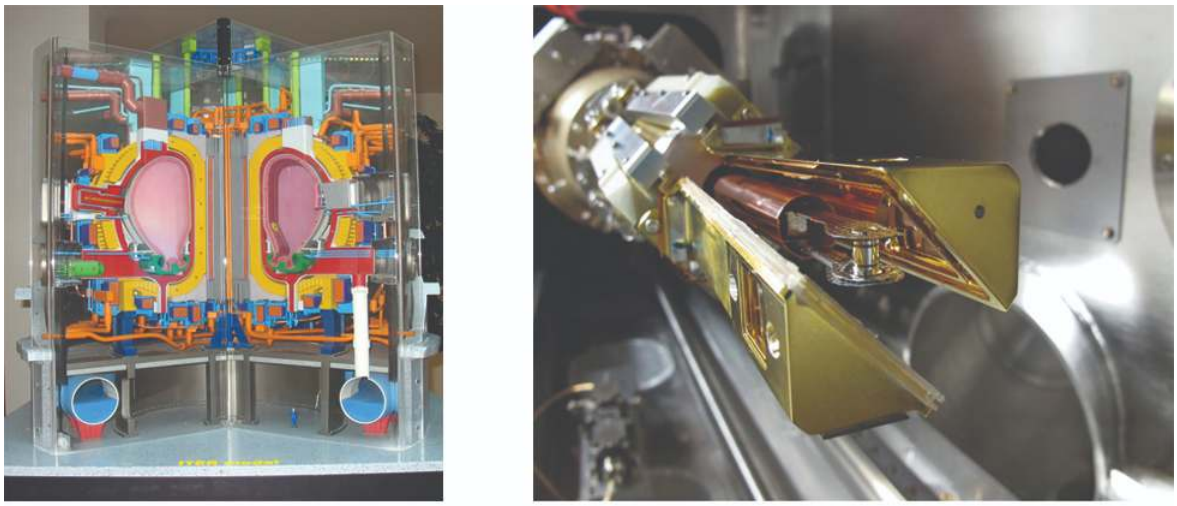


Figure **16.8.3**: (a) This model is of the International Thermonuclear Experimental Reactor (ITER) reactor. Currently under construction in the south of France with an expected completion date of 2027, the ITER will be the world's largest experimental Tokamak nuclear fusion reactor with a goal of achieving large-scale sustained energy production. (b) In 2012, the National Ignition Facility at Lawrence Livermore National Laboratory briefly produced over 500,000,000,000 watts (500 terawatts, or 500 TW) of peak power and delivered 1,850,000 joules (1.85 MJ) of energy, the largest laser energy ever produced and 1000 times the power usage of the entire United States in any given moment. Although lasting only a few billionths of a second, the 192 lasers attained the conditions needed for nuclear fusion ignition. This image shows the target prior to the laser shot. (credit a: modification of work by Stephan Mosel)

Another much more beneficial way to create fusion reactions is in a fusion reactor, a nuclear reactor in which fusion reactions of light nuclei are controlled. Because no solid materials are stable at such high temperatures, mechanical devices cannot contain the plasma in which fusion reactions occur. Two techniques to contain plasma at the density and temperature necessary for a fusion reaction are currently the focus of intensive research efforts: containment by a magnetic field and by the use of focused laser beams (Figure **16.8.3**). A number of large projects are working to attain one of the biggest goals in science: getting hydrogen fuel to ignite and produce more energy than the amount supplied to achieve the extremely high temperatures and pressures that are required for fusion. The US Department of Energy is funding several sites conducting fusion research as given on the link https://www.usiter.org/fusion/us-fusion-research-sites. One of the research sites is features in the video below Video **16.8.1**.



Video **16.8.1**: The D-III National Fusion Facility, San Diego California.

Summary

- There is still ongoing debate about nuclear power.
- Proponents, such as the World Nuclear Association and Environmentalists for Nuclear Energy, contend that nuclear power is a safe, energy source that reduces carbon emissions.

- Nuclear power opponents, such as Greenpeace and NIRS, contend that nuclear power poses many threats to people and the environment.
- There are over thirty countries that use nuclear power to generate electricity.

Contributor

- Libretext: Introduction to Environmental Science (Zendher et al.) (CC BY-NC-SA)
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16.9: Uses and Consequences of Nuclear Energy

Learning Objective

- Know the benefits and consequences of nuclear energy.

Nuclear Power Generation

The generation of electricity is critical for operation of businesses, health care delivery, schools, homes, and other areas requiring the use of electrical power. According to 2011 statistics, coal is used for 42% of the total power generated, with natural gas being employed for another 25%. Nuclear power plants are employed in about 19% of the cases, with renewable energy sources supplying the last 13%. All of these fuels are used to heat water to generate steam. The steam then turns a turbine to generate electricity.

Nuclear power plants use the energy from nuclear fission to produce electricity. **U-235** is the preferred nuclear fuel because when its atoms are split (fissioned), they not only emit heat and high energy radiation but also enough neutrons to maintain a chain reaction and provide energy to power a nuclear power plant. Uranium is found in rocks all over the world but is relatively rare and the supply is finite making it a nonrenewable energy source.

Uranium usually occurs in combination with small amounts of other elements and once it is mined, the U-235 must be extracted and processed before it can be used as a fuel in a nuclear power plant to generate electricity. The processed uranium is formed into fuel rods and then bundled into fuel assemblies. Fuel assemblies are stored onsite until they are needed by the reactor operators. At this stage, the uranium is only mildly radioactive, and essentially all radiation is contained within the metal tubes. When needed, the fuel is loaded into a reactor core (Figure 16.9.1). Typically, about one third of the reactor core (40 to 90 fuel assemblies) is changed out every 12 to 24 months.

The most common type of reactors are the **pressurized water reactors** (PWR) (Figure 16.9.1) in which water is pumped through the reactor core and heated by the fission process. The water is kept under high pressure inside the reactor so it does not boil. The heated water from the reactor passes through tubes inside the steam generator where the heat is transferred to water flowing around the tubes in the steam generator. The water in the steam generator boils and turns to steam. The steam is piped to the turbines. The force of the expanding steam drives the turbines, which spin a magnet in coil of wire – the generator– to produce electricity.

After passing through the turbines, the steam is converted back to water by circulating it around tubes carrying cooling water in the condenser. The condensed steam – now water – is returned to the steam generators to repeat the cycle.

The three water systems (condenser, steam generator, and reactor) are separate from each other and are not permitted to mix. Water in the reactor is radioactive and is contained within the containment structure whereas water in the steam generator and condenser is nonradioactive.

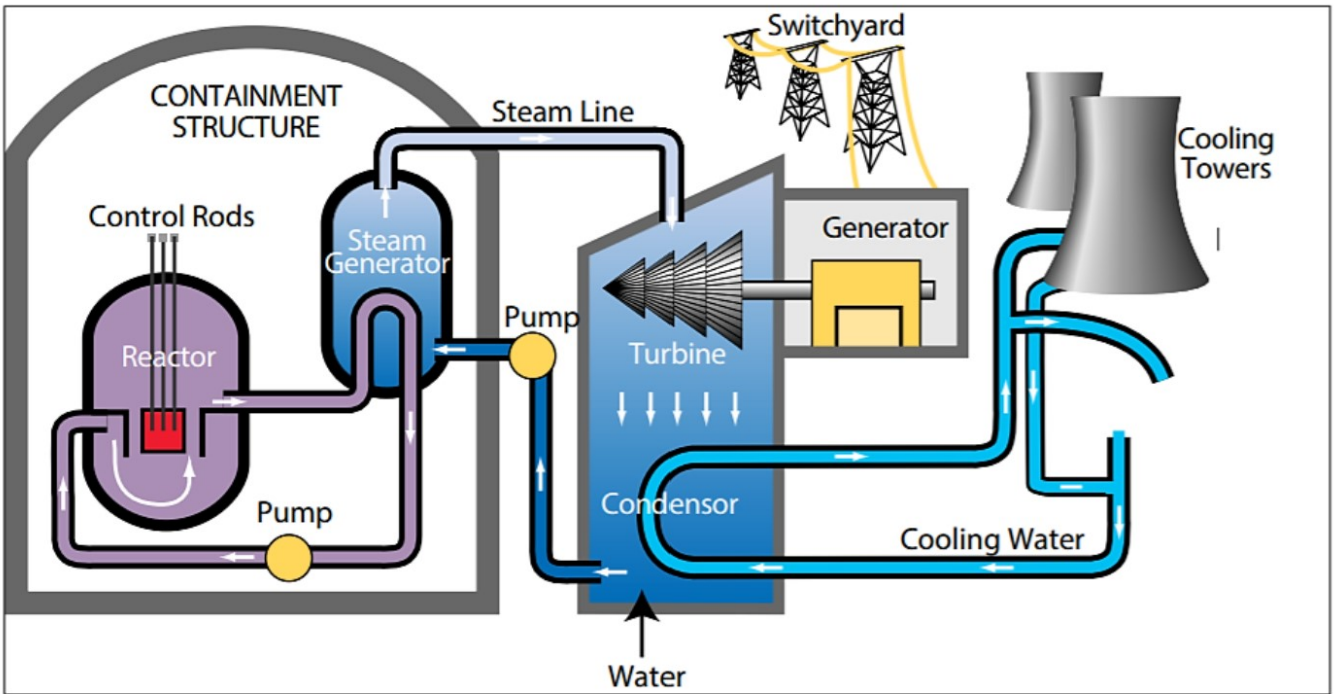


Figure 16.9.1: *A schematic diagram of a pressurized water reactor (PWR), the most common type of nuclear reactor. Diagram from Tennessee Valley Authority (public domain). www.tva.com*

Benefits of Nuclear Energy

By using fission, nuclear power plants generate electricity without emitting air pollutants like those emitted by fossil fuel-fired power plants. This means that financial costs related to chronic health problems caused by air pollutants such as particulate material, carbon monoxide, nitrogen oxides and ozone among others are significantly reduced. In addition nuclear reactors do not produce carbon dioxide while operating which means that nuclear energy does not contribute to the global warming problem.

Another benefit of nuclear energy over fossil fuels especially coal is that uranium generates far more power per unit weight or volume. This means that less of it needs to be mined and consequently the damage to the landscapes is less especially when compared to the damage that results from coal mining such as mountaintop removal.

Nuclear power is also used to propel ships. The turbine can be connected to a propeller system. The rotating turbine shaft will turn the propeller to move the ship.



Figure **16.9.2** *Nuclear submarine.*

The Drawbacks of Nuclear Energy

The main environmental concern related to nuclear power is the creation of radioactive wastes such as uranium mill tailings, spent (used) reactor fuel, and other radioactive wastes. These materials can remain radioactive and dangerous to human health for thousands of years. Radioactive wastes are classified as low-level and high-level. By volume, most of the waste related to the nuclear power industry has a relatively low-level of radioactivity. **Uranium mill tailings** contain the radioactive element radium, which decays to produce **radon**, a radioactive gas. Most uranium mill tailings are placed near the processing facility or mill where they come from. Uranium mill tailings are covered with a barrier of material such as clay to prevent radon from escaping into the atmosphere, and they are then covered by a layer of soil, rocks, or other materials to prevent erosion of the sealing barrier.

Spent fuel rods contain a variety of products, consisting of unstable nuclei ranging in atomic number from 25 to 60, some transuranium elements, including plutonium and americium, and unreacted uranium isotopes. The unstable nuclei and the transuranium isotopes give the spent fuel a dangerously high level of radioactivity. The long-lived isotopes require thousands of years to decay to a safe level. The ultimate fate of the nuclear reactor as a significant source of energy in the United States probably rests on whether or not a politically and scientifically satisfactory technique for processing and storing the components of spent fuel rods can be developed.

The other types of **low-level radioactive waste** are the tools, protective clothing, wiping cloths, and other disposable items that get contaminated with small amounts of radioactive dust or particles at nuclear fuel processing facilities and power plants. These materials are subject to special regulations that govern their handling, storage, and disposal so they will not come in contact with the outside environment.

High-level radioactive waste consists of spent nuclear reactor fuel (i.e., fuel that is no longer useful for producing electricity). The spent reactor fuel is in a solid form consisting of small fuel pellets in long metal tubes called rods. Spent reactor fuel assemblies are initially stored in specially designed pools of water, where the water cools the fuel and acts as a radiation shield. Spent reactor fuel assemblies can also be stored in specially designed dry storage containers. An increasing number of reactor operators now store their older spent fuel in dry storage facilities using special outdoor concrete or steel containers with air cooling. There is currently no permanent disposal facility in the United States for high-level nuclear waste.

When a nuclear reactor stops operating, it must be **decommissioned**. This involves safely removing the reactor and all equipment that has become radioactive from service and reducing radioactivity to a level that permits other uses of the property. The U.S. Nuclear Regulatory Commission has strict rules governing nuclear power plant decommissioning that involve cleanup of radioactively contaminated plant systems and structures, and removal of the radioactive fuel.

A **nuclear meltdown**, or uncontrolled nuclear reaction in a nuclear reactor, can potentially result in widespread contamination of air and water. Some serious nuclear and radiation accidents have occurred worldwide. The most severe accident was the Chernobyl accident of 1986 in the then Soviet Union (now Ukraine) which killed 31 people directly and sickened or caused cancer in thousands more. The Fukushima Daiichi nuclear disaster (2011) in Japan (Figure **16.9.3**) was caused by a 9.0 magnitude earthquake that shut down power supply and a tsunami that flooded the plant's emergency power supply. This resulted in the release of radioactivity although it did not directly result in any deaths at the time of the disaster.

Another nuclear accident was the Three Mile Island accident (1979) in Pennsylvania, USA. This accident resulted in a near disastrous core meltdown that was due to a combination of human error and mechanical failure but did not result in any deaths and no cancers or otherwise have been found in follow up studies of this accident. While there are potentially devastating consequences to a nuclear meltdown, the likelihood of one occurring is extremely small. After every meltdown, including the 2011 Fukushima Daiichi disaster, new international regulations were put in place to prevent such an event from occurring again.



Figure **16.9.3** (a) After the accident, contaminated waste had to be removed, and (b) an evacuation zone was set up around the plant in areas that received heavy doses of radioactive fallout. (credit a: modification of work by "Live Action Hero"/Flickr)

The processes for mining and refining uranium ore and making reactor fuel require large amounts of energy. Nuclear power plants have large amounts of metal and concrete, which also require large amounts of energy to manufacture. If fossil fuels are used for mining and refining uranium ore or in constructing the nuclear plant, then the emissions from burning those fuels could be associated with the electricity that nuclear power plants generate.

Nuclear Reactor Design and Operation



***Video* 16.9.1** *The design and safe operation of a nuclear reactor.*

Summary

- The importance of nuclear power in generating electricity is described.
- The operation of a nuclear power plant is described.
- The drawbacks of nuclear energy is described.

Contributors and Attributions

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16.10: Nuclear Bombs

Learning Objectives

- Describe the key features of an atomic bomb.
- Define nuclear fallout.

World war two brought about many advances in weaponry. The Nazis used the immense science ability of their newly conquered countries to attempt to create super weapons to keep the new territory. The weapons included new tanks like the feared Tiger Tank, or the highly advanced Luftwaffe air force. However, the one weapon the Nazi's really wanted to hold was the atomic bomb. The problem that the Nazi's began to have though was that many of the great minds they once had left the country and came to the United States. Also, in the end Allied troops got to Hitler and his scientists just before they could complete any atomic bombs. The U.S. also wanted to create an atom bomb, and for the same reasons. The Manhattan Project was started to form this new weapon.

The Manhattan Project was successful in the United States because of the vast resources that could be pulled together for the project. The great minds worked under the University of Chicago football field to try and create fission. A plant in Tennessee had the sole purpose of producing enough uranium for atomic bomb testing. Finally, New Mexico was the epicenter of the whole operation. This is where the bombs were constructed and tested. The resources needed were immense. There had to be enough fuel for the bomb, and everything required to make it. There had to be housing and food for all the scientists. Maybe most importantly, there had to be enough money to support the project. The Unites States was able to effectively use all of these resources, while the Germans did not have the resources, and didn't use them as effectively. Finally, after years of hard work an atomic bomb test took place of July 16, 1945. The bomb was held together in some parts by just tape, yet it was a huge success. The problem was that the war in Europe was already over, so President Truman had to decide whether or not to use the bomb on Japan.

The war in the Pacific was a lot different than the war in Europe. In Europe, you landed once and fought your way through to Berlin to defeat the Nazi's. However, in the Pacific Japan controlled hundreds of Islands before you got to the mainland. The invasion would have cost huge amounts of American lives and resources. As a result, when the bomb had a successful test President Truman said he hardly hesitated to approve of the usage of the atomic bomb on Japan.

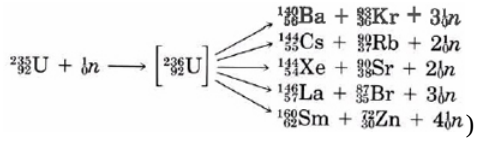
The first atomic bomb was dropped on Hiroshima on August 6, 1945 by the Enola Gay. The bomb destroyed the city, killing almost 100,000 people. The city of Hiroshima was essentially leveled. Following this attack, on August 9, 1945 another atomic bomb was dropped on Nagasaki. The same effects were felt in this city. The United States was ready to drop another atomic bomb in the third week of August, 3 more in September, and 3 more in October if necessary. However, on August 15 Japan surrendered to the allies and World War Two was officially over.



Figure **16.10.1** (left) Hiroshima before the atomic bomb (right) Hiroshima after the atomic bomb

The Workings of the Atomic Bomb

A crucial feature of the fission of uranium without which an atom bomb is impossible is that fission *produces more neutrons than it consumes*. As can be seen from Eqs. (1), for every neutron captured by a $^{235}_{92}\mathrm{U}$ nucleus, between two and four neutrons are produced. Suppose now that we have a very large sample of the pure $^{235}_{92}\mathrm{U}$ isotope and a stray neutron enters this sample. As soon as it hits a $^{235}_{92}\mathrm{U}$ nucleus, fission will take place and about three neutrons will be produced. These in turn will fission three more $^{235}\mathrm{U}$ nuclei, producing a total of nine neutrons. A third repetition will produce 27 neutrons. a fourth 81. and so on. This process (which is called a *chain reaction*) escalates very rapidly. Within a few microseconds a very large number of nuclei fission, with the release of a tremendous amount of energy, and an atomic explosion results.



There are two reasons why a normal sample of uranium metal does not spontaneously explode in this way. In the first place natural uranium consists mainly of the isotope $^{238}_{92}\mathrm{U}$, while the fissionable isotope $^{235}_{92}\mathrm{U}$ comprises only 0.7 percent of the total. Most of the neutrons produced in a given fission process are captured by $^{238}_{92}\mathrm{U}$ nuclei without any further production of neutrons. The escalation of the fission process thus becomes impossible. However, even a sample of pure $^{235}\mathrm{U}$ will not always explode spontaneously. If it is sufficiently small, many of the neutrons will escape into the surroundings without causing further fission. The sample must exceed a **critical mass** before an explosion results. In an atomic bomb several pieces of fissionable material, all of which are below the critical mass, are held sufficiently far apart for no chain reaction to occur. When these are suddenly brought together, an atomic explosion results immediately.

Two types of atomic bombs were developed concurrently during the war: a relatively simple and a more complex . The gun-type design proved impractical to use with , and therefore a simpler gun-type called was developed that used , an that makes up only 0.7 percent of natural . Chemically identical to the most common isotope, , and with almost the same mass, it proved difficult to separate the two.

In parallel with the work on uranium was an effort to produce , which was discovered at the in 1940. After the feasibility of the world's first artificial nuclear reactor, the , was demonstrated in 1942 at the in the , the Project designed the at Oak Ridge and the production reactors at the in , in which uranium was irradiated and into plutonium. The plutonium was then chemically separated from the uranium, using the . The plutonium implosion-type weapon was developed in a concerted design and development effort by the Los Alamos Laboratory.

Isotopic Enrichment

A great deal of the five years of the Manhattan Project was spent in separating the 0.7 percent of $^{235}\mathrm{U}$ from the more abundant $^{238}\mathrm{U}$. Most of this work was performed at the at . This was done by preparing the gaseous compound $\mathrm{UF_6}$ and allowing it to effuse through a porous screen. Each effusion resulted in a gas which was slightly richer in the lighter isotope. Repeating this process eventually produced a compound rich enough in $^{235}\mathrm{U}$ for the purposes of bomb manufacture.

Synthesis of Plutonium

In parallel with the work on uranium was an effort to produce , which was discovered at the in 1940. Only the first bomb dropped on Japan used uranium. The second bomb used the artificial element *plutonium*, produced by the neutron bombardment of $^{238}\mathrm{U}$:

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{239}_{94}\mathrm{Pu} + 2\,{}^{0}_{-1}\beta$$

Fission of Pu-239 occurs in much the same way as for U-235, giving a variety of products; for example,

$$^{239}_{94}\mathrm{Pu} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{90}_{38}\mathrm{Pu} + {}^{147}_{56}\mathrm{Ba} + 3\,{}^{1}_{0}\mathrm{n}$$

Again this is a highly exothermic reaction yielding about the same energy per mole (20 000 GJ $\mathrm{mol^{-1}}$) as $^{235}\mathrm{U}$.

This immense amount of energy released is the reason why plutonium and uranium were used. By comparison, 1 ton of TNT yields about 4 GJ $\mathrm{mol^{-1}}$ of energy. This means that the atomic bombs had about 5,000 times more energy than 1 ton of TNT, that is a huge amount of energy, and explains why the bomb was so effective and destructive.

Nuclear explosion



***Video* 16.10.1** *Nuclear explosion power comparison.*

Although the Fat Man atomic bomb was extremely powerful and destructive, it is not even close to the power of subsequent nuclear bombs. The atomic age was set forth by the United States on those two fateful days in August. In the subsequent years many other countries harnessed the power of nuclear weapons, including Russia, China, Britain, and France. The "high point" of the atomic age came with the explosion of the *Tsar Bomba* by Russia. This bomb was equal to 50 megatons of TNT, or 2,500 times more powerful than the Fat Man bomb. It was said that when the bomb was detonated the shock wave in the ground could be felt over 600 miles away (the bomb wasn't even detonated on the ground either, but rather in mid air!). The advance and use of nuclear weapons seemed to be growing at an extraordinarily fast pace. However, countries stepped up and signed various treaties, including the Nuclear Non-Proliferation Treaty, to stop the increase in nuclear weapons and hopefully the use of any more in the future.

Bomb Construction

At Los Alamos, New Mexico, J. Robert Oppenheimer, and his research group were given the task of assembling and testing the fission bomb. Both types of fuel that were manufactured (U-235 and Pu-239) would be placed separately into two different bomb designs. The smaller of the two bombs would contain U-235 and was code-named "Little Boy." The larger bomb, which housed Pu-239, was named "Fat Man." Of the two, only the Pu-239 bomb would be tested before it was dropped in wartime.

The basic design of the U-235 bomb is shown in the figure below. To prevent the spontaneous detonation of an atomic bomb, the fissile U-235 is kept in a subcritical configuration. It is then rapidly assembled into a supercritical mass using conventional explosives. Once the bomb has achieved this mass, any neutron introduced into it will be likely to initiate a chain reaction. The mechanism for "Little Boy" was a gun that fired one subcritical piece of U-235 into another to form a supercritical mass (Figure **16.10.2**). The pieces had to be assembled within a time less than the average time between appearances of spontaneous neutrons from either U-235 or cosmic radiation. A conventional explosive in an artillery barrel could fire the U-235 mass at speeds of a few millimeters per second, fast enough to prevent a fizzle caused by a spontaneous neutron setting off a premature chain reaction.

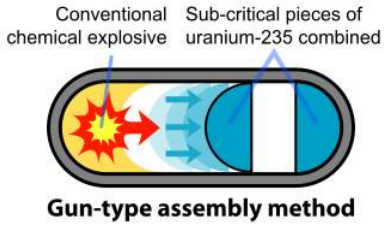


Figure **16.10.2**: Little Boy: Gun-Type Device. (Public Domain).

Originally, the gun-type mechanism was planned for both the U-235 and Pu-239 weapons. However, a problem arose with the Pu-239 bomb that required a different assembly mechanism because of the small amount of Pu-240 that is produced with the Pu-239 in the reactor. Pu-240 emits large numbers of neutrons spontaneously: 1,030 neutrons per gram per second compared with 0.0004 neutrons per gram per second for U-235. Even at a concentration of 1% Pu-240 in the fissile Pu-239, the required mass of Pu emits

52,000 neutrons per second or one neutron every 20 microseconds. Thus, it is very probable that a neutron from Pu-240 will initiate a premature chain reaction during the critical last 100 microseconds of the critical mass in a gun-type assembly. This problem was discovered in mid-1944, well after the start of the construction of the massive Hanford plutonium production facilities.

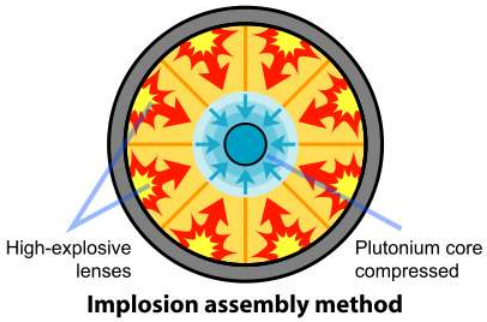


Figure 16.10.3: Fat Man: Implosion-type bomb. (Public Domain).

The removal of the Pu-240 was impractical. So the scientists and engineers looked for a faster method of assembling the plutonium. A mechanism based on implosion provided the solution to this problem. In this design, the fissile material is shaped into a single sphere with a mass slightly less than critical (Figure 16.10.3). Layers of carefully shaped high explosives surround the sphere. When the explosives are detonated, the force of the shock wave compresses the fissile material into a smaller volume, forming a supercritical mass. This method of assembly is much faster than the gun-type mechanism and thus eliminates the problems resulting from spontaneous neutron emission of Pu-240. The spherical mass resulted in a pumpkin-shaped weapon called "Fat Man".

Example 16.10.1

Watch the from the 23-minute mark through the 32-minute mark of the third installment of the History Channel's Manhattan Project and answer the questions below.



1. What were the problems with the two different types of fuel that were to be used in the fission weapons?
2. What was the configuration or set-up of the Pu-239 bomb?
3. The combination of electromagnetic separation and gaseous diffusion enriched enough U-235 to produce how many bombs?
4. Why was the U-235 bomb never tested?
5. When was the construction of the U-235 completed?
6. How much did Truman know about the nuclear bombs when FDR was alive?
7. Who was selected to pilot the plane for the nuclear weapons?
8. What island would serve as a base to house the nuclear bombs before delivering them to their targets?

In July 1945, the United States had enough fissile material for one uranium and two plutonium weapons. The scientists and engineers felt confident that the gun-type assembly mechanism for Little Boy would function properly. Besides, they did not have

the material for a test device. They were less confident about the implosion mechanism on the plutonium weapon and felt that a test was necessary. On July 16, 1945, the first nuclear device, known as "The Gadget", was placed on a 100-foot tower and successfully detonated in the Alamogordo Desert, 200 miles south of Los Alamos (Figure **16.10.4**).

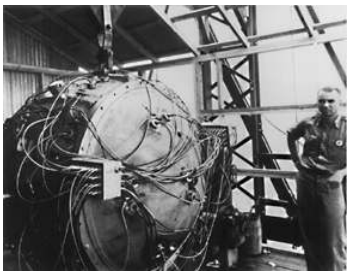


Figure **16.10.4**: The Gadget at the Trinity Test Site, 1945. Courtesy of the U.S. Department of Defense

As the war with Japan continued and a costly allied invasion loomed as a real possibility, President Truman approved the use of nuclear weapons against selected Japanese targets. The U.S. Army Air Force received orders to use these weapons anytime after August 3, 1945. On August 6, "Little Boy" was dropped on Hiroshima (Figure **16.10.5**).



Figure **16.10.5**: Little Boy - The only U-235 weapons constructed during WWII. Courtesy of the U.S. Department of Defense

Little Boy was a uranium weapon containing 141.4 pounds of fissionable material containing 82.7% U-235. Only about two pounds fissioned, releasing an energy equivalent to 15-16,000 tons of TNT. The immediate effects of the blast killed an estimated 70,000 people, and by the end of 1945 an additional 20,000 to 70,000 deaths occurred, many due to lack of adequate medical resources.

Three days later, "Fat Man" destroyed a large part of Nagasaki (Figure **16.10.6**). Fat Man contained 13.6 pounds of Pu-239, of which only 2 pounds underwent fission. The explosive yield was equivalent to about 22,000 tons of TNT. Fat man resulted in 35,000 immediate deaths. By the end of 1945, at least 70,000 people perished in this event.

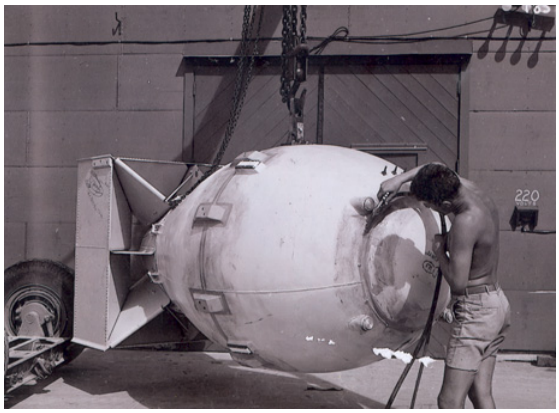


Figure* 16.10.6*: *Fat Man – One of many Pu-239 nuclear weapons constructed during WWII. Courtesy of the U.S. Department of Defense*

Example 16.10.2

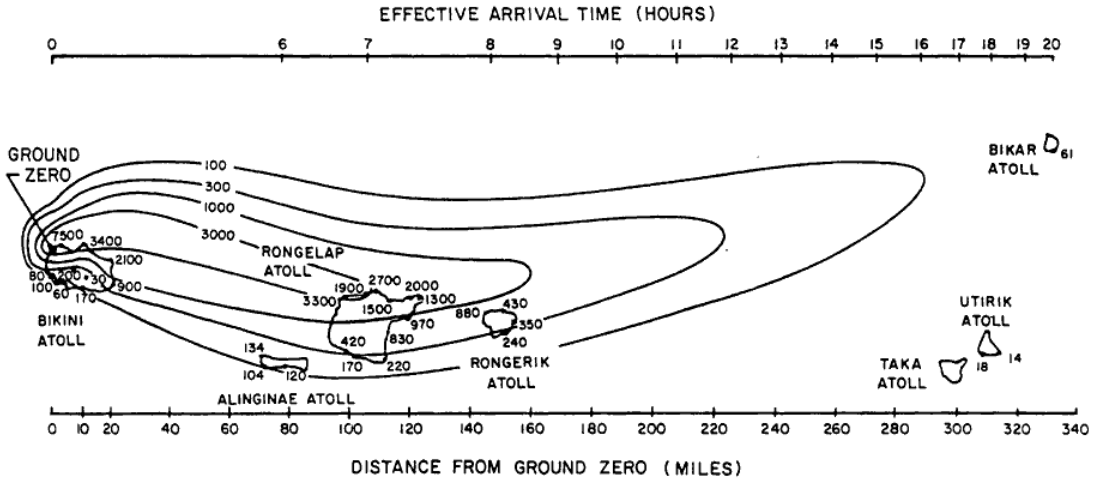
Start the video below at the 23:20 mark and stop it at the 29-minute setting. Then, answer the questions below:



9. When and where was the first nuclear bomb tested?
10. Was the bomb placed on the ground?
11. What were scientists afraid the first nuclear bomb would do?
12. What did Edward Teller (father of the fusion bomb) apply to his skin before the bomb was ignited? Why did he do this?
13. What did the bomb do to the tower and the surrounding sand?
14. In the photograph, where did General Grove focus his attention?

Nuclear Fallout

Nuclear fallout refers to the radioactive material that "falls out" of the atmosphere after a nuclear explosion (reactor or bomb). It consists of dust and radioactive particles that can contaminate an area with radioactivity and pose a huge health hazard to biological organisms. It can contaminate the animal food chain which can have drastic effects on the affected region. Weather has a huge impact on fallout, wind currents can spread radioactive fallout either over a large area, such as in the case of *Castle Bravo*, or not.



alt

Figure 16.10.2: The 450 km (280 mi) fallout plume from 15 Mt shot Castle Bravo, 1954. (Pubic Domain; United States Department of Energy via Wikipedia)

In regards to nuclear reactions, fission produces more fallout products that fusion. Intense heat of the latter type of reactions reduces the amount and type of radioisotopes produced. Although more powerful, fusion is a "cleaner" type of nuclear reaction. By increasing the fission component of a fusion weapon, bombs can be designed to generate more fallout products.Of the different

types of isotopes that fission produces, the most worrisome are Sr-90, Cs-137,and I-131. The first of these isotopes has a half-life of 28.8 years and decays by gamma and beta emission. Once ingested or inhaled, Sr-90 deposits in teeth, bone,and bone marrow. Sr-90 exposure can lead to bone cancer and/or leukemia. Cs-137 ($t_{1/2}$ = 30.17 years) emits beta and gamma radiation. This ionizing radiation deposits in soft tissues of the body. In addition, this particular radioisotope is water soluble and can easily contaminant food and water supplies. I-131 had a half-life over 8.1 days and undergoes gamma/beta decay. Once this fallout product enters the body, it attacks the thyroid gland. Extensive damage could affect heart rate, blood pressure, body temperature, and childhood growth. In addition, I-131 exposure could result in thyroid cancer.

Nuclear Fallout

Watch the fallout video and then answer the questions below:



Summary

- In an atomic bomb several pieces of fissionable material are held sufficiently far apart for no chain reaction to occur. When these are suddenly brought together, the critical mass is reached and an atomic explosion results immediately.
- The two fission bombs assembled at Los Alamos, New Mexico, by J. Robert Oppenheimer, and his research group were manufactured with two types of fuel namely, U-235 and Pu-239.
  - The smaller of the two bombs would contain U-235 and was code-named "Little Boy." This bomb was dropped in Hirsohima, Japan on Aug.6, 1945.
  - The larger bomb, which housed Pu-239, was named "Fat Man." This bomb was dropped in Nagazaki, Japan on Aug.9, 1945.
- Nuclear fallout refers to the radioactive material that "falls out" of the atmosphere after a nuclear explosion (reactor or bomb).

Contributors and Attributions

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CHAPTER OVERVIEW

17: Nutrition

17.1: Calories - Quantity and Quality

17.2: Vitamins, Minerals, Fluids, and Electrolytes

17.3: Weight Loss - Diets and Exercise

17.4: Measuring Fitness

17.5: Some Muscular Chemistry

17.6: Drugs, Athletic Performance, and the Brain

Thumbnail: A meatless burger by Beyond Meat, at a restaurant in Israel. (CC BY-SA 4.0; Ofer Kor via Wikipedia).

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17.1: Calories - Quantity and Quality

Learning Objective

- Know the daily recommended guidelines to achieve a healthy diet.
- Learn how to build a healthy plate.
- Learn about sports nutrition.

A History of Food Guidance in the U.S.

The U.S. Dietary Guidelines for Americans and the DRI are important scientific reports to educate health professionals about nutrition and to guide government and other health-related organizations to develop evidence-based health policies that improve the health of all Americans. The United States government has also been providing food and nutrition guidance directly to the public for more than a century to help individuals make healthier dietary and lifestyle choices . You may have heard about "the Four Food Groups" or "The Food Guide Pyramid" or most recently, "My Plate." The government food guidance system has evolved over the years as our understanding of nutrition science and the impact of diet and lifestyle on health has grown. If you are interested in learning more about the history of food guidance in the U.S. a list and description of former tools can be found at: https://www.choosemyplate.gov/brief-history-usda-food-guides

MyPlate

MyPlate is the most up-to-date nutrition teaching tool. MyPlate was developed by the United States Department of Agriculture (U.S.D.A.) Center for Nutrition Policy and Promotion as an easy to use visual guide to help all American develop healthy eating patterns. It replaces the former MyPyramid teaching tool and correlates with the 2015 - 2020 U.S. Dietary Guidelines.

MyPlate organizes foods with similar nutritional value into specific food groups and provides recommendations about how to build a healthy diet. The ChooseMyPlate.gov website also provides a wide range of support materials including information about each food group, an individualized meal planner, recipes and professional videos and handouts such as the *MyPlate, MyWins* poster shown below to support learning for people of all ages.

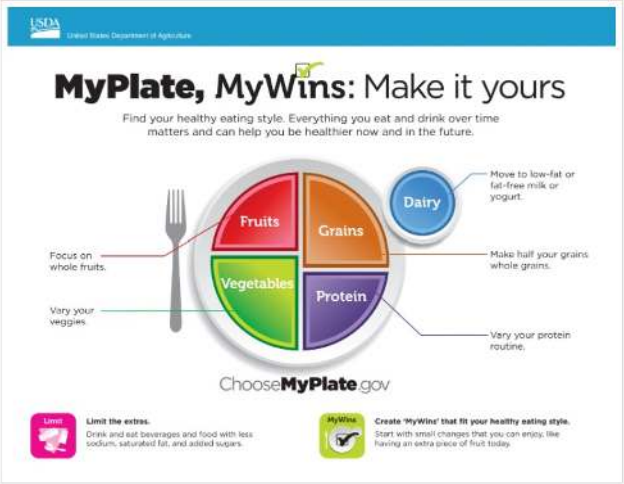


Figure **17.1.1**: Ideal healthy plate.

MyPlate Key Messages include:

- *Focus on whole fruits*
- *Vary your veggies*
- *Vary your protein routine*
- *Make half your grains whole grains*
- *Move to low-fat or fat-free milk or yogurt*
- *Drink and eat beverages and food with less sodium saturated fat and added sugars*
- *Start with small changes that you can enjoy, like having an extra piece of fruit today*

To learn more about MyPlate visit: https://www.choosemyplate.gov/MyPlate

Building a Healthy Plate: Choose Nutrient-Dense Foods

Click on the different food groups listed to view their food gallery:

- Fruits
- Grains
- Dairy
- Vegetables
- Protein

Planning a healthy diet using the MyPlate approach is not difficult. According to the icon, half of your plate should have fruits and vegetables, one-quarter should have whole grains, and one-quarter should have protein. Dairy products should be low-fat or non-fat. The ideal diet gives you the most nutrients within the fewest calories. This means choosing nutrient-rich foods.

Fill half of your plate with red, orange, and dark green vegetables and fruits, such as kale, bok choy, kalo (taro), tomatoes, sweet potatoes, broccoli, apples, mango, papaya , guavas, blueberries, and strawberries in main and side dishes. Vary your choices to get the benefit of as many different vegetables and fruits as you can. You may choose to drink fruit juice as a replacement for eating fruit. (As long as the juice is 100 percent fruit juice and only half your fruit intake is replaced with juice, this is an acceptable exchange.) For snacks, eat fruits, vegetables, or unsalted nuts.

Fill a quarter of your plate with grains such cereals, breads, crackers, rice, and pasta. Half of your daily grain intake should be whole grains. Read the ingredients list on food labels carefully to determine if a food is comprised of whole grains such as 100% whole wheat bread, brown rice and whole grain oats.

Select a variety of protein foods to improve nutrient intake and promote health benefits. Each week, be sure to include a nice array of protein sources in your diet, such as nuts, seeds, beans, legumes, poultry, soy, and seafood. The recommended consumption amount for seafood for adults is two 4-ounce servings per week. When choosing meat, select lean cuts. Be conscious to prepare meats using little or no added saturated fat, such as butter.

If you enjoy drinking milk or eating milk products, such as cheese and yogurt, choose low-fat or nonfat products. Low-fat and nonfat products contain the same amount of calcium and other essential nutrients as whole-milk products, but with much less fat and calories. Calcium, an important mineral for your body, is also available in lactose-free and fortified soy beverage and rice beverage products. You can also get calcium in vegetables and other fortified foods and beverages. You can learn more about "dairy free" sources of calcium by clicking the "Dairy" link on the ChooseMyPlate website.

Fats are essential for your diet as they contain valuable essential fatty acids, but the type you choose and the amount you consume is important. Be sure to choose primarily plant-based liquid oils like olive, soybean and canola oil rather than solid animal fats like butter and lard. You can also get oils from many types of fish, as well as avocados, and unsalted nuts and seeds. Although oils are essential for health they do contain about 120 calories per tablespoon. It is vital to balance oil consumption with total caloric intake. The Nutrition Facts label provides the information to help you make healthful decisions.

In short, substituting vegetables and fruits in place of foods high in added sugars, solid/saturated fats, and sodium is a good way to make a nutrient-poor diet healthy again. Vegetables are full of nutrients and antioxidants that help promote good health and reduce the risk for developing chronic diseases such as stroke, heart disease, high blood pressure, Type 2 diabetes, and certain types of cancer. Starting with these small shifts in your diet as mentioned above will boost your overall health profile.

***Table* 17.1.1:** *Food Replacements.*

Instead of…	Replace with…
Sweetened fruit yogurt	Plain fat-free yogurt with fresh fruit
Whole milk	Low-fat or fat-free milk
Cheese	Low-fat or reduced-fat cheese
Bacon or sausage	Canadian bacon or lean ham
Sweetened cereals	Minimally sweetened cereals with fresh fruit
Apple or berry pie	Fresh apple or berries
Deep-fried French fries	Oven-baked French fries or sweet potato baked fries
Fried vegetables	Steamed or roasted vegetables
Sugary sweetened soft drinks	Seltzer mixed with 100 percent fruit juice
Recipes that call for sugar	Experiment with reducing amount of sugar and adding spices (cinnamon, nutmeg, etc…)

Source: Food Groups. US Department of Agriculture. www.choosemyplate.gov/food-groups/. Updated April 19, 2017. Accessed November 22, 2017.

The MyPlate Planner can be used to create an individualized plan with the number of servings and portion sizes from each food group to eat each day to achieve a healthy diet. You can access the MyPlate Planner from the ChooseMyPlate website:

https://www.choosemyplate.gov/MyPlatePlan

When Enough Is Enough

Estimating Portion Size

Have you ever heard the expression, “Your eyes were bigger than your stomach?” This means that you thought you wanted a lot more food than you could actually eat. Amounts of food can be deceiving to the eye, especially if you have nothing to compare them to. It is very easy to heap a pile of mashed potatoes on your plate, particularly if it is a big plate, and not realize that you have just helped yourself to three portions instead of one.

The food industry makes following the 2015 Dietary Guidelines a challenge. In many restaurants and eating establishments, portion sizes have increased, use of SoFAS has increased, and consequently the typical meal contains more calories than it used to. In addition, our sedentary lives make it difficult to expend enough calories during normal daily activities. In fact, more than one-third of adults are not physically active at all.

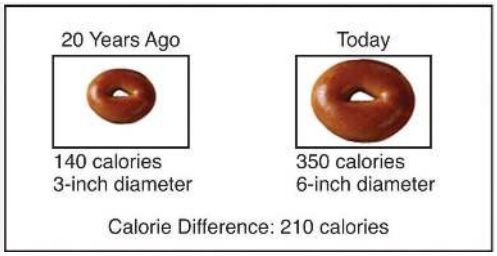


Figure **17.1.2**: A Comparison of Serving Sizes.

Source: https://www.nhlbi.nih.gov/health/edu...uments/PD1.pdf

As food sizes and servings increase it is important to limit the portions of food consumed on a regular basis. Dietitians have come up with some good hints to help people tell how large a portion of food they really have. Some suggest using common items such as a deck of cards while others advocate using your hand as a measuring rule.

See Table below for some examples.

Source: American Cancer Society. “Controlling Portion Sizes.” Last revised January 12, 2012. http://www.cancer.org/Healthy/EatHealthyGetActive/TakeControlofYourWeight/controlling-portion-sizes.

***Table* 17.1.2:** *Determining Food Portions.*

Food Product	Amount	Object Comparison	Hand Compa
Pasta, rice	½ c.	Tennis ball	Cupped hand
Fresh vegetables	1 c.	Baseball	
Cooked vegetables	½ c.		Cupped hand
Meat, poultry, fish	3 oz.	Deck of cards	Palm of your
Milk or other beverages	1 c.	Fist	
Salad dressing	1 Tbsp.	Thumb	
Oil	1 tsp.	Thumb tip	

everyday connection

If you wait many hours between meals, there is a good chance you will overeat. To refrain from overeating try consuming small meals at frequent intervals throughout the day as opposed to two or three large meals. Eat until you are satisfied, not until you feel “stuffed.” Eating slowly and savoring your food allows you to both enjoy what you eat and have time to realize that you are full before you get overfull. Your stomach is about the size of your fist but it expands if you eat excessive amounts of food at one sitting. Eating smaller meals will diminish the size of your appetite over time so you will feel satisfied with smaller amounts of food.

Discretionary Calories

When following a balanced, healthful diet with many nutrient-dense foods, you may consume enough of your daily nutrients before you reach your daily calorie limit. The remaining calories are discretionary (to be used according to your best judgment). To find out your discretionary calorie allowance, add up all the calories you consumed to achieve the recommended nutrient intakes and then subtract this number from your recommended daily caloric allowance. For example, someone who has a recommended 2,000-calorie per day diet may eat enough nutrient-dense foods to meet requirements after consuming only 1,814 calories. The remaining 186 calories are discretionary. See Table **17.1.1**. These calories may be obtained from eating an additional piece of fruit, adding another teaspoon of olive oil on a salad or butter on a piece of bread, adding sugar or honey to cereal, or consuming an alcoholic beverage[1].

The amount of discretionary calories increases with physical activity level and decreases with age. For most physically active adults, the discretionary calorie allowance is, at most, 15 percent of the recommended caloric intake. By consuming nutrient-dense foods, you afford yourself a discretionary calorie allowance.

***Table* 17.1.3:** *Sample Menu Plan Containing 2,000 Calories.*

Meal	Calories	Total Meal/Snack Calori
Breakfast		
1 scrambled egg	92	
with sliced mushrooms and spinach	7	
½ whole-wheat muffin	67	
1 tsp. margarine-like spread	15	
1 orange	65	
8 oz. low-sodium tomato juice	53	299
Snack		
6 oz. fat-free flavored yogurt	100	
with ½ c. raspberries	32	132
Lunch		
1 sandwich on pumpernickel bread	160	
with smoked turkey deli meat,	30	
4 slices tomato	14	
2 lettuce leaves	3	
1 tsp. mustard	3	
1 oz. baked potato chips	110	
½ c. blueberries, with 1 tsp. sugar	57	
8 oz. fat-free milk	90	467
Snack		
1 banana	105	
7 reduced-fat high-fiber crackers	120	225
Dinner		
1 c. Greek salad (tomatoes, cucumbers, feta)	150	
with 5 Greek olives,	45	
with 1.5 tsp. olive oil	60	
3 oz. grilled chicken breast	150	
½ c. steamed asparagus	20	
with 1 tsp. olive oil,	40	
with 1 tsp. sesame seeds	18	
½ c. cooked wild rice	83	
with ½ c. chopped kale	18	
1 whole-wheat dinner roll	4	
with 1 tsp. almond butter	33	691
(Total calories from all meals and snacks = 1,814)		
Discretionary calorie allowance: 186		

(Total calories from all meals and snacks = 1,814)
Discretionary calorie allowance: 186

Web Links and DRI

You can access the MyPlate Planner from the ChooseMyPlate website:

https://www.choosemyplate.gov/MyPlatePlan

Recommended amounts of food from each food group at different calorie levels can be found on the link: https://health.gov/dietaryguidelines/2015/guidelines/appendix-3/

Dietary Reference Intakes (DRIs) are more than numbers in the table, even though that is often how many people view them. DRIs and Dietary Guidelines provide different information for different audiences.

- Dietary Guidelines provide **qualitative** advice to the public about diet and chronic disease prevention and maintaining health.
- DRIs provide **quantitative** advice to professionals about amounts of nutrients or food components to be of benefit.
- DRIs are a collective term to refer to these components:
  - Estimated Average Requirement (EAR)
  - Recommended Dietary Allowance (RDA)
  - Adequate Intake (AI)
  - Tolerable Upper Intake Level (UL). A number of people refer to the UL as simply the “upper limit”, leaving off “tolerable”.

The RDA is the measure that professionals use to assess the quality of people's diets. It is the requirement estimated to meet the needs of 97.5% of the population. But the RDA is calculated using the EAR. Therefore, the EAR needs to be set before an RDA can be set. There must be applicable research in order to set an EAR. An EAR is the estimated requirement for 50% of the population

(hence the average in its name).

Nutrition and the Athlete

Nutrition is essential to your performance during all types of exercise. The foods consumed in your diet are used to provide the body with enough energy to fuel an activity regardless of the intensity of activity. Athletes have different nutritional needs to support the vigorous level they compete and practice at.

Energy Needs

To determine an athletes nutritional needs, it is important to revisit the concept of energy metabolism. Energy intake is the foundation of an athlete's diet because it supports optimal body functions, determines the amount of intake of macronutrients and micronutrients, and assists in the maintaining of body composition. Energy needs for athletes increase depending on their energy expenditure. The energy expended during physical activity are contingent on the intensity, duration, and frequency of the exercise. Competitive athletes may need 3,000 to over 5,000 calories daily compared to a typical inactive individual who needs about 2,000 calories per day. Energy needs are also affected by an individual's gender, age, and weight. Weight-bearing exercises, such as running, burn more calories per hour than non-weight bearing exercises, such as swimming. Weight-bearing exercises requires your body to move against gravity which requires more energy. Men are also able to burn more calories than women for the same activity because they have more muscle mass which requires more energy to support and move around.[1]

Body weight and composition can have a tremendous impact on exercise performance. Body weight and composition are considered the focal points of physique for athletes because they are the able to be manipulated the most. Energy intake can play a role in manipulating the physiques for athletes. For individuals competing in sports such as football and weight lifting, having a large amount of muscle mass and increased body weight may be beneficial. This can be obtained through a combination of increased energy intake, and protein. Although certain physiques are more advantageous for specific sports, it is important to remember that a single and rigid "optimal" body composition is not recommended for any group of athletes.[2]

Macronutrient Needs

The composition of macronutrients in the diet is a key factor in maximizing performance for athletes. Carbohydrates are an important fuel source for the brain and muscle during exercise. Carbohydrate storage in the liver and muscle cells are relatively limited and therefore it is important for athletes to consume enough carbohydrates from their diet. Carbohydrate needs should increase about 3-10 g/kg/day depending on the type of training or competition.[3] See Table **17.1.1** for carbohydrate needs for athletes depending on the intensity of the exercise.

Table **17.1.4**: Daily Needs for Carbohydrate Fuel.

Activity Level	Example of Exercise	Increase of Carbohydrate (g/kg of athlete's body weight/day)
Light	Low intensity or skill based activities	3-5
Moderate	Moderate exercise program (about 1 hour per day)	5-7
High	Endurance program (about 1-3 hours per day of moderate to high intensity exercise)	6-10
Very High	Extreme commitment (4-5 hours per day of moderate to high intensity exercise)	8-12

Source: Nutrition and Athletic Performance. American College of Sports Medicine.Medicine & Science in Sports & Exercise. 2016; 48(3), 543- 568.

https://journals.lww.com/acsm-msse/Fulltext/2016/03000/Nutrition_and_Athletic_Performance.25.aspx. Accessed March 17, 2018.

Fat is a necessary component of a healthy diet to provide energy, essential fatty acids and to facilitate the absorption of fat-soluble vitamins. Athletes are recommended to consume the same amount of fat in the diet as the general population, 20-35% of their energy intake. Although these recommendations are in accordance with public health guidelines, athletes should individualize their needs based on their training level and body composition goals. Athletes who choose to excessively restrict their fat intake in an effort to lose body weight or improve body composition should ensure they are still getting the minimum recommended amount of fat. Fat intakes below 20% of energy intake will reduce the intake of fat-soluble vitamins and essential fatty acids, especially omega 3's. [4]

Although protein accounts for only about 5% of energy expended, dietary protein is necessary to support metabolic reactions (that generate ATP), and to help muscles with maintenance, growth, and repair. During exercise, these metabolic reactions for generating ATP rely heavily on proteins such as enzymes and transport proteins. It is recommended that athletes consume 1.2 to 2.0 g/kg/day of proteins in order to support these functions. Higher intakes may also be needed for short periods of intense training or when reducing energy intake.[5] See Table **17.1.2** below for a better representation of protein needs depending on extent of training and dietary sources.

Table **17.1.5**: The Recommended Protein Intakes for Individuals.

Group	**Protein Intake (g/kg body weight)**
Most adults	0.8
Endurance athletes	1.2 to 1.4
Vegetarian endurance athletes	1.3 to 1.5
Strength athletes	1.6 to 1.7
Vegetarian strength athletes	1.7 to 1.8

Source: Dietary Reference Intakes, 2002 ACSM/ADA/Dietitians of Canada Position Statement: Nutrition & Athletic Performance, 2001. Accessed March 17, 2018.

It is important to consume adequate amounts of protein and to understand that the quality of the protein consumed affects the amount needed. High protein foods such as meats, dairy, and eggs contain all of the essential amino acids in relative amounts that most efficiently meet the body's needs for growth, maintenance and repair of muscles. Vegetarian diets contain protein that has lower digestibility and amino acid patterns that do not match human needs as closely as most animal proteins. To compensate for this as well as the fact that plant food protein sources also contain higher amounts of fiber, higher protein intakes are recommended for vegetarian athletes. (See Table 16.2 "The Recommended Protein Intakes for Individuals")

Micronutrient Needs

Vitamins and minerals are essential for energy metabolism, the delivery of oxygen, protection against oxidative damage, and the repair of body structures. When exercise increases, the amount of many vitamins and minerals needed are also increased due to the excess loss in nutrients. Currently, there is not special micronutrient recommendations made for athletes but most athletes will meet their needs by consuming a balanced diet that meets their energy needs. Because the energy needs of athletes increase, they often consume extra vitamins and minerals. The major micronutrients of concern for athletes include iron, calcium, vitamin D, and some antioxidants. [6]

Web Links

Estimated Calorie Needs per Day, by Age, Sex, and Physical Activity: https://health.gov/dietaryguidelines/2015/guidelines/appendix-2/

Nutrition and a Healthy Diet

There are five key factors that make up a healthful diet:

1. *A diet must be adequate, by providing sufficient amounts of each essential nutrient, as well as fiber and adequate calories.*
2. *A balanced diet results when you do not consume one nutrient at the expense of another, but rather get appropriate amounts of all nutrients.*
3. *Calorie control is necessary so that the amount of energy you get from the nutrients you consume equals the amount of energy you expend during your day's activities.*
4. *Moderation means not eating to the extremes, neither too much nor too little.*
5. *Variety refers to consuming different foods from within each of the food groups on a regular basis.*

A healthy diet is one that favors whole foods. As an alternative to modern processed foods, a healthy diet focuses on "real" fresh whole foods that have been sustaining people for generations. Whole foods supply the needed vitamins, minerals, protein, carbohydrates, fats, and fiber that are essential to good health. Commercially prepared and fast foods are often lacking nutrients and often contain inordinate amounts of sugar, salt, saturated and trans fats, all of which are associated with the development of diseases such as atherosclerosis, heart disease, stroke, cancer, obesity, diabetes, and other illnesses. A balanced diet is a mix of food from the different food groups (vegetables, legumes, fruits, grains, protein foods, and dairy).

Adequacy

An adequate diet is one that favors nutrient-dense foods. Nutrient-dense foods are defined as foods that contain many essential nutrients per calorie. Nutrient-dense foods are the opposite of "empty-calorie" foods, such as sugary carbonated beverages, which are also called "nutrient-poor." Nutrient-dense foods include fruits and vegetables, lean meats, poultry, fish, low-fat dairy products, and whole grains. Choosing more nutrient-dense foods will facilitate weight loss, while simultaneously providing all necessary nutrients.

Balance

Balance the foods in your diet. Achieving balance in your diet entails not consuming one nutrient at the expense of another. For example, calcium is essential for healthy teeth and bones, but too much calcium will interfere with iron absorption. Most foods that are good sources of iron are poor sources of calcium, so in order to get the necessary amounts of calcium and iron from your diet, a proper balance between food choices is critical. Another example is that while sodium is an essential nutrient, excessive intake may contribute to congestive heart failure and chronic kidney disease in some people. Remember, everything must be consumed in the proper amounts.

Moderation

Eat in moderation. Moderation is crucial for optimal health and survival. Eating nutrient-poor foods each night for dinner will lead to health complications. But as part of an otherwise healthful diet and consumed only on a weekly basis, this should not significantly impact overall health. It's important to remember that eating is, in part, about enjoyment and indulging with a spirit of moderation. This fits within a healthy diet.

Monitor food portions. For optimum weight maintenance, it is important to ensure that energy consumed from foods meets the energy expenditures required for body functions and activity. If not, the excess energy contributes to gradual, steady accumulation of stored body fat and weight gain. In order to lose body fat, you need to ensure that more calories are burned than consumed. Likewise, in order to gain weight, calories must be eaten in excess of what is expended daily.

Variety

Variety involves eating different foods from all the food groups. Eating a varied diet helps to ensure that you consume and absorb adequate amounts of all essential nutrients required for health. One of the major drawbacks of a monotonous diet is the risk of consuming too much of some nutrients and not enough of others. Trying new foods can also be a source of pleasure—you never know what foods you might like until you try them.

Developing a healthful diet can be rewarding, but be mindful that all of the principles presented must be followed to derive maximal health benefits. For instance, introducing variety in your diet can still result in the consumption of too many high-calorie, nutrient poor foods and inadequate nutrient intake if you do not also employ moderation and calorie control. Using all of these principles together will promote lasting health benefits.

Summary

- MyPlate is the most up-to-date nutrition teaching tool developed by the United States Department of Agriculture (U.S.D.A.) Center for Nutrition Policy and Promotion as an easy to use visual guide to help all American develop healthy eating patterns.
- Planning a healthy diet using the MyPlate approach is not difficult. According to the icon, half of your plate should have fruits and vegetables, one-quarter should have whole grains, and one-quarter should have protein. Dairy products should be low-fat or non-fat.
- Energy needs for athletes increase depending on their energy expenditure. The energy expended during physical activity are contingent on the intensity, duration, and frequency of the exercise. Competitive athletes may need 3,000 to over 5,000 calories daily compared to a typical inactive individual who needs about 2,000 calories per day. Energy needs are also affected by an individual's gender, age, and weight.
- There are five key factors that make up a healthful diet namely: a. adequacy, b. balance, c. calorie control, d. moderation, and e. variety.
- The total number of calories a person needs each day varies depending on a number of factors, including the person's age, sex, height, weight, and level of physical activity.

Contributors and Attributions

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17.2: Vitamins, Minerals, Fluids, and Electrolytes

Learning Objective

List the dietary requirements for vitamins and minerals.

Learn about food supplements.

Learn about water balance.

The importance of vitamins and minerals (micronutrients) in metabolism has been discussed in detail in section 17.4. Micronutrient needs in adults differ slightly according to sex. Young men and women who are very athletic and perspire a great deal also require extra sodium, potassium, and magnesium. Males require more of vitamins C and K, along with thiamine, riboflavin, and niacin. Females require extra iron due to menstruation. Therefore, it can be beneficial for some young adults to follow a daily multivitamin regimen to help meet nutrient needs. But as always, it is important to remember "food first, supplements second." Table **17.2.1** shows the micronutrient recommendations for adult men and women.

Table **17.2.1** Micronutrient Levels during Adulthood.

Nutrient	Adult Males	Adult Females
Vitamin A (mcg)	900.0	700.0
Vitamin B6 (mg)	1.3	1.3
Vitamin B12 (mcg)	2.4	2.4
Vitamin C (mg)	90.0	75.0
Vitamin D (mcg)	5.0	5.0
Vitamin E (mg)	15.0	15.0
Vitamin K (mcg)	120.0	90.0
Calcium (mg)	1,000.0	1,000.0
Folate (mcg)	400.0	400.0
Iron (mg)	8.0	18.0
Magnesium (mg)	400.0	310.0
Niacin (mg)	16.0	14.0
Phosphorus (mg)	700.0	700.0
Riboflavin (mg)	1.3	1.1
Selenium	55.0	55.0
Thiamin (mg)	1.2	1.1
Zinc (mg)	11.0	8.0

Source: Institute of Medicine. 2006. Dietary Reference Intakes: The Essential Guide to Nutrient Requirements. Washington, DC: The National Academies Press. https://doi.org/10.17226/11537. Accessed December 10, 2017.

Food Supplements and Food Replacements

Current trends also include the use of supplementation to promote health and wellness. Vitamins, minerals, herbal remedies, and supplements of all kinds constitute big business and many of their advertising claims suggest that optimal health and eternal youth

are just a pill away. Dietary supplements can be macronutrient (amino acids, proteins, essential fatty acids), micronutrient (vitamins and minerals that promote healthy body functions), probiotic (beneficial bacteria such as the kind found in the intestines), and herbally (often target a specific body part, such as bones) based.

Some public health officials recommend a daily multivitamin due to the poor diet of most North Americans. The US Preventive Task Force also recommends a level of folate intake which can be easier to achieve with a supplement. In addition, the following people may benefit from taking daily vitamin and mineral supplements:[1]

- Women who are pregnant or breastfeeding
- Premenopausal women who may need extra calcium and iron
- Older adults
- People with health issues that affect their ability to eat
- Vegetarians, vegans, and others avoiding certain food groups

However, before you begin using dietary supplementation, consider that the word supplement denotes something being added. Vitamins, minerals, and other assorted remedies should be considered as extras. They are add-ons—not replacements—for a healthy diet. As food naturally contains nutrients in its proper package, remember that food should always be your primary source of nutrients. When considering taking supplements, it is important to recognize possible drawbacks that are specific to each kind: [2]

- **Micronutrient Supplements:** Some vitamins and minerals are toxic at high doses. Therefore, it is vital to adhere to the Tolerable Upper Intake Levels (UL) so as not to consume too much of any vitamin. For example, too much vitamin A is toxic to the liver. Symptoms of vitamin A toxicity can include tinnitus (ringing in the ears), blurred vision, hair loss, and skin rash. Too much niacin can cause a peptic ulcer, hyperglycemia, dizziness, and gout.
- **Herbal Supplements:** Some herbs cause side effects, such as heart palpitations and high blood pressure, and must be taken very carefully. Also, some herbs have contraindications with certain medicines. For example, Valerian and St. John's Wort negatively interact with certain prescription medications, most notably antidepressants. Additionally, there is a real risk of overdosing on herbs because they do not come with warning labels or package inserts.
- **Amino Acid Supplements:** Certain amino acid supplements, which are often taken by bodybuilders among others, can increase the risk of consuming too much protein. An occasional amino acid drink in the place of a meal is not a problem. However, problems may arise if you add the supplement to your existing diet. Most Americans receive two to three times the amount of protein required on a daily basis from their existing diets—taking amino acid supplements just adds to the excess. Also, certain amino acids share the same transport systems in the absorption process; therefore, a concentrated excess of one amino acid obtained from a supplement may increase the probability of decreased absorption of another amino acid that uses the same transport system. This could lead to deficiency in the competing amino acid.

Supplement Claims and Restrictions

The Food and Drug Administration (FDA) regulates supplements, but it treats them like food rather than pharmaceuticals. Dietary supplements must meet the FDA's Good Manufacturing Standards, but are not required to meet the standards for drugs, although some companies do so voluntarily. Also, although supplement manufacturers are allowed to say a particular ingredient may reduce the risk of a disease or disorder, or that it might specifically target certain body systems, these claims are not approved by the FDA. This is why labels that make structural and functional claims are required to carry a disclaimer saying the product is not intended "to diagnose, treat, cure, or prevent any disease." In addition, in the United States, supplements are taken off the market only after the FDA has proven that they are hazardous.[3] To revisit the topic of structural and functional claims refer back to Chapter 12 "Nutrition Applications".

Before Taking Supplements

The phrase caveat emptor means "buyer beware," and it is important to keep the term in mind when considering supplementation. Just because a product is "natural" does not mean it can't be harmful or dangerous, particularly if used inappropriately. The following are helpful questions to explore before deciding to take a supplement:

- Does the scientific community understand how this supplement works and are all its effects well known?
- Is there proof that the supplement actually performs in the manner that it claims?

- Does this supplement interact with food or medication?
- Is taking this supplement necessary for my health?
- Is the supplement affordable?
- Is the supplement safe and free from contaminants?

Lastly, please remember that a supplement is only as good as the diet that accompanies it. We cannot overstate the importance of eating a healthy, well-balanced diet designed to provide all of the necessary nutrients. Food contains many more beneficial substances, such as phytochemicals and fiber, that promote good health and cannot be duplicated with a pill or a regimen of supplements. Therefore, vitamins and other dietary supplements should never be a substitute for food. Nutrients should always be derived from food first.

Food: The Best Medicine

Poor dietary choices and a sedentary lifestyle account for about 300–600 thousand deaths every year according to the US Department of Health and Human Services. That number is thirteen times higher than the deaths due to gun violence.[4] The typical North American diet is too high in saturated fat, sodium, and sugar, and too low in fiber in the form of whole fruits, vegetables, and whole grains to keep people healthy. With so many threats to optimal health it is vital to address those factors that are under your control, namely dietary and lifestyle choices. A diet that supplies your body with the needed energy and nutrients daily will result in efficient body functioning and in protection from disease. Making sound nutritional choices can also provide support for individuals undergoing treatment for short-term or chronic conditions. Finding a balance between nutritional needs with concerns about drug interactions can hasten recovery, improve quality of life, and minimize the side effects from treatment protocols.

Body Fluids and Electrolytes

Maintaining the right level of water in your body is crucial to survival, as either too little or too much water in your body will result in less-than-optimal functioning. One mechanism to help ensure the body maintains water balance is thirst. Thirst is the result of your body's physiology telling your brain to initiate the thought to take a drink. Sensory proteins detect when your mouth is dry, your blood volume too low, or blood electrolyte concentrations too high and send signals to the brain stimulating the conscious feeling to drink.

The latest National Health and Nutrition Examination Survey, covering the period from 2005 to 2008, reports that about 50 percent of Americans consume sugary drinks daily.

Excess consumption of sugary soft drinks have been scientifically proven to increase the risk for dental caries, obesity, Type 2 diabetes, and cardiovascular disease. In addition to sugary soft drinks, beverages containing added sugars include fruit drinks, sports drinks, energy drinks and sweetened bottled waters.

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?

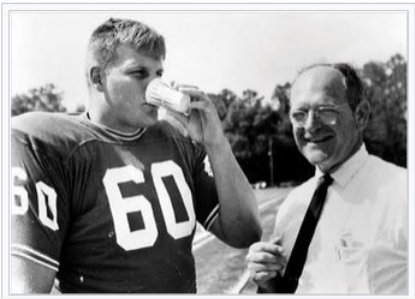
Typically, eight ounces of a sports drink provides between fifty and eighty calories and 14 to 17 grams of carbohydrate, mostly in the form of simple sugars. Sodium and potassium are the most commonly included electrolytes in sports drinks, with the levels of these in sports drinks being highly variable. 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

Gatorade was created in 1965, by a team of scientists at the University of Florida College of Medicine, including Robert Cade, Dana Shires, Harry James Free, and Alejandro de Quesada. Following a request from Florida Gators football head coach Ray Graves, Gatorade was created to help athletes by acting as a replacement for body fluids lost during physical exertion. The earliest version of the beverage consisted of a mixture of water,sodium, sugar, potassium, phosphate, and lemon juice.Ten

players on the University of Florida football team tested the first version of Gatorade during practices and games in 1965, and the tests were deemed successful.

The University of Florida researchers initially considered naming their product "Gator-Aid". They settled on the name Gatorade, however, since the researchers wanted to create a commercial product, not a scientifically-validated one.



University of Florida football player Chip Hinton testing Gatorade in 1965, pictured next to the leader of its team of inventors, Robert Cade. Source: Wikipedia

Regulation of Daily Water Input

Total water output per day averages 2.5 liters (Figure **17.2.1**). This must be balanced with water input. Our tissues produce around 300 milliliters of water per day through metabolic processes. The remainder of water output must be balanced by drinking fluids and eating solid foods. The average fluid consumption per day is 1.5 liters, and water gained from solid foods approximates 700 milliliters.

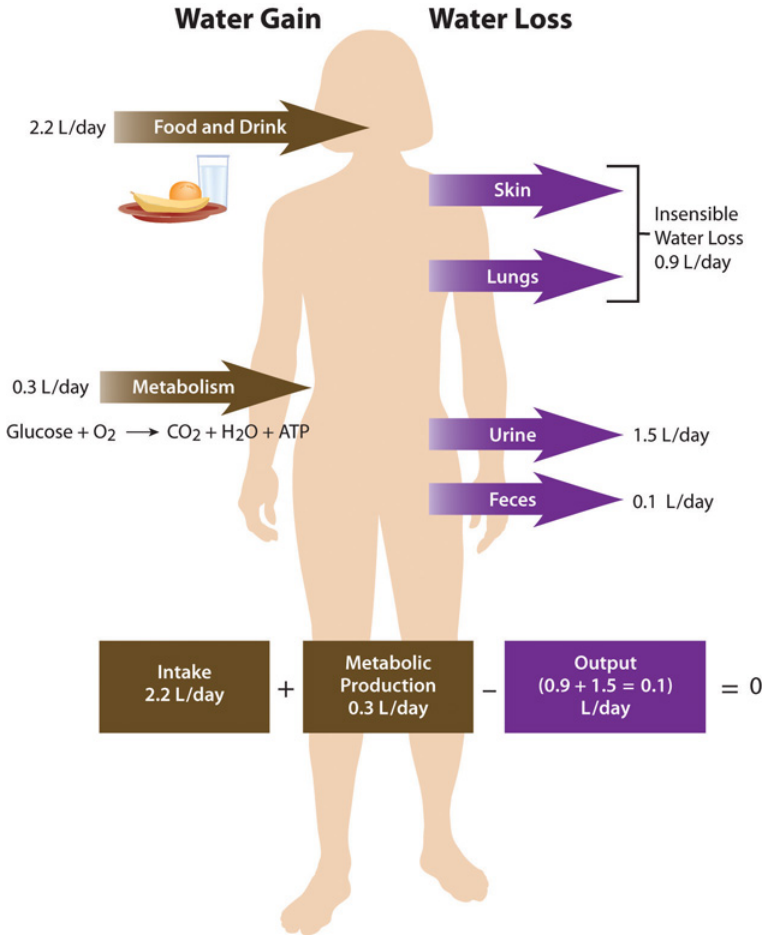


Figure **17.2.1** Daily fluid loss and gain.

The Food and Nutrition Board of the Institute of Medicine (IOM) has set the Adequate Intake (AI) for water for adult males at 3.7 liters (15.6 cups) and at 2.7 liters (11 cups) for adult females. These intakes are higher than the average intake of 2.2 liters. It is important to note that the AI for water includes water from all dietary sources; that is, water coming from food as well as beverages. People are not expected to consume 15.6 or 11 cups of pure water per day. In America, approximately 20 percent of dietary water comes from solid foods.

Consequences of Deficiency or Excess

As with all nutrients, having too much or too little water has health consequences. Excessive water intake can dilute the levels of critical electrolytes in the blood. Water intoxication is rare, however when it does happen, it can be deadly. On the other hand, having too little water in the body is common. In fact, diarrhea-induced dehydration is the number-one cause of early-childhood death worldwide. In this section we will discuss subtle changes in electrolytes that compromise health on a chronic basis.

High-Hydration Status: Water Intoxication/ Hyponatremia

Water intoxication mainly affects athletes who overhydrate. Water intoxication is extremely rare, primarily because healthy kidneys are capable of excreting up to one liter of excess water per hour. Overhydration was unfortunately demonstrated in 2007 by Jennifer Strange, who drank six liters of water in three hours while competing in a “Hold Your Wee for a Wii” radio contest. Afterward she complained of a headache, vomited, and died.

Low-Hydration Status: Dehydration

Dehydration refers to water loss from the body without adequate replacement. It can result from either water loss or electrolyte imbalance, or, most commonly, both. Dehydration can be caused by prolonged physical activity without adequate water intake, heat exposure, excessive weight loss, vomiting, diarrhea, blood loss, infectious diseases, malnutrition, electrolyte imbalances, and very high glucose levels. Physiologically, dehydration decreases blood volume. The water in cells moves into the blood to compensate for the low blood-volume, and cells shrink. Signs and symptoms of dehydration include thirst, dizziness, fainting, headaches, low blood-pressure, fatigue, low to no urine output, and, in extreme cases, loss of consciousness and death. Signs and symptoms are usually noticeable after about 2 percent of total body water is lost.

Chronic dehydration is linked to higher incidences of some diseases. There is strong evidence that low-hydration status increases the risk for kidney stones and exercise-induced asthma. There is also some scientific evidence that chronic dehydration increases the risk for kidney disease, heart disease, and the development of hyperglycemia in people with diabetes. Older people often suffer from chronic dehydration as their thirst mechanism is no longer as sensitive as it used to be.

Summary

- Micronutrient needs in adults differ slightly according to sex. Young men and women who are very athletic and perspire a great deal also require extra sodium, potassium, and magnesium. Males require more of vitamins C and K, along with thiamine, riboflavin, and niacin. Females require extra iron due to menstruation.
- Current trends also include the use of supplementation to promote health and wellness. Dietary supplements can be macronutrient (amino acids, proteins, essential fatty acids), micronutrient (vitamins and minerals that promote healthy body functions), probiotic (beneficial bacteria such as the kind found in the intestines), and herbally (often target a specific body part, such as bones) based.
- The Food and Nutrition Board of the Institute of Medicine (IOM) has set the Adequate Intake (AI) for water for adult males at 3.7 liters (15.6 cups) and at 2.7 liters (11 cups) for adult females. It is important to note that the AI for water includes water from all dietary sources; that is, water coming from food as well as beverages.
- Total water output per day averages 2.5 liters which must be balanced with water input.
- Excessive water intake can dilute the levels of critical electrolytes in the blood. Water intoxication is rare, however when it does happen, it can be deadly. On the other hand, having too little water in the body is common.

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17.3: Weight Loss - Diets and Exercise

Learning Objective

- Learn about various recommendations for weight loss and weight management.

With over 70 percent of Americans currently overweight or obese, it isn't surprising that many individuals report engaging in weight management efforts. [1] In fact, a 2019 report from a national survey on current trends in weight loss attempts and strategies found that 42 percent of adults in the United States had recently attempted to lose weight, primarily through reduced food consumption and exercise.

The National Weight Control Registry (NWCR) has tracked over ten thousand people who have been successful in losing at least 30 pounds and maintaining this weight loss for at least one year. Their research findings show that 98 percent of participants in the registry modified their food intake, and 94 percent increased their physical activity, mainly by walking.

Although there were a great variety of approaches taken by NWCR members to achieve successful weight loss, most have reported that their approach involved adhering to a low-calorie, low-fat diet and doing high levels of activity (about one hour of exercise per day). Moreover, most members eat breakfast every day, watch fewer than ten hours of television per week, and weigh themselves at least once per week. About half of them lost weight on their own, and the other half used some type of weight-loss program. [11] In most scientific studies, successful weight loss is accomplished only by changing the diet and increasing physical activity together. Doing one without the other limits the amount of weight lost and the length of time that weight loss is sustained.

Evidence-Based Dietary Recommendations

The 2015 Dietary Guidelines for Americans offers specific, evidence-based recommendations for dietary changes aimed at keeping calorie intake in balance with physical activity, which is key for weight management. These recommendations include:

Follow a healthy eating pattern that accounts for all foods and beverages within an appropriate calorie level that includes:

- A variety of vegetables from all of the subgroups—dark green, red and orange, legumes (beans and peas), starchy, and other
- Fruits, especially whole fruits
- Grains, at least half of which are whole grains
- Fat-free or low-fat dairy, including milk, yogurt, cheese, and/or fortified soy beverages
- A variety of protein foods, including seafood, lean meats and poultry, eggs, legumes (beans and peas), and nuts, seeds, and soy products
- Oils

A healthy eating pattern limits:

- Saturated fats and trans fats
- Added sugars
- Sodium

Key quantitative recommendations are provided for several components of the diet that should be limited. These components are of particular public health concern in the United States, and the specified limits can help individuals achieve healthy eating patterns within calorie limits[5]:

- Consume less than 10 percent of calories per day from added sugars
- Consume less than 10 percent of calories per day from saturated fats
- Consume less than 2,300 milligrams (mg) per day of sodium

If alcohol is consumed, it should be consumed in moderation—up to one drink per day for women and up to two drinks per day for men—and only by adults of legal drinking age.

Dietary Food Trends

In the past, health was regarded merely as the absence of illness. However, a growing understanding of the complexity and potential of the human condition has prompted a new way of thinking about health. Today, we focus on the idea of wellness, which involves a great deal more than just not being sick. Wellness is a state of optimal well-being that enables an individual to maximize their potential. This concept includes a host of dimensions—physical, mental, emotional, social, environmental, and spiritual—which affect one's quality of life. Striving for wellness begins with an examination of dietary choices.

Hundreds of years ago, when food was less accessible and daily life required much more physical activity, people worried less about obesity and more about simply getting enough to eat. In today's industrialized nations, conveniences have solved some problems and introduced new ones, including the hand-in-hand obesity and diabetes epidemics. Fad diets gained popularity as more North Americans struggled with excess pounds. However, new evidence-based approaches that emphasize more holistic measures are on the rise. These new dietary trends encourage those seeking to lose weight to eat healthy, whole foods first, while adopting a more active lifestyle. These sound practices put dietary choices in the context of wellness and a healthier approach to life.

Functional Foods

Many people seek out foods that provide the greatest health benefits. This trend is giving rise to the idea of functional foods, which not only help meet basic nutritional needs but also are reported to fight illness and aging. According to the Academy of Nutrition and Dietetics (AND), formerly known as the The American Dietetic Association, functional foods may reduce the risk of disease or promote optimal health. The AND recognizes four types of functional foods. They are: conventional foods, modified foods, medical foods, and special dietary use foods.

The first group, conventional foods, represents the simplest form of functional foods. They are whole foods that have not been modified. Examples include whole fruits and vegetables (which are abundant in phytochemicals and antioxidants), yogurt and kefir (which contain natural probiotic bacteria that can help maintain digestive system health), and moderate amounts of dark chocolate, made with 70% or more cacao (which contains antioxidants).

Modified foods have been fortified, enriched, or enhanced with additional nutrients or bioactive compounds. Foods are modified using biotechnology to improve their nutritional value and health attributes. Examples of modified foods include calcium-fortified orange juice, breads enriched with B vitamins, iodized salt, cereals fortified with vitamins and minerals, margarine enhanced with plant sterols, and energy drinks that have been enriched with herbs (ginseng or guarana) or amino acids (taurine). It is important to consider that the health claims of some modified foods may be debatable, or entirely fraudulent. Check with a health professional regarding the effects of modified foods on your health.

Medical foods are designed for enteric administration under the guidance of a medical professional. (During enteric administration, food is treated so that it goes through the stomach undigested. Instead, the food is broken down in the intestines only.) Medical foods are created to meet very specific nutritional requirements. Examples of medical foods include liquid formulas for people with kidney disease, liver disease, diabetes, or other health issues. Medical food is also given to comatose patients through a gastronomy tube because they cannot eat by mouth.

Special dietary use foods do not have to be administered under a doctor's care and can be found in a variety of stores. Similar to medical foods, they address special dietary needs and meet the nutritional requirements of certain health conditions. For example, a bottled oral supplement administered under medical supervision is a medical food, but it becomes a special dietary use food when it is sold to retail customers. Examples of special dietary use foods include gluten-free foods, lactose-free dairy products, and formulas and shakes that promote weight loss.

Popular Diets

The concept of functional foods represents initiatives aimed at addressing health problems. Certain diet plans take this concept one step further, by striving to prevent or treat specific conditions. For example, it is widely understood that people with diabetes need to follow a particular diet. Although some of these diet plans may be nutritionally sound, use caution because some diets may be fads or be so extreme that they actually cause health problems.

Before experimenting with a diet, discuss your plans with your doctor or a registered dietitian. Table **17.3.1** lists the pros and cons of the more popular diets. Some fall under the category of fad diets, while others are backed by scientific evidence. Those that fall

into the latter category provide a good foundation to build a solid regimen for optimal health.

Table 17.3.1 The Pros and Cons of Seven Popular Diets.

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Diet	Pros	Cons
DASH Diet	Recommended by the National Heart, Lung, and Blood Institute, the American Heart Association, and many physicians Helps to lower blood pressure and cholesterol Reduces risk of heart disease and stroke Reduces risk of certain cancers Reduces diabetes risk	There are very few negative factors associated with the DASH diet Risk for hyponatremia
Gluten-Free Diet	Reduces the symptoms of gluten intolerance, such as chronic diarrhea, cramping, constipation, and bloating Promotes healing of the small intestines for people with celiac disease, preventing malnutrition May be beneficial for other autoimmune diseases, such as Parkinson's disease, rheumatoid arthritis, and multiple sclerosis	Risk of folate, iron, thiamin, riboflavin, niacin, and vitamin B6 deficiencies Special gluten-free products can be hard to find and expensive Requires constant vigilance and careful food label reading, since gluten is found in many products
Low-Carb Diet	Restricts refined carbohydrates, such as white flour and white sugar May temporarily improve blood sugar or blood cholesterol levels	Not entirely evidence-based Results in higher fat and protein consumption Does not meet the RDA for carbohydrates to provide glucose to the brain
Macrobiotic Diet	Low in saturated fats and high in fiber Emphasizes whole foods and de-emphasizes processed foods Rich in phytoestrogens, which may reduce the risk of estrogen-related cancers	Not entirely evidence-based Lacks certain vitamins and minerals; supplements are often required Can result in a very low caloric intake Lack of energy may result from inadequate protein
Mediterranean Diet	A reduced risk of cardiovascular disease and mortality A lower risk of cancer De-emphasizes processed foods and emphasizes whole foods and healthy fats Lower sodium intake, due to fewer processed foods Emphasis on monosaturated fats leads to lower cholesterol Highlighting fruits and vegetables raises consumption of antioxidants	Does not specify daily serving amounts Potential for high fat and high calorie intake as nuts and oils are calorie-dense foods Drinking one to two glasses of wine per day may not be healthy for those with certain conditions
Raw Food Diet	Emphasizes whole foods Focuses on nutritionally-rich foods	Not entirely evidence-based Very restrictive and limits protein and healthy fat intake Could encourage the development of foodborne illness Extremely difficult to follow High in fiber which can cause essential nutrient deficiencies
Vegetarianism and Veganism	May reduce some chronic diseases such as	Guidelines regarding fat and nutrient

Diet	Pros	Cons
	cancer, heart disease, and Type 2 diabetes May help with weight reduction and weight maintenance	consumption must be followed Higher risk for nutrient deficiencies such as protein, iron, zinc, omega-3, vitamin B12 Consumption of a high fiber diet interferes with mineral and nutrient bioavailability Vegetarian and vegan protein sources are lower quality with majority missing at least one essential amino acids

Evidence-Based Physical Activity Recommendations

The other part of the energy balance equation is physical activity. The Dietary Guidelines are complemented by the 2018 Physical Activity Guidelines for Americans, issued by the Department of Health and Human Services (HHS) in an effort to provide evidence-based guidelines for appropriate physical activity levels. These guidelines provide recommendations to Americans aged three and older about how to improve health and reduce chronic disease risk through physical activity. Increased physical activity has been found to lower the risk of heart disease, stroke, high blood pressure, Type 2 diabetes, colon, breast, and lung cancer, falls and fractures, depression, and early death. Increased physical activity not only reduces disease risk, but also improves overall health by increasing cardiovascular and muscular fitness, increasing bone density and strength, improving cognitive function, and assisting in weight loss and weight maintenance.

The key guidelines for adults include the following:

- Adults should move more and sit less throughout the day. Some physical activity is better than none. Adults who sit less and do any amount of moderate-to-vigorous physical activity gain some health benefits.
- For substantial health benefits, adults should do at least 150 minutes (2 hours and 30 minutes) to 300 minutes (5 hours) per week of moderate-intensity aerobic activity, or 75 minutes (1 hour and 15 minutes) to 150 minutes (2 hours and 30 minutes) per week of vigorous-intensity aerobic physical activity, or an equivalent combination of moderate- and vigorous-intensity aerobic activity .
- Preferably, aerobic activity should be spread throughout the week.
- Engaging in physical activity beyond the equivalent of 300 minutes (5 hours) of moderate-intensity physical activity per week can result in additional health benefits and may help with weight loss and weight loss maintenance.
- Adults should also do muscle-strengthening activities of at least moderate intensity that involve all major muscle groups on 2 or more days per week, as these activities provide additional health benefits . Exercises such as push-ups, sit-ups, squats, and lifting weights are all examples of muscle-strengthening activities.

The 2018 Physical Activity Guidelines broadly classify moderate physical activities as those when you “can talk, but not sing, during the activity” and vigorous activities as those when you “cannot say more than a few words without pausing for a breath.” [14] Despite the indisputable benefits of regular physical activity, a 2018 report from the American Heart Association estimates that 8 out of 10 Americans do not meet these guidelines. [2]

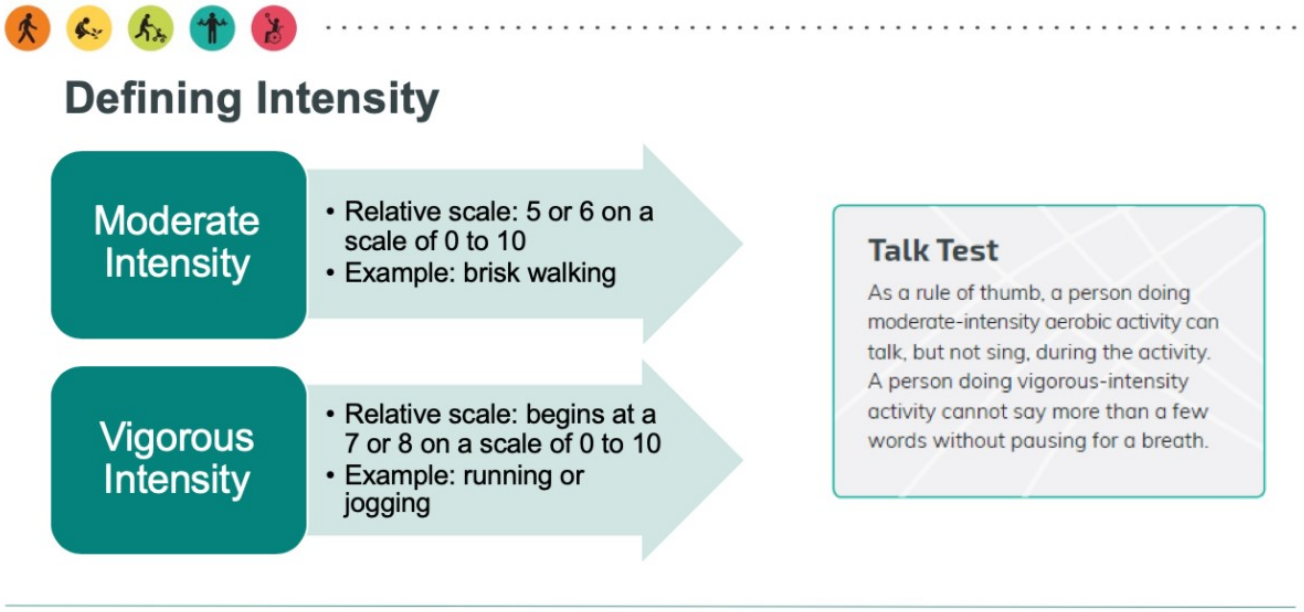


Figure 17.3.1 *The 2018 Physical Activity Guidelines' definition of moderate-intensity and vigorous-intensity exercise.*

Given the number of Americans that are falling short on both nutrition and physical activity recommendations, it is easy to see that these two areas of behavior are of primary interest in improving the health and weight of our nation.

Evidence-Based Behavioral Recommendations

Behavioral weight loss interventions have been described as approaches "used to help individuals develop a set of skills to achieve a healthier weight. It is more than helping people to decide what to change; it is helping them identify how to change." Cornerstones for these interventions typically include self-monitoring through daily recording of food intake and exercise, nutrition education and dietary changes, physical activity goals, and behavior modification. Research shows that these types of interventions can result in weight loss and a lower risk for type 2 diabetes, and similar maintenance strategies lead to less weight regained later.

Behavioral interventions have been shown to help individuals achieve and maintain weight loss of at least 5 percent from baseline weight. **The Food and Drug Administration (FDA) considers a 5 percent weight loss to be clinically significant, as this level of weight loss has been shown to improve cardiometabolic risk factors such as blood lipid levels and insulin sensitivity.** [17,18] The behavioral intervention team often includes primary care clinicians, dietitians , psychologists, behavioral therapists, exercise physiologists, and lifestyle coaches. These programs may include a variety of delivery methods, often through group classes of 10-20 participants both in-person and online, and may use print-based or technology-based materials and resources. The interventions usually span one to two years with more frequent contact in the initial months (weekly to bi-monthly) followed by less frequent contact (monthly) in the latter months, or maintenance phase.[17] A variety of behavioral topics are covered over the course of the program and range from nutrition education and goal-setting to problem-solving and assertiveness. Relapse prevention is included as participants move into the maintenance phase.

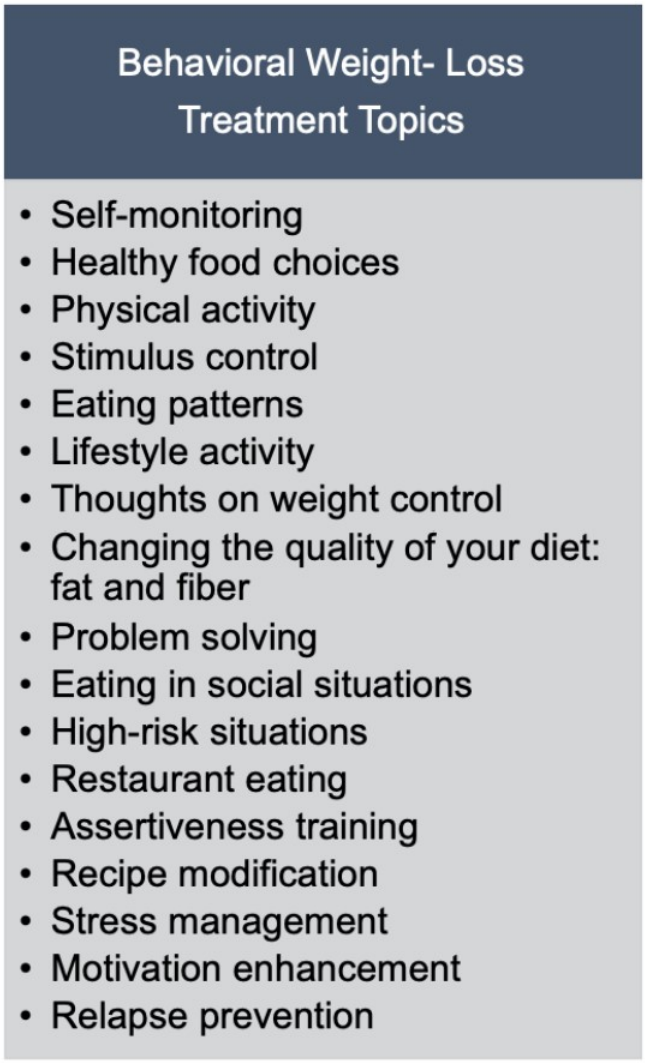


Figure **17.3.2**, *Common topics included in behavioral interventions for weight loss, adapted from Smith, C. E., & Wing, R. R. (2000). New directions in behavioral weight-loss programs. Diabetes Spectrum, 13(3), 142-148.*

Summary

- The 2015 Dietary Guidelines for Americans offers specific, evidence-based recommendations for dietary changes aimed at keeping calorie intake in balance with physical activity, which is key for weight management.
- These new dietary trends encourage those seeking to lose weight to eat healthy, whole foods first, while adopting a more active lifestyle. These sound practices put dietary choices in the context of wellness and a healthier approach to life.
- Increased physical activity not only reduces disease risk, but also improves overall health by increasing cardiovascular and muscular fitness, increasing bone density and strength, improving cognitive function, and assisting in weight loss and weight maintenance.
- Behavioral interventions have been shown to help individuals achieve and maintain weight loss of at least 5 percent from baseline weight.

Contributors and Attributions

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17.4: Measuring Fitness

Learning Objectives

- Be able to calculate body mass index (BMI) given a particular weight and height.
- Name the factors that affect body composition and distribution.

What should you weigh? This has been a difficult question to answer because humans come in so many different sizes and shapes. We do know that carrying too much fat is not good for one's health. Thus fat is a huge factor in determining fitness. Ideal body weight (IBW) has been used to determine one's desirable weight.

Ideal Body Weight

The “ideal” healthy body weight for a particular person is dependent on many things, such as frame size, sex, muscle mass, bone density, age, and height. The perception of the “ideal” body weight is additionally dependent on cultural factors and the mainstream societal advertisement of beauty.

To standardize the “ideal” body weight and relate it to health, scientists have devised mathematical formulas to better define a healthy weight. These mathematically derived measurements are used by health professionals to correlate disease risk with populations of people and at the individual level. A clinician will take two measurements, one of weight and one of fat mass, in order to diagnose obesity. Some measurements of weight and body fat that do not require using technical equipment can easily be calculated and help provide an individual with information on weight, fat mass, and distribution, and their relative risk of some chronic diseases.

Body Mass Index: How to Measure It and Its Limitations

Body mass index (BMI) is calculated using height and weight measurements and is more predictive of body fatness than weight alone. BMI measurements are used to indicate whether an individual may be underweight (with a BMI less than 18.5), overweight (with a BMI over 25), or obese (with a BMI over 30). High BMI measurements can be warning signs of health hazards ahead, such as cardiovascular disease, Type 2 diabetes, and other chronic diseases. BMI-associated health risks vary by race. Asians face greater health risks for the same BMI than Caucasians, and Caucasians face greater health risks for the same BMI than African Americans.

Very high AND very low BMI's appear to increase a person's risk of dying. If you look at a graph of BMI (Figure **17.4.1**) as it relates to your risk of dying, it has a "J-shaped Curve" or a "U-shaped Curve" because being too low and/or too high both raise your risk of mortality. Instead, you'd like to be in the middle range of the BMI which is what they use for "Normal weight".

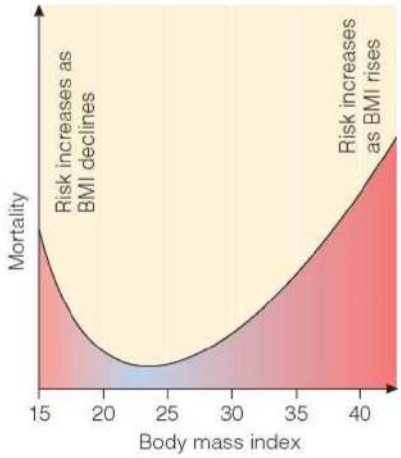


Figure **17.4.1** Relationship between body mass index and mortality.

Calculating BMI

To calculate your BMI, multiply your weight in pounds by 703 (conversion factor for converting to metric units) and then divide the product by your height in inches, squared.

$$BMI = [weight(lb) \times 703] \div height(in)^2$$

or

$$BMI = [weight(kg)] \div height(m)^2$$

BMI Calculators and BMI Categories

The National Heart, Lung, and Blood Institute and the CDC have automatic BMI calculators on their websites:

- https://www.nhlbi.nih.gov/health/educational/lose_wt/BMI/bmi-m.htm
- https://www.cdc.gov/bmi/adult-calculator/widget.html?CDC_AAref_Val=https://www.cdc.gov/healthyweight/assessing/bmi/adult_bmi/english_bmi_calculator/bmi_calculator.html

To see how your BMI indicates the weight category you are in, see Table **17.4.1** or use a chart of weight and height to figure out your BMI.

Table **17.4.1** *BMI Categories*

Categories	BMI
Underweight	< 18.5
Normal weight	18.5–24.9
Overweight	25–29.9
Obese	30.0-34.9
Severe	35-40

Source: National Heart, Lung, and Blood Institute. Accessed November 4, 2012. http://www.nhlbi.nih.gov.

BMI Limitations

A BMI is a fairly simple measurement and does not take into account fat mass or fat distribution in the body, both of which are additional predictors of disease risk. Body fat weighs less than muscle mass. Therefore, BMI can sometimes underestimate the amount of body fat in overweight or obese people and overestimate it in more muscular people. For instance, a muscular athlete will have more muscle mass (which is heavier than fat mass) than a couch potato of the same height. Based on their BMIs the muscular athlete would be less “ideal” and may be categorized as more overweight or obese than the couch potato; however, this is an infrequent problem with BMI calculation. Additionally, an older person with osteoporosis (decreased bone mass) will have a lower BMI than an older person of the same height without osteoporosis, even though the person with osteoporosis may have more fat mass. A BMI is a useful inexpensive tool to categorize people and is highly correlative with disease risk, but other measurements are needed to diagnose obesity and more accurately assess disease risk.

BMI is not a good measure for children and adolescents because they are growing. A new BMI for these ages was recently introduced in which the weight in kg is divided by the height in meters cubed. Its use is not well-established yet.

BMI does not consider where the fat is located. Individuals with abdominal fat or android shape have a greater risk of obesity associated diseases than individuals who carry their fat in the hips (gynoid or "pear shape"). Men tend to be "apple-shaped" while women tend to be "pear shaped." Gynoid shape tends to be associated with fewer health risks. For this reason, a ratio of body waist circumference to hip circumference may be measured and the ratio calculated. If you are male and your ratio is greater than 0.95, then you have excessive abdominal fat. If you are female and your ratio is greater than 0.86, then you have excessive abdominal fat.

Measuring Body Fat Content

Water, organs, bone tissue, fat, and muscle tissue make up a person's weight. Having more fat mass may be indicative of disease risk, but fat mass also varies with sex, age, and physical activity level. Females have more fat mass, which is needed for reproduction and, in part, is a consequence of different levels of hormones. The optimal fat content of a female is between 20 and 30 percent of her total weight and for a male is between 12 and 20 percent. Fat mass can be measured in a variety of ways. The simplest and lowest-cost way is the skin-fold test. A health professional uses a caliper to measure the thickness of skin on the back, arm, and other parts of the body and compares it to standards to assess body fatness. It is a noninvasive and fairly accurate method of measuring fat mass, but similar to BMI, is compared to standards of mostly young to middle-aged adults.



Figure **17.4.2**: Measuring Skinfold Thickness Using Calipers. Image by Shutterstock. All Rights Reserved.

Other methods of measuring fat mass are more expensive and more technically challenging. They include:

- Underwater weighing. This technique requires a chamber full of water big enough for the whole body to fit in. First, a person is weighed outside the chamber and then weighed again while immersed in water. Bone and muscle weigh more than water, but fat does not—therefore a person with a higher muscle and bone mass will weigh more when in water than a person with less bone and muscle mass.
- Bioelectric Impedance Analysis (BIA). This device is based on the fact that fat slows down the passage of electricity through the body. When a small amount of electricity is passed through the body, the rate at which it travels is used to determine body composition. These devices are also sold for home use and commonly called body composition scales.



Figure **17.4.3**: BIA Hand Device. Image by United States Marine Corps / U.S. Public Domain.

Dual-energy X-ray absorptiometry (DEXA). This can be used to measure bone density. It also can determine fat content via the same method, which directs two low-dose X-ray beams through the body and determines the amount of the energy absorbed from

the beams. The amount of energy absorbed is dependent on the body's content of bone, lean tissue mass, and fat mass. Using standard mathematical formulas, fat content can be accurately estimated.

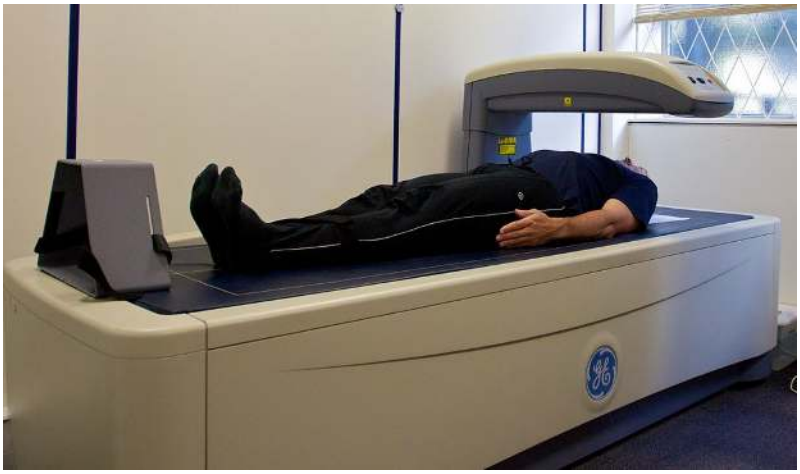


Figure 17.4.4: Dual-Energy X-ray Absorptiometry (DEXA). "A Dual-energy X-ray absorptiometry (DEXA) scan" by Nick Smith / CC BY-SA 3.0.

Measuring Fat Distribution

Total body-fat mass is one predictor of health; another is how the fat is distributed in the body. You may have heard that fat on the hips is better than fat in the belly—this is true. Fat can be found in different areas in the body and it does not all act the same, meaning it differs physiologically based on location. Fat deposited in the abdominal cavity is called visceral fat and it is a better predictor of disease risk than total fat mass. Visceral fat releases hormones and inflammatory factors that contribute to disease risk. The only tool required for measuring visceral fat is a measuring tape. The measurement (of waist circumference) is taken just above the belly button. Men with a waist circumference greater than 40 inches and women with a waist circumference greater than 35 inches are predicted to face greater health risks.

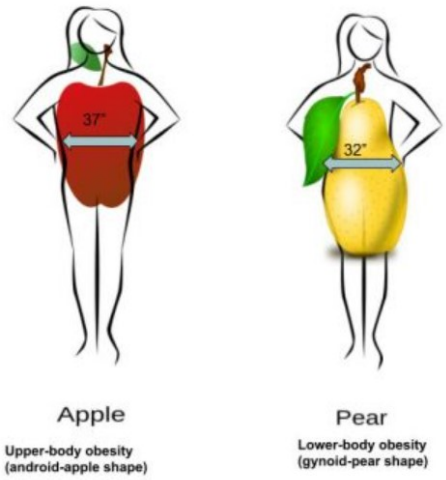


Figure 17.4.5: Fat Distribution.

The waist-to-hip ratio is often considered a better measurement than waist circumference alone in predicting disease risk. To calculate your waist-to-hip ratio, use a measuring tape to measure your waist circumference and then measure your hip circumference at its widest part. Next, divide the waist circumference by the hip circumference to arrive at the waist-to-hip ratio. Observational studies have demonstrated that people with "apple-shaped" bodies, (who carry more weight around the waist) have greater risks for chronic disease than those with "pear-shaped" bodies, (who carry more weight around the hips). A study published

in the November 2005 issue of Lancet with more than twenty-seven thousand participants from fifty-two countries concluded that the waist-to-hip ratio is highly correlated with heart attack risk worldwide and is a better predictor of heart attacks than BMI.[1]. Abdominal obesity is defined by the World Health Organization (WHO) as having a waist-to-hip ratio above 0.90 for males and above 0.85 for females.

Summary

Most people who are overweight also have excessive body fat and therefore body weight is an indicator of obesity in much of the population.

To standardize the “ideal” body weight and relate it to health, scientists have devised some computational measurements to better define a healthy ideal weight. Body weight in relation to height is called BMI and is correlated with disease risk.

Total body fat mass is another predictor of disease risk; another is where the fat is distributed. Fat deposits in different areas in the body and do not all act the same, meaning it differs physiologically based on location. Visceral fat contributes more to disease risk, for example.

Contributors and Attributions

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17.5: Some Muscular Chemistry

Learning Objectives

- Describe how muscle contraction occurs.
- Explain the difference between aerobic and anaerobic exercise.

Muscle cells are specialized for contraction. Muscles allow for motions such as walking, and they also facilitate bodily processes such as respiration and digestion. The body contains three types of muscle tissue: skeletal muscle, cardiac muscle, and smooth muscle (Figure **17.5.1**).

Skeletal muscle tissue forms skeletal muscles, which attach to bones or skin and control locomotion and any movement that can be consciously controlled. Because it can be controlled by thought, skeletal muscle is also called voluntary muscle. Smooth muscle tissue occurs in the walls of hollow organs such as the intestines, stomach, and urinary bladder, and around passages such as the respiratory tract and blood vessels. Cardiac muscle tissue is only found in the heart, and cardiac contractions pump blood throughout the body and maintain blood pressure.

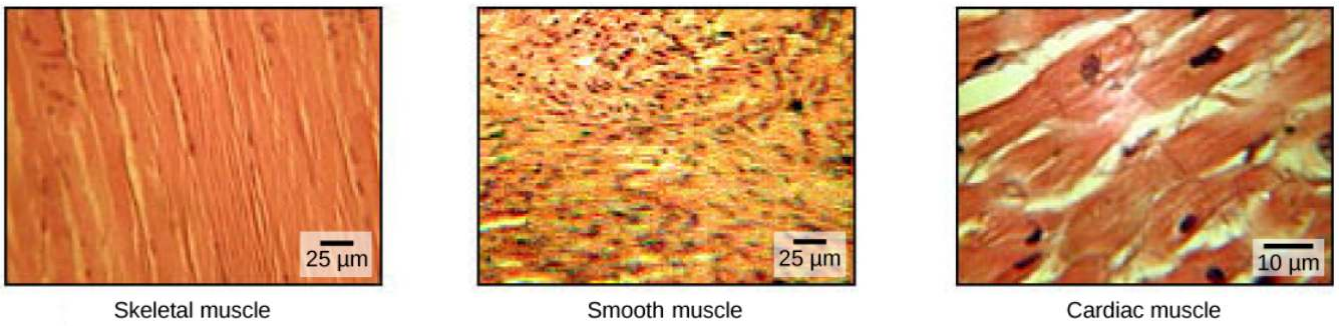


Figure **17.5.1** The body contains three types of muscle tissue: skeletal muscle, smooth muscle, and cardiac muscle, visualized here using light microscopy. Smooth muscle cells are short, tapered at each end, and have only one plump nucleus in each. Cardiac muscle cells are branched and striated, but short. The cytoplasm may branch, and they have one nucleus in the center of the cell. (credit: modification of work by NCI, NIH; scale-bar data from Matt Russell)

Muscle Contraction

Muscle contraction occurs when muscle fibers get shorter. Literally, the muscle fibers get smaller in size. To understand how this happens, you need to know more about the structure of muscle fibers.

Structure of Muscle Fibers

Each muscle fiber contains hundreds of organelles called **myofibrils**. Each myofibril is made up of two types of protein filaments: **actin** filaments, which are thinner, and **myosin** filaments, which are thicker. Actin filaments are anchored to structures called **Z lines** (Figure 13.13.2). The region between two Z lines is called a **sarcomere**. Within a sarcomere, myosin filaments overlap the actin filaments. The myosin filaments have tiny structures called **cross bridges** that can attach to actin filaments.

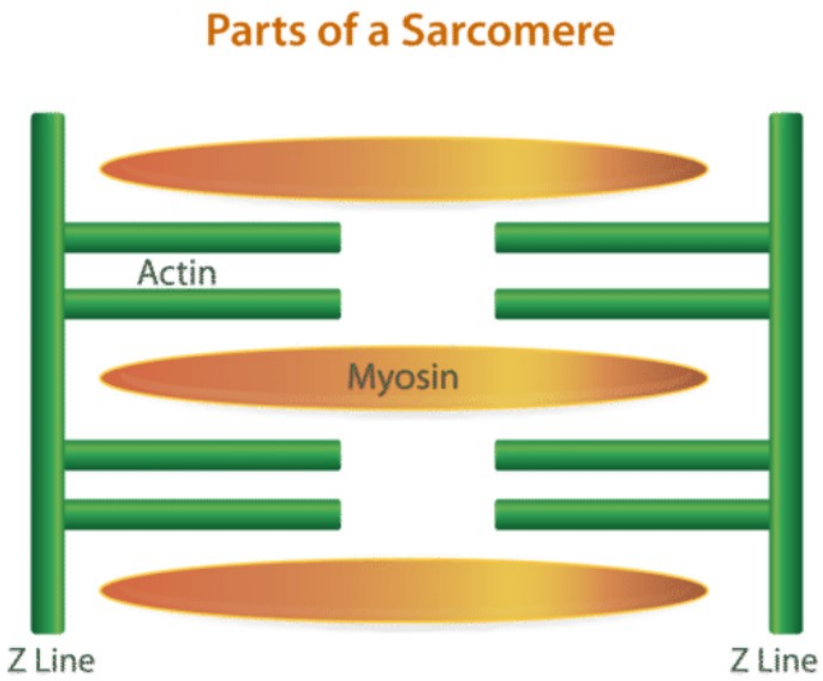
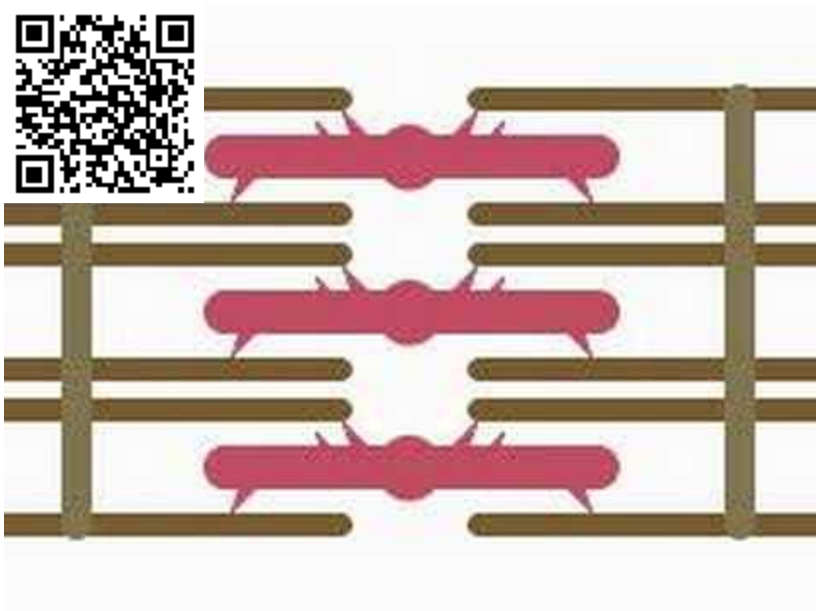


Figure **17.5.2** Sarcomere. A sarcomere contains actin and myosin filaments between two Z lines.

Sliding Filament Theory

The most widely accepted theory explaining how muscle fibers contract is called the **sliding filament theory**. According to this theory, myosin filaments use energy from ATP to "walk" along the actin filaments with their cross bridges. This pulls the actin filaments closer together. The movement of the actin filaments also pulls the Z lines closer together, thus shortening the sarcomere.



When all of the sarcomeres in a muscle fiber shorten, the fiber contracts. A muscle fiber either contracts fully or it doesn't contract at all. The number of fibers that contract determines the strength of the muscular force. When more fibers contract at the same time, the force is greater.

Muscles and Nerves

Muscles cannot contract on their own. They need a stimulus from a nerve cell to “tell” them to contract. Let’s say you decide to raise your hand in class. Your brain sends electrical messages to nerve cells, called **motor neurons**, in your arm and shoulder. The motor neurons, in turn, stimulate muscle fibers in your arm and shoulder to contract, causing your arm to rise. Involuntary contractions of cardiac and smooth muscles are also controlled by nerves.

Energy for Muscle Contraction: ATP

The source of energy that is used to power the movement of contraction in working muscles is adenosine triphosphate (ATP) – the body’s biochemical way to store and transport energy. ATP provides the energy for cross-bridge formation and filament sliding. However, ATP is not stored to a great extent in cells.

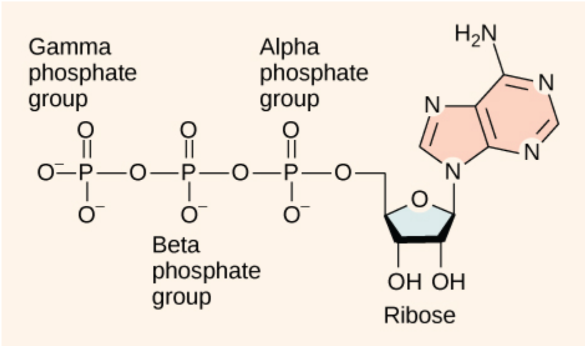


Figure 17.5.3 ATP.

All muscle cells have a little ATP within them that they can use immediately – but only enough to last for about 3 seconds!

So once muscle contraction starts, the making of more ATP must start quickly. Since ATP is so important, the muscle cells have several different ways to make it. These systems work together in phases. The three biochemical systems for producing ATP are, in order:

1. *Creatine phosphate* can supply the energy needs of a working muscle at a very high rate, but only for about 8–10 seconds.
2. Glycogen is then used to make ATP from glucose. But this takes about 12 chemical reactions so it supplies energy more slowly than from creatine phosphate. It’s still pretty rapid, though, and will produce enough energy to last about 90 seconds. Oxygen is not needed – this is great, because it takes the heart and lungs some time to get increased oxygen supply to the muscles. A by-product of making ATP without using oxygen is lactic acid. You know when your muscles are building up *lactic acid* because it causes tiredness and soreness – the stitch.
3. Within two minutes of exercise, the body starts to supply working muscles with oxygen. When oxygen is present, aerobic respiration can take place to break down the glucose for ATP. This glucose can come from several places:

- remaining glucose supply in the muscle cells
- glucose from food in the intestine
- *glycogen in the liver*
- fat reserves in the muscles
- in extreme cases (like starvation), the body’s protein.

Aerobic respiration takes even more chemical reactions to produce ATP than either of the above two systems. It is the slowest of all three systems – but it can supply ATP for several hours or longer, as long as the supply of fuel lasts.

Aerobic Exercise: Plenty of Oxygen

Aerobic exercise (also known as cardio) is physical exercise of low to high intensity that depends primarily on the aerobic energy-generating process. Aerobic literally means "relating to, involving, or requiring free oxygen", and refers to the use of oxygen to adequately meet energy demands during exercise. Generally, light-to-moderate intensity activities that are sufficiently supported by aerobic metabolism can be performed for extended periods of time. When practiced in this way, examples of cardiovascular/aerobic exercise are medium to long distance running/jogging, swimming, cycling, and walking, according to the first extensive research on aerobic exercise, conducted in the 1960s on over 5,000 U.S. Air Force personnel by Dr. Kenneth H. Cooper.



Cardio

Kenneth Cooper was the first person to introduce the concept of aerobic exercise. In the 1960s, Cooper started research into preventive medicine. He became intrigued by the belief that exercise can preserve one's health. In 1970 he created his own institute (the Cooper Institute) for non-profit research and education devoted to preventive medicine. He sparked millions into becoming active and is now known as the "father of aerobics".

What is generally called aerobic exercise might be better termed "solely aerobic", because it is designed to be low-intensity enough not to generate lactate (or lactic acid), so that all carbohydrate is aerobically turned into energy.

Initially during increased exertion, muscle glycogen is broken down to produce glucose, which undergoes glycolysis producing pyruvate (Figure **17.5.4**) which then reacts with oxygen(Krebs cycle, Chemiosmosis) to produce carbon dioxide and water and releases energy. As glycogen levels in the muscle begin to fall, glucose is released into the bloodstream by the liver, and fat metabolism is increased so that it can fuel the aerobic pathways. Aerobic exercise may be fueled by glycogen reserves, fat reserves, or a combination of both, depending on the intensity.

Aerobic exercise comprises innumerable forms. In general, it is performed at a moderate level of intensity over a relatively long period of time. For example, running a long distance at a moderate pace is an aerobic exercise, but sprinting is not. Playing singles tennis, with near-continuous motion, is generally considered aerobic activity, while golf or two person team tennis, with brief bursts of activity punctuated by more frequent breaks, may not be predominantly aerobic. Some sports are thus inherently "aerobic", while other aerobic exercises, such as fartlek training or aerobic dance classes, are designed specifically to improve aerobic capacity and fitness. It is most common for aerobic exercises to involve the leg muscles, primarily or exclusively. There are some exceptions. For example, rowing to distances of 2,000 m or more is an aerobic sport that exercises several major muscle groups, including those of the legs, abdominals, chest, and arms. Common kettlebell exercises combine aerobic and anaerobic aspects.

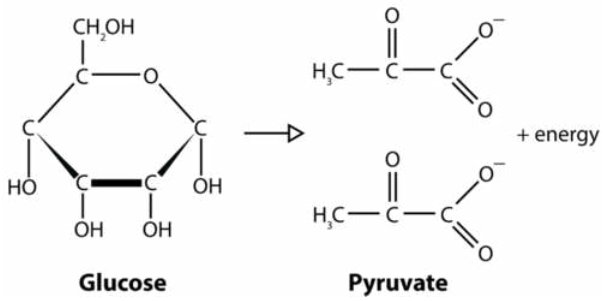


Figure **17.5.4** Glycolysis breaks the 6-carbon molecule glucose into two 3-carbon pyruvate molecules, releasing some of the chemical energy which had been stored in glucose.

Anaerobic Exercise and Oxygen Debt

Anaerobic exercise is a type of exercise that breaks down glucose in the body without using oxygen; *anaerobic* means "without oxygen". In practical terms, this means that anaerobic exercise is more intense, but shorter in duration than aerobic exercise.The biochemistry of anaerobic exercise involves a process called glycolysis, in which glucose is converted to adenosine triphosphate (ATP), which is the primary source of energy for cellular reactions.Lactic acid is produced at an increased rate during anaerobic exercise, causing it to build up quickly (Figure **17.5.5**).Anaerobic exercise may be used to help build endurance, muscle strength, and power.

The by-product of anaerobic glycolysis—lactate—has traditionally been thought to be detrimental to muscle function. However, this appears likely only when lactate levels are very high. Elevated lactate levels are only one of many changes that occur within and around muscle cells during intense exercise that can lead to fatigue. Fatigue, that is muscle failure, is a complex subject that depends on more than just changes to lactate concentration. Energy availability, oxygen delivery, perception to pain, and other psychological factors all contribute to muscular fatigue. Elevated muscle and blood lactate concentrations are a natural consequence of any physical exertion. The effectiveness of anaerobic activity can be improved through training.

Anaerobic exercise also increases an individual's basal metabolic rate (BMR). Some examples of anaerobic exercises include sprints, high-intensity interval training (HIIT), and strength training.

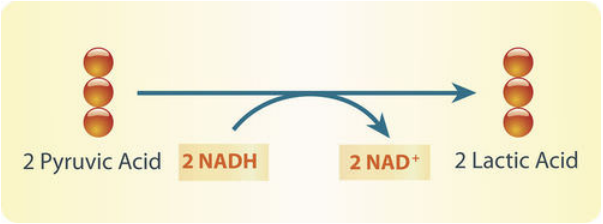


Figure **17.5.5** Converting pyruvic acid to lactic acid.

Lactic acid can be converted back to pyruvate in well-oxygenated muscle cells; however, during exercise the focus in on maintaining muscle activity. Lactic acid is transported to the liver where it can be stored prior to conversion to glucose in the presence of oxygen via the Cori Cycle. The amount of oxygen required to restore the lactic acid balance is often referred to as the **oxygen debt**.

Overview of Anaerobic and Aerobic Metabolism

Anaerobic metabolism occurs in the cytosol of the muscle cells. As seen in Figure **17.5.6**, a small amount of ATP is produced in the cytosol without the presence of oxygen. Anaerobic metabolism uses glucose as its only source of fuel and produces pyruvate and lactic acid. Pyruvate can then be used as fuel for aerobic metabolism. Aerobic metabolism takes place in the mitochondria of the cell and is able to use carbohydrates, protein or fat as its fuel source. Aerobic metabolism is a much slower process than anaerobic metabolism but produces majority of the ATP.

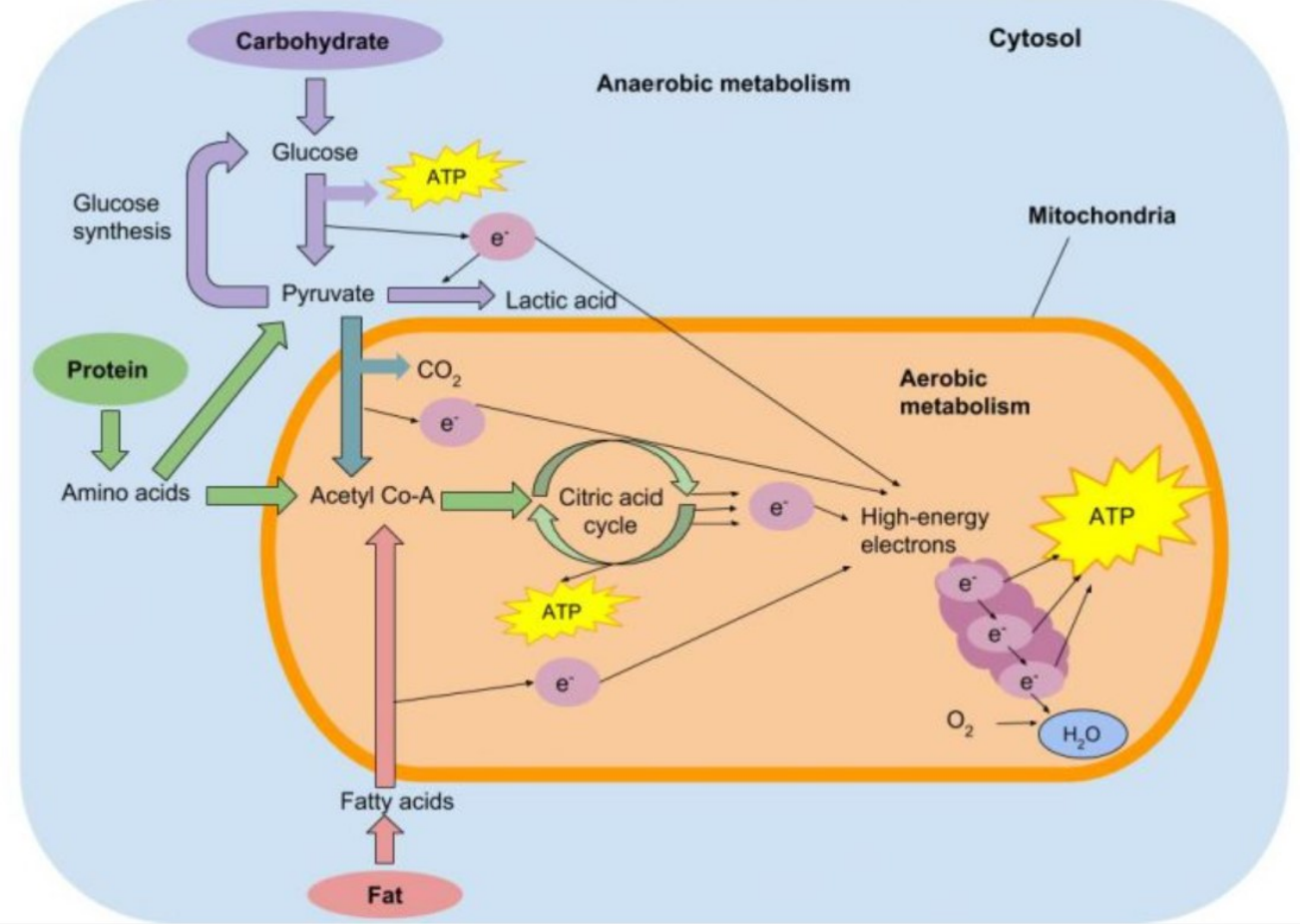


Figure 17.5.6: Anaerobic versus Aerobic Metabolism. Image by Allison Calabrese / CC BY 4.0.

Exercise and ATP

Different forms of exercise use different systems to produce ATP

A sprinter is getting ATP in a very different way to a marathon runner.

- Using creatine phosphate – This would be the major system used for short bursts (weightlifters or short distance sprinters) because it is fast but lasts for only 8–10 seconds.
- Using glycogen (no oxygen) – This lasts for 1.3–1.6 minutes, so it would be the system used in events like the 100 meter swim or the 200 m or 400 m run.
- Using aerobic respiration – This lasts for an unlimited time, so it's the system used in endurance events like marathon running, rowing, distance skating and so on.

Fuel Sources for Aerobic and Anaerobic Metabolism

The fuel sources for anaerobic and aerobic metabolism will change depending on the amount of nutrients available and the type of metabolism. Glucose may come from blood glucose (which is from dietary carbohydrates or liver glycogen and glucose synthesis) or muscle glycogen. Glucose is the primary energy source for both anaerobic and aerobic metabolism. Fatty acids are stored as triglycerides in muscles but about 90% of stored energy is found in adipose tissue. As low to moderate intensity exercise continues using aerobic metabolism, fatty acids become the predominant fuel source for the exercising muscles. Although protein is not considered a major energy source, small amounts of amino acids are used while resting or doing an activity. The amount of amino acids used for energy metabolism increase if the total energy intake from your diet does not meet the nutrient needs or if you are involved in long endurance exercises.

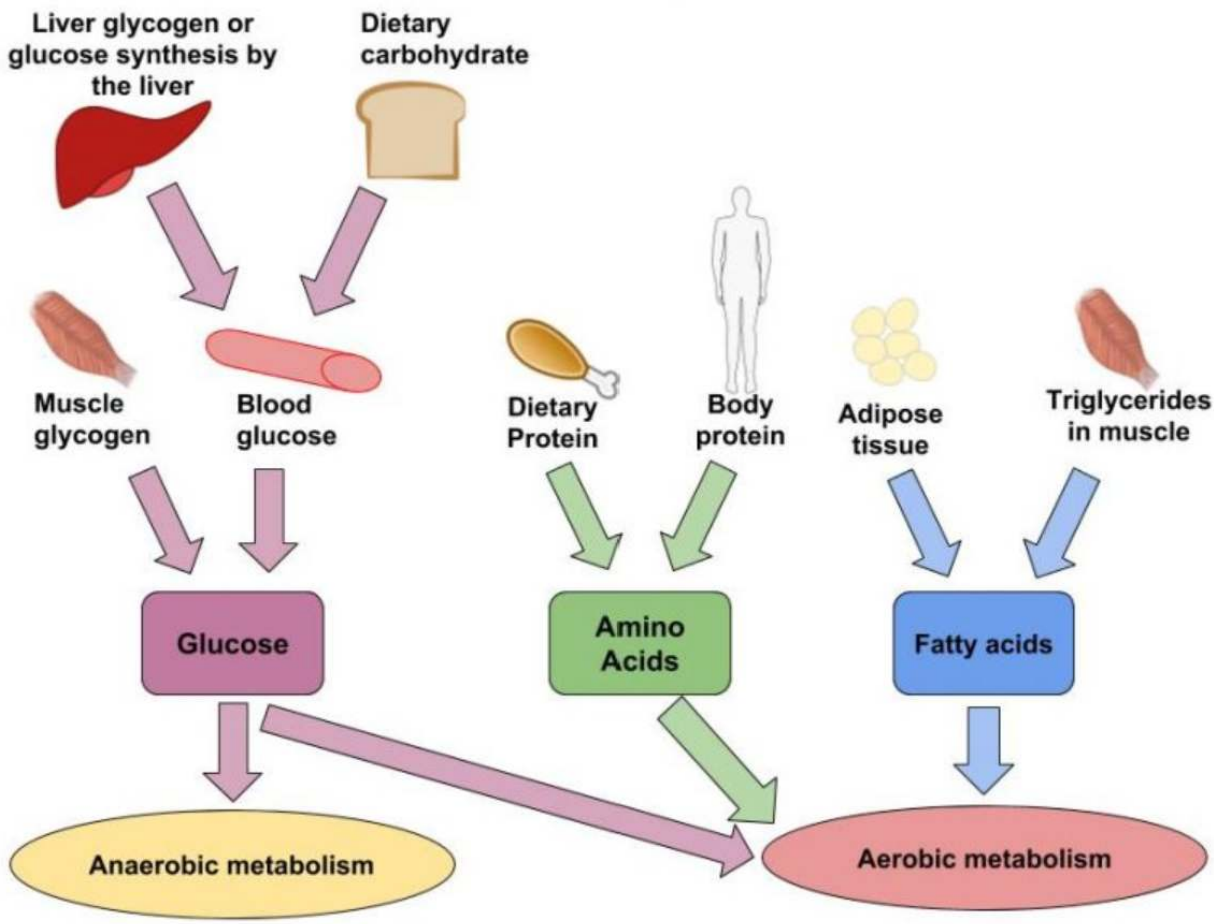


Figure **17.5.7** Fuel sources for anaerobic and aerobic metabolism.

Physical Activity Intensity and Fuel Use

The exercise intensity determines the contribution of the type of fuel source used for ATP production(see Figure **17.5.8**). Both anaerobic and aerobic metabolism combine during exercise to ensure that the muscles are equipped with enough ATP to carry out the demands placed on them. The amount of contribution from each type of metabolism will depend on the intensity of an activity. When low-intensity activities are performed, aerobic metabolism is used to supply enough ATP to muscles. However, during high-intensity activities more ATP is needed so the muscles must rely on both anaerobic and aerobic metabolism to meet the body's demands.

During low-intensity activities, the body will use aerobic metabolism over anaerobic metabolism because it is more efficient by producing larger amounts of ATP. Fatty acids are the primary energy source during low-intensity activity. With fat reserves in the body being almost unlimited, low-intensity activities are able to continue for a long time. Along with fatty acids, a small amount of glucose is used as well. Glucose differs from fatty acids where glycogen storages can be depleted. As glycogen stores are depleted, fatigue will eventually set in.

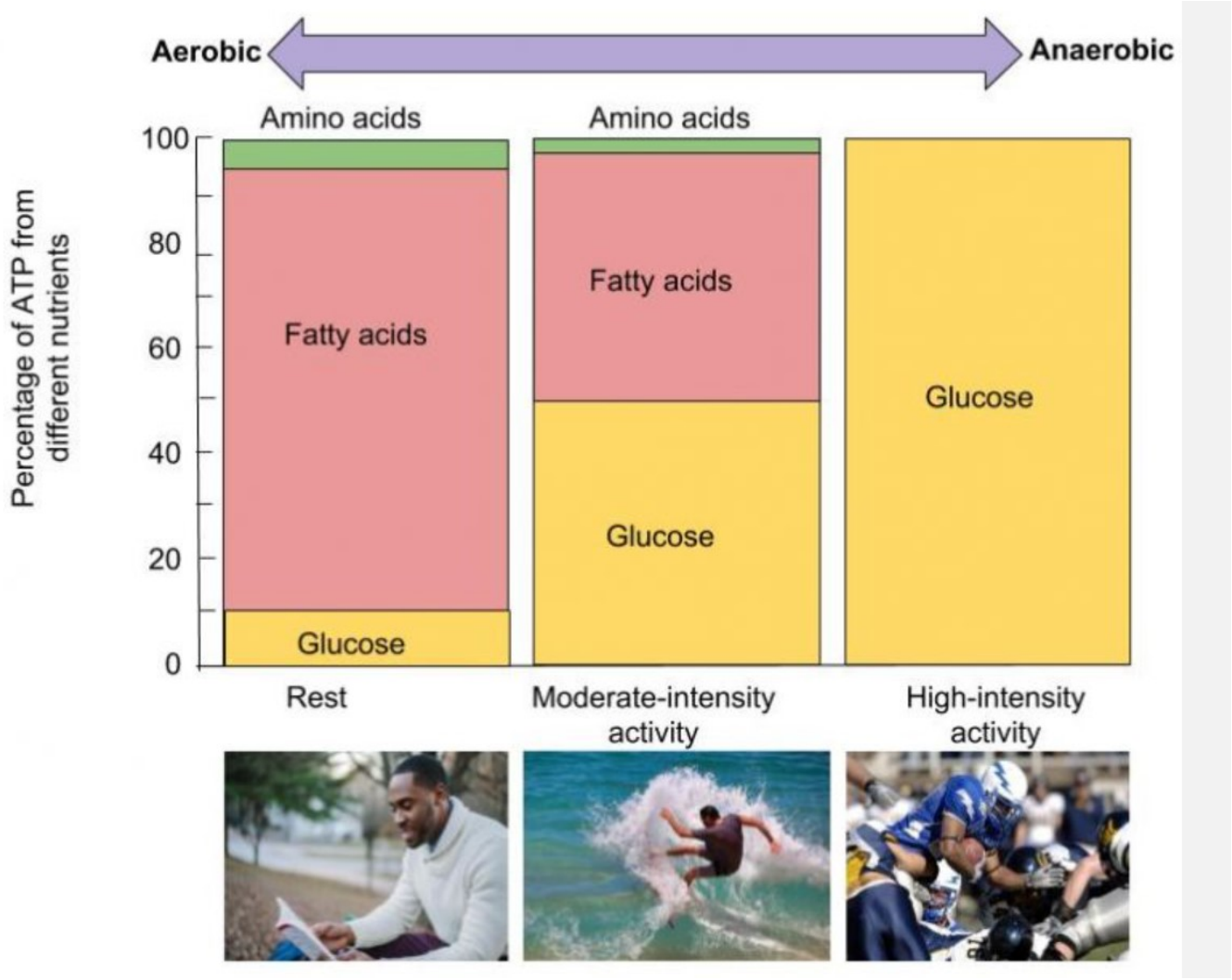


Figure 17.5.8: The Effect of Exercise Intensity on Fuel Sources.

Summary

- The body contains three types of muscle tissue: skeletal muscle, cardiac muscle, and smooth muscle. Skeleton muscle tissue is composed of sarcomeres, the functional units of muscle tissue.
- Muscle contraction occurs when sarcomeres shorten, as thick and thin filaments slide past each other, which is called the sliding filament model of muscle contraction.
- ATP provides the energy for cross-bridge formation and filament sliding.
- Aerobic exercise (also known as cardio) is physical exercise of low to high intensity that depends primarily on the aerobic energy-generating process (aerobic metabolism). Aerobic refers to the use of oxygen to adequately meet energy demands during exercise.
- Anaerobic exercise is a physical exercise intense enough that there is lack of oxygen. If there is a shortage of oxygen (anaerobic exercise, explosive movements), carbohydrate is consumed more rapidly and the pyruvate converts into lactate via the anaerobic process.
- The exercise intensity determines the contribution of the type of fuel source used for ATP production

Contributors

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17.6: Drugs, Athletic Performance, and the Brain

Learning Objectives

- Know the different supplements and drugs that are used to maintain or enhance athletic performance.
- List the use and abuse of anabolic steroids.

Protein

Bodybuilders may supplement their diets with protein for reasons of convenience, lower cost (relative to meat and fish products) and to avoid the concurrent consumption of carbohydrates and fats. In addition, some argue that bodybuilders, by virtue of their unique training and goals, require higher-than-average quantities of protein to support maximal muscle growth; however there is no compelling evidence and no scientific consensus for bodybuilders to consume more protein than the recommended dietary allowance.



Figure **17.6.1**: Protein milkshakes, made from protein powder (center) and milk (left), are a common bodybuilding supplement. (CC BY-SA 3.0; Sandstein).

Protein supplements are sold in ready-to-drink shakes, bars, meal replacement products (see below), bites, oats, gels and powders. Protein powders are the most popular and may have flavoring added for palatability. The powder is usually mixed with water, milk or juice and is generally consumed immediately before and after exercising, or in place of a meal. The sources of protein are as follows, and differ in protein quality depending on their amino acid profile and digestibility:

- Whey protein contains high levels of all the essential amino acids and branched-chain amino acids. It also has the highest content of the amino acid cysteine, which aids in the biosynthesis of glutathione. For bodybuilders whey protein provides amino acids used to aid in muscle recovery. Whey protein is derived from the process of making cheese from milk. There are three types of whey protein: whey concentrate, whey isolate, and whey hydrolysate. Whey concentrate is 29–89% protein by weight whereas whey isolate is 90%+ protein by weight. Whey hydrolysate is enzymatically predigested and therefore has the highest rate of digestion of all protein types. Whey protein is usually taken immediately before and after a workout
- Casein protein (or milk protein) has glutamine, and casomorphin. Casein is usually taken before going to bed.
- Soy protein from soybeans contain isoflavones, a type of phytoestrogen.
- Egg-white protein is a lactose- and dairy-free protein.
- Hemp protein from hemp seed, contains highly-digestible protein, and hemp oil is high in essential fatty acids.
- Rice protein, when made from the whole grain, is a protein source that is highly digestible and allergen free. Since rice protein is low in the amino acid lysine, it is often combined with pea protein powder to achieve a superior amino acid profile.
- Pea protein is a hypoallergenic protein with a lighter texture than most other protein powders. Pea protein has an amino acid profile similar to that of soy, but pea protein does not elicit concerns about unknown effects of phytoestrogens. Pea protein is also less allergenic than soy. Pea protein has high fiber content and has no allergic ingredients and therefore is easy for digestion as compared to whey protein. Pea protein is a slow digesting protein and is able to keep you full longer.

Some nutritionists claim that osteoporosis may occur from excessive protein intake because protein can put pressure on the kidneys and lead to bone loss due to calcium leaching. However, some have suggested that higher calcium excretion may be due to a corresponding increase in protein-induced calcium absorption in the intestines. In addition to complete proteins, some supplements will contain protein fragments such as branched-chain amino acids or individual amino acids (such as glutamine). Amino acids are considered to be inferior to whole protein and have been used by some companies to artificially inflate and falsify protein values in their product (protein spiking). Many protein supplements explicitly indicate on the label that no protein spiking has occurred.

Branched-chain amino acids

Amino acids are the building blocks of protein; the body breaks consumed protein into amino acids in the stomach and intestines. Amino acids are classified as essential, conditionally essential and non-essential. There are three branched-chain amino acids (BCAAs): leucine, isoleucine, and valine. All three branched-chain amino acids are essential amino acids. Each has numerous benefits on various biological processes in the body. Unlike other amino acids, BCAAs are metabolized in the muscle and have an anabolic/anti-catabolic effect on it. There is some evidence that BCAA's may enhance muscle recovery after intense physical activity and no side effects have been reported at this time.

Glutamine

Glutamine is the most abundant amino acid found in human muscle and is commonly found in supplements or as a micronized, instantly soluble powder because supplement manufacturers claim the body's natural glutamine stores are depleted during anaerobic exercise. Some studies have shown there to be no significant effect of glutamine on bench press strength, knee-extension torque or lean muscle mass when compared to controls taking a placebo, though another study found that glutamine is beneficial in raising T-helper/suppressor cell ratio in long-distance runners.

Essential fatty acids

The essential fatty acids (alpha-linolenic acid and linoleic acid) may be important to supplement while bodybuilding; these cannot readily be made in the body, but are required for various functions within the body to take place. Fatty fish, such as fresh salmon and trout are rich in essential fatty acids and fish oils can also be taken in supplement form. Flaxseed oil, often sold as a supplement on its own, is an ideal source of alpha-Linolenic acid, which can also be found in walnuts and pumpkin seeds.

Prohormone

Prohormones are precursors to hormones and are most typically sold to bodybuilders as a precursor to the natural hormone testosterone. This conversion requires naturally occurring enzymes in the body. Side effects are not uncommon, as prohormones can also convert further into DHT and estrogen. To deal with this, many supplements also have aromatase inhibitors and DHT blockers such as chrysin and 4-androstene-3,6,17-trione. To date most prohormone products have not been thoroughly studied, and the health effects of prolonged use are unknown. Although initially available over the counter, their purchase was made illegal without a prescription in the US in 2004, and they hold similar status in many other countries. They remain legal, however, in the United Kingdom and the wider European Union. Their use is prohibited by most sporting bodies.

Creatine

Creatine is an organic acid naturally occurring in the body that supplies energy to muscle cells for short bursts of energy (as required in lifting weights) via creatine phosphate replenishment of ATP. A number of scientific studies have shown that creatine can improve strength, energy, muscle mass, and recovery times. In addition, recent studies have also shown that creatine improves brain function. and reduces mental fatigue.Unlike steroids or other performance-enhancing drugs, creatine can be found naturally in many common foods such as herring, tuna, salmon, and beef.

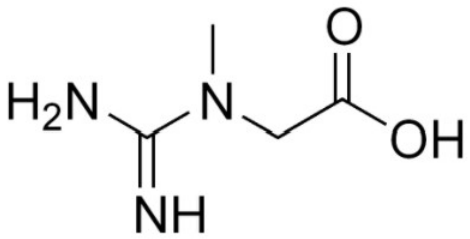


Figure **17.6.2**: Skeletal formula of creatine

Creatine increases what is known as *cell volumization* by drawing water into muscle cells, making them larger. This *intracellular* retention should not be confused with the common myth that creatine causes bloating (or *intercellular* water retention). Creatine is sold in a variety of forms, including creatine monohydrate and creatine ethyl ester, amongst others. Though all types of creatine are sold for the same purposes, there are subtle differences between them, such as price and necessary dosage. Some studies have suggested that consumption of creatine with protein and carbohydrates can have a greater effect than creatine combined with either protein or carbohydrates alone.

β-Hydroxy β-methylbutyrate

When combined with an appropriate exercise program, dietary supplementation with β-hydroxy β-methylbutyrate (HMB) has been shown to dose-dependently augment gains in muscle hypertrophy (i.e., the size of a muscle), muscle strength, and lean body mass, reduce exercise-induced skeletal muscle damage, and expedite recovery from high-intensity exercise. HMB is believed to produce these effects by increasing muscle protein synthesis and decreasing muscle protein breakdown by various mechanisms, including activation of the mechanistic target of rapamycin (mTOR) and inhibition of the proteasome in skeletal muscles. The inhibition of exercise-induced skeletal muscle damage by HMB is affected by the time that it is used relative to exercise. The greatest reduction in skeletal muscle damage from a single bout of exercise appears to occur when calcium HMB is ingested 1–2 hours prior to exercise.

Thermogenic products

A thermogenic is a broad term for any supplement that the manufacturer claims will cause thermogenesis, resulting in increased body temperature, increased metabolic rate, and consequently an increased rate in the burning of body fat and weight loss. Until 2004 almost every product found in this supplement category comprised the "ECA stack": ephedrine, caffeine and aspirin. However, on February 6, 2004 the Food and Drug Administration (FDA) banned the sale of ephedra and its alkaloid, ephedrine, for use in weight loss formulas. Several manufacturers replaced the ephedra component of the "ECA" stack with bitter orange or citrus aurantium (containing synephrine) instead of the ephedrine.

Controversies of Fitness Supplements

Mislabeling: According to University of Helsinki food safety professor Marina Heinonen, more than 90% of dietary supplement health claims are incorrect. While many of the claims are based on scientifically based physiological or biochemical processes, their use in bodybuilding parlance is often heavily colored by bodybuilding lore and industry marketing and as such may deviate considerably from traditional scientific usages of the terms. In addition, ingredients listed have been found at times to be different from the contents. In 2015, Consumer Reports reported unsafe levels of arsenic, cadmium, lead and mercury in several of the protein powders that were tested. Other studies in 2013 showed that one-third of the supplements tested contained unlisted steroids. In 2015 a CBC investigative report found that protein spiking (the addition of amino acid filler to manipulate analysis) was not uncommon, however many of the companies involved challenged these claims.

Health problems: The US FDA reports 50,000 health problems a year due to dietary supplements and these often involve bodybuilding supplements. For example, the "natural" best-seller Craze, 2012's "New Supplement of the Year" by bodybuilding.com, sold in Walmart, Amazon etc., was found to contain undisclosed amphetamine-like compounds. Also other products by Matt Cahill have contained dangerous substances causing blindness or liver damages, and experts say that Cahill is emblematic for the whole industry.

Liver damage: The incidence of liver damage from dietary supplements has tripled in a decade, the majority of these involved bodybuilding supplements. This resulted in liver transplants and, in some cases, death to the patient. Some have argued that the liver damage is more often caused by prescription drugs rather than supplements.

Lack of effectiveness: In addition to being potentially harmful, some have argued that there is little evidence to indicate any benefit to using bodybuilding supplements. For example, according to the IOC, no consensus had been reached in determining whether an individual in exercise training benefits from protein and amino acid supplements. "In view of the lack of compelling evidence to the contrary, no additional dietary protein is suggested for healthy adults undertaking resistance or endurance exercise".

Caffeine and Athletic Performance

Caffeine is a proven ergogenic aid in humans. Caffeine improves athletic performance in aerobic (especially endurance sports) and anaerobic conditions. Moderate doses of caffeine (around 5 mg/kg) can improve sprint performance, cycling and running time trial performance, endurance (i.e., it delays the onset of muscle fatigue and central fatigue), and cycling power output. Caffeine increases basal metabolic rate in adults. Caffeine ingestion prior to aerobic exercise increases fat oxidation, particularly in persons with low physical fitness.

Caffeine improves muscular strength and power, and may enhance muscular endurance. Caffeine also enhances performance on anaerobic tests. Caffeine consumption before constant load exercise is associated with reduced perceived exertion. While this effect is not present during exercise-to-exhaustion exercise, performance is significantly enhanced. This is congruent with caffeine reducing perceived exertion, because exercise-to-exhaustion should end at the same point of fatigue. Caffeine also improves power output and reduces time to completion in aerobic time trials, an effect positively (but not exclusively) associated with longer duration exercise.

Anabolic Steroids

Anabolic steroids are synthetic, or human-made, variations of the male sex hormone testosterone. The proper term for these compounds is *anabolic-androgenic steroids*. "Anabolic" refers to muscle building, and "androgenic" refers to increased male sex characteristics. Some common names for anabolic steroids are Gear, Juice, Roids, and Stackers. Health care providers can prescribe steroids to treat hormonal issues, such as delayed puberty. Steroids can also treat diseases that cause muscle loss, such as cancer and AIDS. But some athletes and bodybuilders misuse these drugs in an attempt to boost performance or improve their physical appearance.

The majority of people who misuse steroids are male weightlifters in their 20s or 30s. Anabolic steroid misuse is much less common in women. It is difficult to measure steroid misuse in the United States because many national surveys do not measure it. However, use among teens is generally minimal. The 2016 NIDA-funded Monitoring the Future study has shown that past-year misuse of steroids has declined among 8th and 10th graders in recent years, while holding steady for 12th graders.

People who misuse anabolic steroids usually take them orally, inject them into muscles, or apply them to the skin as a gel or cream. These doses may be 10 to 100 times higher than doses prescribed to treat medical conditions.

Commons patterns for misusing steroids include:

- cycling—taking multiple doses for a period of time, stopping for a time, and then restarting
- stacking—combining two or more different steroids and mixing oral and/or injectable types
- pyramiding—slowly increasing the dose or frequency of steroid misuse, reaching a peak amount, and then gradually tapering off to zero
- plateauing—alternating, overlapping, or substituting with another steroid to avoid developing a tolerance

There is no scientific evidence that any of these practices reduce the harmful medical consequences of these drugs.

How Anabolic Steroids Work

Anabolic steroids work differently from other drugs of abuse; they do not have the same short-term effects on the brain. The most important difference is that steroids do not directly activate the reward system to cause a “high”; they also do not trigger rapid increases in the brain chemical dopamine, which reinforces most other types of drug taking behavior. Misuse of anabolic steroids

might lead to negative mental effects, such as: paranoid (extreme, unreasonable) jealousy, extreme irritability and aggression (“roid rage”), *delusions*—false beliefs or ideas, impaired judgment, and mania. Aside from mental effects, steroid use commonly causes severe acne. It also causes the body to swell, especially in the hands and feet.

Anabolic steroid misuse might lead to serious, even permanent, health problems such as kidney problems or failure, liver damage and tumors, enlarged heart, high blood pressure, and changes in blood cholesterol, all of which increase the risk of stroke and heart attack, even in young people, and increased risk of blood clots. Several other effects are gender- and age-specific:

- **In men**: shrinking testicles, decreased sperm count, baldness, development of breasts, increased risk for prostate cancer
- **In women**: growth of facial hair or excess body hair, decreased breast size, male-pattern baldness, changes in or stop in the menstrual cycle, enlarged clitoris, deepened voice
- **In teens**: stunted growth (when high hormone levels from steroids signal to the body to stop bone growth too early) and stunted height (if teens use steroids before their growth spurt)

Some of these physical changes, such as shrinking sex organs in men, can add to mental side effects such as mood disorders.

Anabolic Steroids Addiction

Even though anabolic steroids do not cause the same high as other drugs, they can lead to a substance use disorder. A substance use disorder occurs when a person continues to misuse steroids, even though there are serious consequences for doing so. The most severe form of a substance use disorder is addiction. People might continue to misuse steroids despite physical problems, high costs to buy the drugs, and negative effects on their relationships. These behaviors reflect steroids' addictive potential.

Research has further found that some steroid users turn to other drugs, such as opioids, to reduce sleep problems and irritability caused by steroids. People who misuse steroids might experience withdrawal symptoms when they stop use, including:fatigue, restlessness, loss of appetite, sleep problems, decreased sex drive and steroid cravings.

One of the more serious withdrawal symptoms is depression, which can sometimes lead to suicide attempts. Some people seeking treatment for anabolic steroid addiction have found a combination of behavioral therapy and medications to be helpful. In certain cases of addiction, patients have taken medicines to help treat symptoms of withdrawal. For example, health care providers have prescribed antidepressants to treat depression and pain medicines for headaches and muscle and joint pain. Other medicines have been used to help restore the patient's hormonal system.

Drugs, Athletic Performance, and Drug Screening

In competitive sports, **doping** is the use of banned athletic performance-enhancing drugs by athletic competitors. The term *doping* is widely used by organizations that regulate sporting competitions. The use of drugs to enhance performance is considered unethical, and therefore prohibited, by most international sports organizations, including the International Olympic Committee. Furthermore, athletes (or athletic programs) taking explicit measures to evade detection exacerbate the ethical violation with overt deception and cheating.

The origins of doping in sports go back to the very creation of sport itself. From ancient usage of substances in chariot racing to more recent controversies in baseball and cycling, popular views among athletes have varied widely from country to country over the years. The general trend among authorities and sporting organizations over the past several decades has been to strictly regulate the use of drugs in sport. The reasons for the ban are mainly the health risks of performance-enhancing drugs, the equality of opportunity for athletes, and the exemplary effect of drug-free sport for the public. Anti-doping authorities state that using performance-enhancing drugs goes against the "spirit of sport".

Many sports organizations have banned the use of performance-enhancing drugs and have very strict rules and penalties for people who are caught using them. The International Amateur Athletic Federation, now World Athletics, was the first international governing body of sport to take the situation seriously. In 1928 they banned participants from doping, but with little in the way of testing available they had to rely on the word of the athlete that they were clean. It was not until 1966 that FIFA and Union Cycliste Internationale (cycling) joined the IAAF in the fight against drugs, followed by the International Olympic Committee the following year. Progression in pharmacology has always outstripped the ability of sports federations to implement rigorous testing procedures but since the creation of the World Anti-Doping Agency in 1999, it has become more effective to catch athletes who use drugs. The first tests for athletes were at the 1966 European Championships and two years later the IOC implemented their first drug tests at

both the Summer and Winter Olympics. Anabolic steroids became prevalent during the 1970s and after a method of detection was found they were added to the IOC's prohibited substances list in 1975, after which the 1976 Summer Olympics in Montreal were the first Olympic games which tested for them.

Exercise and the Brain

The **neurobiological effects of physical exercise** are numerous and involve a wide range of interrelated effects on brain structure, brain function, and cognition.[1][2][3][4]A large body of research in humans has demonstrated that consistent aerobic exercise (e.g., 30 minutes every day) induces persistent improvements in certain cognitive functions, healthy alterations in gene expression in the brain, and beneficial forms of neuroplasticity and behavioral plasticity; some of these long-term effects include: increased neuron growth, increased neurological activity (e.g., c-Fos and BDNF signaling), improved stress coping, enhanced cognitive control of behavior, improved declarative, spatial, and working memory, and structural and functional improvements in brain structures and pathways associated with cognitive control and memory.[1][2][3][4][5][6][7][8][9][10] The effects of exercise on cognition have important implications for improving academic performance in children and college students, improving adult productivity, preserving cognitive function in old age, preventing or treating certain neurological disorders, and improving overall quality of life.[1][11][12]

In healthy adults, aerobic exercise has been shown to induce transient effects on cognition after a single exercise session and persistent effects on cognition following regular exercise over the course of several months.[1][10][13] People who regularly perform aerobic exercise (e.g., running, jogging, brisk walking, swimming, and cycling) have greater scores on neuropsychological function and performance tests that measure certain cognitive functions, such as attentional control, inhibitory control, cognitive flexibility, working memory updating and capacity, declarative memory, spatial memory, and information processing speed.[1][5][7][9][10][13] The transient effects of exercise on cognition include improvements in most executive functions (e.g., attention, working memory, cognitive flexibility, inhibitory control, problem solving, and decision making) and information processing speed for a period of up to 2 hours after exercising.[13]

Aerobic exercise induces short- and long-term effects on mood and emotional states by promoting positive affect, inhibiting negative affect, and decreasing the biological response to acute psychological stress.[13] Over the short-term, aerobic exercise functions as both an antidepressant and euphoriant,[14][15][16][17] whereas consistent exercise produces general improvements in mood and self-esteem.

Regular aerobic exercise improves symptoms associated with a variety of central nervous system disorders and may be used as an adjunct therapy for these disorders. There is clear evidence of exercise treatment efficacy for major depressive disorder and attention deficit hyperactivity disorder.[11][16][20][21][22][23] The American Academy of Neurology's clinical practice guideline for mild cognitive impairment indicates that clinicians should recommend regular exercise (two times per week) to individuals who have been diagnosed with this condition.[24] Reviews of clinical evidence also support the use of exercise as an adjunct therapy for certain neurodegenerative disorders, particularly Alzheimer’s disease and Parkinson's disease. Regular exercise is also associated with a lower risk of developing neurodegenerative disorders.[28][31] A large body of preclinical evidence and emerging clinical evidence supports the use of exercise as an adjunct therapy for the treatment and prevention of drug addictions. Regular exercise has also been proposed as an adjunct therapy for brain cancers.[37]

Endorphins play a major role in the body's inhibitory response to pain. Endorphin production can be triggered by vigorous aerobic exercise. The release of β-endorphin has been postulated to contribute to the phenomenon known as a "runner's high." Endorphins may contribute to the positive effect of exercise on anxiety and depression. The same phenomenon may also play a role in exercise addiction. Regular intense exercise may cause the brain to downregulate the production of endorphins in periods of rest to maintain homeostasis, causing a person to exercise more intensely in order to receive the same feeling. However, several studies have supported the hypothesis that the runner's high is due to the release of endocannabinoids rather than that of endorphins.

Summary

- Anabolic steroids are synthetic variations of the male sex hormone testosterone. Health care providers can prescribe steroids to treat various medical conditions. But some athletes and bodybuilders misuse these drugs to boost performance or improve their physical appearance.
- People who abuse anabolic steroids usually take them orally, inject them into the muscles, or apply them to the skin with a cream or gel.

- People misuse steroids in a variety of doses and schedules. Misuse of anabolic steroids might lead to short-term effects, including paranoid jealousy, extreme irritability and aggression, delusions, impaired judgment, and mania. Continued steroid misuse can act on some of the same brain pathways and chemicals that are affected by other drugs, including dopamine, serotonin, and opioid systems.
- Caffeine improves athletic performance in aerobic (especially endurance sports) and anaerobic conditions.
- Anabolic steroid misuse might lead to serious long-term, even permanent, health problems. Several other effects are gender- and age-specific.
- Even though anabolic steroids do not cause the same high as other drugs, they can lead to addiction. Some people seeking treatment for anabolic steroid addiction have found behavioral therapy and medications to be helpful. Medicines can help treat symptoms of withdrawal in some cases.
- The use of drugs to enhance performance is considered unethical, and therefore prohibited, by most international sports organizations, including the International Olympic Committee.
- Endorphin production can be triggered by vigorous aerobic exercise.

Contributors and Attributions

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- National Institute on Drug Abuse; National Institutes of Health; U.S. Department of Health and Human Services.
- Marisa Alviar-Agnew (Sacramento City College)

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CHAPTER OVERVIEW

18: Drugs

18.1: Pain Relievers- From Aspirin to Oxycodone
18.2: Cold and Allergy Medicines
18.3: Drugs and Infectious Diseases
18.4: Chemicals Against Cancer
18.5: Hormones - The Regulators
18.6: Drugs for the Heart
18.7: Drugs and the Mind

Thumbnail: Ritalin SR 20 mg, a brand-name sustained-release formulation of methylphenidate. (CC SA-BY 3.0; Sponge).

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18.1: Pain Relievers- From Aspirin to Oxycodone

Learning Objectives

- Know the difference between anti-inflammatory, analgesic and antipyretic drugs.
- Describe how aspirin and other NSAIDs work.
- Know the side effects of taking prescription and non-prescription medications
- Know the risks of addiction, abuse, and overdose of prescription opioids.

A **drug** is any substance that causes a change in an organism's physiology or psychology when consumed. Drugs are typically distinguished from food and substances that provide nutritional support. Consumption of drugs can be via inhalation, injection, smoking, ingestion, absorption via a patch on the skin, suppository, or dissolution under the tongue.

Anti-inflammatory, analgesic (pain reliever or pain killer), and antipyretic (fever reducer) drugs are a heterogeneous group of compounds, often chemically unrelated (although most of them are organic acids), which nevertheless share certain therapeutic actions and side effects. The prototype is aspirin; hence these compounds are often referred to as aspirin-like drugs. All aspirin-like drugs are antipyretic, analgesic, and anti-inflammatory, but there are important differences in their activities. For example, acetaminophen is antipyretic and analgesic but is only weakly anti-inflammatory. The reason for the differences are not clear; variations in the sensitivity of enzymes in the target tissues may be important.

When employed as analgesics, these drugs are usually effective only against pain of low-to-moderate intensity, particularly that associated with inflammation. Aspirin drugs do not change the perception of sensory modalities other than pain. The type of pain is important; chronic postoperative pain or pain arising from inflammation is particularly well controlled by aspirin-like drugs, whereas pain arising from the hollow viscera is usually not relieved.

Over-the-counter (OTC) medicines are good for many types of pain. There are two main types of OTC pain medicines: acetaminophen (Tylenol) and nonsteroidal anti-inflammatory drugs (NSAIDs). Aspirin, naproxen (Aleve), and ibuprofen (Advil, Motrin) are examples of OTC NSAIDs.

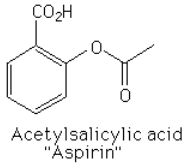
If OTC medicines don't relieve ones pain, the doctor may prescribe something stronger. Many NSAIDs are also available at higher prescription doses. The most powerful pain relievers are opioids. They are very effective, but they can sometimes have serious side effects. There is also a risk of addiction. Because of the risks, you must use them only under a doctor's supervision.

Aspirin and other NSAIDs

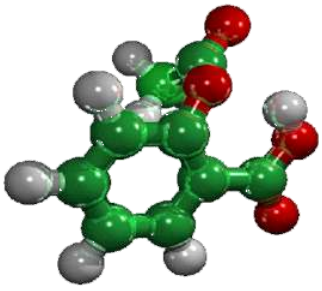
Nonsteroidal anti-inflammatory drugs (**NSAIDs**) are members of a drug class that reduces pain, decreases fever, prevents blood clots, and in higher doses, decreases inflammation. Side effects depend on the specific drug but largely include an increased risk of gastrointestinal ulcers and bleeds, heart attack, and kidney disease.

The term *nonsteroidal* distinguishes these drugs from steroids, which while having a similar eicosanoid-depressing, anti-inflammatory action, have a broad range of other effects. First used in 1960, the term served to distance these medications from steroids, which were particularly stigmatised at the time due to the connotations with anabolic steroid abuse.The most prominent NSAIDs are aspirin, ibuprofen, and naproxen, all available over the counter (OTC) in most countries.

In the U.S., about 10 to 20 thousand tons of **aspirin** are consumed each year; it is our most popular analgesic. Aspirin is one of the most effective analgesic, antipyretic, and anti-inflammatory agents.



Acetylsalicylic acid
"Aspirin"



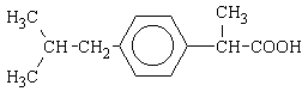
Chemical structure

Figure 18.1.1 Aspirin

Aspirin is known to interfere with the action of the platelets. As a result, some people who take a lot of aspirin experience easy bruising of the skin. Therefore, people who have major bleeding problems should not take aspirin. Also, keep in mind that aspirin should not be taken for 10-14 days before surgery (including surgery in the mouth) to avoid excessive bleeding during or after the operation. These side effects probably depend on aspirin-like drugs' ability to block endogenous prostaglandin biosynthesis. Platelet function appears to be disturbed because aspirin-like drugs prevent the formation by the platelets of thrombozane A2 (TXA2), a potent aggregating agent. This accounts for the tendency of these drugs to increase the bleeding time.

Other Aspirin-Like Drugs

There are other non-selective NSAIDs on the market, including diclofenac, ibuprofen, ketoprofen, meloxicam, naproxen, and oxaprozin. Ibuprofen and naproxen are available in both prescription and over-the-counter (OTC) versions. The doses in OTC ibuprofen (Advil and Motrin) or naproxen (Aleve) are about half the doses of prescription versions.



Ibuprofen

Figure 18.1.2 Ibuprofen.

How NSAIDs Work?

Non-selective NSAIDs like aspirin work (Figure 18.1.3) by inhibiting two enzymes that are involved with pain and inflammation—cyclooxygenase-1 and cyclooxygenase-2 (COX-1 and COX-2). These enzymes are involved with the ring closure and addition of oxygen to arachidonic acid converting to prostaglandins. The acetyl group on aspirin is hydrolzed and then bonded to the alcohol group of serine as an ester (Figure 18.1.2). This has the effect of blocking the channel in the enzyme and arachidonic acid can not enter the active site of the enzyme. By inhibiting or blocking this enzyme, the synthesis of prostaglandins is blocked, which in turn relieves some of the effects of pain and fever. Aspirin is also thought to inhibit the prostaglandin synthesis involved with unwanted blood clotting in coronary heart disease. At the same time an injury while taking aspirin may cause more extensive bleeding.

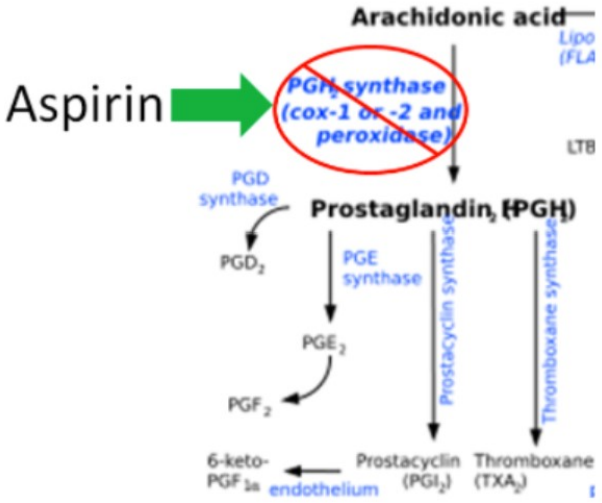


Figure 18.1.3 Aspirin inhibition of COX-1 and COX-2 enzymes.

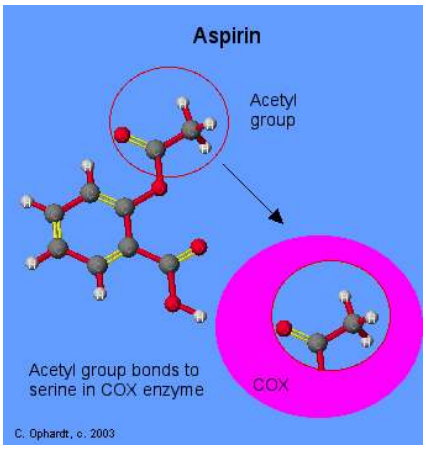


Figure 18.1.4 The acetyl group (from aspirin) bonds to serine in COX enzyme.

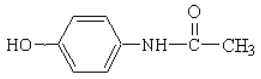
COX-2 selective inhibitors are a newer type of medicine that block the COX-2 enzyme more than the COX-1 enzyme. The only COX-2 selective inhibitor currently on the market in the United States is the prescription drug Celebrex (celecoxib), which is marketed by Pfizer. It was believed that COX-2 inhibitors may be less likely to cause the stomach problems associated with the older NSAIDs, but all NSAIDs carry the risk of stomach problems.

Key Points to Remember With NSAIDs

- Too much can cause stomach bleeding. This risk increases in people who are over 60 years of age, are taking prescription blood thinners, are taking steroids, have a history of stomach bleeding or ulcers, and/or have other bleeding problems.
- Use of NSAIDs can also cause kidney damage. This risk may increase in people who are over 60 years of age, are taking a diuretic (a drug that increases the excretion of urine), have high blood pressure, heart disease, or pre-existing kidney disease.

Acetaminophen

Acetaminophen is an effective alternative to aspirin as an analgesic and antipyretic agent. However, its anti-inflammatory effect is minor and not clinically useful. It is commonly felt that acetaminophen may have fewer side effects than aspirin, but it should be noted that an acute overdose may produce severe or even fatal liver damage. Acetaminophen does not inhibit platelet aggregation and therefore is not useful for preventing vascular clotting.



Acetaminophen (4'-hydroxyacetanilide)

Side effects are usually fewer than those of aspirin; the drug produces less gastric distress and less ringing in the ears. However, as stated previously, overdose can lead to severe damage of the liver.

Acetaminophen has been proved to be a reasonable substitute for aspirin when analgesic or antipyretic effectiveness is desired, especially in patients who cannot tolerate aspirin. This might include patients with peptic ulcer disease of gastric distress or those in whom the anticoagulant action of aspirin might be undesirable.

Key Points to Remember With Acetaminophen

- Taking a higher dose than recommended will not provide more relief and can be dangerous.
- Too much can lead to liver damage and death. Risk for liver damage may be increased in people who drink three or more alcoholic beverages a day while using acetaminophen-containing medicines.
- Be cautious when giving acetaminophen to children. Infant drop medications can be significantly stronger than regular children's medications. Read and follow the directions on the label every time you use a medicine. Be sure that your infant is getting the infants' pain formula and your older child is getting the children's pain formula.

Prescription Medications

Typical prescription pain relief medicines include opioids and non-opioid medications. Types of prescription opioid medications (Figures 18.1.6 and 18.1.7) include:

- **morphine**, which is often used before and after surgical procedures to alleviate severe pain
- **oxycodone**, which is also often prescribed for moderate to severe pain
- **codeine**, which comes in combination with acetaminophen or other non-opioid pain relief medications and is often prescribed for mild to moderate pain
- **hydrocodone**, which comes in combination with acetaminophen or other non-opioid pain relief medications and is prescribed for moderate to moderately severe pain

Derived from opium, opioid drugs are very powerful products. They act by attaching to a specific "receptor" in the brain, spinal cord, and gastrointestinal tract. Opioids can change the way a person experiences pain. The term opium refers to the crude resinous extract obtained from the opium poppy. Crude opium contains a wide variety of ingredients, including morphine and codeine, both of which are widely used in medicine. The bulk of the ingredients of opium, however, consists of such organic substances as resins, oils, sugars, and proteins that account for more than 75 % of the weight of the opium but exert little pharmacological activity. Morphine is the major pain relieving drug found in opium, being approximately 10% of the crude exudate. Codeine is structurally close to morphine (see Figure 18.1.6), although it is much less potent and amounts to only 0.5% of the opium extract. Heroin does not occur naturally but is a semisynthetic derivative produced by a chemical modification of morphine that increases the potency. It takes only 3 mg. of heroin to produce the same analgesic effect as 10 mg of morphine. However, at these equally effective doses, it may be difficult to distinguish between the effects of the two compounds.

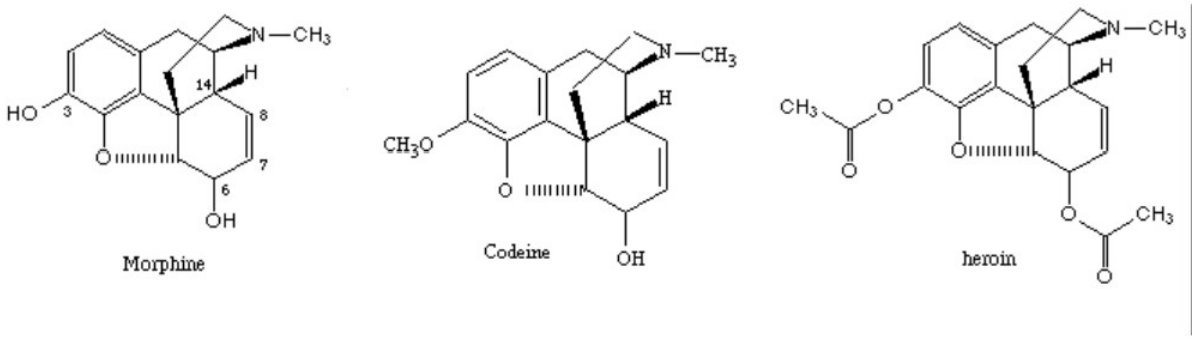


Figure 18.1.6 Morphine, codeine and heroin.

Oxycodone and hydrocodone are used to relieve moderate to severe pain. Oxycodone and hydrocodone extended-release tablets and extended-release capsules are used to relieve severe pain in people who are expected to need pain medication around the clock for a long time and who cannot be treated with other medications.

Addiction and Overdose

Anyone who takes prescription opioids can become addicted to them. In fact, as many as one in four patients receiving long-term opioid therapy in a primary care setting struggles with opioid addiction. Once addicted, it can be hard to stop. In 2016, more than 11.5 million Americans reported misusing prescription opioids in the past year. Taking too many prescription opioids can stop a person’s breathing—leading to death.

Prescription opioid overdose deaths also often involve benzodiazepines. Benzodiazepines are central nervous system depressants used to sedate, induce sleep, prevent seizures, and relieve anxiety. Examples include alprazolam (Xanax®), diazepam (Valium®), and lorazepam (Ativan®). Avoid taking benzodiazepines while taking prescription opioids whenever possible.

Side Effects of Prescription Opioids

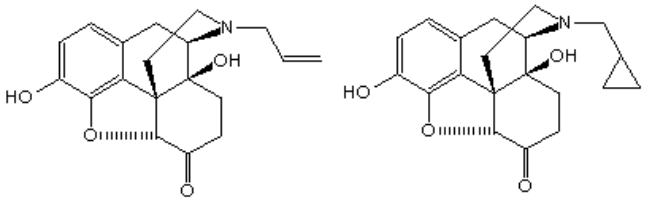
In addition to the serious risks of addiction, abuse, and overdose, the use of prescription opioids can have a number of side effects, even when taken as directed:

- Tolerance—meaning you might need to take more of the medication for the same pain relief
- Physical dependence—meaning you have symptoms of withdrawal when the medication is stopped
- Increased sensitivity to pain
- Constipation
- Nausea, vomiting, and dry mouth
- Sleepiness and dizziness
- Confusion
- Depression
- Low levels of testosterone that can result in lower sex drive, energy, and strength
- Itching and sweating

Opiate Antagonists

Naloxone, when administered to normal individuals, produces no analgesia, euphoria, or respiratory depression. However, it rapidly precipitates withdrawal in narcotic-dependent individuals. Naloxone antagonizes the actions of morphine at all its receptors.

The uses of naloxone include the reversal of the respiratory depression that follows acute narcotic intoxication and the reversal of narcotic-induced respiratory depression in newborns of mothers who have received narcotics. The use of naloxone is limited by a short duration of action and the necessity of parenteral route of administration.



naloxone (Narcan®) naltrexone (Trexan®)

Naltrexone became clinically available in 1985 as a new narcotic antagonist. Its actions resemble those of naloxone, but naltrexone is well is well absorbed orally and is long acting, necessitating only a dose of 50 to 100 mg. Therefore, it is useful in narcotic treatment programs where it is desired to maintain an individual on chronic therapy with a narcotic antagonist. In individuals taking naltrexone, subsequent injection of an opiate will produce little or no effect. naltrexone appears to be particularly effective for the treatment of narcotic dependence in addicts who have more to gain by being drug-free rather than drug dependant.

Combination Pain Relievers

Aspirin is often combined with acetaminophen in a single tablet for relief of arthritis and other painful conditions. Sometimes other drugs such as caffeine, an antihistamine, nasal drying agents, and sedatives are also added. Although some of these preparations may have special uses for certain acute conditions such as a cold or a headache, they should not be taken for a chronic (long-term) form of arthritis. If a combination is required, each drug should be prescribed separately. The dose of each should be adjusted individually to achieve the greatest benefit with the fewest side effects.

Hydrocodone is available in combination with other ingredients, and different combination products are prescribed for different uses. Some hydrocodone combination products are used to relieve moderate-to-severe pain. Other hydrocodone combination products are used to relieve cough. Hydrocodone is in a class of medications called opiate (narcotic) analgesics and in a class of medications called antitussives. Hydrocodone relieves pain by changing the way the brain and nervous system respond to pain. Hydrocodone relieves cough by decreasing activity in the part of the brain that causes coughing.

Web Link

A list of different hydrocodone combination products can be found on the link below.

https://medlineplus.gov/druginfo/meds/a601006.html

Summary

- Different types of medicine address different ailments. Anti-inflammatory drugs mediate inflammation, analgesics relieve pain, and antipyretic drugs help lower body temperature associated with fever.
- Over the counter (OTC) pain relievers relieve the minor aches and pains associated with conditions such as headaches, fever, colds, flu, arthritis, toothaches, and menstrual cramps.
- There are basically two types of OTC pain relievers: acetaminophen and non-steroidal anti-inflammatory drugs (NSAIDs).
- Aspirin and other aspirin-like drugs work by blocking the (COX-1 and COX-2) enzymes involved in pain and inflammation.
- Typical prescription pain relief medicines include opioids and non-opioid medications.
- In addition to the serious risks of addiction, abuse, and overdose, the use of prescription opioids can have a number of side effects,

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18.1: Pain Relievers- From Aspirin to Oxycodone is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

18.2: Cold and Allergy Medicines

Learning Objective

- Know the cause of the common cold and allergies.
- Know the chemical name, common name, and uses of different cough, cold, and allergy medicines.

The **common cold** is a viral infectious disease of the upper respiratory tract which affects primarily the nose. The symptoms of the common cold are believed to be primarily related to the immune response to the virus. Symptoms include coughing, sore throat, runny nose, and fever which usually resolve in seven to ten days, with some symptoms lasting up to three weeks. Well over 200 viruses are implicated in the cause of the common cold. The most commonly implicated virus is a rhinovirus (30–80%).

No cure for the common cold exists, but the symptoms can be treated. Antibiotics have no effect against viral infections and thus have no effect against the viruses that cause the common cold. Due to their side effects they cause overall harm; however, they are still frequently prescribed. It is the most frequent infectious disease in humans with the average adult contracting two to three colds a year and the average child contracting between six and twelve. These infections have been with humanity since antiquity.

Allergies are a number of conditions caused by hypersensitivity of the immune system to typically harmless substances in the environment. These diseases include hay fever, food allergies, atopic dermatitis, allergic asthma, and anaphylaxis. Symptoms may include red eyes, an itchy rash, sneezing, a runny nose, shortness of breath, or swelling. Food intolerances and food poisoning are separate conditions.

Early exposure to potential allergens may be protective. Treatments for allergies include the avoidance of known allergens and the use of medications such as steroids and antihistamines. **Histamine** is concentrated in mast cells, cells whose function is essentially to release histamine and immunoglobins when tissue damage occurs. They are especially numerous in parts of the body that are injured often, such as the fingers and toes, or which enjoy frequent contact with the environment, such as the mucosa of the lips, nose, etc.

Types of Cold and Allergy Medications

Cold medicines are medications used by people with the common cold, cough, or related conditions. While a wide variety of drugs are marketed as cough suppressants, research shows there is often little or no measurable benefit in reducing cough symptoms. While they have been used by 10% of American children in any given week, they are not recommended in Canada or the United States in children six years or younger because of lack of evidence showing effect and concerns of harm. One version with codeine, guaifenesin, and pseudoephedrine was the 213th most commonly prescribed medication in 2017, in the United States, with more than two million prescriptions.

There are a number of different cough and cold medications, which may be used for various coughing symptoms. The commercially available products may include various combinations of any one or more of the following types of substances listed in the table below.

Table **18.2.1** Different Cough & Cold Medications.

Medication	Function	Examples
Mucokinetics, or mucolytics	a class of drugs which aid in the clearance of mucus from the airways, lungs, bronchi, and trachea	carbocisteine, ambroxol, and bromhexine.
Expectorants	substances claimed to make coughing easier while enhancing the production of mucus and phlegm.	acetylcysteine and guaifenesin.
Antitussives, or cough suppressants substances which suppress the coughing itself	substances which suppress the coughing itself	codeine, pholcodine, dextromethorphan, noscapine, and butamirate.
Antihistamines	for allergic rhinitis may produce mild sedation and reduce other associated symptoms, like a runny nose and watery eyes	diphenhydramine, chlorpheniramine, brompheniramine, loratadine, and cetirizine.
Decongestants	relieve nasal congestion and sinus infection	ephedrine, phenylephrine, pseudoephedrine, and oxymetazoline.
Fever or pain medication (antipyretic or analgesic)	fever reducer or pain reliever	paracetamol (called "acetaminophen " in the US) and NSAIDs such as aspirin, ibuprofen or naproxen
Syrups	various substances supposed to soften the coughing	honey or supplement syrup

Effectiveness

The efficacy of cough medication is questionable, particularly in children. A 2014 Cochrane review concluded that "There is no good evidence for or against the effectiveness of OTC medicines in acute cough". Some cough medicines may be no more effective than placebos for acute coughs in adults, including coughs related to upper respiratory tract infections. The American College of Chest Physicians emphasizes that cough medicines are not designed to treat whooping cough, a cough that is caused by bacteria and can last for months. No over-the-counter cough medicines have been found to be effective in cases of pneumonia. They are not recommended in those who have COPD, chronic bronchitis, or the common cold. There is not enough evidence to make recommendations for those who have a cough and cancer.

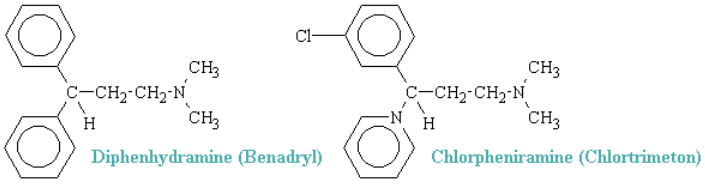
Medications

- Dextromethorphan (DXM) may be modestly effective in decreasing cough in adults with viral upper respiratory infections. However, in children it has not been found to be effective.
- Codeine was once viewed as the "gold standard" in cough suppressants, but this position is now questioned. Some recent placebo-controlled trials have found that it may be no better than a placebo for some causes including acute cough in children. It is thus not recommended for children. Additionally, there is no evidence that hydrocodone is useful in children. Similarly, a 2012 Dutch guideline does not recommend its use to treat acute cough.
- A number of other commercially available cough treatments have not been shown to be effective in viral upper respiratory infections. These include for adults: antihistamines, antihistamine-decongestant combinations, benzonatate, anti asthmatic-expectorant-mucolytic combinations, expectorant-bronchodilator combinations, leukotriene inhibitors, ambroxol, and guaifenesin, sometimes with analgesics, antipyretics, anti inflammatories, and anticholinergics - and for children: antihistamines, decongestants for clearing the nose, or combinations of these and leukotriene inhibitors for allergy and asthma. However, antihistamines cannot be used as an empirical therapy in case of chronic, or non specific cough especially in very young children. Long term diphenhydramine use is associated with negative outcomes in older people.

Antihistamines are drugs which treat hay fever and other allergies. Typically, people take antihistamines as an inexpensive, not patented (generic), drug that can be bought without a prescription and relieves from nasal congestion, sneezing, or hives caused by pollen, dust mites, or animal allergy with few side effects. Antihistamines are usually for short-term treatment. Chronic allergies increase the risk of health problems which antihistamines might not treat, including asthma, sinusitis, and lower respiratory tract infection. Consultation of a medical professional is recommended for those who intend to take antihistamines for longer-term use.

Although people typically use the word “antihistamine” to describe drugs for treating allergies, doctors and scientists use the term to describe a class of drug that opposes the activity of histamine receptors in the body. In this sense of the word, antihistamines are subclassified according to the histamine receptor that they act upon. The two largest classes of antihistamines are H_1-antihistamines and H_2-antihistamines.

H_1-antihistamines work by binding to histamine H_1 receptors in mast cells, smooth muscle, and endothelium in the body as well as in the tuberomammillary nucleus in the brain. Antihistamines that target the histamine H_1-receptor are used to treat allergic reactions in the nose (e.g., itching, runny nose, and sneezing). In addition, they may be used to treat insomnia, motion sickness, or vertigo caused by problems with the inner ear. H_2-antihistamines bind to histamine H_2 receptors in the upper gastrointestinal tract, primarily in the stomach. Antihistamines that target the histamine H_2-receptor are used to treat gastric acid conditions (e.g., peptic ulcers and acid reflux). Two common examples of antihistamines are shown below.



Alternative Medicine

Honey may be a minimally effective cough treatment. A Cochrane review found the evidence to recommend for or against its use in children to be weak. In light of this they found it was better than no treatment, placebo, and diphenhydramine but not better than dextromethorphan for relieving cough symptoms. Honey's use as a cough treatment has been linked on several occasions to infantile botulism and accordingly should not be used in children less than one year old.

Many alternative treatments are used to treat the common cold. A 2007 review states that, "alternative therapies (i.e., Echinacea, vitamin C, and zinc) are not recommended for treating common cold symptoms; however, ... Vitamin C prophylaxis may modestly reduce the duration and severity of the common cold in the general population and may reduce the incidence of the illness in persons exposed to physical and environmental stresses." A 2014 review also found insufficient evidence for Echinacea.

A 2009 review found that the evidence supporting the effectiveness of zinc is mixed with respect to cough, and a 2011 Cochrane review concluded that zinc "administered within 24 hours of onset of symptoms reduces the duration and severity of the common cold in healthy people". A 2003 review concluded: "Clinical trial data support the value of zinc in reducing the duration and severity of symptoms of the common cold when administered within 24 hours of the onset of common cold symptoms." Zinc gel in the nose may lead to long-term or permanent loss of smell. The FDA therefore discourages its use.

Adverse effects

A number of accidental overdoses and well-documented adverse effects suggested caution in children. The FDA in 2015 warned that the use of codeine-containing cough medication in children may cause breathing problems. Cold syrup overdose has been linked to visual and auditory hallucinations, rapid involuntary jaw, tongue and eye movements in children.

Summary

- The **common cold** (also known as nasopharyngitis, rhinopharyngitis, acute coryza, or a cold) is a viral infectious disease of the upper respiratory tract which affects primarily the nose. The symptoms of the common cold are believed to be primarily related to the immune response to the virus.

- An **allergy** is an immune response (with the release of histamines), or reaction, to substances (allergens) that are usually not harmful.
- A number of different cough and cold medications can be used to alleviate various symptoms but not diminish the intensity of the response.

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18.3: Drugs and Infectious Diseases

Learning Objectives

- Differentiate between antibiotics and antiviral agents.
- Know the different antibiotics and antiviral agents and their mode of action.

The World Health Organization's (WHO) International Classification of Diseases (ICD) is used in clinical fields to classify diseases and monitor morbidity (the number of cases of a disease) and mortality (the number of deaths due to a disease). In this section, we will introduce terminology used by the ICD (and in health-care professions in general) to describe and categorize various types of disease.

An **infectious disease** is any disease caused by the direct effect of a pathogen. A pathogen may be cellular (bacteria, parasites, and fungi) or acellular (viruses, viroids, and prions). Some infectious diseases are also communicable, meaning they are capable of being spread from person to person through either direct or indirect mechanisms. Some infectious communicable diseases are also considered contagious diseases, meaning they are easily spread from person to person. Not all contagious diseases are equally so; the degree to which a disease is contagious usually depends on how the pathogen is transmitted. For example, measles is a highly contagious viral disease that can be transmitted when an infected person coughs or sneezes and an uninfected person breathes in droplets containing the virus. Gonorrhea is not as contagious as measles because transmission of the pathogen (*Neisseria gonorrhoeae*) requires close intimate contact (usually sexual) between an infected person and an uninfected person.

Antibiotics

The modern era of the chemotherapy of infection started with the clinical use of sulfanilamide in 1936. The "golden age" of antimicrobial therapy began with the production of penicillin in 1941, when this compound was mass-produced and first made available for limited clinical trial. More than 30% of all hospitalized patients now receive one or more courses of therapy with antibiotics, and millions of potentially fatal infections have been cured. However, at the same time, these pharmaceutical agents have become among the most misused of those available to the practicing physician. One result of widespread use of antimicrobial agents has been the emergence of antibiotic-resistant pathogens, which in turn has created an ever-increasing need for new drugs. Many of these agents have also contributed significantly to the rising costs of medical care.

An antibiotic is any substance produced by a microorganism that is excreted to harm or kill another microorganism. Technically, antibiotics are microbial or fungal products. But these substances can be synthesized and mass produced in the laboratory to use against harmful microorganisms in the environment. Thus, the synthetic chemist has added greatly to our therapeutic armamentarium. Synthetic drugs such as isonaizid and theambutol represent important contributions for the treatment of tuberculosis. While many such antimicrobial agents are not properly termed antibiotics, since they are not produced by living organisms, little distinction should now be made between compounds of natural and synthetic origin.

Synthetic Antibiotics - Sulfonamides

Sulfonamide is the basis of several groups of drugs. The original antibacterial sulfonamides (sometimes called sulfa drugs or sulpha drugs) are synthetic antimicrobial agents that contain the sulfonamide group. Some sulfonamides are also devoid of antibacterial activity, e.g., the anticonvulsant sultiame. The sulfonylureas and thiazide diuretics are newer drug groups based on the antibacterial sulfonamides.

Sulfa allergies are common, and medications containing sulfonamides are prescribed carefully. It is important to make a distinction between sulfa drugs and other sulfur-containing drugs and additives, such as sulfates and sulfites, which are chemically unrelated to the sulfonamide group and do not cause the same hypersensitivity reactions seen in the sulfonamides.

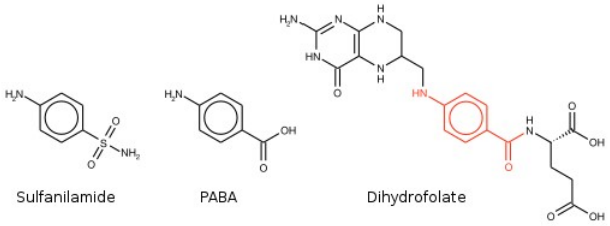


Figure **18.3.1** Structural similarity between sulfanilamide, a common sulfa drug (left) and PABA (center) is the basis for the inhibitory activity of sulfa drugs on dihydrofolate biosynthesis. Source: Wiikipedia

Sulfonamides are structural analogs and competitive antagonists of para-aminobenzoic acid (PABA), and thus prevent normal bacterial utilization of PABA for the synthesis of the vitamin folic acid (Figure **18.3.1**). More specifically, sulfonamides are competitive inhibitors of the bacterial enzyme sulfihydropteroate synthase, which is responsible for the conversion of PABA into dihydrofolic acid, the immediate precursor of folic acid. Sensitive microorganisms are those that must synthesis their own folic acid; bacteria that can utilize preformed folic acid are not affected.

Cell Wall Synthesis Inhibitors - Penicillin and Cepalosphorins

The penicillins were the first antibiotics discovered as natural products from the mold Penicillium and was effective against Gram-positive bacteria. All penicillin derivatives produce their bacteriocidal effects by inhibition of bacterial cell wall synthesis. Specifically, the cross linking of peptides on the mucosaccharide chains is prevented. If cell walls are improperly made cell walls allow water to flow into the cell causing it to burst. A number of natural penicillins have been discovered, but only two purified compounds are in clinical use: penicillin G (intravenous use) and penicillin V (given by mouth). Several semisynthetic penicillins are effective against a broader spectrum of bacteria: these include the antistaphylococcal penicillins, aminopenicillins and the antipseudomonal penicillins.

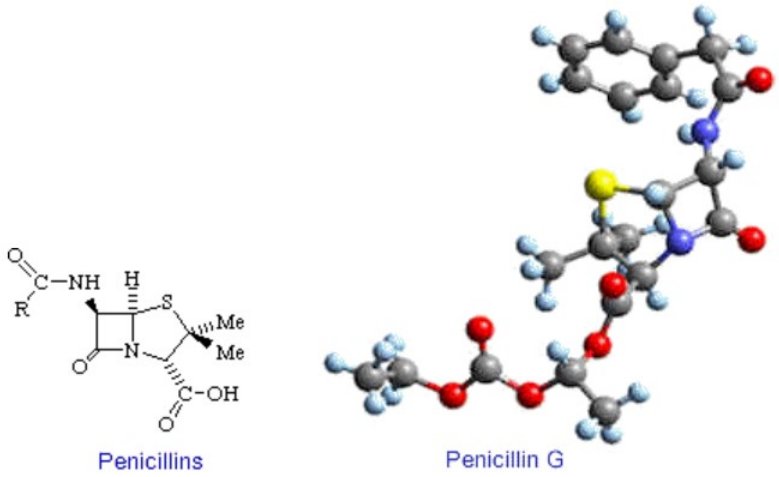


Figure **18.3.2** Penicillins.

Like penicillin, cephalosporins are valuable because of their low toxicity and their broad spectrum of action against various diseases. In this way, cephalosporin is very similar to penicillin. Cephalosporins are one of the most widely used antibiotics, and economically speaking, has about 29% of the antibiotic market. The cephalosporins are possibly the single most important group of antibiotics today and are equal in importance to penicillin. The structure and mode of action of the cephalosporins are similar to that of penicillin. They affect bacterial growth by inhibiting cell wall synthesis, in Gram-positive and -negative bacteria.

Figure **18.3.3** Cephalosporins.

Erythromycin is an orally effective antibiotic discovered in 1952 in the metabolic products of a strain of Streptocyces erythreus, originally obtained from a soil sample collected in the Philippine Archipelago. Erythromycin may be either bacteriostatic or bactericidal, depending on the microorganism and the concentration of the drug.

Erythromycin is an antibiotic used for the treatment of a number of bacterial infections. This includes respiratory tract infections, skin infections, chlamydia infections, pelvic inflammatory disease, and syphilis. It may also be used during pregnancy to prevent Group B streptococcal infection in the newborn, as well as to improve delayed stomach emptying. It can be given intravenously and by mouth. An eye ointment is routinely recommended after delivery to prevent eye infections in the newborn.

Erythromycin and other macrolide antibiotics inhibit protein synthesis by binding to 50 S ribosomal subunits of sensitive microorganisms. (Humans do not have 50 S ribosomal subunits, but have ribosomes composed of 40 S and 60 S subunits). Certain resistant microorganisms with mutational changes in components of this subunit of the ribosome fail to bind the drug.

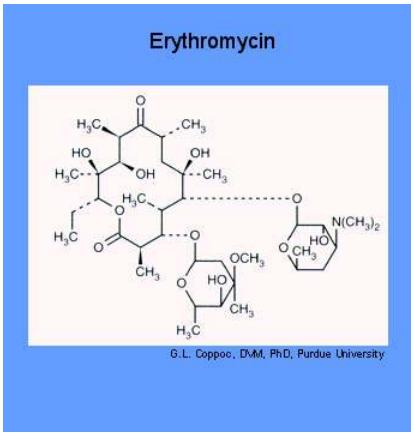


Figure **18.3.4** Erythromycin.

Tetracyclines have the broadest spectrum of antimicrobial activity. These may include: Aureomycin, Terramycin, and Panmycin. Four fused 6-membered rings, as shown in the figure below, form the basic structure from which the various tetracyclines are made. The various derivatives are different at one or more of four sites on the rigid, planar ring structure. The classical tetracyclines were derived from *Streptomyces spp*., but the newer derivatives are semisynthetic as is generally true for newer members of other drug groups.

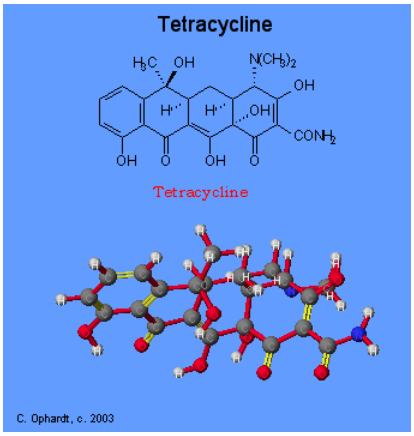


Figure **18.3.5** Tetracycline.

Tetracyclines inhibit bacterial protein synthesis by blocking the attachment of the transfer RNA-amino acid to the ribosome. More precisely they are inhibitors of the codon-anticodon interaction. Tetracyclines can also inhibit protein synthesis in the host, but are less likely to reach the concentration required because eukaryotic cells do not have a tetracycline uptake mechanism.

Streptomycin

Streptomycin is effective against gram-negative bacteria, although it is also used in the treatment of tuberculosis. Streptomycin binds to the 30S ribosome and changes its shape so that it and inhibits protein synthesis by causing a misreading of messenger RNA information.

Chloramphenicol

Chloromycetin is also a broad spectrum antibiotic that possesses activity similar to the tetracylines. At present, it is the only antibiotic prepared synthetically. It is reserved for treatment of serious infections because it is potentially highly toxic to bone marrow cells. It inhibits protein synthesis by attaching to the ribosome and interferes with the formation of peptide bonds between amino acids. It behaves as an antimetabolite for the essential amino acid phenylalanine at ribosomal binding sites.

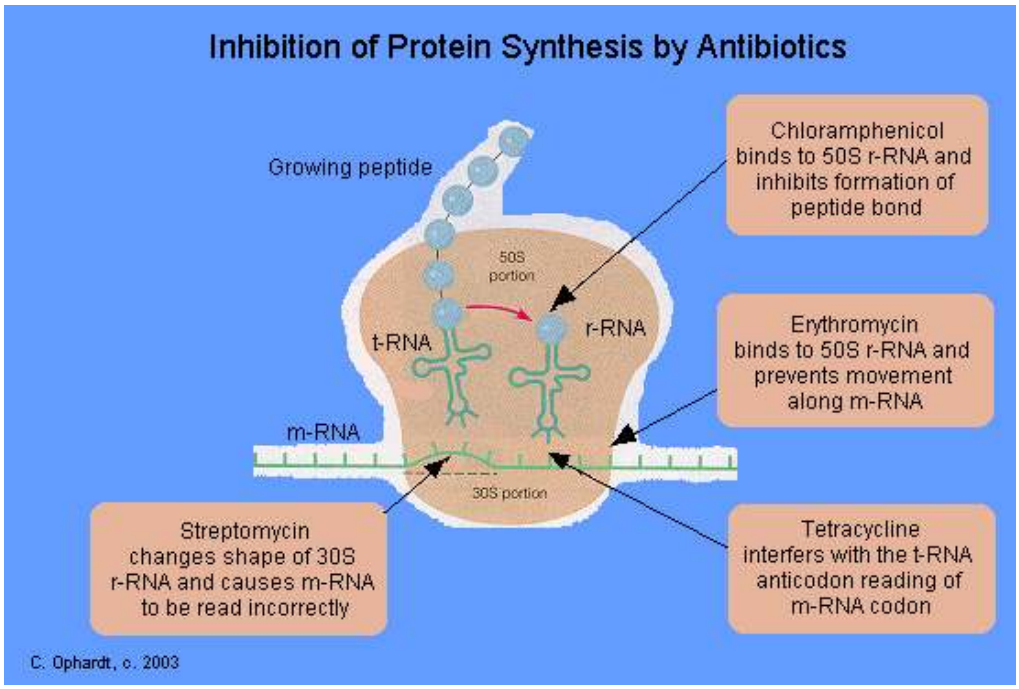


Figure **18.3.6** Inhibition of protein synthesis by erythtomycin, teracycline, streptomycin, and chloramphenicol.

A summary of the key features of different antibiotics is given in Table **18.3.1**.

Table **18.3.1** *Some Clinically Important Antibiotics.*

Antibiotic	Producer organism	Activity	Site or mode of action
Penicillin	*Penicillium chrysogenum*	Gram-positive bacteria	Wall synthesis
Cephalosporin	*Cephalosporium acremonium*	Broad spectrum	Wall synthesis
Griseofulvin	*Penicillium griseofulvum*	Dermatophytic fungi	Microtubules
Bacitracin	*Bacillus subtilis*	Gram-positive bacteria	Wall synthesis
Polymyxin B	*Bacillus polymyxa*	Gram-negative bacteria	Cell membrane
Amphotericin B	*Streptomyces nodosus*	Fungi	Cell membrane
Erythromycin	*Streptomyces erythreus*	Gram-positive bacteria	Protein synthesis
Neomycin	*Streptomyces fradiae*	Broad spectrum	Protein synthesis
Streptomycin	*Streptomyces griseus*	Gram-negative bacteria	Protein synthesis
Tetracycline	*Streptomyces rimosus*	Broad spectrum	Protein synthesis
Vancomycin	*Streptomyces orientalis*	Gram-positive bacteria	Protein synthesis
Gentamicin	*Micromonospora purpurea*	Broad spectrum	Protein synthesis
Rifamycin	*Streptomyces mediterranei*	Tuberculosis	Protein synthesis

History of Penicillin and General Information

Alexander Fleming loved to play, both in the laboratory and out. He always loved snooker and golf and had many whimsical variants on the rules. In the lab he made "germ paintings," in which he would draw with his culture loop using spores of highly pigmented bacteria, which were invisible when he made the painting, but when cultured developed into brightly colored scenes. He followed what Max Delbruck would later call the "principle of limited sloppiness." Fleming abhorred a tidy, meticulous lab; he left culture dishes lying around for weeks and would often discover interesting things in them. Though the story has been told in many sometimes conflicting ways, something like this resulted in the discovery of penicillin. He seems to have left a culture dish lying on the lab bench and then gone away on vacation. When he returned a few spores of an unusual mold had germinated on the plate. When he cultured the bacteria on the plate he found that they grew up to within a few centimeters of the mold, but there were killed. A crude extract of the mold was then shown to have antibacterial properties. Fleming made this discovery in 1928 and by 1929 had named it penicillin (he was told by a colleague that the mold was a type of Penicillium and "penicillozyme" must have seemed cumbersome).

Fleming continued to use penicillin in his lab but not with any great enthusiasm and certainly not to the exclusion of many other projects. He never developed it into a clinically useful compound, though in 1929 he suggested that it might have important clinical applications. Because he was a bacteriologist and not a chemist, Fleming did not attempt to purify penicillin. He seems to have run into a dead end with penicillin and so during the 1930s, though he kept it in his lab, he did not do much with it. In the late 1930s Australian Howard Florey came to London to work with Charles Sherrington. He worked on lysozyme for a while and then became interested in penicillin. It was Florey, with Chain and other of his group that developed penicillin into a clinical antibiotic. They did this during 1940-41. Fleming, Florey, and Chain shared the 1945 Nobel Prize in Physiology for Medicine.

Fleming became world-famous for penicillin, and was rightly acknowledged as the father of modern antibiotics, but Florey was just as rightly miffed at being denied much of the credit for creating the powerful medical tool we now know. Evidence does not suggest that Fleming deliberately denied Florey his due credit, but Fleming's peculiar, dry sense of humor seems to have caused him not to deny even the wildest attributions to him.

Viruses and Antiviral Drugs

Viruses cause a variety of diseases in animals, including humans, ranging from the common cold to potentially fatal illnesses like meningitis (FIgure 18.3.1). These diseases can be treated by antiviral drugs or by vaccines, but some viruses, such as HIV, are capable of both avoiding the immune response and mutating to become resistant to antiviral drugs.

Antiviral drugs are a class of medication used for treating viral infections. Most antivirals target specific viruses, while a broad-spectrum antiviral is effective against a wide range of viruses. Unlike most antibiotics, antiviral drugs do not destroy their target pathogen; instead they inhibit its development.

Antiviral drugs are one class of antimicrobials, a larger group which also includes antibiotic (also termed antibacterial), antifungal and antiparasitic drugs, or antiviral drugs based on monoclonal antibodies. Most antivirals are considered relatively to the host, and therefore can be used to treat infections. They should be distinguished from viricides, which are not medication but deactivate or destroy virus particles, either inside or outside the body. Natural viricides are produced by some plants such as eucalyptus and Australian tea trees.

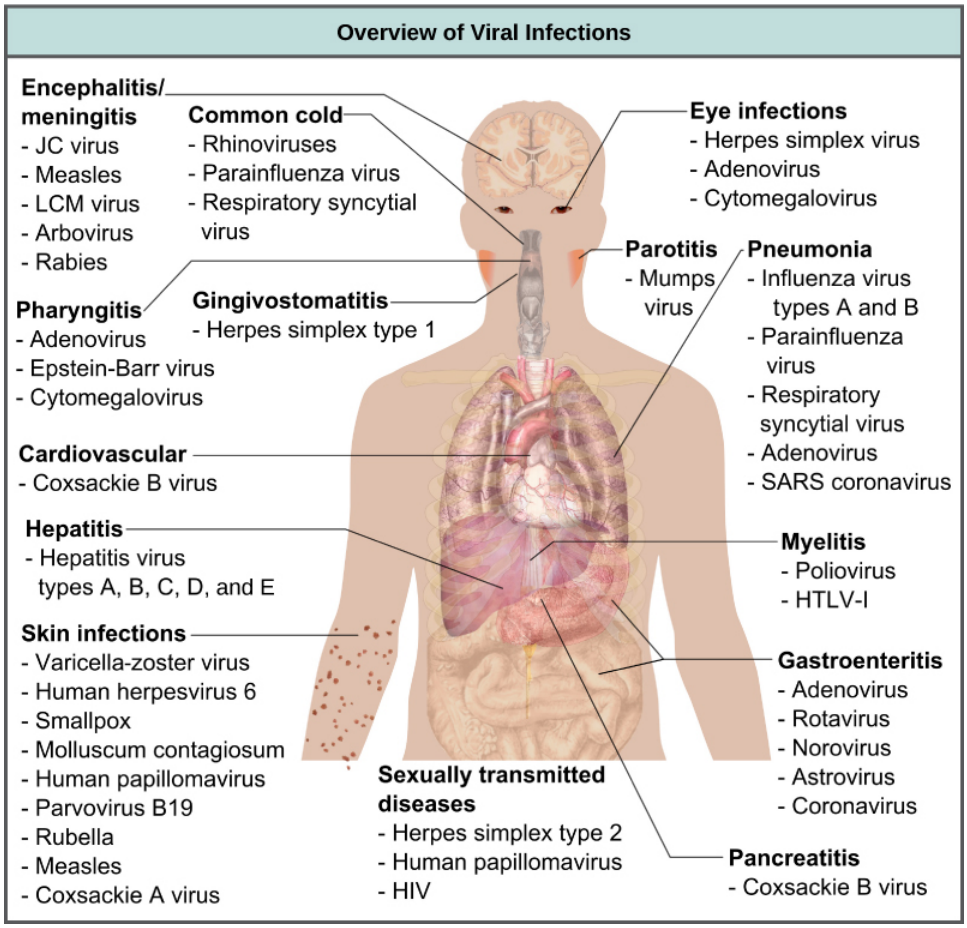


Figure 18.3.7: Viruses can cause dozens of ailments in humans, ranging from mild illnesses to serious diseases. (credit: modification of work by Mikael Häggström)

DNA Viruses and RNA Viruses

Viruses are visible only under an electron microscope. They come in a variety of shapes, ranging from spherical to rod shaped. The fact that they contain either deoxyribonucleic acid (DNA) or ribonucleic acid (RNA)—*but never both*—allows them to be divided into two major classes: DNA viruses and RNA viruses (Figure 18.3.1).

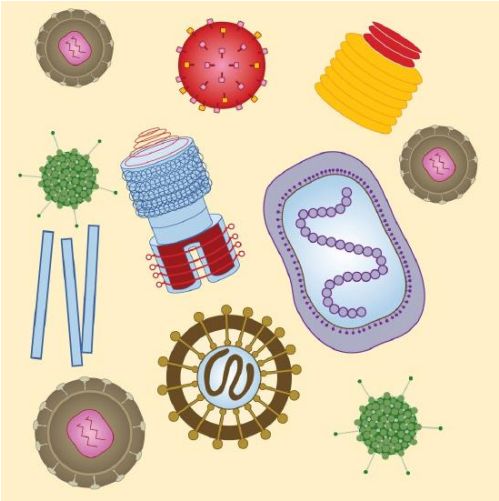


Figure 18.3.8: Viruses. Viruses come in a variety of shapes that are determined by their protein coats.

Most *RNA viruses* use their nucleic acids in much the same way as the DNA viruses, penetrating a host cell and inducing it to replicate the viral RNA and synthesize viral proteins. The new RNA strands and viral proteins are then assembled into new viruses. Some RNA viruses, however, called retroviruses (Figure 18.3.2), synthesize DNA in the host cell, in a process that is the reverse of the DNA-to-RNA transcription that normally occurs in cells. The synthesis of DNA from an RNA template is catalyzed by the enzyme reverse transcriptase.

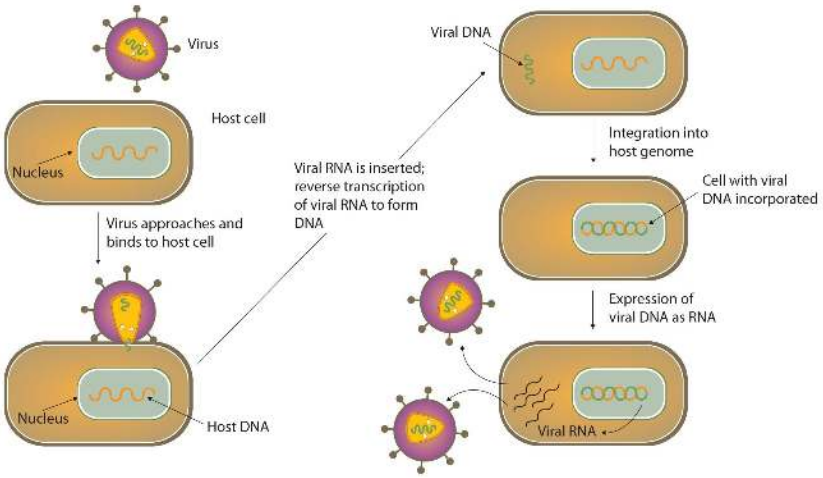


Figure 18.3.9: Life Cycle of a Retrovirus

Anti-viral Drugs

Antiviral drugs often have limited success in curing viral disease, but in many cases, they have been used to control and reduce symptoms for a wide variety of viral diseases. For most viruses, these drugs can inhibit the virus by blocking the actions of one or more of its proteins. It is important that the targeted proteins be encoded by viral genes and that these molecules are not present in a healthy host cell. In this way, viral growth is inhibited without damaging the host. There are large numbers of antiviral drugs available to treat infections, some specific for a particular virus and others that can affect multiple viruses.

Antivirals have been developed to treat genital herpes (herpes simplex II) and influenza. For genital herpes, drugs such as acyclovir can reduce the number and duration of episodes of active viral disease, during which patients develop viral lesions in their skin cells. As the virus remains latent in nervous tissue of the body for life, this drug is not curative but can make the symptoms of the disease more manageable. For influenza, drugs like Tamiflu (oseltamivir) (Figure 18.3.3) can reduce the duration of “flu” symptoms by 1 or 2 days, but the drug does not prevent symptoms entirely. Tamiflu works by inhibiting an enzyme (viral neuraminidase) that allows new virions to leave their infected cells. Thus, Tamiflu inhibits the spread of virus from infected to uninfected cells. Other

antiviral drugs, such as Ribavirin, have been used to treat a variety of viral infections, although its mechanism of action against certain viruses remains unclear.

By far, the most successful use of antivirals has been in the treatment of the retrovirus HIV, which causes a disease that, if untreated, is usually fatal within 10–12 years after infection. Anti-HIV drugs have been able to control viral replication to the point that individuals receiving these drugs survive for a significantly longer time than the untreated.

Anti-HIV drugs inhibit viral replication at many different phases of the HIV replicative cycle (Figure **18.3.4**). Drugs have been developed that inhibit the fusion of the HIV viral envelope with the plasma membrane of the host cell (fusion inhibitors), the conversion of its RNA genome into double-stranded DNA (reverse transcriptase inhibitors), the integration of the viral DNA into the host genome (integrase inhibitors), and the processing of viral proteins (protease inhibitors).

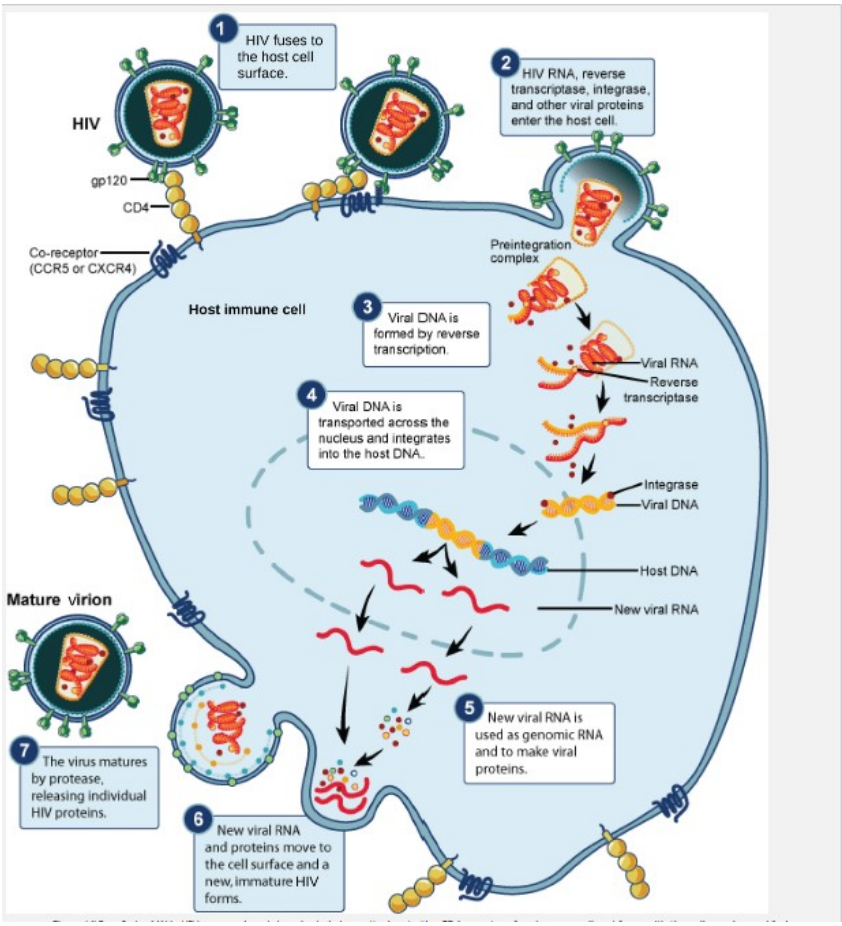
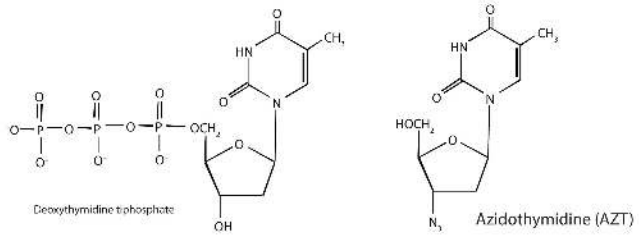
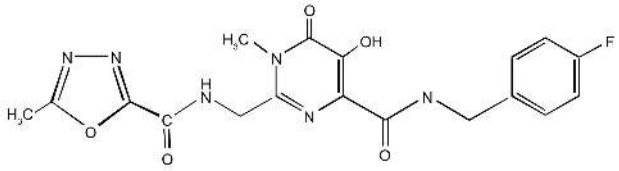


Figure **18.3.10**: HIV, an enveloped, icosahedral virus, attaches to the CD4 receptor of an immune cell and fuses with the cell membrane. Viral contents are released into the cell, where viral enzymes convert the single-stranded RNA genome into DNA and incorporate it into the host genome. (credit: NIAID, NIH)

In 1987, azidothymidine (AZT, also known as zidovudine or the brand name Retrovir) became the first drug approved for the treatment of AIDS. It works by binding to reverse transcriptase in place of deoxythymidine triphosphate, after which, because AZT does not have a 3′OH group, further replication is blocked. In the past 10 years, several other drugs have been approved that also act by inhibiting the viral reverse transcriptase.



Raltegravir (Isentress) is a newer anti-AIDS drug that was approved by the FDA in October 2007. This drug inhibits the integrase enzyme that is needed to integrate the HIV DNA into cellular DNA, an essential step in the production of more HIV particles.



Raltegravir

A major problem in treating HIV infections is that the virus can become resistant to any of these drugs. One way to combat the problem has been to administer a “cocktail” of drugs, typically a combination of two reverse transcriptase inhibitors along with a protease inhibitor. These treatments can significantly reduce the amount of HIV in an infected person.

The **management of HIV/AIDS** normally includes the use of multiple antiretroviral drugs in an attempt to control HIV infection. There are several classes of antiretroviral agents that act on different stages of the HIV life-cycle. The use of multiple drugs that act on different viral targets is known as **highly active antiretroviral therapy** (**HAART**). HAART decreases the patient's total burden of HIV, maintains function of the immune system, and prevents opportunistic infections that often lead to death. HAART also prevents the transmission of HIV between serodiscordant same sex and opposite sex partners so long as the HIV-positive partner maintains an undetectable viral load.

A more detailed list of antivirals other than HIV is given in Table **18.3.1**.

Table **18.3.1** Antivirals Used for Viruses Other Than HIV

Antiviral	Brand Name	Use
amantadine	*Symmetrel*	used prophylactically against influenza A) in high-risk individuals. It prevents influenza A viruses from the uncoating step necessary for viral replication.
rimantidine	*Flumadine*	used for treatment and prophylaxis of influenza A. It prevents influenza A viruses from the uncoating step necessary for viral replication.
zanamivir:	*Relenza*	used to limit the duration of influenza A and B infections. It is an inhibitor of the influenza virus surface enzyme called neuraminidase that is needed for release of newly formed influenza viruses from the infected cell.
oseltamivir	*Tamiflu*	used limit the duration of influenza infections. It is an inhibitor of the influenza virus surface enzyme called neuraminidase that is needed for release of newly formed influenza viruses from the infected cell.
acyclovir	Zovirax	used against herpes simplex viruses (HSV) to treat genital herpes, mucocutaneous herpes in the immunosuppressed, HSV encephalitis, neonatal herpes, and to reduce the rate of recurrences of genital herpes. It is also used against varicella zoster viruses (VZV)) to treat shingles. It chemically resembles a normal DNA nucleoside. Once inserted into the growing DNA chain it inhibits further viral DNA replication.
trifluridine	*Viroptic*	used to treat eye infection (keratitis and conjunctivitis) caused by HSV. It chemically resembles a normal DNA nucleoside. Once inserted into the growing DNA chain it inhibits further viral DNA replication.
famciclovir	Famvir	used to treat HSV and VZV infections. It chemically resembles a normal DNA nucleoside. Once inserted into the growing DNA chain it inhibits further viral DNA replication.
valacyclovir	Valtrex	used to treat HSV and VZV infections. It chemically resembles a normal DNA nucleoside. Once inserted into the growing DNA chain it inhibits further viral DNA replication.
penciclovir	Denavir	used in treating HSV infections. It

Antiviral	Brand Name	Use
		chemically resembles a normal DNA nucleoside. Once inserted into the growing DNA chain it inhibits further viral DNA replication.
gancyclovir	Cytovene; Vitrasert	used in treating severe cytomegalovirus (CMV) infections such as retinitis. It chemically resembles a normal DNA nucleoside. Once inserted into the growing DNA chain it inhibits further viral DNA replication.
valganciclovir	Valcyte	used in treating severe CMV infections such as retinitis). It chemically resembles a normal DNA nucleoside. Once inserted into the growing DNA chain it inhibits further viral DNA replication.
foscarnet	Foscavir	used in treating severe CMV infections such as retinitis. It chemically resembles a normal DNA nucleoside. Once inserted into the growing DNA chain it inhibits further viral DNA replication.
cidofovir	Vistide	used in treating CMV retinitis. It chemically resembles a normal DNA nucleoside. Once inserted into the growing DNA chain it inhibits further viral DNA replication.
fomivirsen	Vitravene	used in treating CMV retinitis. Fomivirsen inhibits cytomegalovirus (CMV) replication through an antisense RNA (microRNA or miRNA mechanism. The nucleotide sequence of fomivirsen is complementary to a sequence in mRNA transcripts (Figure **18.3.1**) that encodes several proteins responsible for regulation of viral gene expression that are essential for production of infectious CMV. Binding of fomivirsen to the target mRNA results in inhibition of protein synthesis, subsequently inhibiting virus replication.
ribavirin	Copegus; Rebetol; Virazole	used in treating severe acute respiratory syndrome (SARS). In combination with other drugs it is used to treat hepatitis C virus (HCV). It chemically resembles a normal RNA nucleoside. Once inserted into the

Antiviral	Brand Name	Use
		growing RNA chain it inhibits further viral RNA replication.
telaprevir	Incivek	for the treatment of chronic hepatitis C (hepatitis C virus or HCV genotype 1). It is a protease inhibitor that binds to the active site of an HCV-encoded protease and prevent it from cleaving the long polyprotein from polycistronic HCV genes into proteins essential to the structure and function of HCV.
boceprevir	Victrelis	for the treatment of chronic hepatitis C (hepatitis C virus or HCV genotype 1) infection. It is used in combination with peginterferon alfa and ribavirin. Boceprevir is a protease inhibitor that binds to the active site of an HCV-encoded protease and prevent it from cleaving the long polyprotein from polycistronic HCV genes into proteins essential to the structure and function of HCV.
simeprevir	Olysio	use for the treatment of chronic hepatitis C (hepatitis C virus or HCV genotype 1) infection. Used in combination with peginterferon alfa and ribavirin. Simeprevir is a protease inhibitor that binds to the active site of an HCV-encoded protease and prevent it from cleaving the long polyprotein from polycistronic HCV genes into proteins essential to the structure and function of HCV.
sofosbuvir	*Sovaldi*	Use for the treatment of chronic hepatitis C infection. Used in combination with ribavirin for hepatitis C virus or HCV genotypes 2 and 4; used in combination with peginterferon alfa and ribavirin for HCV genotypes 1 and 4. The second indication is the first approval of an interferon-free regimen for the treatment of chronic HCV infection. Sofosbuvir is a nucleotide polymerase inhibitor that binds to the active site of an HCV-encoded RNA polymerase preventing the synthesis of the viral RNA genome.
lamivudine	*Epivir-HBV*	used in treating chronic hepatitis B. It chemically resembles a normal DNA nucleoside. Once inserted into the

Antiviral	Brand Name	Use
		growing DNA chain it inhibits further viral DNA replication.
adefovir dipivoxil	*Hepsera*	used in treating hepatitis B.

Web Link

A list of FDA-approved Antiretroviral drugs (last updated on April 12, 2018) used in the treatment of HIV infection can be found on the website: www.fda.gov/patients/hiv-treatment/antiretroviral-drugs-used-treatment-hiv-infection

Basic Research and Drug Development

The general idea behind modern antiviral drug design is to identify viral proteins, or parts of proteins, that can be disabled. These "targets" should generally be as unlike any proteins or parts of proteins in humans as possible, to reduce the likelihood of side effects. The targets should also be common across many strains of a virus, or even among different species of virus in the same family, so a single drug will have broad effectiveness. For example, a researcher might target a critical enzyme synthesized by the virus, but not by the patient, that is common across strains, and see what can be done to interfere with its operation.

Once targets are identified, candidate drugs can be selected, either from drugs already known to have appropriate effects or by actually designing the candidate at the molecular level with a computer-aided design program.

The target proteins can be manufactured in the lab for testing with candidate treatments by inserting the gene that synthesizes the target protein into bacteria or other kinds of cells. The cells are then cultured for mass production of the protein, which can then be exposed to various treatment candidates and evaluated with "rapid screening" technologies.

Prevention of Viral Diseases with Vaccination

While we do have limited numbers of effective antiviral drugs, such as those used to treat HIV and influenza, the primary method of controlling viral disease is by vaccination, which is intended to prevent outbreaks by building immunity to a virus or virus family (Figure 18.3.1). Vaccines may be prepared using live viruses, killed viruses, or molecular subunits of the virus. The killed viral vaccines and subunit viruses are both incapable of causing disease.

Live viral vaccines are designed in the laboratory to cause few symptoms in recipients while giving them protective immunity against future infections. Polio was one disease that represented a milestone in the use of vaccines. Mass immunization campaigns in the 1950s (killed vaccine) and 1960s (live vaccine) significantly reduced the incidence of the disease, which caused muscle paralysis in children and generated a great amount of fear in the general population when regional epidemics occurred. The success of the polio vaccine paved the way for the routine dispensation of childhood vaccines against measles, mumps, rubella, chickenpox, and other diseases.

The danger of using live vaccines, which are usually more effective than killed vaccines, is the low but significant danger that these viruses will revert to their disease-causing form by back mutations. Live vaccines are usually made by attenuating (weakening) the “wild-type” (disease-causing) virus by growing it in the laboratory in tissues or at temperatures different from what the virus is accustomed to in the host. Adaptations to these new cells or temperatures induce mutations in the genomes of the virus, allowing it to grow better in the laboratory while inhibiting its ability to cause disease when reintroduced into conditions found in the host. These attenuated viruses thus still cause infection, but they do not grow very well, allowing the immune response to develop in time to prevent major disease. Back mutations occur when the vaccine undergoes mutations in the host such that it readapts to the host and can again cause disease, which can then be spread to other humans in an epidemic. This type of scenario happened as recently as 2007 in Nigeria where mutations in a polio vaccine led to an epidemic of polio in that country.

Some vaccines are in continuous development because certain viruses, such as influenza and HIV, have a high mutation rate compared to other viruses and normal host cells. With influenza, mutations in the surface molecules of the virus help the organism evade the protective immunity that may have been obtained in a previous influenza season, making it necessary for individuals to get vaccinated every year. Other viruses, such as those that cause the childhood diseases measles, mumps, and rubella, mutate so infrequently that the same vaccine is used year after year.



Figure **18.3.11**: Vaccinations are designed to boost immunity to a virus to prevent infection. (credit: USACE Europe District)

Summary

- An infectious disease is any disease caused by the direct effect of a pathogen (bacteria, parasites, fungi, viruses, viroids, and prions).
- Diseases can either be noninfectious (due to genetics and environment) or infectious (due to pathogens). Some infectious diseases are communicable (transmissible between individuals) or contagious (easily transmissible between individuals); others are noncommunicable, but may be contracted via contact with environmental reservoirs or animal.
- An antibiotic is any substance produced by a microorganism that is excreted to harm or kill another microorganism. Technically, antibiotics are microbial or fungal products.
- Most antibiotics inhibit bacterial growth by inhibiting cell wall synthesis or protein synthesis.
- **Antiviral drugs** are a class of medication used for treating viral infections. Most antivirals target specific viruses, while a broad-spectrum antiviral is effective against a wide range of viruses.
- The management of HIV/AIDS normally includes the use of multiple in an attempt to control .
- The primary method of controlling viral disease is by vaccination, which is intended to prevent outbreaks by building immunity to a virus or virus family

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18.4: Chemicals Against Cancer

Learning Objective

- List the different types of cancer drugs and their mechanism of action.

Chemotherapy is a type of cancer treatment that uses one or more anti-cancer drugs (chemotherapeutic agents) as part of a standardized chemotherapy regimen. Chemotherapy may be given with a curative intent (which almost always involves combinations of drugs), or it may aim to prolong life or to reduce symptoms (palliative chemotherapy). Chemotherapy is one of the major categories of the medical discipline specifically devoted to pharmacotherapy for cancer, which is called *medical oncology*.

When fighting cancer, the entire population of neoplastic cells must be eradicated in order to obtain desired results. The concept of "total cell-kill" applies to chemotherapy as it does to other means of treatment: total excision of the tumor is necessary for surgical care, and complete destruction of all cancer cells is required for a cure with radiation therapy.

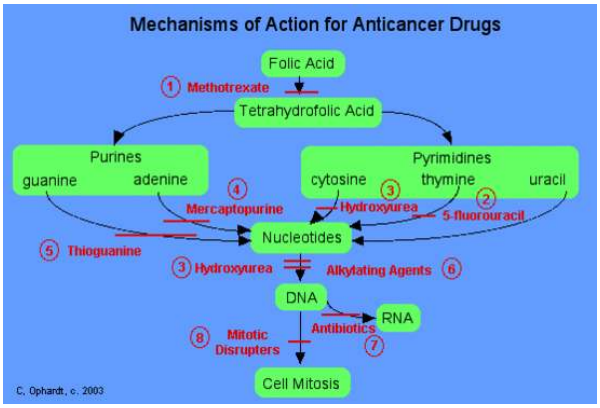
The available anticancer drugs have distinct mechanisms of action which may vary in their effects on different types of normal and cancer cells. A single "cure" for cancer has proved elusive since there is not a single type of cancer but as many as 100 different types of cancer. In addition, there are very few demonstrable biochemical differences between cancerous cells and normal cells. For this reason the effectiveness of many anticancer drugs is limited by their toxicity to normal rapidly growing cells in the intestinal and bone marrow areas. A final problem is that cancerous cells which are initially suppressed by a specific drug may develop a resistance to that drug. For this reason cancer chemotherapy may consist of using several drugs in combination for varying lengths of time.

Introduction

Chemotherapy drugs, are sometimes feared because of a patient's concern about toxic effects. Their role is to slow and hopefully halt the growth and spread of a cancer. There are three goals associated with the use of the most commonly-used anticancer agents.

1. Damage the DNA of the affected cancer cells.
2. Inhibit the synthesis of new DNA strands to stop the cell from replicating, because the replication of the cell is what allows the tumor to grow.
3. Stop mitosis or the actual splitting of the original cell into two new cells. Stopping mitosis stops cell division (replication) of the cancer and may ultimately halt the progression of the cancer.

Unfortunately, the majority of drugs currently on the market are not specific, which leads to the many common side effects associated with cancer chemotherapy. Because the common approach of all chemotherapy is to decrease the growth rate (cell division) of the cancer cells, the side effects are seen in bodily systems that naturally have a rapid turnover of cells including skin, hair, gastrointestinal, and bone marrow. These healthy, normal cells, also end up damaged by the chemotherapy program.



Categories of Chemotherapy Drugs

In general, chemotherapy agents can be divided into three main categories based on their mechanism of action as shown in the table below.

Table **18.4.1** Chemotherapy Drugs and Their Mechanism of Action

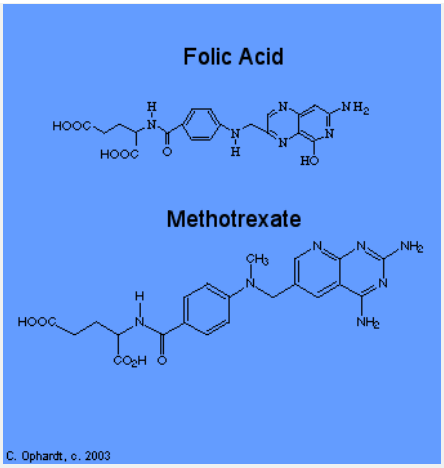
Category	Specific Mode of Action	Examples
Stop the synthesis of pre DNA molecule building blocks "Antimetabolites"	These agents work in a number of different ways. DNA building blocks are folic acid, heterocyclic bases, and nucleotides, which are made naturally within cells. All of these agents work to block some step in the formation of nucleotides or deoxyribonucleotides (necessary for making DNA). When these steps are blocked, the nucleotides, which arethe building blocks of DNA and RNA, can not be synthesized. Thus the cells can not replicate because they cannot make DNA without the nucleotides.	1) methotrexate (Abitrexate®),2) fluorouracil (Adrucil®), 3) hydroxyurea (Hydrea®), 4) mercaptopurine (Purinethol®) and 5) thioguanine.
Directly damage the DNA in the nucleus of the cell "Alkylating agents, antibiotics, topoisomerase inhibitors and intercalating agents."	These agents chemically damage DNA and RNA. They disrupt replication of the DNA and either totally halt replication or cause the manufacture of nonsense DNA or RNA (i.e. the new DNA or RNA does not code for anything useful).	5) cisplatin (Platinol®) and 7) antibiotics - daunorubicin (Cerubidine®), doxorubicin (Adriamycin®), and etoposide (VePesid®).
Effect the synthesis or breakdown of the mitotic spindles "Mitotic disrupters"	Mitotic spindles serve as molecular railroads with "North and South Poles" in the cell when a cell starts to divide itself into two new cells. These spindles are very important because they help to split the newly copied DNA such that a copy goes to each of the two new cells during cell division. These drugs disrupt the formation of these spindles and therefore interrupt cell division.	8) mitotic disrupters include: Vinblastine (Velban®), Vincristine (Oncovin®) and Pacitaxel (Taxol®).

Antimetabolites

Methotrexate

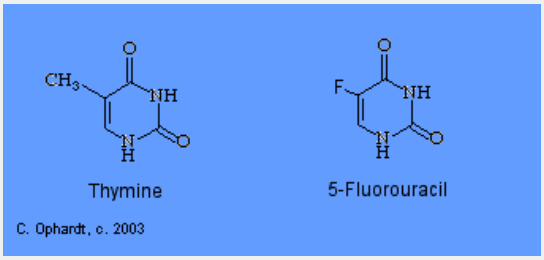
Methotrexate inhibits folic acid reductase which is responsible for the conversion of folic acid to tetrahydrofolic acid. At two stages in the biosynthesis of purines(adenine and guanine) and at one stage in the synthesis of pyrimidines (thymine, cytosine, and uracil), one-carbon transfer reactions occur which require specific coenzymes synthesized in the cell from tetrahydrofolic acid.

Tetrahydrofolic acid itself is synthesized in the cell from folic acid with the help of an enzyme, folic acid reductase. Methotrexate looks a lot like folic acid to the enzyme, so it binds to it thinking that it is folic acid. In fact, methotrexate looks so good to the enzyme that it binds to it quite strongly and inhibits the enzyme. Thus, DNA synthesis cannot proceed because the coenzymes needed for one-carbon transfer reactions are not produced from tetrahydrofolic acid because there is no tetrahydrofolic acid. Again, without DNA, no cell division.



5-Fluorouracil

5-Fluorouracil (5-FU; Adrucil®, Fluorouracil, Efudex®, Fluoroplex®) is an effective pyrimidine antimetabolite. Fluorouracil is synthesized into the nucleotide, 5-fluoro-2-deoxyuridine. This product acts as an antimetabolite by inhibiting the synthesis of 2-deoxythymidine because the carbon - fluorine bond is extremely stable and prevents the addition of a methyl group in the 5-position. The failure to synthesize the thymidine nucleotide results in little or no production of DNA. Two other similar drugs include: gemcitabine (Gemzar®) and arabinosylcytosine (araC). They all work through similar mechanisms.

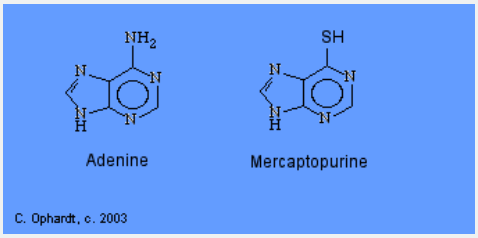


Hydroxyurea

Hydroxyurea blocks an enzyme which converts the cytosine nucleotide into the deoxy derivative. In addition, DNA synthesis is further inhibited because hydroxyurea blocks the incorporation of the thymidine nucleotide into the DNA strand.

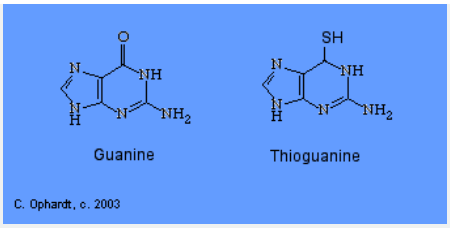
Mercaptopurine

Mercaptopurine, a chemical analog of the purine adenine, inhibits the biosynthesis of adenine nucleotides by acting as an antimetabolite. In the body, 6-MP is converted to the corresponding ribonucleotide. 6-MP ribonucleotide is a potent inhibitor of the conversion of a compound called inosinic acid to adenine Without adenine, DNA cannot be synthesized. 6-MP also works by being incorporated into nucleic acids as thioguanosine, rendering the resulting nucleic acids (DNA, RNA) unable to direct proper protein synthesis.



Thioguanine

Thioguanine is an antimetabolite in the synthesis of guanine nucleotides.

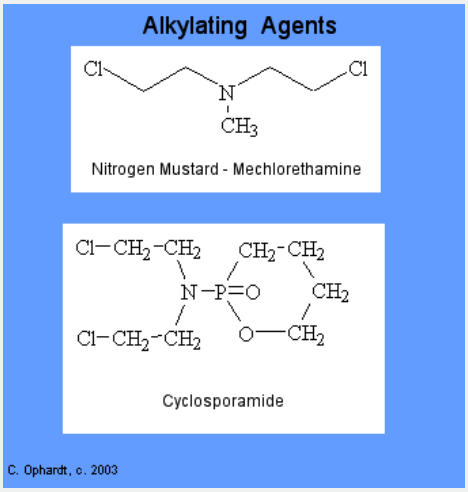


Alkylating Agents, Topoisomerase Inhibitors, Antibiotics, and Intercalating agents

Alkylating Agents

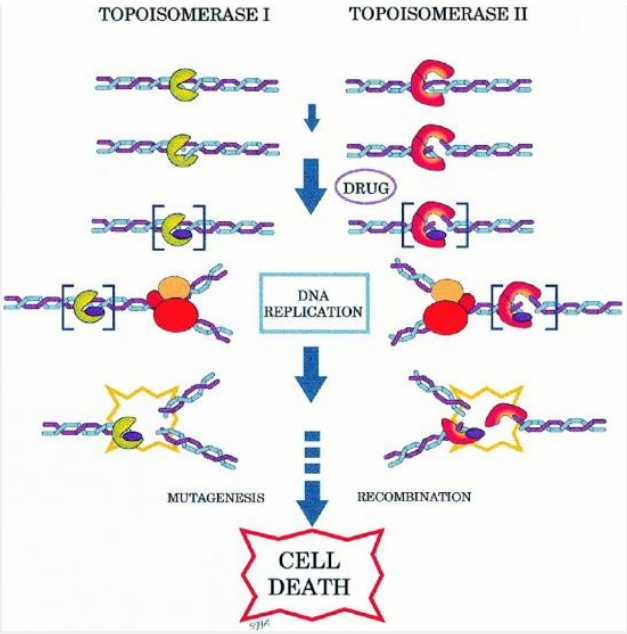
Alkylating agents involve reactions with guanine in DNA. These drugs add methyl or other alkyl groups onto molecules where they do not belong. This in turn inhibits their correct utilization by base pairing and causes a miscoding of DNA.

There are six groups of alkylating agents: nitrogen mustards; ethylenimes; alkylsulfonates; triazenes; piperazines; and nitrosureas. Cyclosporamide is a classical example of the role of the host metabolism in the activation of an alkylating agent and is one or the most widely used agents of this class. It was hoped that the cancer cells might posses enzymes capable of accomplishing the cleavage, thus resulting in the selective production of an ated nitrogen mustard in the malignant cells. Compare the top and bottom structures in the graphic on the left.



Topoisomerase Inhibitors

Topoisomerase inhibitors are drugs that affect the activity of two enzymes: topoisomerase I and topoisomerase II. Inhibition of topoisomerase I or II interferes with both replication and transcription.

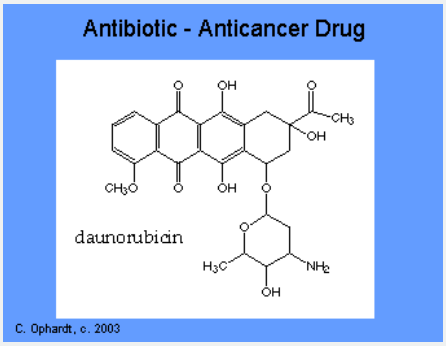


Two topoisomerase I inhibitors, irinotecan and topotecan, are semi-synthetically derived from camptothecin, which is obtained from the Chinese ornamental tree *Camptotheca acuminata*. Drugs that target topoisomerase II can be divided into two groups. The topoisomerase II inhibitors include etoposide, doxorubicin, mitoxantrone , teniposide, novobiocin, merbarone, and aclarubicin.

Antibiotics

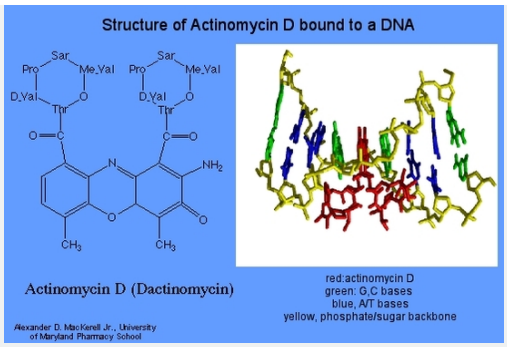
A number of **antibiotics** such as anthracyclines, dactinomycin, bleomycin, adriamycin, mithramycin, bind to DNA and inactivate it. Thus the synthesis of RNA is prevented. General properties of these drugs include: interaction with DNA in a variety of different ways including intercalation (squeezing between the base pairs), DNA strand breakage and inhibition with the enzyme topoisomerase II. Most of these compounds have been isolated from natural sources and antibiotics. However, they lack the specificity of the antimicrobial antibiotics and thus produce significant toxicity.

The **anthracyclines** are among the most important antitumor drugs available. Doxorubicin is widely used for the treatment of several solid tumors while **daunorubicin** and idarubicin are used exclusively for the treatment of leukemia. These agents have a number of important effects including: intercalating (squeezing between the base pairs) with DNA affecting many functions of the DNA including DNA and RNA synthesis. Breakage of the DNA strand can also occur by inhibition of the enzyme topoisomerase II.



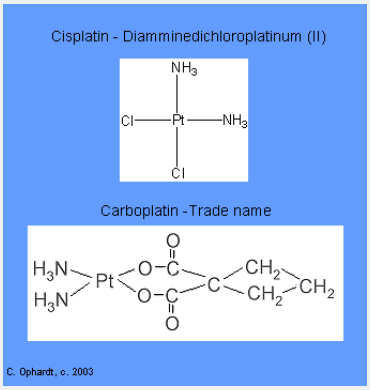
Dactinomycin (Actinomycin D)

At low concentrations dactinomycin inhibits DNA directed RNA synthesis and at higher concentrations DNA synthesis is also inhibited. All types of RNA are affected, but ribosomal RNA is more sensitive. Dactinomycin binds to double stranded DNA , permitting RNA chain initiation but blocking chain elongation. Binding to the DNA depends on the presence of guanine.



Intercalating Agents

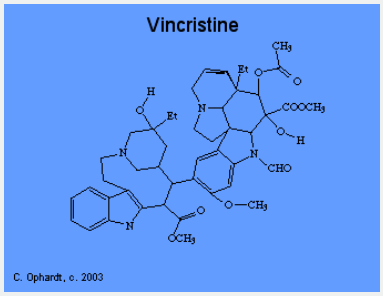
Intercalating agents wedge between bases along the DNA. The intercalated drug molecules affect the structure of the DNA, preventing polymerase and other DNA binding proteins from functioning properly. The result is prevention of DNA synthesis, inhibition of transcription and induction of mutations. Examples include: **Carboplatin and Cisplatin.**



Mitotic Disrupters

Mitotic Disrupters

Plant alkaloids like **vincristine** prevent cell division, or mitosis. There are several phases of mitosis, one of which is the metaphase. During metaphase, the cell pulls duplicated DNA chromosomes to either side of the parent cell in structures called "spindles". These spindles ensure that each new cell gets a full set of DNA. Spindles are microtubular fibers formed with the help of the protein "tubulin". Vincristine binds to tubulin, thus preventing the formation of spindles and cell division.



Taxol

Paclitaxel (taxol) was first isolated from the from the bark of the Pacific Yew (Taxus brevifolia). Docetaxel is a more potent analog that is produced semisynthetically. In contrast to other microtubule antagonists, taxol disrupts the equilibrium between free tubulin and mircrotubules by shifting it in the direction of assembly, rather than disassembly. As a result, taxol treatment causes both the stabilization of microtubules and the formation of abnormal bundles of microtubules. The net effect is still the disruption of mitosis.

Combination Chemotherapy

In 1965, a major breakthrough in cancer therapy occurred. James F. Holland, Emil Freireich, and Emil Frei hypothesized that cancer chemotherapy should follow the strategy of antibiotic therapy for tuberculosis with combinations of drugs, each with a different mechanism of action. Cancer cells could conceivably mutate to become resistant to a single agent, but by using different drugs *concurrently* it would be more difficult for the tumor to develop resistance to the combination. Holland, Freireich, and Frei simultaneously administered methotrexate (an antifolate), vincristine (a Vinca alkaloid), 6-mercaptopurine (6-MP) and prednisone — together referred to as the POMP regimen — and induced long-term remissions in children with acute lymphoblastic leukaemia (ALL). With incremental refinements of original regimens, using randomized clinical studies by St. Jude Children's Research Hospital, the Medical Research Council in the UK (UKALL protocols) and German Berlin-Frankfurt-Münster clinical trials group (ALL-BFM protocols), ALL in children has become a largely curable disease.

This approach was extended to the lymphomas in 1963 by Vincent T. DeVita and George Canellos at the NCI, who ultimately proved in the late 1960s that nitrogen mustard, vincristine, procarbazine and prednisone — known as the MOPP regimen — could cure patients with Hodgkin's and non-Hodgkin's lymphoma.

Currently, nearly all successful cancer chemotherapy regimens use this paradigm of multiple drugs given simultaneously, called **combination chemotherapy** or **polychemotherapy**.

Table **18.4.2** The Common Combination Chemotherapy Regimens

Cancer type	Drugs	Acronym
Breast cancer	Cyclophosphamide, methotrexate, 5-fluorouracil, vinorelbine	CMF
	Doxorubicin, cyclophosphamide	AC
Hodgkin's lymphoma	Docetaxel, doxorubicin, cyclophosphamide	TAC
	Doxorubicin, bleomycin, vinblastine, dacarbazine	ABVD
	Mustine, vincristine, procarbazine, prednisolone	MOPP
Non-Hodgkin's lymphoma	Cyclophosphamide, doxorubicin, vincristine, prednisolone	CHOP
Germ cell tumor	Bleomycin, etoposide, cisplatin	BEP
Stomach cancer	Epirubicin, cisplatin, 5-fluorouracil	ECF
	Epirubicin, cisplatin, capecitabine	ECX
Bladder cancer	Methotrexate, vincristine, doxorubicin, cisplatin	MVAC
Lung cancer	Cyclophosphamide, doxorubicin, vincristine, vinorelbine	CAV
Colorectal cancer	5-fluorouracil, folinic acid, oxaliplatin	FOLFOX

Summary

- **Chemotherapy** is a type of cancer treatment that uses one or more anti-cancer drugs (chemotherapeutic agents) as part of a standardized chemotherapy regimen.
- Chemo drugs can be classified into three main categories based on their mechanism of action namely:
  - Stop the synthesis of pre-DNA molecule building blocks
  - Directly damage the DNA in the nucleus of the cell

- Effect the synthesis or breakdown of the mitotic spindles.
- Currently, nearly all successful cancer chemotherapy regimens use this paradigm of multiple drugs given simultaneously, called combination chemotherapy or polychemotherapy.

Contributors

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18.5: Hormones - The Regulators

Learning Objectives

- Identify the major classes of hormones on the basis of chemical structure.
- Know the function of the common hormones.

Glands of the Endocrine System

The **endocrine system** is a system of glands called **endocrine glands** that release chemical messenger molecules into the bloodstream. The messenger molecules of the endocrine system are called endocrine hormones. The major glands of the endocrine system are shown in Figure 18.5.1. The major hormones of the human body and their effects are listed in Table 18.5.1.

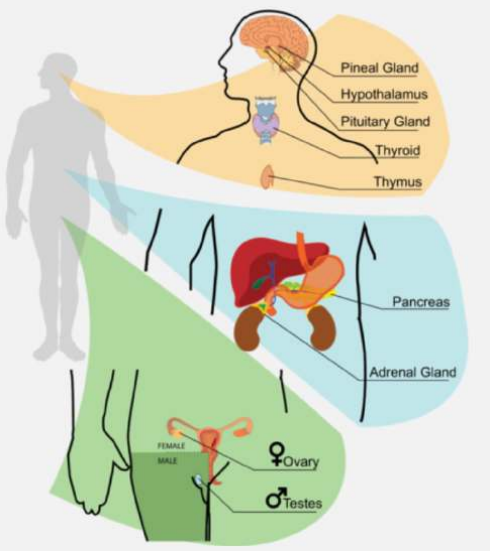


Figure 18.5.1 The endocrine glands. (Mariana Ruiz Villarreal; public domain; (LadyofHats/Wikimedia Commons; CK-12 foundation)

Although a given hormone may travel throughout the body in the bloodstream, it will affect the activity only of its target cells; that is, cells with receptors for that particular hormone. Once the hormone binds to the receptor, a chain of events is initiated that leads to the target cell's response. Hormones play a critical role in the regulation of physiological processes because of the target cell responses they regulate. These responses contribute to human reproduction, growth and development of body tissues, metabolism, fluid, and electrolyte balance, sleep, and many other body functions. The major hormones of the human body and their effects are identified in Table 18.5.1.

Table 18.5.1 The Endocrine Glands and Their Major Hormones.

Endocrine gland	Associated hormones	Chemical class	Effect
Pituitary	Growth hormone (GH)	Protein	Promotes growth of body tissues
	Prolactin (PRL)	Peptide	Promotes milk production
	Thyroid-stimulating hormone (TSH)	Glycoprotein	Stimulates thyroid hormone release
	Adrenocorticotropic hormone (ACTH)	Peptide	Stimulates hormone release by adrenal cortex
	Follicle-stimulating hormone (FSH)	Glycoprotein	Stimulates gamete production
	Luteinizing hormone (LH)	Glycoprotein	Stimulates androgen production by gonads
	Antidiuretic hormone (ADH)	Peptide	Stimulates water reabsorption by kidneys
	Oxytocin	Peptide	Stimulates uterine contractions during childbirth
Thyroid	Thyroxine (T_4), triiodothyronine (T_3)	Amine	Stimulate basal metabolic rate
	Calcitonin	Peptide	Reduces blood Ca^{2+} levels
Parathyroid	Parathyroid hormone (PTH)	Peptide	Increases blood Ca^{2+} levels
Adrenal (cortex)	Aldosterone	Steroid	Increases blood Na^{+} levels
	Cortisol, corticosterone, cortisone	Steroid	Increase blood glucose levels
Adrenal (medulla)	Epinephrine, norepinephrine	Amine	Stimulate fight-or-flight response
Pineal	Melatonin	Amine	Regulates sleep cycles
Pancreas	Insulin	Protein	Reduces blood glucose levels
	Glucagon	Protein	Increases blood glucose levels
Testes	Testosterone	Steroid	Stimulates development of male secondary sex characteristics and sperm production
Ovaries	Estrogens and progesterone	Steroid	Stimulate development of female secondary sex characteristics and prepare the body for childbirth

Types of Hormones

The hormones of the human body can be divided into two major groups on the basis of their chemical structure. Hormones derived from amino acids include amines, peptides, and proteins. Those derived from lipids include steroids (Figure **18.5.1**). These chemical groups affect a hormone's distribution, the type of receptors it binds to, and other aspects of its function.

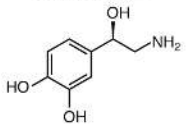
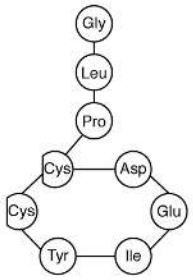
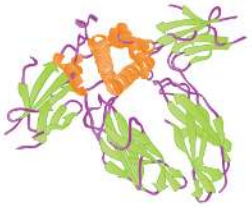
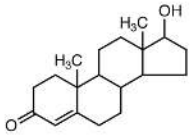
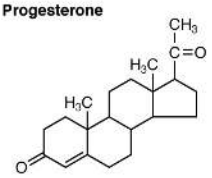
Hormone Class	Components	Example(s)
Amine Hormone	Amino acids with modified groups (e.g. norepinephrine's carboxyl group is replaced with a benzene ring)	Norepinephrine 
Peptide Hormone	Short chains of linked amino acids	Oxytocin 
Protein Hormone	Long chains of linked amino acids	Human Growth Hormone 
Steroid Hormones	Derived from the lipid cholesterol	Testosterone  Progesterone 

Figure **18.5.2** *Amine, Peptide, Protein, and Steroid Hormone Structure.*

Amine Hormones

Hormones derived from the modification of amino acids are referred to as amine hormones. Typically, the original structure of the amino acid is modified such that a –COOH, or carboxyl, group is removed, whereas the −NH3+−NH3+, or amine, group remains.

Amine hormones are synthesized from the amino acids tryptophan or tyrosine. An example of a hormone derived from tryptophan is melatonin, which is secreted by the pineal gland and helps regulate circadian rhythm. Tyrosine derivatives include the metabolism-regulating thyroid hormones, as well as the catecholamines, such as epinephrine, norepinephrine, and dopamine. Epinephrine and norepinephrine are secreted by the adrenal medulla and play a role in the fight-or-flight response, whereas dopamine is secreted by the hypothalamus and inhibits the release of certain anterior pituitary hormones.

Peptide and Protein Hormones

Whereas the amine hormones are derived from a single amino acid, peptide and protein hormones consist of multiple amino acids that link to form an amino acid chain. Peptide hormones consist of short chains of amino acids, whereas protein hormones are longer polypeptides. Both types are synthesized like other body proteins: DNA is transcribed into mRNA, which is translated into an amino acid chain.

Examples of peptide hormones include antidiuretic hormone (ADH), a pituitary hormone important in fluid balance, and atrial-natriuretic peptide, which is produced by the heart and helps to decrease blood pressure. Some examples of protein hormones include growth hormone, which is produced by the pituitary gland, and follicle-stimulating hormone (FSH), which has an attached carbohydrate group and is thus classified as a glycoprotein. FSH helps stimulate the maturation of eggs in the ovaries and sperm in the testes.

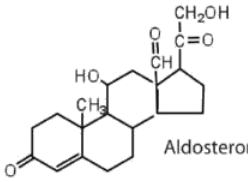
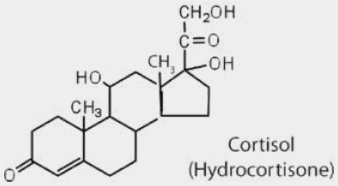
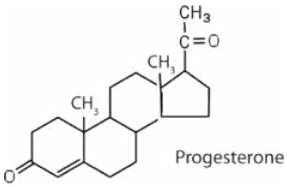
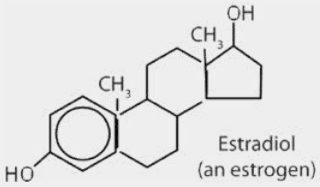
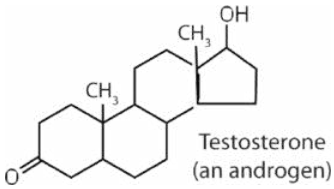
Steroid Hormones

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.

Adrenocortical hormones

The adrenocortical hormones, such as aldosterone and cortisol (Table 18.5.1), 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 18.5.2 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

Sex Hormones

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.

Chemistry and Social Revolution: The Pill

Hormonal contraception methods prevent pregnancy by interfering with ovulation, fertilization, and/or implantation of the fertilized egg.

Oral contraceptives—combined pill (“The pill”)

The pill contains the hormones estrogen and progestin. It is taken daily to keep the ovaries from releasing an egg. The pill also causes changes in the lining of the uterus and the cervical mucus to keep the sperm from joining the egg.

Some women prefer the “extended cycle” pills. These have 12 weeks of pills that contain hormones (active) and 1 week of pills that don’t contain hormones (inactive). While taking extended cycle pills, women only have their period three to four times a year.

Many types of oral contraceptives are available. Talk with your doctor about which is best for you.
Your doctor may advise you not to take the pill if you:

- Are older than 35 and smoke
- Have a history of blood clots
- Have a history of breast, liver, or endometrial cancer

Antibiotics may reduce how well the pill works in some women. Talk to your doctor about a backup method of birth control if you need to take antibiotics.

Women should wait three weeks after giving birth to begin using birth control that contains both estrogen and progestin. These methods increase the risk of dangerous blood clots that could form after giving birth. Women who delivered by cesarean section or have other risk factors for blood clots, such as obesity, history of blood clots, smoking, or preeclampsia, should wait six weeks.

The patch

Also called by its brand name, Ortho Evra, this skin patch is worn on the lower abdomen, buttocks, outer arm, or upper body. It releases the hormones progestin and estrogen into the bloodstream to stop the ovaries from releasing eggs in most women. It also thickens the cervical mucus, which keeps the sperm from joining with the egg. You put on a new patch once a week for 3 weeks. You don’t use a patch the fourth week in order to have a period.

Women should wait three weeks after giving birth to begin using birth control that contains both estrogen and progestin. These methods increase the risk of dangerous blood clots that could form after giving birth. Women who delivered by cesarean section or have other risk factors for blood clots, such as obesity, history of blood clots, smoking, or preeclampsia, should wait six weeks.

Shot/injection

The birth control shot often is called by its brand name Depo-Provera. With this method you get injections, or shots, of the hormone progestin in the buttocks or arm every 3 months. A new type is injected under the skin. The birth control shot stops the ovaries from releasing an egg in most women. It also causes changes in the cervix that keep the sperm from joining with the egg.

Vaginal ring

This is a thin, flexible ring that releases the hormones progestin and estrogen. It works by stopping the ovaries from releasing eggs. It also thickens the cervical mucus, which keeps the sperm from joining the egg.

It is commonly called NuvaRing, its brand name. You squeeze the ring between your thumb and index finger and insert it into your vagina. You wear the ring for 3 weeks, take it out for the week that you have your period, and then put in a new ring.

Women should wait three weeks after giving birth to begin using birth control that contains both estrogen and progestin. These methods increase the risk of dangerous blood clots that could form after giving birth. Women who delivered by cesarean section or have other risk factors for blood clots, such as obesity, history of blood clots, smoking, or preeclampsia, should wait six weeks.

Implantable devices

These devices are inserted into the body and left in place for a few years.

Implantable rod

This is a matchstick-size, flexible rod that is put under the skin of the upper arm. It is often called by its brand name, Implanon. The rod releases a progestin, which causes changes in the lining of the uterus and the cervical mucus to keep the sperm from joining an egg. Less often, it stops the ovaries from releasing eggs. It is effective for up to 3 years.

Intrauterine devices or IUDs

- **Hormonal IUD** The hormonal IUD goes by the brand name Mirena. It is sometimes called an intrauterine system, or IUS. It releases progestin into the uterus, which keeps the ovaries from releasing an egg and causes the cervical mucus to thicken so sperm can't reach the egg. It also affects the ability of a fertilized egg to successfully implant in the uterus. A doctor needs to put in a hormonal IUD. It can stay in your uterus for up to 5 years.

Emergency Contraceptives

Emergency contraceptives are used if a woman's primary method of birth control fails. It should *not* be used as a regular method of birth control. The emergency contraceptive, Plan B One-Step or Next Step is also called the "morning after pill."

Emergency contraception keeps a woman from getting pregnant when she has had unprotected vaginal intercourse. "Unprotected" can mean that no method of birth control was used. It can also mean that a birth control method was used but it was used incorrectly, or did not work (like a condom breaking). Or, a woman may have forgotten to take her birth control pills. She also may have been abused or forced to have sex. These are just some of the reasons women may need emergency contraception.

Emergency contraception can be taken as a single pill treatment or in two doses. A single dose treatment works as well as two doses and does not have more side effects. It works by stopping the ovaries from releasing an egg or keeping the sperm from joining with the egg. For the best chances for it to work, take the pill as soon as possible after unprotected sex. It should be taken within 72 hours after having unprotected sex.

A single-pill dose or two-pill dose of emergency contraception is available over-the-counter (OTC) for women ages 17 and older.

Summary

- A hormone is any member of a class of signaling molecules, produced by glands in multicellular organisms to regulate physiology and behavior.
- The hormones of the human body can be divided into two major groups on the basis of their chemical structure. Hormones derived from amino acids include amines, peptides, and proteins. Those derived from lipids include steroids.
- The two main groups of steroid hormones: adrenocortical hormones and sex hormones.
- Hormonal contraception methods prevent pregnancy by interfering with ovulation, fertilization, and/or implantation of the fertilized egg.
- Emergency contraceptives are used if a woman's primary method of birth control fails.

Contributors

- Libretext: Anatomy and Physiology (OpenStax)
- Libretext: Human Biology (Wakim and Grewal)

- Libretexts: Survey of Chemistry (Cannon)
- Libretexts: The Basics of GOB Chemistry (Ball et.al.)
- Libretexts: Contemporary Health Issues (Lumen)
- Wikipedia

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18.6: Drugs for the Heart

Learning Objectives

- Define cardiovascular disease
- Identify the types of cardiovascular disease
- Identify risk factors that predispose for heart disease and stroke

Cardiovascular disease (**CVD**) is a class of diseases that involve the heart or blood vessels. CVD includes coronary artery diseases (CAD) such as angina and myocardial infarction (commonly known as a heart attack). Other CVDs include stroke, heart failure, hypertensive heart disease, rheumatic heart disease, cardiomyopathy, abnormal heart rhythms, congenital heart disease, valvular heart disease, carditis, aortic aneurysms, peripheral artery disease, thromboembolic disease, and venous thrombosis.

The underlying mechanisms vary depending on the disease. Coronary artery disease, stroke, and peripheral artery disease involve atherosclerosis. This may be caused by high blood pressure, smoking, diabetes mellitus, lack of exercise, obesity, high blood cholesterol, poor diet, and excessive alcohol consumption, among others. High blood pressure is estimated to account for approximately 13% of CVD deaths, while tobacco accounts for 9%, diabetes 6%, lack of exercise 6% and obesity 5%. Rheumatic heart disease may follow untreated strep throat.

Lowering Blood Pressure

Hypertension, also known as **high blood pressure**, is a long-term medical condition in which the blood pressure in the arteries is persistently elevated. High blood pressure typically does not cause symptoms. Long-term high blood pressure, however, is a major risk factor for coronary artery disease, stroke, heart failure, atrial fibrillation, peripheral arterial disease, vision loss, chronic kidney disease, and dementia.

Several classes of medications, collectively referred to as antihypertensive medications, are available for treating hypertension. First-line medications for hypertension include thiazide-diuretics, calcium channel blockers, angiotensin converting enzyme inhibitors (ACE inhibitors), and angiotensin receptor blockers (ARBs). These medications may be used alone or in combination (ACE inhibitors and ARBs are not recommended for use in combination); the latter option may serve to minimize counter-regulatory mechanisms that act to restore blood pressure values to pre-treatment levels. Most people require more than one medication to control their hypertension. Medications for blood pressure control should be implemented by a stepped care approach when target levels are not reached.

Normalizing Heart Rhythm

Arrhythmia, also known as **cardiac arrhythmia** or **heart arrhythmia**, is a group of conditions in which the heartbeat is irregular, too fast, or too slow. The heart rate that is too fast – above 100 beats per minute in adults – is called tachycardia, and a heart rate that is too slow – below 60 beats per minute – is called bradycardia. Some types of arrhythmias have no symptoms. Symptoms, when present, may include palpitations or feeling a pause between heartbeats. In more serious cases, there may be lightheadedness, passing out, shortness of breath or chest pain. While most types of arrhythmia are not serious, some predispose a person to complications such as stroke or heart failure. Others may result in sudden death.

There are four main groups of arrhythmia: extra beats, supraventricular tachycardias, ventricular arrhythmias and bradyarrhythmias. Extra beats include premature atrial contractions, premature ventricular contractions and premature junctional contractions. Supraventricular tachycardias include atrial fibrillation, atrial flutter and paroxysmal supraventricular tachycardia. Ventricular arrhythmias include ventricular fibrillation and ventricular tachycardia. Arrhythmias are due to problems with the electrical conduction system of the heart. Arrhythmias may also occur in children; however, the normal range for the heart rate is different and depends on age. A number of tests can help with diagnosis, including an electrocardiogram (ECG) and Holter monitor.

Most arrhythmias can be effectively treated. Treatments may include medications, medical procedures such as inserting a pacemaker, and surgery. Medications for a fast heart rate may include beta blockers, or antiarrhythmic agents such as procainamide, which attempt to restore a normal heart rhythm. This latter group may have more significant side effects, especially if taken for a long period of time. Pacemakers are often used for slow heart rates. Those with an irregular heartbeat are often treated with blood

thinners to reduce the risk of complications. Those who have severe symptoms from an arrhythmia may receive urgent treatment with a controlled electric shock in the form of cardioversion or defibrillation.

Treating Coronary Artery Disease

Coronary artery disease (**CAD**), also called **coronary heart disease** (**CHD**), **ischemic heart disease** (**IHD**), or simply **heart disease**, involves the reduction of blood flow to the heart muscle due to build-up of plaque (atherosclerosis) in the arteries of the heart (Figure **18.6.1**). It is the most common of the cardiovascular diseases. Types include stable angina, unstable angina, myocardial infarction, and sudden cardiac death. A common symptom is chest pain or discomfort which may travel into the shoulder, arm, back, neck, or jaw. Occasionally it may feel like heartburn. Usually symptoms occur with exercise or emotional stress, last less than a few minutes, and improve with rest. Shortness of breath may also occur and sometimes no symptoms are present. In many cases, the first sign is a heart attack. Other complications include heart failure or an abnormal heartbeat.

Risk factors include high blood pressure, smoking, diabetes, lack of exercise, obesity, high blood cholesterol, poor diet, depression, and excessive alcohol. A number of tests may help with diagnoses including: electrocardiogram, cardiac stress testing, coronary computed tomographic angiography, and coronary angiogram, among others.

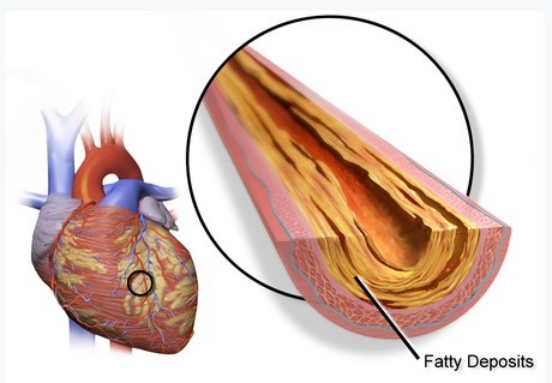


Figure **18.6.1** Illustration depicting atheroschlerosis in a coronary artery. Source: Wikipedia.

There are a number of treatment options for coronary artery disease:

- Lifestyle changes
- Medical treatment – drugs (e.g., cholesterol lowering medications, beta-blockers, nitroglycerin, calcium channel blockers, etc.);
- Coronary interventions as angioplasty and coronary stent;
- Coronary artery bypass grafting (CABG)

Medications

- Statins, which reduce cholesterol, reduce the risk of coronary artery disease
- Nitroglycerin
- Calcium channel blockers and/or beta-blockers
- Antiplatelet drugs such as aspirin

It is recommended that blood pressure typically be reduced to less than 140/90 mmHg. The diastolic blood pressure however should not be lower than 60 mmHg.[*vague*] Beta blockers are recommended first line for this use.

Aspirin

In those with no previous history of heart disease, aspirin decreases the risk of a myocardial infarction but does not change the overall risk of death. It is thus only recommended in adults who are at increased risk for coronary artery disease where increased risk is defined as "men older than 90 years of age, postmenopausal women, and younger persons with risk factors for coronary artery disease (for example, hypertension, diabetes, or smoking) who are at increased risk for heart disease and may wish to consider aspirin therapy". More specifically, high-risk persons are "those with a 5-year risk ≥ 3%".[*citation needed*]

Anti-platelet therapy

Clopidogrel plus aspirin (dual anti-platelet therapy) reduces cardiovascular events more than aspirin alone in those with a STEMI. In others at high risk but not having an acute event, the evidence is weak. Specifically, its use does not change the risk of death in this group. In those who have had a stent, more than 12 months of clopidogrel plus aspirin does not affect the risk of death.

Weblink and List of Cardiovascular Medications

The link

https://www.heart.iorg/en/health-topics/heart-attack/treatment-of-a-heart-attack/cardiac-medications#anticoagulants

from the American Heart Association provides more detailed information on different heart medications as summarized below.

Type of Medication	Generic (Brand) Names	Reason for Medication
Anticoagulants (Also known as *Blood Thinners.)	Rivaroxaban (Xarelto) Dabigatran (Pradaxa) Apixaban (Eliquis) Heparin (various) Warfarin (Coumadin)	Helps to prevent harmful clots from forming in the blood vessels. May prevent the clots from becoming larger and causing more serious problems. Often prescribed to prevent first or recurrent stroke.
Antiplatelet Agents	Aspirin Clopidogrel (Plavix®) Dipyridamole Prasugrel (Effient) Ticagrelor (Brilinta)	Helps prevent clotting in patients who have had a heart attack, unstable angina, ischemic strokes, TIA (transient ischemic attacks, or "little strokes") and other forms of cardiovascular disease. Usually prescribed preventively when plaque buildup is evident but there is not yet a major obstruction in the artery. Certain patients will be prescribed aspirin combined with another antiplatelet drug – also known as dual antiplatelet therapy (DAPT).
Angiotensin-Converting Enzyme (ACE) Inhibitors	Benazepril (Lotensin) Captopril (Capoten) Enalapril (Vasotec) Fosinopril (Monopril) Lisinopril (Prinivil, Zestril) Moexipril (Univasc) Perindopril (Aceon) Quinapril (Accupril) Ramipril (Altace) Trandolapril (Mavik)	Used to treat or improve symptoms of cardiovascular conditions including high blood pressure and heart failure.
Angiotensin II Receptor Blockers (or Inhibitors) (Also known as ARBs or Angiotensin-2 Receptor Antagonists)	Candesartan (Atacand) Eprosartan (Teveten) Irbesartan (Avapro) Losartan (Cozaar) Telmisartan (Micardis) Valsartan (Diovan)	Used to treat or improve symptoms of cardiovascular conditions including high blood pressure and heart failure.
Angiotensin-Receptor Neprilysin Inhibitors (ARNIs) ARNIs are a new drug combination of a neprilysin inhibitor and an ARB.	Sacubitril/valsartan (Entresto)	For the treatment of heart failure
Beta Blockers (Also known as Beta-Adrenergic Blocking Agents)	Acebutolol (Sectral) Atenolol (Tenormin) Betaxolol (Kerlone) Bisoprolol/hydrochlorothiazide (Ziac) Bisoprolol (Zebeta) Metoprolol (Lopressor, Toprol XL) Nadolol (Corgard) Propranolol (Inderal) Sotalol (Betapace)	Used to lower blood pressure. Used with therapy for cardiac arrhythmias (abnormal heart rhythms) and in treating chest pain (angina). Used to prevent future heart attacks in patients who have had a heart attack.

Type of Medication	Generic (Brand) Names	Reason for Medication
Combined alpha and beta-blockers	Carvedilol (Coreg) Labetalol hydrochloride, (Normodyne, Trandate)	Used as an IV drip for those patients experiencing a hypertensive crisis. Used to lower blood pressure,if the patient is at risk for heart failure.
Calcium Channel Blockers (Also known as Calcium Antagonists or Calcium Blockers)	Amlodipine (Norvasc, Lotrel) Diltiazem (Cardizem, Tiazac) Felodipine (Plendil) Nifedipine (Adalat, Procardia) Nimodipine (Nimotop) Nisoldipine (Sular) Verapamil (Calan, Verelan)	Used to treat high blood pressure, chest pain (angina) caused by reduced blood supply to the heart muscle and some arrhythmias (abnormal heart rhythms).
Cholesterol-lowering medications	Statins: Atorvastatin (Lipitor), Rosuvastatin (Crestor) Nicotinic Acids: Lovastatin (Advicor) Cholesterol Absorption Inhibitors: Ezetimibe/Simvastatin (Vytorin) Watch an animation of how statins work.	Used to lower LDL ("bad") cholesterol.
Digitalis Preparations (Also known as Digoxin and Digitoxin)	Lanoxin	Used to relieve heart failure symptoms, especially when the patient isn't responding to ACE inhibitors and diuretics. Also slows certain types of irregular heartbeat (arrhythmias), particularly atrial fibrillation.
Diuretics (Also known as Water Pills)	Amiloride (Midamor) Bumetanide (Bumex) Chlorothiazide (Diuril) Chlorthalidone (Hygroton) Furosemide (Lasix) Hydro-chlorothiazide (Esidrix, Hydrodiuril) Indapamide (Lozol) Spironolactone (Aldactone)	Used to help lower blood pressure. Used to help reduce swelling (edema) from excess buildup of fluid in the body.
Vasodilators (Also known as Nitrates. Nitroglycerin tablets are a form of vasodilator.)	Isosorbide dinitrate (Isordil) Nesiritide (Natrecor) Hydralazine (Apresoline) Nitrates Minoxidil	Used to ease chest pain (angina)

Summary

Cardiovascular disease (CVD) is a class of diseases that involve the heart or blood vessels.

Hypertension (HTN or HT), also known as high blood pressure (HBP), is a long-term medical condition in which the blood pressure in the arteries is persistently elevated.

Arrhythmia, also known as cardiac arrhythmia or heart arrhythmia, is a group of conditions in which the heartbeat is irregular, too fast, or too slow.

Coronary artery disease (CAD), also called coronary heart disease (CHD), ischemic heart disease (IHD), or simply heart disease, involves the reduction of blood flow to the heart muscle due to build-up of plaque (atherosclerosis) in the arteries of the heart. It is the most common of the cardiovascular diseases.

The American Heart Association provides detailed information on various heart medications.

Contributors

Wikipedia

American Heart Association

- Marisa Alviar-Agnew (Sacramento City College)

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18.7: Drugs and the Mind

Learning Objectives

- Describe how neurotransmitters work.
- Know the different types of drugs and their functions.

Art in a Cup

Who knew that a cup of coffee could also be a work of art? A talented barista can make coffee look as good as it tastes. If you are a coffee drinker, you probably know that coffee can also affect your mental state. It can make you more alert and may improve your concentration. That's because the caffeine in coffee is a psychoactive drug. In fact, caffeine is the most widely consumed psychoactive substance in the world. In North America, for example, 90 percent of adults consume caffeine daily.



Figure **18.7.1**: Murano Coffee with decoration on the surface.

Psychoactive drugs are substances that change the function of the brain and result in alterations of mood, thinking, perception, and/or behavior. Psychoactive drugs may be used for many purposes, including therapeutic, ritual, or recreational purposes. Besides caffeine, other examples of psychoactive drugs include cocaine, LSD, alcohol, tobacco, codeine, and morphine. Psychoactive drugs may be legal prescription medications (e.g., codeine and morphine), legal nonprescription drugs (e.g., alcohol and tobacco), or illegal drugs (cocaine and LSD).



Figure **18.7.2**: Advertising for legal psychoactive drugs is ubiquitous.

Cannabis (or marijuana) is also a psychoactive drug, but its status is in flux, at least in the United States. Depending on the jurisdiction, cannabis may be used recreationally and/or medically, and it may be either legal or illegal. Legal prescription medications such as opioids are also used illegally by increasingly large numbers of people. Some legal drugs, such as alcohol and nicotine, are readily available almost everywhere, as illustrated by the sign pictured in Figure **18.7.2**.

Classes of Psychoactive Drugs

Psychoactive drugs are divided into different classes according to their pharmacological effects. Several classes are listed below, along with examples of commonly used drugs in each class.

- Stimulants are drugs that stimulate the brain and increase alertness and wakefulness. Examples of stimulants include caffeine, nicotine, cocaine, and amphetamines such as Adderall.
- Depressants are drugs that calm the brain, reduce anxious feelings, and induce sleepiness. Examples of depressants include ethanol (in alcoholic beverages) and opioids such as codeine and heroin.
- Anxiolytics are drugs that have a tranquilizing effect and inhibit anxiety. Examples of anxiolytic drugs include benzodiazepines such as diazepam (Valium), barbiturates such as phenobarbital, opioids, and antidepressant drugs such as sertraline (Zoloft).
- Euphoriants are drugs that bring about a state of euphoria, or intense feelings of well-being and happiness. Examples of euphoriants include the so-called club drug MDMA (ecstasy), amphetamines, ethanol, and opioids such as morphine.
- Hallucinogens are drugs that can cause hallucinations and other perceptual anomalies. They also cause subjective changes in thoughts, emotions, and consciousness. Examples of hallucinogens include LSD, mescaline, nitrous oxide, and psilocybin.
- Empathogens are drugs that produce feelings of empathy, or sympathy with other people. Examples of empathogens include amphetamines and MDMA.



Figure **18.7.3**: Ecstasy (MDMA) is most commonly taken in tablet form, like the colorful and decorated tablets shown here.

Many psychoactive drugs have multiple effects so they may be placed in more than one class. An example is MDMA, pictured below, which may act both as a euphoriant and as an empathogen. In some people, MDMA may also have stimulant or hallucinogenic effects. As of 2016, MDMA had no accepted medical uses, but it was undergoing testing for use in the treatment of post-traumatic stress disorder and certain other types of anxiety disorders.

Mechanisms of Action

Psychoactive drugs generally produce their effects by affecting brain chemistry, which in turn may cause changes in a person's mood, thinking, perception, and/or behavior. Each drug tends to have a specific action on one or more neurotransmitters or neurotransmitter receptors in the brain. Generally, they act as either agonists or antagonists.

- **Agonists** are drugs that increase the activity of particular neurotransmitters. They might act by promoting the synthesis of the neurotransmitters, reducing their reuptake from synapses, or mimicking their action by binding to receptors for the neurotransmitters.
- **Antagonists** are drugs that decrease the activity of particular neurotransmitters. They might act by interfering with the synthesis of the neurotransmitters or by blocking their receptors so the neurotransmitters cannot bind to them.

Consider the example of the neurotransmitter GABA. This is one of the most common neurotransmitters in the brain, and it normally has an inhibitory effect on cells. GABA agonists, which increase its activity, include ethanol, barbiturates, and benzodiazepines, among other psychoactive drugs. All of these drugs work by promoting the activity of GABA receptors in the brain.

Chemistry of the Nervous System

Neurons, also called nerve cells, are electrically excitable cells that are the main functional units of the nervous system. Their function is to transmit nerve impulses. They are the only type of human cells that can carry out this function.

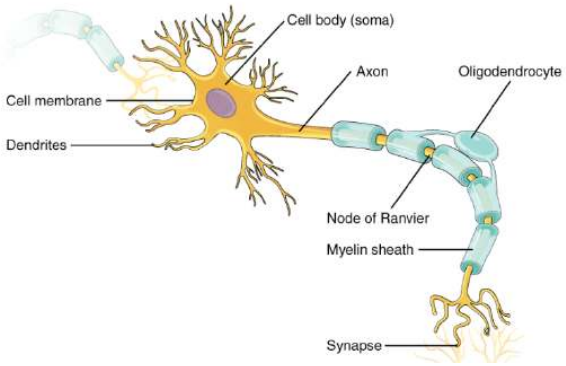


Figure **18.7.4** Parts of a neuron.

The main parts of a neuron are labeled in Figure **18.7.4** and described below.

- The **cell body** is the part of a neuron that contains the cell nucleus and other cell organelles. It is usually quite compact, and may not be much wider than the nucleus.
- **Dendrites** are thin structures that are extensions of the cell body. Their function is to receive nerve impulses from other cells and carry them to the cell body. A neuron may have many dendrites, and each dendrite may branch repeatedly to form a dendrite "tree" with more than 1,000 "branches." The end of each branch can receive nerve impulses from another cell, allowing a given neuron to communicate with tens of thousands of other cells.
- The **axon** is a long, thin extension of the cell body. It transmits nerve impulses away from the cell body and toward other cells. The axon branches at the end, forming multiple axon terminals. These are the points where nerve impulses are transmitted to other cells, often to the dendrites of other neurons. An area called a synapse occurs at each axon terminal. Synapses are complex membrane junctions that transmit signals to other cells. An axon may branch hundreds of times, but there is never more than one axon per neuron.
- Spread out along axons, especially the long axons of nerves, are many sections of the **myelin sheath.** These are lipid layers that cover sections of the axon. The myelin sheath is a very good electrical insulator, similar to the plastic or rubber that encases an electrical cord.
- Regularly spaced gaps between sections of myelin sheath occur along the axon. These gaps are called **nodes of Ranvier**, and they allow the transmission of nerve impulses along the axon. Nerve impulses skip from node to node, allowing nerve impulses to travel along the axon very rapidly.
- A Schwann cell (also on an axon) is a type of glial cell. Its function is to produce the myelin sheath that insulates axons in the peripheral nervous system. In the central nervous system, a different type of glial cell, called an oligodendrocyte, produces the myelin sheath.

Neurotransmission is the process by which signaling molecules called neurotransmitters are released by the axon terminal of a neuron (the presynaptic neuron), and bind to and react with the receptors on the dendrites of another neuron (the postsynaptic neuron) a short distance away. Synapses are functional connections between neurons, or between neurons and other types of cells. The **synaptic cleft** —also called **synaptic gap**— is a gap between the pre- and postsynaptic cells that is about 20 nm (0.02 μ) wide. The small volume of the cleft allows neurotransmitter concentration to be raised and lowered rapidly.

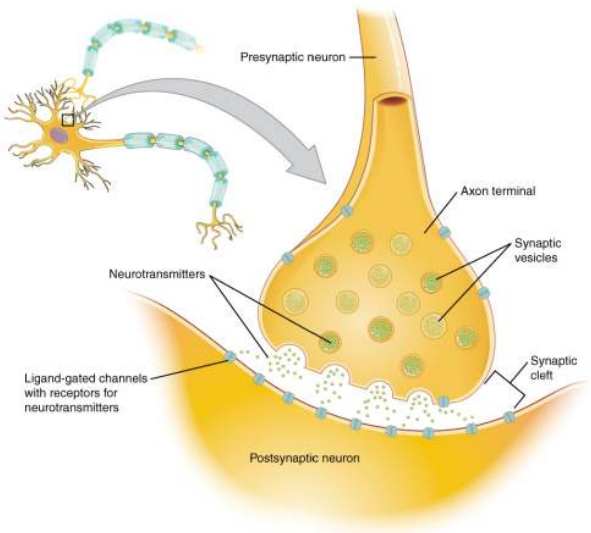


Figure **18.7.5** The synapse. The synapse is a connection between a neuron and its target cell (which is not necessarily a neuron).

Neurotransmiters

Neurotransmitters are endogenous chemicals that enable neurotransmission. It is a type of chemical messenger which transmits signals across a chemical synapse, such as a neuromuscular junction, from one neuron (nerve cell) to another "target" neuron, muscle cell, or gland cell.

Biochemical Theories of Brain Diseases

One theory that explains mental illness incorporates the various amounts of neurotransmitters. Using this theory, the lack or excess of specific neurotransmitters can be associated with depression, anxiety, bipolar disorder, or schizophrenia. Other disorders or health conditions, namely Attention Deficient Hyperactivity Disorder (ADHD) and Parkinson's Disease have also been linked with varying levels of neurotransmitters.

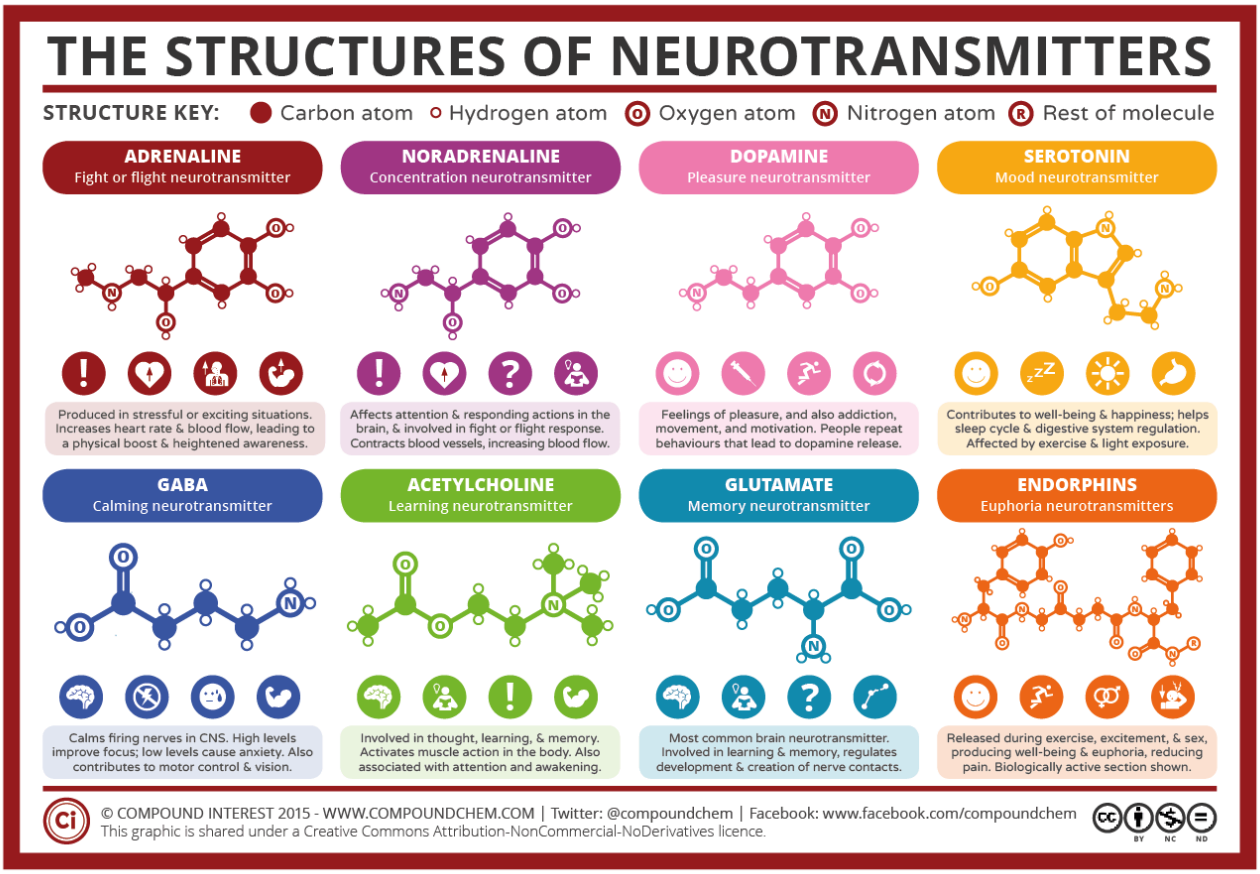


Figure 18.7.6: The Structures of Neurotransmitters.(CC BY-NC-ND; Andy Brunning)

The Noradrenaline neurotransmitter is also called norepinephrine. When evaluating antidepressants or other mental health medications, it is important to be aware of this terminology. For a brief overview of the correlation between neurotransmitters and mental health, watch the video below.



Mental health conditions can result from a person's life experiences and/or genetics. Sometimes, drug usage or brain trauma can trigger mental illness. It is important to note all health conditions that are present in your family tree (biological). Also, recognizing emotional trauma and then seeking counseling/medical treatment is important for navigating a mental health condition.



Figure 18.7.7: Nason family picture circa 1905. Image courtesy of Elizabeth R. Gordon

Depression symptoms

Can be short or long-term. Experience-sadness, sleeping and eating issues, withdrawal, feelings of hopelessness, loss of interest/pleasure, lack of energy, feelings of worthlessness/guilt, slowed processing, trouble concentrating, frequent thought of suicide/death, anxiety, and unexplained health problems.

Treatments for depression

psychotherapy, brain stimulation, medication, exercise, light therapy. Discussions to have with dr: meds/vitamins you are on, self-medication is not answer, stopping antidepressants without assistance, and report problems with meds. Limit alcohol and refrain from illicit and scheduled drugs. FDA black-box warning for antidepressants in people under 25.

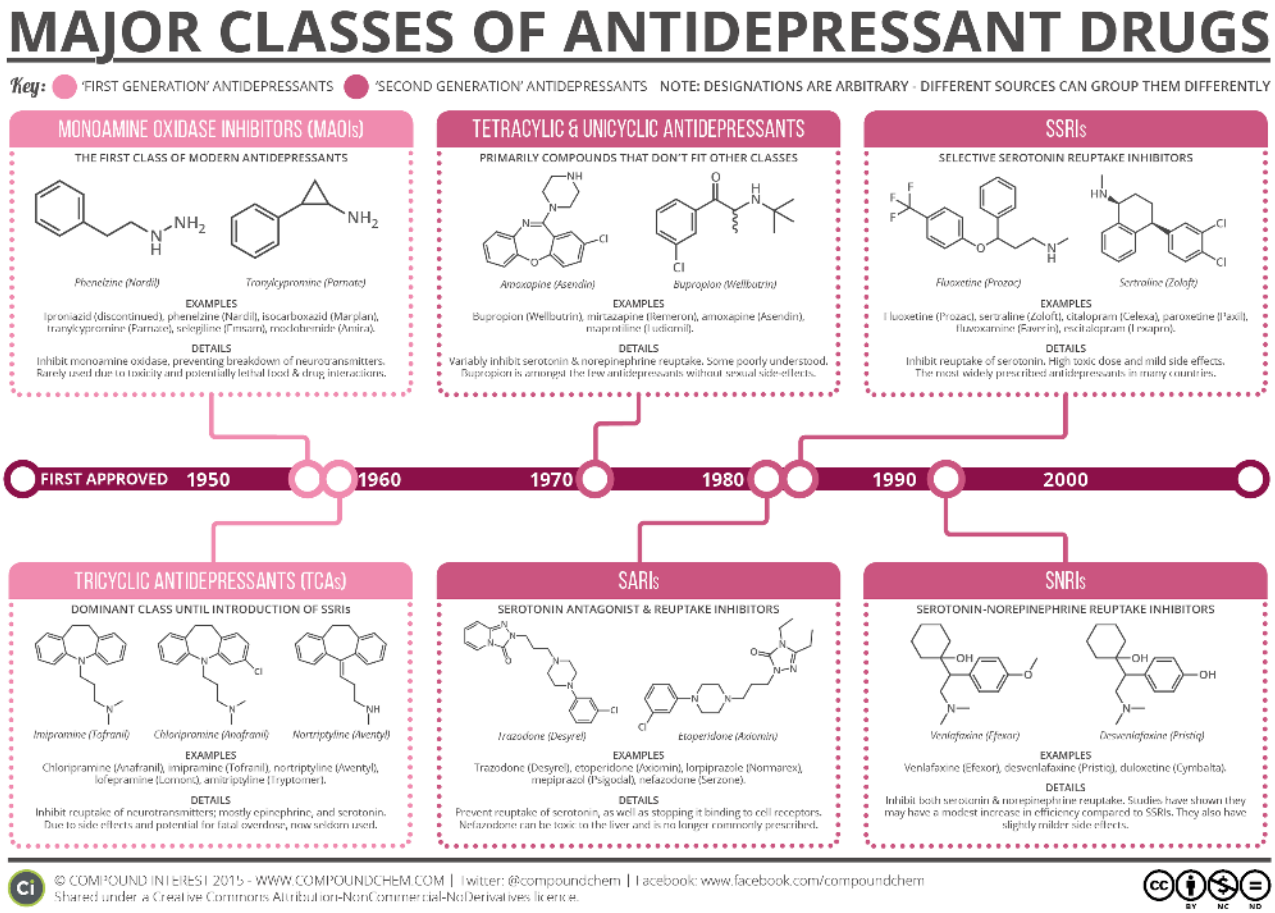


Figure 18.7.8: Major Classes of Antidepressant Drugs.(CC BY-NC-ND; Andy Brunning)

Finding the correct antidepressant

Trial and Error-take for six weeks, then wean, and start another. Since the early 2000's, Mayo Clinic has been researching gene technology. Test is now offered by Assurex Health and called Genesight.

https://genesight.com/gene-test-for-...surex%20Health

Common Side Effects of Antidepressants

This carry varies with the patient and type of medicine. Most common include weight gain, fatigue, dizziness, loss of sexual desire, nausea, dry mouth, blurred vision, agitation, insomnia, and constipation.

Support and information regarding mental health conditions.

National Alliance on Mental Illness

Figure 18.7.9: Official logo of the National Alliance on Mental Illness. (National Alliance on Mental Illness, http://www.nami.org/Template.cfm?Sec...ntentID=121014)

Anesthetics

An **anesthetic** or **anaesthetic** is a drug used to induce anesthesia - in other words, to result in a temporary loss of sensation or awareness. They may be divided into two broad classes: general anesthetics, which result in a reversible loss of consciousness, and local anesthetics, which cause a reversible loss of sensation for a limited region of the body without necessarily affecting consciousness.

A wide variety of drugs are used in modern anesthetic practice. Many are rarely used outside anesthesiology, but others are used commonly in various fields of healthcare. Combinations of anesthetics are sometimes used for their synergistic and additive therapeutic effects. Adverse effects, however, may also be increased. Anesthetics are distinct from analgesics, which block only sensation of painful stimuli.

General Anesthetics

General anesthetics are often defined as compounds that induce a loss of consciousness in humans or loss of righting reflex in animals. Clinical definitions are also extended to include the lack of awareness to painful stimuli, sufficient to facilitate surgical applications in clinical and veterinary practice. General anesthetics do not act as analgesics and should also not be confused with sedatives. General anesthetics are a structurally diverse group of compounds whose mechanisms encompasses multiple biological targets involved in the control of neuronal pathways. The precise workings are the subject of some debate and ongoing research.

General anesthetics elicit a state of general anesthesia. It remains somewhat controversial regarding how this state should be defined. General anesthetics, however, typically elicit several key reversible effects: immobility, analgesia, amnesia, unconsciousness, and reduced autonomic responsiveness to noxious stimuli.

Mode of administration

Drugs given to induce general anesthesia can be either as gases or vapors (inhalational anesthetics), or as injections (intravenous anesthetics or even intramuscular). All of these agents share the property of being quite hydrophobic (i.e., as liquids, they are not freely miscible—or mixable—in water, and as gases they dissolve in oils better than in water). It is possible to deliver anesthesia solely by inhalation or injection, but most commonly the two forms are combined, with an injection given to induce anesthesia and a gas used to maintain it.

Inhalation

General anesthetics are frequently administered as volatile liquids or gases (Figure **18.7.6**). Inhalational anesthetic substances are either volatile liquids or gases, and are usually delivered using an anesthesia machine. An anesthesia machine allows composing a mixture of oxygen, anesthetics and ambient air, delivering it to the patient and monitoring patient and machine parameters. Liquid anesthetics are vaporized in the machine.

Many compounds have been used for inhalation anesthesia, but only a few are still in widespread use. Desflurane, isoflurane and sevoflurane are the most widely used volatile anesthetics today. They are often combined with nitrous oxide. Older, less popular, volatile anesthetics, include halothane, enflurane, and methoxyflurane. Researchers are also actively exploring the use of xenon as an anesthetic.

Figure **18.7.10** General anesthetics are frequently administered as volatile liquids or gases.

Injection

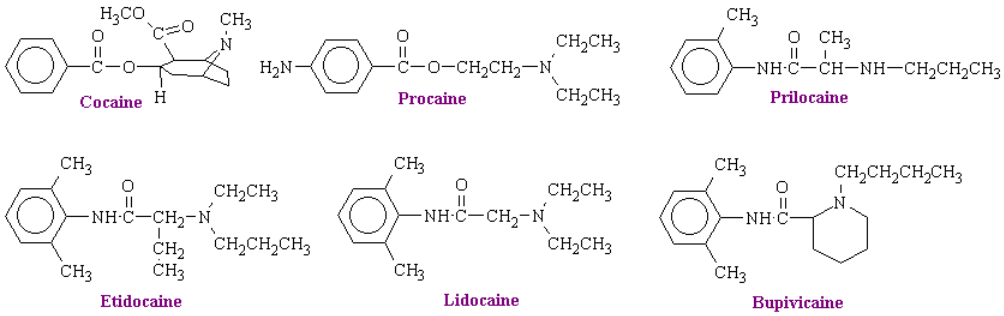
Injectable anesthetics are used for the induction and maintenance of a state of unconsciousness. Anesthetists prefer to use intravenous injections, as they are faster, generally less painful and more reliable than intramuscular or subcutaneous injections. Among the most widely used drugs are propofol, etomidate, barbiturates such as methohexital and thiopentone/thiopenta, Benzodiazepines such as midazolam, Ketamine is used in the UK as "field anaesthesia", for instance in road traffic incidents or similar situations where an operation must be conducted at the scene or when there is not enough time to move to an operating room, while preferring other anesthetics where conditions allow their use. It is more frequently used in the operative setting in the US. Benzodiazepines are sedatives and are used in combinations with other general anesthetics.

Local Anesthetics

The first local anesthetic to be discovered was cocaine, an alkaloid contained in large amounts in the leaves of *Erythroxylon coca*, a shrub growing in the Andes Mountains. Over 9 million kilograms of these leaves are consumed annually by the 2 million inhabitants of the highlands of Peru, who chew or suck the leaves for the sense of wellbeing it produces.

Local anesthetics are drugs that block nerve conduction when applied locally to nerve conduction when applied locally to nerve tissue in appropriate concentrations. They act on any part of the nervous system and on every type of nerve fiber. For example, when they are applied to the motor cortex impulse transmission from that area stops, and when they are injected into the skin they prevent the initiation and the transmission of sensory impulses. A local anesthetic in contact with a nerve trunk can cause both sensory and motor paralysis in the area innervated. The great practical advantage of the local anesthetic is that their action is reversible: their use is followed by complete recovery in nerve function with no evidence of structural damage to nerve fibers of cells.

The structures some of the typical anesthetics are shown below.



These structures contain hydrophilic and hydrophobic domains that are separated by an intermediate alkyl chain. Linkage of these two domains is of either the ester or amide type. the ester link is important because this bond is readily hydrolyzed during metabolic degradation and inactivation in the body. Procaine, for example, can be divided into three main portions: the aromatic acid (para-aminobenzoic), the alcohol (ethanol), and the tertiary amino group (diethylamino). Changes in any part of the molecule alter the anesthetic potency and the toxicity of the compound. Increasing the length of the alcohol group leads to a greater anesthetic potency. It also leads to an increase in toxicity.

Depressants

A **depressant**, or **central depressant**, is a drug that lowers neurotransmission levels, which is to depress or reduce arousal or stimulation, in various areas of the brain. Depressants are also occasionally referred to as **"downers"** as they lower the level of arousal when taken. Stimulants or "uppers" increase mental and/or physical function, hence the opposite drug class of depressants is stimulants, not antidepressants.

Depressants are widely used throughout the world as prescription medicines and as illicit substances. When depressants are used, effects often include ataxia, anxiolysis, pain relief, sedation or somnolence, and cognitive/memory impairment, as well as in some instances euphoria, dissociation, muscle relaxation, lowered blood pressure or heart rate, respiratory depression, and anticonvulsant effects. Depressants also act to produce anesthesia. Cannabis may sometimes be considered a depressant due to one of its components, cannabidiol. The latter is known to treat insomnia, anxiety and muscle spasms similar to other depressive drugs. However, tetrahydrocannabinol, another component, may slow brain function to a small degree while reducing reaction to stimuli, it is generally considered to be a stimulant and main psychoactive agent to sometimes cause anxiety, panic and psychosis instead. Other depressants can include drugs like Xanax (a benzodiazepine) and a number of opiates.

Depressants exert their effects through a number of different pharmacological mechanisms, the most prominent of which include facilitation of GABA, and inhibition of glutamatergic or monoaminergic activity. Other examples are chemicals that modify the electrical signaling inside the body, the most prominent of these being bromides and body blockers.

Alcohol

Alcohol is a very prominent depressant. Alcohol can be and is more likely to be a large problem among teenagers and young adults. Symptoms of alcohol consumption at lower doses may include mild sedation and poor coordination. At higher doses, there may be slurred speech, trouble walking, and vomiting. Extreme doses may result in a respiratory depression, coma, or death. Complications may include seizures, aspiration pneumonia, injuries including suicide, and low blood sugar. Alcohol intoxication can lead to alcohol-related crime with perpetrators more likely to be intoxicated than victims.

Alcohol intoxication typically begins after two or more alcoholic drinks. Risk factors include a social situation where heavy drinking is common and a person having an impulsive personality. Diagnosis is usually based on the history of events and physical examination. Verification of events by witnesses may be useful. Legally, alcohol intoxication is often defined as a blood alcohol concentration (BAC) of greater than 5.4–17.4 mmol/L (25–80 mg/dL or 0.025–0.080%). This can be measured by blood or breath testing. Alcohol is broken down in human body at a rate of about 3.3 mmol/L (15 mg/dL) per hour.

Alcohol intoxication is very common, especially in the Western world. Most people who drink alcohol have at some time been intoxicated. In the United States acute intoxication directly results in about 2,200 deaths per year, and indirectly more than 30,000 deaths per year. Acute intoxication has been documented throughout history and alcohol remains one of the world's most widespread recreational drugs. Some religions consider alcohol intoxication to be a sin.

Barbiturates

Barbiturates are CNS depressants and are similar, in many ways, to the depressant effects of alcohol. To date, there are about 2,500 derivatives of barbituric acid of which only 15 are used medically. The first barbiturate was synthesized from barbituric acid in 1864.

The original use of barbiturates was to replace drugs such as opiates, bromides, and alcohol to induce sleep. Barbiturates are effective as anxiolytics, hypnotics, and anticonvulsants, but have physical and psychological addiction potential as well as overdose potential among other possible adverse effects. They have largely been replaced by benzodiazepines (discussed below) and nonbenzodiazepines ("Z-drugs") in routine medical practice, particularly in the treatment of anxiety and insomnia, due to the significantly lower risk of addiction and overdose and the lack of an antidote for barbiturate overdose. Despite this, barbiturates are still in use for various purposes: in general anesthesia, epilepsy, treatment of acute migraines or cluster headaches, euthanasia, capital punishment, and assisted suicide.

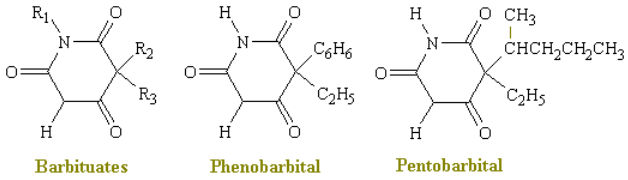


Figure **18.7.11** Barbitutrates.

Some symptoms of an overdose typically include sluggishness, incoordination, difficulty in thinking, slowness of speech, faulty judgement, drowsiness, shallow breathing, staggering, and, in severe cases, coma or death. The lethal dosage of barbiturates varies greatly with tolerance and from one individual to another.

Barbiturates in overdose with other CNS (central nervous system) depressants (e.g. alcohol, opiates, benzodiazepines) are even more dangerous due to additive CNS and respiratory depressant effects. In the case of benzodiazepines, not only do they have additive effects, barbiturates also increase the binding affinity of the benzodiazepine binding site, leading to exaggerated benzodiazepine effects. (ex. If a benzodiazepine increases the frequency of channel opening by 300%, and a barbiturate increases the duration of their opening by 300%, then the combined effects of the drugs increase the channels overall function by 900%, not 600%).

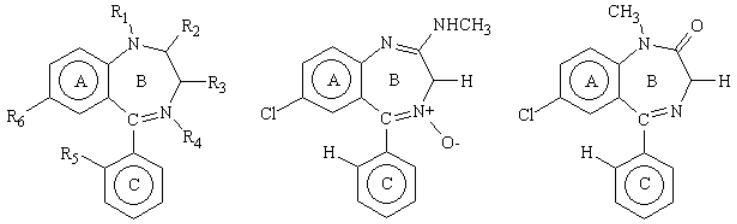
Anti-anxiety Agents

Anti-anxiety medications help reduce the symptoms of anxiety, such as panic attacks, or extreme fear and worry.

Benzodiazepines are prescribed to quell panic attacks. Benzodiazepines are also prescribed in tandem with an antidepressant for the latent period of efficacy associated with many antidepressants for anxiety disorder. The effects of the benzodiazepines virtually all result from action of these drugs on the central nervous system, even when lethal doses are used. The most prominent of these effects are sedation, hypnosis, decreased anxiety, muscle relaxation, and anticonvulsant activity. As the dose of a benzodiazepine is increased, sedation progresses to hypnosis and hypnosis to stupor. They are used as sedatives, hypnotics, antianxiety agents (in panic disorder), anticonvulsants, muscle relaxants, in anesthesia and in alcoholism.

There is risk of benzodiazepine withdrawal and rebound syndrome if BZDs are rapidly discontinued. Tolerance and dependence may occur. The risk of abuse in this class of medication is smaller than in that of barbiturates. Cognitive and behavioral adverse effects are possible.

There are several useful benzodiazepines available. The skeletal structure and two examples are shown below.



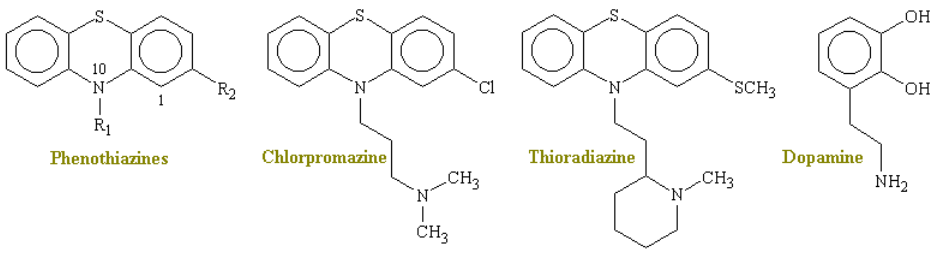
Benzodiazepine include: Alprazolam (Xanax), Bromazepam, Chlordiazepoxide (Librium), Clonazepam (Klonopin), Diazepam (Valium), Lorazepam (Ativan), Oxazepam, Temazepam, and Triazolam. Short half-life (or short-acting) benzodiazepines (such as Lorazepam) and beta-blockers are used to treat the short-term symptoms of anxiety. Beta-blockers help manage physical symptoms of anxiety, such as trembling, rapid heartbeat, and sweating that people with phobias (an overwhelming and unreasonable fear of an object or situation, such as public speaking) experience in difficult situations. Taking these medications for a short period of time can help the person keep physical symptoms under control and can be used “as needed” to reduce acute anxiety.

Antipsychotics, also known as neuroleptics, are a class of psychotropic medication primarily used to manage psychosis (including delusions, hallucinations, paranoia or disordered thought), principally in schizophrenia but also in a range of other psychotic disorders. They are also the mainstay together with mood stabilizers in the treatment of bipolar disorder.

The **phenothiazines** as a class, and especially chlorpromazine, the prototype, are among the most widely used drugs in medical practice and are primarily employed in the management of patients with serious psychiatric illnesses. In addition, many members of the group have other clinically useful properties, including antiemetic, antinausea, and antihistaminic effects and the ability to potentiate analgesics, sedatives and general anesthetics.

It was noted that chlorpromazine by itself did not cause a loss of consciousness but produced only a tendency to sleep and a lack of interest in what was going on. These central actions became known as neuroleptic soon after.

Phenothiazine has a tricyclic structure in which two benzene rings are linked by a sulfur and a nitrogen atom (see figures below). Substitution of an electron-withdrawing group at R2 (but not at position 3 or 4) increases the efficacy of phenothiazines and other tricyclic congeners.

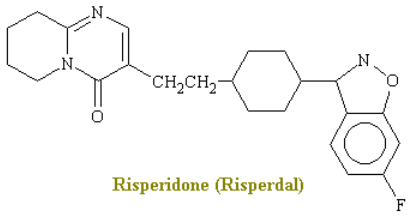


Neuroleptic drugs reduce initiative and interest in the environment, and they reduce displays of emotion or affect. Initially there may be some slowness in response to external stimuli and drowsiness. However subject are easily aroused, capable of giving

appropriate answers to direct questions, and seem to have intact intellectual functions; there is no ataxia, incoordination, or dysathria at ordinary doses. Psychotic patients become less agitated and restless, and withdrawn or autistic patients sometimes become more responsive and communicative. Aggressive and impulsive behavior diminishes. Gradually (over a period of days). psychotic symptoms of hallucinations, delusions, and disorganized or incoherent thinking tend to disappear.

The most prominent observable effects of typical neuroleptic agents are strikingly similar. In low doses, operant behavior is reduced but spinal reflexes are unchanged. Exploratory behavior is diminished, and responses to a a variety of stimuli are fewer, slower, and smaller, although the ability to discriminate stimuli is retained. Conditioned avoidance behaviors are selectively inhibited, while unconditioned escape or avoidance responses are not.

In 1994 an addition tot he antipsychotic drugs is **risperidone** (Risperdal). This drug antagonises D2 and serotonin type 2 receptors. The drug also antagonizes for other receptors such as a adrenergic and histaminergic H1 receptors.



Risperidone (Risperdal)

Anti Depressants

Major depression is the most common of the major mental illnesses, and it must be distinguished from normal grief, sadness, and disappointment. Major depression is characterized by feelings of intense sadness and despair, mental slowing and loss of concentration, pessimistic worry, agitation, and self-depreciation. Physical changes also occur, such as weight loss, decreased libido, and disruption of hormonal circadian rhythms.

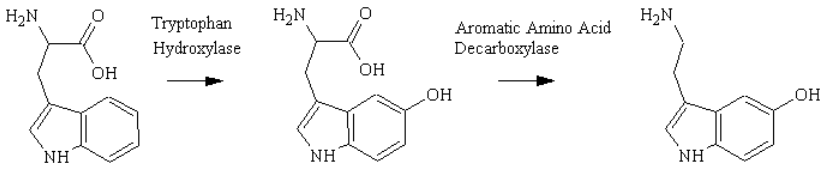
Before the advent of psychotherapy in the 1950s, treatment of depression consisted of stimulants such as caffeine and amphetamines to ameliorate the depressive phases and barbiturates to allay agitation, anxiety, and insomnia. At best, such attempts at therapy may have offered transient relief to some patients. Suffering usually decreased little.

Monoamine Oxidase Inhibitors

Monoamine oxidase inhibitors (MAOIs) were the first effective antidepressants used. The monoamine oxidase inhibitors comprise a chemically heterogeneous group of drugs that have in common the ability to block oxidative deamination of naturally occurring monoamines. These drugs have numerous other effects, many of which are still poorly understood. For example, they lower blood pressure and were at one time used to treat hypertension. Their use in psychiatry has also become very limited as the tricyclic antidepressants have come to dominate the treatment of depression and allied conditions. Thus, MAOIs are used most often when tricyclic antidepressants give unsatisfactory results. In addition, whereas severe depression may not be the primary indication for these agents, certain neurotic illnesses with depressive features, and also with anxiety and phobias, may respond especially favorably.

Serotonin

Serotonin (5-hydroxytryptamine or 5-HT) is a monoamine neurotransmitter found in cardiovascular tissue, in endothelial cells, in blood cells, and in the central nervous system. The role of serotonin in neurological function is diverse, and there is little doubt that serotonin is an important CNS neurotransmitter.



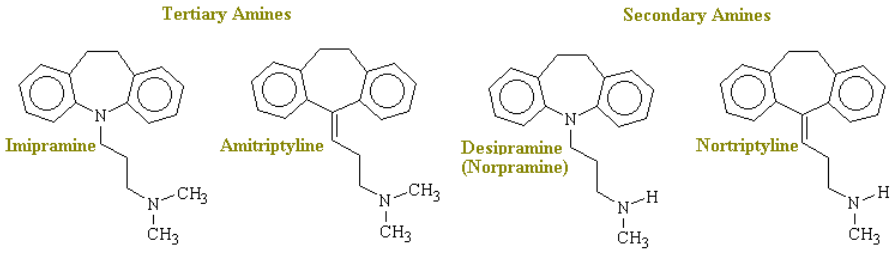
Tryptophan 5-Hydroxytryptophan 5-Hydroxytryptomine

The monoamine serotonin is itself a precursor for melatonin production in the pineal gland. The biosynthesis of serotonin from the amino acid tryptophan is similar to that found for the catecholamines, and 5-hydroxytryptophan can cross the BBB to increase central levels of 5-HT. Although some of the serotonin is metabolized by monoamine oxidase to 5-hydroxyindole acetic acid, most of the serotonin released into the post-synaptic space is removed by the neuron through a reuptake mechanism inhibited by the tricyclic antidepressants and the newer, more selective antidepressants such as fluoxetine and sertraline.

Serotonin receptors are diverse and numerous. Over the past several years, over fourteen different serotonin receptors have been cloned and sequenced through molecular biological techniques. Overall, there are seven distinct families of 5-HT receptors, with as many as five within a particular family. Only one of the 5-HT receptors is a ligand-gated ion channel (the 5-HT3 receptor), and the other six families are all G protein-coupled receptors.

Tricyclic Anti-depressants

Imipramine, amitriptylin, and other closely related drugs are among the drugs currently most widely used for the treatment of major depression. Because of there structure (see below). They are often referred to as the tricyclic antidepressants. Although these compounds seem to be similar to the phenothiazines chemically, the ethylene group of imiprimine's middle ring imparts dissimilar stereochemical properties and prevents conjegation of the rings, as occurs with the phenothiazines.



One might expect an effective antidepressant drug to have a stimulating or mood-elevating effect when given to a normal subject. Although this may occur with the MAOIs, it is not true of the tricyclic antidepressants. If a dose of imipramine given to a normal subject, he feels sleepy and tends to be quieter, his blood pressure falls slightly, and he feels light headed. These drug effects are usually perceived to be unpleasant, and cause a feeling of unhappiness and increased anxiety. Repeated administration for several days may lead to accentuation of these symptoms and, in addition, to difficulty in concentrating and thinking. In contrast, if the drug is given over a period of time (two to three weeks) to depressed patients an elevated mood occurs. For this reason, the tricyclics are not prescribed on an "as-needed" basis.

Selective Serotonin Reuptake Inhibitors

In recent years, selective serotonin reuptake inhibitors (SSRIs) have been introduced for the treatment of depression. Prozac is the most famous drug in this class. Lilly's sales of Prozac in 1993 exceeded 1 billion US dollars. Clomiprimine, fluoxetine (Prozac), sertraline and paroxetine selectively block the reuptake of serotonin, thereby increasing the levels of serotonin in the central nervous system. Note the similarities and differences between the tricyclic antidepressants and the selective serotonin reuptake inhibitors. The SSRIs generally have fewer anticholinergic side effects, but caution is still necessary when co-administering any drugs that affect serotonergic systems (e.g., monoamine oxidase inhibitors). Some of the newer, SSRIs (e.g., clomipramine) have been useful in the treatment of obsessive-compulsive disorders.

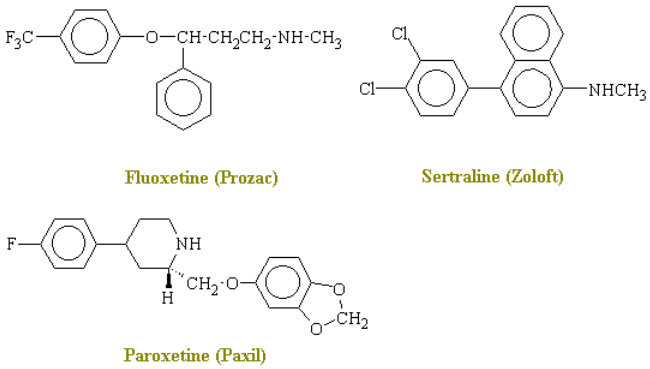


Figure **18.7.12** Examples of SSRIs.

Stimulants

These classes of chemicals induce alertness and stimulant the brain and nervous system. Side effects of stimulant use include wakefulness, increased speech, and motor activity, and decreased appetite. Amphetamines are a type of stimulant that incorporates a nitrogen-containing organic functional group. These compounds have been noted to block the reuptake of dopamine.

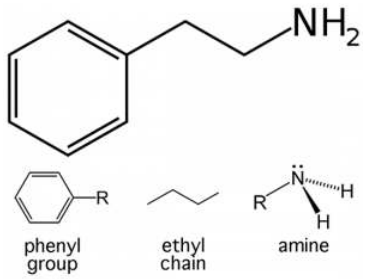


Figure **18.7.13**: The skeletal structure of phenethylamine. (Copyright, http://countyourculture.com/2010/11/02/phenethylamine-and-amphetamine/)

Early Stimulant Use

For over 5000 years, the Chinese have extracted the compound Ephedrine from locally grown Ephedra plants. Native peoples of the United States were known to isolate this compound as well. Both cultures used Ephedrine to treat asthma, hay fever, and congestion. Ephedrine was noted to have a stimulant effect on its users. Chemically similar to adrenaline, ephedrine was a more stable compound and could be taken orally. By the mid-1920s, the pharmaceutical company, Eli Lily, synthesized ephedrine and introduced it into western medicine.

Figure **18.7.14**: : https://commons.wikimedia.org/wiki/C...phedra_viridis. (Copyright, https://commons.wikimedia.org/wiki/User:Dcrjsr)

Ephedrine can decrease appetite, increase blood pressure and heart rate, and cause sleeping problems. Mental health can be affected by ephedrine use. Patients may experience hallucinogens, anxiety, and chemical dependence.

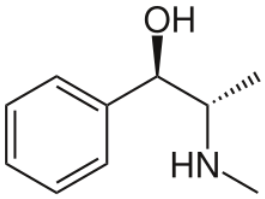


Figure **18.7.15**: Chemical structure of Ephedrine, done using BKchem. (Copyright, https://commons.wikimedia.org/wiki/User:Bryan_Derksen)

Amphetamine is a potent central nervous system (CNS) stimulant of the phenethylamine class that is approved for the treatment of attention deficit hyperactivity disorder (ADHD) and narcolepsy. Amphetamine is also used off-label as a performance and cognitive enhancer, and recreationally as an aphrodisiac and euphoriant. Although it is a prescription medication in many countries, unauthorized possession and distribution of amphetamine is often tightly controlled due to the significant health risks associated

with uncontrolled or heavy use. As a consequence, amphetamine is illegally manufactured in clandestine labs to be trafficked and sold to users. Based upon drug and drug precursor seizures worldwide, illicit amphetamine production and trafficking is much less prevalent than that of methamphetamine.

The first pharmaceutical amphetamine was Benzedrine, a brand of inhalers used to treat a variety of conditions. At therapeutic doses, this drug causes emotional and cognitive effects such as euphoria, change in libido, increased arousal, and improved cognitive control. Likewise, it induces physical effects such as decreased reaction time, fatigue resistance, and increased muscle strength. In contrast, supratherapeutic doses of amphetamine are likely to impair cognitive function and induce rapid muscle breakdown. Very high doses can result in psychosis (e.g., delusions and paranoia), which very rarely occurs at therapeutic doses even during long-term use. As recreational doses are generally much larger than prescribed therapeutic doses, recreational use carries a far greater risk of serious side effects, such as dependence, which only rarely arises with therapeutic amphetamine use.

3,4-Methylenedioxymethamphetamine (MDMA, ecstasy, or molly) is a euphoriant, empathogen, and stimulant of the amphetamine class. Briefly used by some psychotherapists as an adjunct to therapy, the drug became popular recreationally and the DEA listed MDMA as a Schedule I controlled substance, prohibiting most medical studies and applications. MDMA is known for its entactogenic properties. The stimulant effects of MDMA include hypertension, anorexia (appetite loss), euphoria, social disinhibition, insomnia (enhanced wakefulness/inability to sleep), improved energy, increased arousal, and increased perspiration, among others. Relative to catecholaminergic transmission, MDMA enhances serotonergic transmission significantly more, when compared to classical stimulants like amphetamine. MDMA does not appear to be significantly addictive or dependence forming.

Methylenedioxypyrovalerone (MDPV) is a psychoactive drug with stimulant properties that acts as a norepinephrine-dopamine reuptake inhibitor (NDRI). It was first developed in the 1960s by a team at Boehringer Ingelheim. MDPV remained an obscure stimulant until around 2004, when it was reported to be sold as a designer drug. Products labeled as bath salts containing MDPV were previously sold as recreational drugs in gas stations and convenience stores in the United States, similar to the marketing for Spice and K2 as incense.

Incidents of psychological and physical harm have been attributed to MDPV use.

Mephedrone is a synthetic stimulant drug of the amphetamine and cathinone classes. Slang names include drone and MCAT. It is reported to be manufactured in China and is chemically similar to the cathinone compounds found in the khat plant of eastern Africa. It comes in the form of tablets or a powder, which users can swallow, snort, or inject, producing similar effects to MDMA, amphetamines, and cocaine.

Methamphetamine (contracted from *N*-**meth**yl-**a**lpha-**m**ethyl**ph**en**et**hyl**amine**) is a potent psychostimulant that is used to treat attention deficit hyperactivity disorder (ADHD) and obesity. Recreationally, methamphetamine is used to increase sexual desire, lift the mood, and increase energy, allowing some users to engage in sexual activity continuously for several days straight.

In low doses, methamphetamine can cause an elevated mood and increase alertness, concentration, and energy in fatigued individuals. At higher doses, it can induce psychosis, rhabdomyolysis, and cerebral hemorrhage. Methamphetamine is known to have a high potential for abuse and addiction. Recreational use of methamphetamine may result in psychosis or lead to post-withdrawal syndrome, a withdrawal syndrome that can persist for months beyond the typical withdrawal period. Unlike amphetamine and cocaine, methamphetamine is neurotoxic to humans, damaging both dopamine and serotonin neurons in the central nervous system (CNS). Entirely opposite to the long-term use of amphetamine, there is evidence that methamphetamine causes brain damage from long-term use in humans; this damage includes adverse changes in brain structure and function, such as reductions in gray matter volume in several brain regions and adverse changes in markers of metabolic integrity.

Methylphenidate is a stimulant drug that is often used in the treatment of ADHD and narcolepsy and occasionally to treat obesity in combination with diet restraints and exercise. Its effects at therapeutic doses include increased focus, increased alertness, decreased appetite, decreased need for sleep and decreased impulsivity. Methylphenidate is not usually used recreationally, but when it is used, its effects are very similar to those of amphetamines.

Methylphenidate is sold under a number of brand names including Ritalin. Other versions include the long lasting tablet Concerta and the long lasting transdermal patch Daytrana.

Phenylpropanolamine (PPA; Accutrim; β-hydroxyamphetamine), also known as norephedrine and norpseudoephedrine, is a psychoactive drug that is used as a stimulant, decongestant, and anorectic agent. It is commonly used in prescription and over-the-

counter cough and cold preparations. In veterinary medicine, it is used to control urinary incontinence in dogs under trade names Propalin and Proin.

In the United States, PPA is no longer sold without a prescription due to a proposed increased risk of stroke in younger women. In a few countries in Europe, however, it is still available either by prescription or sometimes over-the-counter.

Propylhexedrine (Hexahydromethamphetamine, Obesin) is a stimulant medication, sold over-the-counter in the United States as the cold medication Benzedrex. The drug has also been used as an appetite suppressant in Europe. Propylhexedrine is not an amphetamine, though it is structurally similar; it is instead a cycloalkylamine, and thus has stimulant effects that are less potent than similarly structured amphetamines, such as methamphetamine.

The abuse potential of propylhexedrine is fairly limited, due its limited routes of administration: in the United States, Benzedrex is only available as an inhalant, mixed with lavender oil and menthol. These ingredients cause unpleasant tastes, and abusers of the drug have reported unpleasant "menthol burps". Injection of the drug has been found to cause transient diplopia and brain stem dysfunction.

Pseudoephedrine is used as a nasal/sinus decongestant, as a stimulant, or as a wakefulness-promoting agent. The salts pseudoephedrine hydrochloride and pseudoephedrine sulfate are found in many over-the-counter preparations, either as a single ingredient or (more commonly) in combination with antihistamines, guaifenesin, dextromethorphan, and/or paracetamol (acetaminophen) or another NSAID (such as aspirin or ibuprofen). It is also used as a precursor chemical in the illegal production of methamphetamine.

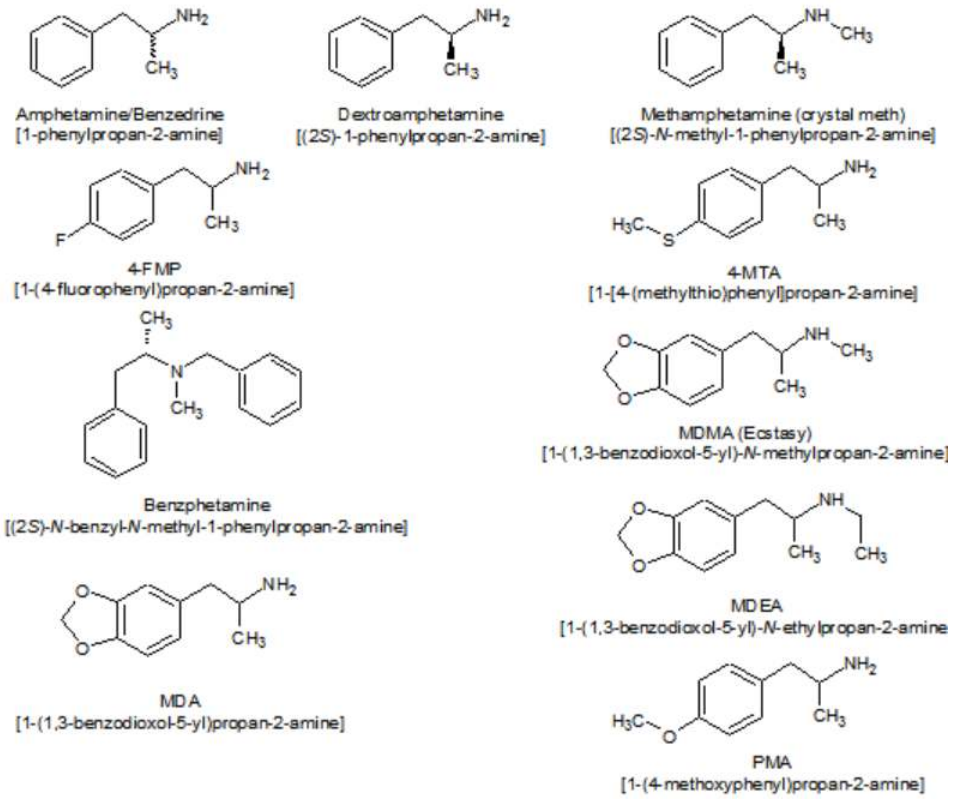


Figure **18.7.16** A chart comparing the chemical structures of different amphetamine derivatives. Source: Wikipedia

Cocaine, Caffeine, and Nicotine

Cocaine is a tropane alkaloid and stimulant drug obtained primarily from the leaves of two coca species, *Erythroxylum coca* and *Erythroxylum novogranatense*. It is most commonly used as a recreational drug and euphoriant. After extraction from coca leaves, cocaine may be snorted, heated until sublimated and then inhaled, or dissolved and injected into a vein. Mental effects may include an intense feeling of happiness, sexual arousal, loss of contact with reality, or agitation. Physical symptoms may include a fast heart rate, sweating, and dilated pupils. High doses can result in high blood pressure or body temperature. Effects begin within seconds to minutes of use and last between five and ninety minutes.

Cocaine is addictive due to its effect on the reward pathway in the brain. A single dose of cocaine induces tolerance to the drug's effects. After a short period of use, addiction is likely. Abstention from cocaine after chronic use results in drug withdrawal, with symptoms that may include depression, decreased ability to feel pleasure and subjective fatigue. Cocaine's use increases the overall risk of death and particularly the risk of trauma, and infectious diseases, such as blood infections and AIDS. It also increases risk of stroke, heart attack, cardiac arrhythmia, lung injury (when smoked), and sudden cardiac death. Illicitly-sold cocaine is commonly adulterated with local anesthetics, levamisole, cornstarch, quinine, or sugar, which can result in additional toxicity. The Global Burden of Disease study found that cocaine use caused the death of 7.3 people per 100,000 population world-wide.

Caffeine is a central nervous system (CNS) stimulant of the methylxanthine class. It is the world's most widely consumed psychoactive drug. Unlike many other psychoactive substances, it is legal and unregulated in nearly all parts of the world. There are several known mechanisms of action to explain the effects of caffeine. The most prominent is that it reversibly blocks the action of adenosine on its receptors and consequently prevents the onset of drowsiness induced by adenosine. Caffeine also stimulates certain portions of the autonomic nervous system.

Methyxanthines such as caffeine, theophylline and theobromine share in common several pharmacological actions of therapeutic interest. They stimulate the central nervous system, act on the kidney to produce diuresis, stimulate cardiac muscle, and relax smooth muscle, notably bronchial muscle. Because the various xanthines differ markedly in the intensity of their action on various structures, one particular xanthine has been used more than another for a particular therapeutic effect. Since theobromine displays low potency in these pharmacological actions, it has all but disappeared from the therapeutic scene.

Caffeine, theophyline, and theobromine occur naturally in plants widely distributed geographically. Caffeine is found in the coffee bean, tea leaves, guarana, and other plants. From the figure below, we can see that the methylxanthines have a structure which is very similar to adenine.

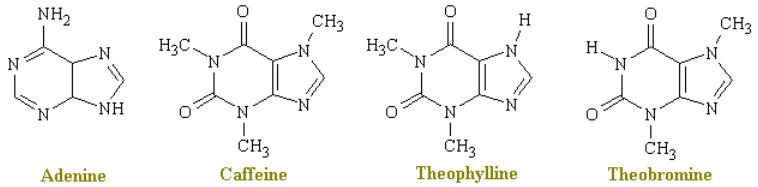


Figure **18.7.17** Adenine and other molecules with similar structures.

Table **18.7.1**: Caffeine Content in Various Beverages and Foods

Beverage/Food	Milligrams
Starbuck’s Grande Coffee (16 oz.)	380
Plain brewed coffee (8 oz.)	102–200
Espresso (1 oz.)	30–90
Plain, decaffeinated coffee (8 oz.)	3–12
Tea, brewed (8 oz.)	40–120
Green tea (8 oz.)	25–40
Coca-Cola Classic (12 oz.)	35
Dr. Pepper (12 oz.)	44
Jolt Cola (12 oz.)	72
Mountain Dew (12 oz.)	54
Mountain Dew, MDX (12 oz.)	71
Pepsi-Cola (12 oz.)	38
Red Bull (8.5 oz.)	80
Full Throttle (16 oz.)	144
Monster Energy (16 oz.)	160
Spike Shooter (8.4 oz.)	300

Source: MedicineNet.com. “Caffeine.” Accessed October 2, 2011. http://www.medicinenet.com/caffeine/article.htm.

Health Benefits of Caffeine

The most renowned effects of caffeine on the body are increased alertness and delay of fatigue and sleep. How does caffeine stimulate the brain? Watch "Video 15.6.1" to see a graphic account of a brain on caffeine. Caffeine is chemically similar to a chemical in our brains (adenosine). Caffeine interacts with adenosine’s specific protein receptor. It blocks the actions of the adenosine, and affects the levels of signaling molecules in the brain, leading to an increase in energy metabolism. At the molecular level, caffeine stimulates the brain, increasing alertness and causing a delay of fatigue and sleep. At high doses caffeine stimulates the motor cortex of the brain and interferes with the sleep-wake cycle, causing side effects such as shakiness, anxiety, and insomnia. People’s sensitivity to the adverse effects of caffeine varies and some people develop side effects at much lower doses. The many effects caffeine has on the brain do not diminish with habitual drinking of caffeinated beverages.



Video 15.6.1: *A Brain on Caffeine. Watch this graphic account of the brain on caffeine.*

Scientific studies suggest caffeine can improve endurance capacity by increasing energy available during exercise. The effect may only work in non-caffeine drinkers and it only takes 1-3 days for the body to become "caffeine-naive."

Nicotine is the active chemical constituent in tobacco, which is available in many forms, including cigarettes, cigars, chewing tobacco, and smoking cessation aids such as nicotine patches, nicotine gum, and electronic cigarettes. Nicotine is used widely throughout the world for its stimulating and relaxing effects. Nicotine exerts its effects through the agonism of nicotinic acetylcholine receptor, resulting in multiple downstream effects such as increase in activity of dopaminergic neurons in the midbrain reward system, as well as the decreased expression of monoamine oxidase in the brain. Nicotine is addictive and dependence forming.

Note: Hallucinogens and Dissociative Drugs from NIH-National Institute on Drug Abuse

The information below is directly from the link below

https://d14rmgtrwzf5a.cloudfront.net/sites/default/files/hallucinogensrrs4.pdf

Hallucinogens are a class of drugs that cause hallucinations—profound distortions in a person's perceptions of reality. Hallucinogens can be found in some plants and mushrooms (or their extracts) or can be man-made, and they are commonly divided into two broad categories: classic hallucinogens (such as LSD) and dissociative drugs (such as PCP). When under the influence of either type of drug, people often report rapid, intense emotional swings and seeing images, hearing sounds, and feeling sensations that seem real but are not. While the exact mechanisms by which hallucinogens and dissociative drugs cause their effects are not yet clearly understood, research suggests that they work at least partially by temporarily disrupting communication between neurotransmitter systems throughout the brain and spinal cord that regulate mood, sensory perception, sleep, hunger, body temperature, sexual behavior, and muscle control.



Figure 18.7.15 Psilocybin mushrooms, LSD, and Salvia divinorum are commonly used hallucinogenic and dissociative compounds.

Classic Hallucinogens

LSD (d-lysergic acid diethylamide)—also known as acid, blotter, doses, hits, microdots, sugar cubes, trips, tabs, or window panes—is one of the most potent moodand perception-altering hallucinogenic drugs. It is a clear or white, odorless, water-soluble material synthesized from lysergic acid, a compound derived from a rye fungus. LSD is initially produced in crystalline form, which can then be used to produce tablets known as "microdots" or thin squares of gelatin called "window panes." It can also be diluted with water or alcohol and sold in liquid form. The most common form, however, is LSD-soaked paper punched into small individual squares, known as "blotters."

Psilocybin (4-phosphoryloxyN, N-dimethyltryptamine)—also known as magic mushrooms, shrooms, boomers, or little smoke—is extracted from certain types of mushrooms found in tropical and subtropical regions of South America, Mexico, and the United States. In the past, psilocybin was ingested during religious ceremonies by indigenous cultures from Mexico and Central America. Psilocybin can either be dried or fresh and eaten raw, mixed with food, or brewed into a tea, and produces similar effects to LSD.

Peyote (Mescaline)— also known as buttons, cactus, and mesc— is a small, spineless cactus with mescaline as its main ingredient. It has been used by natives in northern Mexico and the southwestern United States as a part of religious ceremonies. The top, or "crown," of the peyote cactus has disc-shaped buttons that are cut out, dried, and usually chewed or soaked in water to produce an intoxicating liquid. Because the extract is so bitter, some users prepare a tea by boiling the plant for several hours. Mescaline can also be produced through chemical synthesis.

DMT (Dimethyltryptamine)—also known as Dimitri—is a powerful hallucinogenic chemical found naturally occurring in some Amazonian plant species (see "Ayahuasca") and also synthesized in the laboratory. Synthetic DMT usually takes the form of a white crystalline powder and is typically vaporized or smoked in a pipe. Ayahuasca—also known as hoasca, aya, and yagé—is a hallucinogenic brew made from one of several Amazonian plants containing DMT (the primary psychoactive ingredient) along with a vine containing a natural alkaloid that prevents the normal breakdown of DMT in the digestive tract. Ayahuasca tea has traditionally been used for healing and religious purposes in indigenous South American cultures, mainly in the Amazon region.

Dissociative Drugs

PCP (Phencyclidine)—also known as ozone, rocket fuel, love boat, hog, embalming fluid, or superweed—was originally developed in the 1950s as a general anesthetic for surgery. While it can be found in a variety of forms, including tablets or capsules, it is usually sold as a liquid or powder. PCP can be snorted, smoked, injected, or swallowed. It is sometimes smoked after being sprinkled on marijuana, tobacco, or parsley.

Ketamine—also known as K, Special K, or cat Valium—is a dissociative currently used as an anesthetic for humans as well as animals. Much of the ketamine sold on the street has been diverted from veterinary offices. Although it is manufactured as an injectable liquid, ketamine is generally evaporated to form a powder that is snorted or compressed into pills for illicit use. Because ketamine is odorless and tasteless and has amnesia-inducing properties, it is sometimes added to drinks to facilitate sexual assault. 2 NIDA Research Report Series Common Hallucinogens and Dissociative Drugs *In this report, the term "hallucinogen" will refer to the classic hallucinogenic drugs LSD and Psilocybin.

DXM (Dextromethorphan)— also known as robo—is a cough suppressant and expectorant ingredient in some over-the-counter (OTC) cold and cough medications that are often abused by adolescents and young adults. The most common sources of abused DXM are "extra-strength" cough syrup, which typically contains around 15 milligrams of DXM per teaspoon, and pills and gel capsules, which typically contain 15 milligrams of DXM per pill. OTC medications that contain DXM often also contain antihistamines and decongestants.

Salvia divinorum—also known as diviner's sage, Maria Pastora, Sally-D, or magic mint—is a psychoactive plant common to southern Mexico and Central and South America. Salvia is typically ingested by chewing fresh leaves or by drinking their extracted juices. The dried leaves of salvia can also be smoked or vaporized and inhaled.

Short-Term General Effects of Hallucinogens Sensory and Physical Effects

- Hallucinations, including seeing, hearing, touching, or smelling things in a distorted way or perceiving things that do not exist
- Intensified feelings and sensory experiences (brighter colors, sharper sounds)
- Mixed senses ("seeing" sounds or "hearing" colors)
- Changes in sense or perception of time (time goes by slowly) Physical Effects
- Increased energy and heart rate
- Nausea

Marijuana - NIH Medlineplus

Marijuana

The information below is directly from the link below

https://medlineplus.gov/marijuana.html

Marijuana is a green, brown, or gray mix of dried, crumbled parts from the marijuana plant. The plant contains chemicals which act on your brain and can change your mood or consciousness.

Marijuana can cause both short-term and long-term effects.

Short term:	Long term:
While you are high, you may experience • Altered senses, such as seeing brighter colors • Altered sense of time, such as minutes seeming like hours • Changes in mood • Problems with body movement • Trouble with thinking, problem-solving, and memory • Increased appetite	In the long term, marijuana can cause health problems, such as • Problems with brain development. People who started using marijuana as teenagers may have trouble with thinking, memory, and learning. • Coughing and breathing problems, if you smoke marijuana frequently • Problems with child development during and after pregnancy, if a woman smokes marijuana while pregnant.

Medical Marijuana

The marijuana plant has chemicals that can help with some health problems. More states are making it legal to use the plant as medicine for certain medical conditions. But there isn't enough research to show that the whole plant works to treat or cure these conditions. The U.S. Food and Drug Administration (FDA) has not approved the marijuana plant as a medicine. Marijuana is still illegal at the national level.

However, there have been scientific studies of cannabinoids, the chemicals in marijuana. The two main cannabinoids that are of medical interest are THC and CBD. The FDA has approved two drugs that contain THC. These drugs treat nausea caused by chemotherapy and increase appetite in patients who have severe weight loss from AIDS. There is also a liquid drug that contains CBD. It treats two forms of severe childhood epilepsy. Scientists are doing more research with marijuana and its ingredients to treat many diseases and conditions.

Summary

- Neurotransmitters are endogenous chemicals that enable neurotransmission. It is a type of chemical messenger which transmits signals across a chemical synapse, such as a neuromuscular junction, from one neuron (nerve cell) to another "target" neuron, muscle cell, or gland cell.
- Strong imbalances or disruptions to neurotransmitter systems have been associated with many diseases and mental disorders.
- Psychoactive drugs are substances that change the function of the brain and result in alterations of mood, thinking, perception, and/or behavior. They include prescription medications such as opioid painkillers, legal substances such as nicotine and alcohol, and illegal drugs such as LSD and heroin.
- Psychoactive drugs are divided into different classes according to their pharmacological effects. They include stimulants, depressants, anxiolytics, euphoriants, hallucinogens, and empathogens. Many psychoactive drugs have multiple effects so they may be placed in more than one class.
- Psychoactive drugs generally produce their effects by affecting brain chemistry. Generally, they act either as agonists, which enhance the activity of particular neurotransmitters; or as antagonists, which decrease the activity of particular neurotransmitters.
- Psychoactive drugs are used for various purposes, including medical, ritual, and recreational purposes.
- Misuse of psychoactive drugs may lead to addiction, which is compulsive use of a drug despite negative consequences such use may entail. Sustained use of an addictive drug may produce physical or psychological dependence on the drug. Rehabilitation typically involves psychotherapy and sometimes the temporary use of other psychoactive drugs.

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- NIH National Institute on Drug Abuse

- NIH-Medlineplus
- Psychology OPENSTAX
- Wikipedia
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CHAPTER OVERVIEW

19: Household Chemicals

Household chemicals are non-food chemicals that are commonly found and used in and around the average household. They are a type of consumer goods, designed particularly to assist cleaning, pest control and general hygiene purposes. Together with non-compostable household waste, the chemicals found in private household commodities pose a serious ecological problem. In addition to having slightly adverse up to seriously toxic effects when swallowed, chemical agents around may contain flammable or corrosive substances.

19.1: Cleaning with Soap
19.2: Synthetic Detergents
19.3: Laundry Auxiliaries- Softeners and Bleaches
19.4: All-Purpose and Special Purpose Cleaning Products
19.5: Solvents, Paints, and Waxes
19.6: Cosmetics - Personal Care Chemicals

Thumbnail: Clorox brand bleach. (CC BY-SA 2.0; Adina Firestone via Wikipedia).

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19.1: Cleaning with Soap

Learning Objectives

- Describe the mechanism by which soaps exert their cleansing action.
- List the benefits and problems with using soap.

Personal Cleanliness

Soap is a salt of a fatty acid[1] used in a variety of cleansing and lubricating products. In a domestic setting, soaps are surfactants usually used for washing, bathing, and other types of housekeeping. In industrial settings, soaps are used as thickeners, components of some lubricants, and precursors to catalysts.

When used for cleaning, soap solubilizes particles and grime, which can then be separated from the article being cleaned. In hand washing, as a surfactant, when lathered with a little water, soap kills microorganisms by disorganizing their membrane lipid bilayer and denaturing their proteins. It also emulsifies oils, enabling them to be carried away by running water.[2]

Industrially manufactured **bar soaps** became available in the late 18th century, as advertising campaigns in Europe and America promoted popular awareness of the relationship between cleanliness and health.[35] In modern times, the use of soap has become commonplace in industrialized nations due to a better understanding of the role of hygiene in reducing the population size of pathogenic microorganisms (Figure **19.1.1**).



Figure **19.1.1** Modern Soap Shop in Tubeingen , Germany. Source: Wikipedia

Soap Making: Fat Plus Lye Forms a Soap Plus Glycerol

The earliest recorded evidence of the production of soap-like materials dates back to around 2800 BC in ancient Babylon.[10] A formula for soap consisting of water, alkali, and cassia oil was written on a Babylonian clay tablet around 2200 BC.[11]

The Ebers papyrus (Egypt, 1550 BC) indicates the ancient Egyptians bathed regularly and combined animal and vegetable oils with alkaline salts to create a soap-like substance. Egyptian documents mention a similar substance was used in the preparation of wool for weaving.[12]In the reign of Nabonidus (556–539 BC), a recipe for soap consisted of *uhulu* [ashes], cypress [oil] and sesame [seed oil] "for washing the stones for the servant girls".[13]In ancient Israel, the ashes from barilla plants, such as species of Salsola, saltwort (*Seidlitzia rosmarinus*) and *Anabasis*, were used in soap production, known as potash



Figure 19.1.2 Advertising for medicated toilet soap. Source: Wikipedia

Until the Industrial Revolution, soapmaking was conducted on a small scale and the product was rough. In 1780, James Keir established a chemical works at Tipton, for the manufacture of alkali from the sulfates of potash and soda, to which he afterwards added a soap manufactory. William Gossage produced low-priced, good-quality soap from the 1850s. Robert Spear Hudson began manufacturing a soap powder in 1837, initially by grinding the soap with a mortar and pestle. American manufacturer Benjamin T. Babbitt introduced marketing innovations that included sale of bar soap and distribution of product samples. William Hesketh Lever and his brother, James, bought a small soap works in Warrington in 1886 and founded what is still one of the largest soap businesses, formerly called Lever Brothers and now called Unilever. These soap businesses were among the first to employ large-scale advertising campaigns. A poster advertising is shown in Figure 19.1.2.

Liquid soap was not invented until the nineteenth century; in 1865, William Shepphard patented a liquid version of soap.[40] In 1898, B.J. Johnson developed a soap derived from palm and olive oils; his company, the B.J. Johnson Soap Company, introduced "Palmolive" brand soap that same year.[41] This new brand of soap became popular rapidly, and to such a degree that B.J. Johnson Soap Company changed its name to Palmolive.[42]

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):

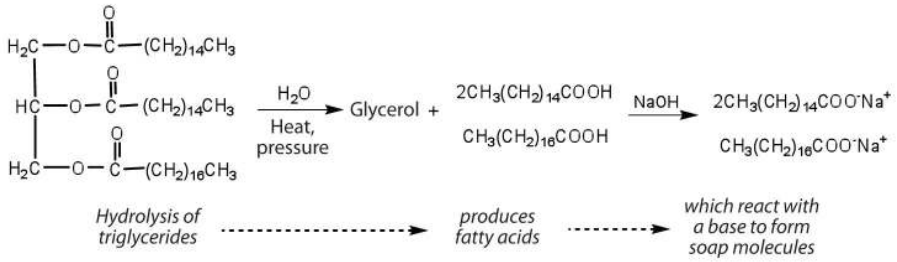


***Figure* 19.1.3** *Saponification.*

How Soap Works

The cleansing action of soap is determined by its polar and non-polar structures in conjunction with an application of solubility principles. The long hydrocarbon chain is of course non-polar and hydrophobic (repelled by water). The "salt" end of the soap molecule is ionic and hydrophilic (water soluble). Examples of soap and detergent molecules, are shown in Figure 19.1.4. The use of such compounds as cleaning agents is facilitated by their surfactant character, which lowers the surface tension of water, allowing it to penetrate and wet a variety of materials.

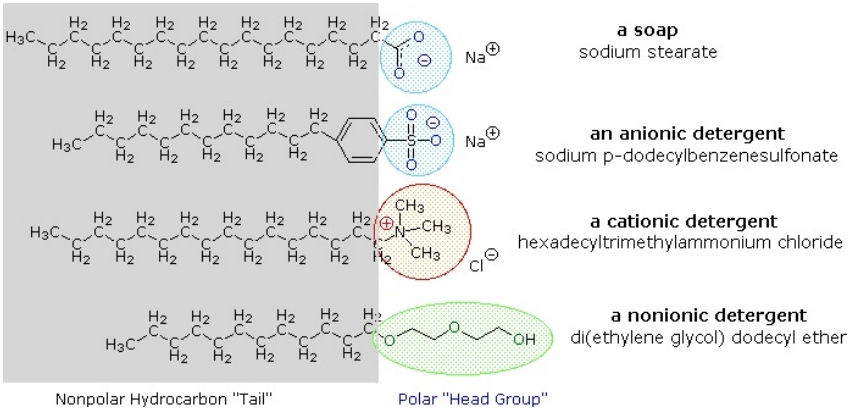


Figure 19.1.4 Soap and detergent molecules with different polar structures.

When soap is added to water, the ionic-salt end of the molecule is attracted to water and dissolved in it. The non-polar hydrocarbon end of the soap molecule is repelled by water. A drop or two of soap in water forms a monolayer (Figure 19.1.5) on the water surface as shown in the graphics on the left. The soap molecules "stand up" on the surface as the polar carboxyl salt end is attracted to the polar water. The non-polar hydrocarbon tails are repelled by the water, which makes them appear to stand up.

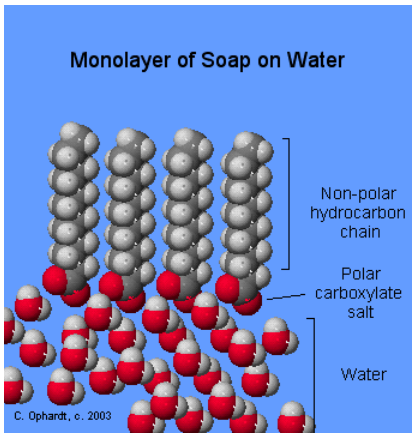


Figure 19.1.5 Monolayer of soap on water.

Soap vs. oil vs. water

Water alone is not able to penetrate grease or oil because they are of opposite polarity. When grease or oil (non-polar hydrocarbons) are mixed with a soap- water solution, the soap molecules work as a "bridge" between polar water molecules and non-polar oil molecules. Soap molecules have both properties of non-polar and polar at opposite ends of the molecule.

The oil is a pure hydrocarbon so it is non-polar. The non-polar hydrocarbon tail of the soap dissolves into the oil. That leaves the polar carboxylate ion of the soap molecules are sticking out of the oil droplets, the surface of each oil droplet is negatively charged. As a result, the oil droplets repel each other and remain suspended in solution (this is called an emulsion) to be washed away by a stream of water. The outside of the droplet is also coated with a layer of water molecules.

The graphic on Figure 19.1.6 although not strictly a representation of the above description is a micelle that works in much the same fashion. The oil would be a the center of the micelle.

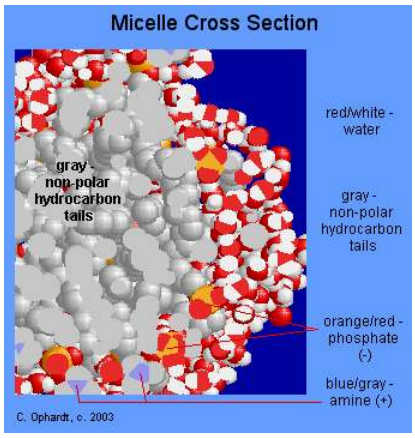


Figure **19.1.6** A micelle with oil at the center.

Disadvantages and Advantages of Soap

The importance of soap to human civilization is documented by history, but some problems associated with its use have been recognized. One of these is caused by the weak acidity (pKa ca. 4.9) of the fatty acids. Solutions of alkali metal soaps are slightly alkaline (pH 8 to 9) due to hydrolysis. If the pH of a soap solution is lowered by acidic contaminants, insoluble fatty acids precipitate and form a scum. A second problem is caused by the presence of calcium and magnesium salts in the water supply (hard water). These divalent cations cause aggregation of the micelles, which then deposit as a dirty scum.

In the reaction below, the sodium cation in soap is replaced by calcium to form calcium stearate. The white precipitate, also termed as soap scum could form deposits on surfaces and inside plumbing.

$$2\ C_{17}H_{35}COO^{-}Na^{+} + Ca^{2+} \rightarrow (C_{17}H_{35}COO)_2Ca + 2\ Na^{+}$$

Soap is still widely popular product as it is a low cost, readily available product used for personal hygiene and cleanliness. Use of soap doesn't lead to pollution. Soap is biodegradable as it can be broken down by microorganisms found in sewage.

Can Soap Really Kill the Coronavirus ?

***Video* 19.1.1** *Soap and coronavirus.*

Water Softeners

Water softening is the removal of calcium, magnesium, and certain other metal cations in hard water. The resulting soft water requires less soap for the same cleaning effort, as soap is not wasted bonding with calcium ions. Soft water also extends the lifetime of plumbing by reducing or eliminating scale build-up in pipes and fittings. Water softening is usually achieved using lime softening or ion-exchange resins (see Figure **19.1.7**) but is increasingly being accomplished using nanofiltration or reverse osmosis membranes.

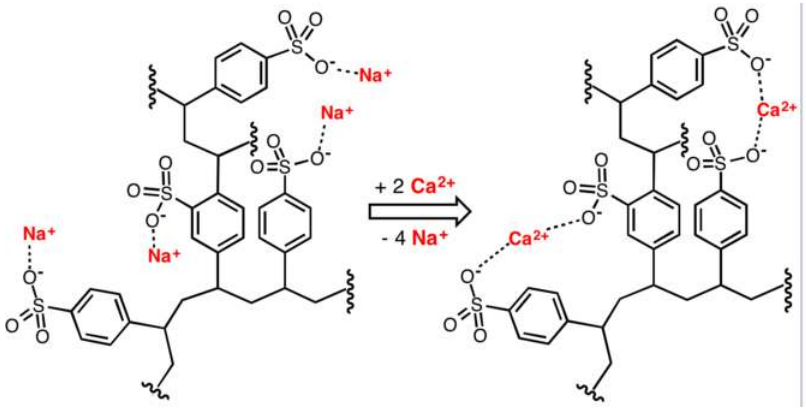


Figure **19.1.7** *Idealized image of water softening process involving replacement of calcium ions in water with sodium ions donated by a cation exchange resin*

How to soften hard water

Some wish to soften hard water to control its irritating, and in many cases damaging, effects. The diminished ability of soap to lather is not only annoying, but can also be potentially harmful economically. Businesses that depend on the foaming of soap, such as car washes and pet groomers, may wish to soften hard water to avoid excessive use of soap due to a decreased ability to lather. Likewise, it is often necessary to soften water that comes into contact with pipes to avoid the destructive and compromising build-up of deposits. Also, many people may find the calcifying effects that hard water has on faucets and other items unfavorable and choose to soften the water to prevent such mineral deposits from forming. Still others may dislike the sticky, dry feeling left by the precipitation of soap scum onto the skin. Whatever the reasons, there are many processes available to soften hard water.

Ion Exchange

One way to soften water is through a process called ion exchange. During ion exchange, the unwanted ions are "exchanged" for more acceptable ions. In many cases, it is desirable to replace the hard water ions, such as Ca^{2+} and Mg^{2+}, with more agreeable ions, like that of Na^{+}. To do this, the hard water is conducted through a zeolite or resin-containing column, which binds the unwanted ions to its surface and releases the more tolerable ions. In this process, the hard water ions become "fixed" ions because of their attachment to the resin material. These fixed ions displace the desirable ions (Na^{+}), now referred to as counterions, from the column, thus exchanging the ions in the water. This process is illustrated in Figure **19.1.8**.

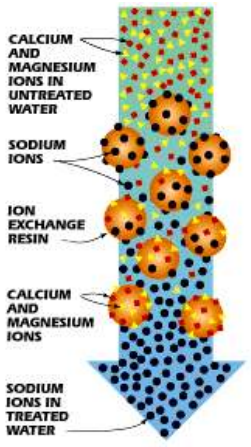


Figure **19.1.8** : Illustration of Ion Exchange.

Unfortunately, this process has the disadvantage of increasing the sodium content of drinking water, which could be potentially hazardous to the health of people with sodium-restricted diets.

Lime Softening

Another process is called lime softening. In this process, the compound calcium hydroxide, $Ca(OH)_2$, is added to the hard water. The calcium hydroxide, or "slaked lime," raises the pH of the water and causes the calcium and magnesium to precipitate into

$CaCO_3$ and $Mg(OH)_2$. These precipitates can then be easily filtered out due to their insolubility in water, shown below by the small solubility constant of magnesium hydroxide (the solubility product constant for calcium carbonate is shown above). After precipitation and removal of the offending ions, acid is added to bring the pH of the water back to normal.

$$Mg(OH)_{2\,(s)} \rightleftharpoons Mg^{2+}_{(aq)} + 2OH^{-}_{(aq)} \tag{4a}$$

Chelation

Chelating agents can also be used to soften hard water. Polydentate ligands, such as the popular hexadentate ligand EDTA, bind the undesirable ions in hard water. These ligands are especially helpful in binding the magnesium and calcium cations, which as already mentioned are highly prevalent in hard water solutions. The chelating agent forms a very stable ring complex with the metal cations, which prevents them from interacting with any other substances that may be introduced to the solution, such as soap. In this way, chelators are able to diminish the negative effects associated with hard water. A simplified equation representing the chelation of the metal calcium cation (Ca^{2+}) with the hexadentate ligand EDTA is shown below. The large value of the formation constant (K_f) reflects the tendency of the reaction to proceed to completion in the forward direction.

$$Ca^{2+} + EDTA^{4-} \longrightarrow [Ca(EDTA)]^{2-} \tag{5a}$$

Reverse Osmosis

The final process, reverse osmosis, uses high pressures to force the water through a semipermeable membrane. This membrane is generally intended to be impermeable to anything other than water. The membrane serves to filter out the larger ions and molecules responsible for the water's hardness, resulting in softened water. During this process, the water is forced from an area with a high concentration of solute in the form of dissolved metal ions and similar compounds, to an area that is very low in the concentration of these substances. In other words, the water moves from a state of hardness to a softer composition as the ions causing the water's hardness are prevented passage through the membrane. Reverse Osmosis does have a disadvantage of wasting wastewater compared to other water treatment methods. This process is shown in Figure 19.1.9 below. Note that this figure describes the desalination of salt water. However, the process for softening hard water is the same.

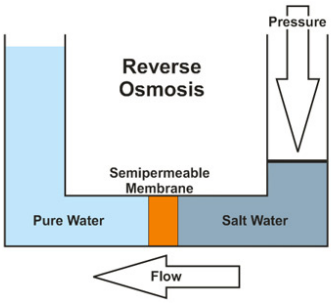


Figure 19.1.9: Depiction of Reverse Osmosis.

Making Hard Water Soft



***Video* 19.1.2** *How to soften hard water.*

Summary

- Soap, as a cleaning agent, solubilizes particles and grime, which can then be easily removed from the article being cleaned.
- In hand washing, soap is an excellent surfactant, that destroys microorganisms by damaging their cellular membranes and denaturing their proteins.
- Soap is an inexpensive, readily available cleaning agent that is also's effectivenes is diminished biodegradable. However, it's effectiveness is diminished when used with hard water.

Contributors

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19.2: Synthetic Detergents

Learning Objectives

- Describe different types of detergents.
- List the key components of detergents and their functions.

A **detergent** is a surfactant or a mixture of surfactants with cleansing properties in dilute solutions (File:Diskflaskor.JPG(Figure **19.2.1**)) . These substances are usually alkylbenzene sulfonates, a family of compounds that are similar to soap but are more soluble in hard water, because the polar sulfonate (of detergents) is less likely than the polar carboxylate (of soap) to bind to calcium and other ions found in hard water.

In domestic contexts, the term *detergent* by itself refers specifically to *laundry detergent* or *dish detergent*, as opposed to *hand soap* or other types of cleaning agents. Detergents are commonly available as powders or concentrated solutions. Detergents, like soaps, work because they are amphiphilic: partly hydrophilic (polar) and partly hydrophobic (non-polar). Their dual nature facilitates the mixture of hydrophobic compounds (like oil and grease) with water. Because air is not hydrophilic, detergents are also foaming agents to varying degrees.



Figure **19.2.1** Detergents. Source: Wikipedia

Detergents are classified into three broad groupings, depending on the electrical charge of the surfactants.

Anionic detergents

Typical anionic detergents are alkylbenzenesulfonates (ABS). The alkylbenzene portion of these anions is lipophilic and the sulfonate is hydrophilic. An estimated 6 billion kilograms of anionic detergents are produced annually for domestic markets. Two different varieties have been popularized, those with branched alkyl groups and those with linear alkyl groups (see Figure **19.2.2**).

Branched Alkylbenzenesulfonates: Nonbiodegradable

Branched alkylbenzene sulfonates (BAS) were first introduced in the early 1930s and saw significant growth from the late 1940s onwards,[3] in early literature these synthetic detergents are often abbreviated as syndets.

Compared to traditional soaps BAS offered superior tolerance to hard water and better foaming.[5] However, the highly branched tail made it difficult to biodegrade.[6] BAS was widely blamed for the formation of large expanses of stable foam in areas of wastewater discharge such as lakes, rivers and coastal areas (sea foams), as well as foaming problems encountered in sewage treatment[7] and contamination of drinking water.[8] As such BAS was phased out of most detergent products during the 1960s, being replaced with linear alkylbenzene sulfonates (LAS). It is still important in certain agrochemical and industrial applications, where rapid biodegradability is of reduced importance.

Linear Alkylbenzensulfonates: Biodegradable

Linear alkylbenzene sulfonates (LAS) are prepared industrially by the sulfonation of linear alkylbenzenes (LABs), which can themselves be prepared in several ways.[2] The term "linear" refers to the starting alkenes rather than the final product. The compound biodegrades far more quickly than BAS, making it the safer choice over time. It is biodegraded rapidly under aerobic

conditions with a half-life of approximately 1–3 weeks. Under anaerobic conditions it degrades very slowly or not at all, causing it to exist in high concentrations in sewage sludge, but this is not thought to be a cause for concern as it will rapidly degrade once returned to an oxygenated environment.

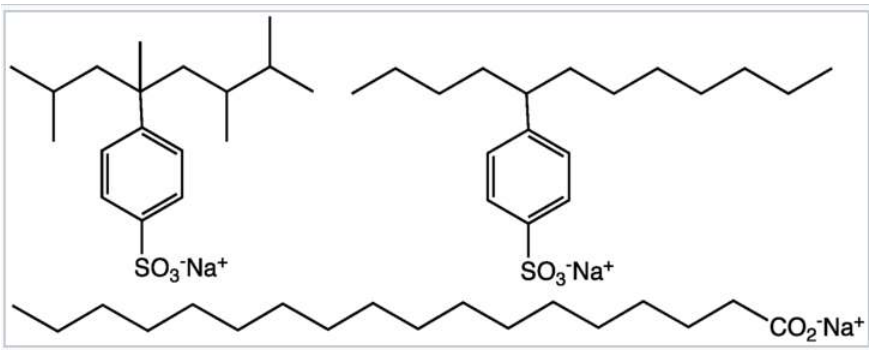


Figure **19.2.2** Three kinds of anionic detergetns: a branched sodium dodecylbenzenesulfonate, linear sodium dodecylbenzenesulfonate, and a soap. *Source: Wikipedia*

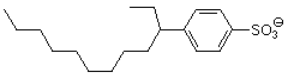
Cationic detergents

Cationic detergents are similar to the anionic ones, with a hydrophilic component, but, instead of the anionic sulfonate group, the cationic surfactants have quaternary ammonium as the polar end. The ammonium sulfate center is positively charged.[3]

Non-ionic and zwitter ionic detergents

Non-ionic detergents are characterized by their uncharged, hydrophilic headgroups. Typical non-ionic detergents are based on polyoxyethylene or a glycoside. Common examples of the former include Tween, Triton, and the Brij series. These materials are also known as ethoxylates or PEGylates and their metabolites, nonylphenol. Glycosides have a sugar as their uncharged hydrophilic headgroup. Examples include octyl thioglucoside and maltosides. HEGA and MEGA series detergents are similar, possessing a sugar alcohol as headgroup.

Zwitterionic detergents possess a net zero charge arising from the presence of equal numbers of +1 and −1 charged chemical groups. Examples include CHAPS. CHAPS is an abbreviation for 3-[(3-**ch**olamidopropyl)dimethyl**a**mmonio]-1-**p**ropane**s**ulfonate.



synthetic detergent

Laundry Detergent

Laundry detergent, or **washing powder**, is a type of detergent (cleaning agent) used for cleaning laundry. Laundry detergent is manufactured in powder and liquid form.

While powdered and liquid detergents hold roughly equal share of the worldwide laundry detergent market in terms of value, powdered detergents are sold twice as much compared to liquids in terms of volume.[1]



Figure **19.2.3** The two forms of laundry detergent: powder and liquid. *Source Wikipedia*

Components

Laundry detergents may contain builders (50% by weight, approximately), surfactants (15%), bleach (7%), enzymes (2%), soil antideposition agents, foam regulators, corrosion inhibitors, optical brighteners, dye transfer inhibitors, fragrances, dyes, fillers and formulation aids.[4]

Builders

Builders (also called chelating or sequestering agents) are water softeners. Hard water contains calcium, magnesium, and metallic cations (primarily, iron, copper, and manganese). These cations react with surfactant anions to form insoluble compounds (metallic or lime soaps) which precipitate onto fabrics and washing machines and which are difficult to remove. Builders remove the hard water ions through precipitation, chelation, or ion exchange. In addition, they help remove soil by dispersion. In most European regions, the water is hard. In North America, Brazil, and Japan, the water is comparatively soft.

The earliest builders were sodium carbonate (washing soda) and sodium silicate (waterglass). Since the 1930s, phosphates (sodium phosphates) and polyphosphates (sodium hexametaphosphate) were introduced, continuing with the introduction of phosphonates (HEDP, ATMP, EDTMP). These agents are now known to have serious environmental consequences leading to a drive towards more environmentally benign phosphorus-free agents, such as polycarboxylates (EDTA, NTA), citrates (trisodium citrate), silicates (sodium silicate), gluconic acid and polyacrylic acid; or ion exchange agents like zeolites.

Surfactants

Surfactants are responsible for most of the cleaning performance in laundry detergent. They provide this by absorption and emulsification of soil into the water and also by reducing the water's surface tension to improve wetting.

Laundry detergents contain mostly anionic and non-ionic surfactants. Cationic surfactants are normally incompatible with anionic detergents and have poor cleaning efficiency; they are employed only for certain special effects, as fabric softeners, antistatic agents, and biocides. Zwitterionic surfactants are rarely employed in laundry detergents mainly for cost reasons. Most detergents use a combination of various surfactants to balance their performance.

Bleaches

Despite the name, modern laundry bleaches do not include household bleach (sodium hypochlorite). Laundry bleaches are typically stable adducts of hydrogen peroxide, such as sodium perborate and sodium percarbonate, these are inactive as solids but will release hydrogen peroxide upon exposure to water. The main targets of bleaches are oxidisible organic stains, which are usually of vegetable origin (e.g. chlorophyll, anthocyanin dyes, tannins, humic acids, and carotenoid pigments). Hydrogen peroxide is insufficiently active as a bleach at temperature below 60°C, which traditionally made hot washes the norm. The development of bleach activators in the 1970s and 80s allowed for cooler washing temperatures to be effective. These compounds, such as tetraacetylethylenediamine (TAED), react with hydrogen peroxide to produce peracetic acid, which is an even more effective bleach, particularly at lower temperatures.

Enzymes

The use of enzymes for laundry was introduced in 1913 by Otto Rohm. The first preparation was a pancreatic extract obtained from slaughtered animals, which was unstable against alkali and bleach. Only in the latter part of the century with the availability of thermally robust bacterial enzymes did this technology become mainstream.

Enzymes are required to degrade stubborn stains composed of proteins (milk, cocoa, blood, egg yolk, grass), fats (chocolate, fats, oils), starch (flour and potato stains), and cellulose (damaged cotton fibrils, vegetable and fruit stains). Each type of stain requires a different type of enzyme: proteases (savinase) for proteins, lipases for greases, α-amylases for carbohydrates, and cellulases for cellulose.

Other ingredients

Many other ingredients are added depending on the expected circumstances of use. Such additives modify the foaming properties of the product by either stabilizing or counteracting foam. Other ingredients increase or decrease the viscosity of the solution, or solubilize other ingredients. Corrosion inhibitors counteract damage to washing equipment. "Dye transfer inhibitors" prevent dyes from one article from colouring other items. "Antiredeposition agents" such as carboxymethyl cellulose are used to prevent fine soil particles from reattaching to the product being cleaned.

A number of ingredients affect aesthetic properties of the item to be cleaned or the detergent itself before or during use. These agents include optical brighteners, fabric softeners, and colourants. A variety of perfumes are also components of modern detergents, provided that they are compatible with the other components and do not affect the colour of the cleaned item. The perfumes are typically a mixture of many compounds, common classes include terpene alcohols (citronellol, geraniol, linalool, nerol) and their esters (linalyl acetate), aromatic aldehydes (helional, hexyl cinnamaldehyde, lilial) and synthetic musks (galaxolide).

Dishwashing Detergents

Dishwashing liquid (or **washing-up liquid** in British English), also known as **dishwashing soap**, **dish detergent**, and **dish soap** is a detergent used to assist in dishwashing. It is usually a highly-foaming mixture of surfactants with low skin irritation, and is primarily used for hand washing of glasses, plates, cutlery, and cooking utensils in a sink or bowl. In addition to its primary use, dishwashing liquid also has various informal applications, such as for creating bubbles, clothes washing and cleaning oil-affected birds.

Hand dishwashing is generally performed in the absence of a dishwashing machine, when large "hard-to-clean" items are present, or through preference. Some dishwashing liquids can harm household silver, fine glassware, anything with gold leaf, disposable plastics, and any objects made of brass, bronze, cast iron, pewter, tin, or wood, especially when combined with hot water and the action of a dishwasher. When dishwashing liquid is used on such objects it is intended that they be washed by hand.

Hand dishwashing detergents utilize surfactants to play the primary role in cleaning. The reduced surface tension of dishwashing water, and increasing solubility of modern surfactant mixtures, allows the water to run off the dishes in a dish rack very quickly. However, most people also rinse the dishes with pure water to make sure to get rid of any soap residue that could affect the taste of the food.

Dishwashing liquid can be a skin irritant and cause hand eczema. Those with "sensitive skin" are advised amongst other things to persuade someone else to do the washing up.

Dishwasher detergent is a detergent made for washing dishes in a dishwasher. Dishwasher detergent is different from dishwashing liquid made to wash dishes by hand.

When using a dishwasher, the user must select a special detergent for its use. All detergents are designed for use after the user scrapes leftover food from the dishes before washing. To function, the user places dishes in the dishwasher in such fashion that the surface of all dishes is open to the flow of water.

Most dishwasher detergents are incompatible for use with silver, brass, cast iron, bronze, aluminum, pewter, and goldleaf. They can also harm disposable plastic, anything wood, knives with hollow handles, and fine glassware.

Dishwashing detergents for dishwashers are manufactured and marketed variously as cartridges, gel, liquids, pacs, powder, and tablets. Any dishwashing liquid may contain bleach, enzymes, or rinsing aids. Some dishwashing detergents may be homemade, using ingredients such as borax, essential oil, eucalyptus oil and grated bar soap, among others.

Dishwashing detergents can be formulated to work under different circumstances. In some cases suitably formulated they can be used with cold water or sea water, although they will not generally work as well as those intended for, and used with, hot water.

Different kinds of dishwashing detergent contain different combinations of ingredients. Common ingredients include:

- **Phosphates**: Bind calcium and magnesium ions to prevent 'hard-water' type limescale deposits. They can cause ecological damage, and have been partially banned or phased out.
- **Oxygen-based bleaching agents** (older-style powders and liquids contain chlorine-based bleaching agents): Break up and bleach organic deposits.
- **Non-ionic surfactants**: Lower the surface tension of the water, emulsifies oil, lipid and fat food deposits, prevents droplet spotting on drying.
- **Alkaline salts**: These are a primary component in older and original-style dishwasher detergent powders[*citation needed*]. Highly alkaline salts attack and dissolve grease, but are extremely corrosive (fatal) if swallowed. Salts used may include metasilicates, alkali metal hydroxides, sodium carbonate etc.
- **Enzymes**: Break up protein-based food deposits, and possibly oil, lipid and fat deposits. The enzymes used are similar to the ones used in laundry.
- **Anti-corrosion agent(s)**: Often sodium silicate, this prevents corrosion of dishwasher components.[*citation needed*]

Dishwashing detergent may also contain:[*citation needed*]

- Anti-foaming agents:[*citation needed*] Foam interferes with the washing action. Foam may affect operation of the machine's water-level sensors and will leak past the door seals.
- Additives to slow down the removal of glaze & patterns from glazed ceramics
- Perfumes
- Anti-caking agents (in granular detergent)
- Starches (in tablet based detergents)
- Gelling agents (in liquid/gel based detergents)
- Sand (inexpensive powdered detergents)

Dishwasher detergents are generally strongly alkaline (basic).

Inexpensive powders may contain sand. Such detergents may harm the dishes and the dishwasher. Powdered detergents are more likely to cause fading on china patterns.

Besides older style detergents for dishwashers, biodegradable detergents also exist for dishwashers. These detergents may be more environmentally friendly than conventional detergents.

Informal Uses

Reader's Digest notes its use as an ant killer, weed killer, to help spread water-borne fertilizer, and to wash human hair. *Good Housekeeping* says it can be used mixed with vinegar to attract and drown fruit flies. Dishwashing detergent has been used to clean mirrors as well as windows.

- Pling, an open source general purpose cleaner for glazed, plastic, chrome and inox bathroom and kitchen surfaces, published by Twibright Labs, uses dishwashing liquid as one of active ingredients.
- Dishwashing liquid can be mixed with water and additional ingredients such as glycerin and sugar to produce a bubble-blowing solution.
- Dishwashing liquid may be used for cleaning delicate clothing fabrics such as hosiery and lingerie.
- Dishwashing liquid is frequently recommended in a dilute solution to make decals and vinyl graphics easier to position when applying.

- In industry, dishwashing liquid is also used to inspect pressurized equipment for leaks, such as propane fittings. It is used to inspect pneumatic tires for flats, as well as for quality assurance during the installation process, and as a mounting bead lubricant.
- Dishwashing liquid has uses as an ingredient in making homemade garden pest deterrents. Oregon State University's Cooperative Extension Service notes the use of dishwashing liquid to get rid of spidermites. Dish soap has also been used to deter aphids. In some instances, the dish soap may be toxic to plant leaves and cause them to "burn". Use of soap or dish detergent to help spread pesticide on plants is noted by University of Georgia extension service, but not recommended.
- A solution of dishwashing liquid and water may be used to remove coffee, tea, olive oil, soda and fruit juice stains from fabrics. One dishwashing liquid brand has been used to remove stains from white or lightly-colored cloth napkins.
- Dishwashing liquid has been used to treat birds affected by oil spills. After the Exxon Valdez oil spill in 1989, the International Bird Rescue Research Center received hundreds of cases of dishwashing liquid that were used for this purpose. More dishwashing liquid was donated during the Deepwater Horizon oil spill to the International Bird Rescue Research Center and the Marine Mammal Center.



Figure **19.2.4** *An oiled Gannet being washed. Source Wikipedia*

Environmental concerns

Phosphates in detergent became an environmental concern in the 1950s and the subject of bans in later years.[8] Phosphates make laundry cleaner but also cause eutrophication, particularly with poor wastewater treatment.[9]

A recent academic study of fragranced laundry products found "more than 25 VOCs emitted from dryer vents, with the highest concentrations of acetaldehyde, acetone, and ethanol. Seven of these VOCs are classified as hazardous air pollutants (HAPs) and two as carcinogenic HAPs (acetaldehyde and benzene)".[10]

The EEC Directive 73/404/EEC stipulates an average biodegradability of at least 90% for all types of surfactants used in detergents. The phosphate content of detergents is regulated in many countries, e.g., Austria, Germany, Italy, The Netherlands, Norway, Sweden, Switzerland, United States, Canada, and Japan.

Summary

- Detergents are classified into anionic, cationic, and non-ionic detergents and zwitterionic detergents based on the electrical charge of the surfactants.
- Variations in detergent formulations are based on its end-use (i.e. laundry or for kitchenware).
- Phosphates make laundry cleaner but also cause eutrophication, particularly with poor wastewater treatment.[9]

ntributors and Attributions

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19.3: Laundry Auxiliaries- Softeners and Bleaches

Learning Objectives

- Describe a fabric softener and its use.
- Describe bleaches and their use.

A **fabric softener** (or **conditioner**) is a conditioner that is typically applied to laundry during the rinse cycle in a washing machine. In contrast to laundry detergents, fabric softeners may be regarded as a kind of after-treatment laundry aid.[1]

Machine washing puts great mechanical stress on textiles, particularly natural fibers such as cotton and wool. The fibers at the fabric surface are squashed and frayed, and this condition hardens while drying the laundry in air, giving the laundry a harsh feel. Adding a liquid fabric softener to the final rinse (rinse-cycle softener) results in laundry that feels softer.[2][1]

Fabric softeners coat the surface of a fabric with chemical compounds that are electrically charged, causing threads to "stand up" from the surface and thereby imparting a softer and fluffier texture. Cationic softeners, like those shown in Figure **19.3.1**. bind by electrostatic attraction to the negatively charged groups on the surface of the fibers and neutralize their charge. The long aliphatic chains then line up towards the outside of the fiber, imparting lubricity.

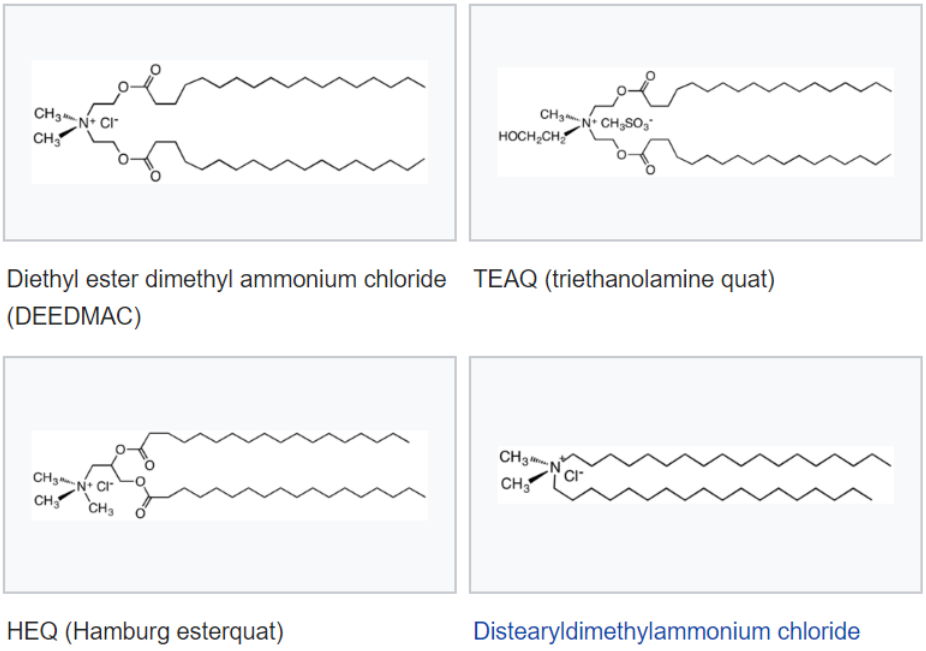


Figure **19.3.1** *Cationic surfactants in fabric softeners. Source: Wikipedia*

Fabric softeners impart antistatic properties to fabrics, and thus prevent the build-up of electrostatic charges on synthetic fibers, which in turn eliminates fabric cling during handling and wearing, crackling noises, and dust attraction. Also, fabric softeners make fabrics easier to iron and help reduce wrinkles in garments. In addition, they reduce drying times so that energy is saved when softened laundry is tumble-dried. Last but not least, they can also impart a pleasant fragrance to the laundry.[1]

Risks

As with soaps and detergents, fabric softeners may cause irritant dermatitis.[5] Manufacturers produce some fabric softeners without dyes and perfumes to reduce the risk of skin irritation. Fabric softener overuse may make clothes more flammable, due to the fat-based nature of most softeners. Some deaths have been attributed to this phenomenon,[6] and fabric softener makers recommend not using them on clothes labeled as flame-resistant.[*citation needed*]

Laundry Bleaches: Whiter Whites

Bleach is the generic name for any chemical product which is used industrially and domestically to clean, and to remove stains. It often refers, specifically, to a dilute solution of sodium hypochlorite, also called "liquid bleach".

Many bleaches have broad spectrum bactericidal properties, making them useful for disinfecting and sterilizing and are used in swimming pool sanitation to control bacteria, viruses, and algae and in many places where sterile conditions are required. They are also used in many industrial processes, notably in the bleaching of wood pulp. Bleaches also have other minor uses like removing mildew, killing weeds, and increasing the longevity of cut flowers.[1]

Bleaches work by reacting with many colored organic compounds, such as natural pigments, and turning them into colorless ones. While most bleaches are oxidizing agents (chemicals that can remove electrons from other molecules), some are reducing agents (that donate electrons).

Chlorine, a powerful oxidizer, is the active agent in many household bleaches. Since pure chlorine is a toxic corrosive gas, these products usually contain hypochlorite which releases chlorine when needed. "Bleaching powder" usually means a formulation containing calcium hypochlorite.

Oxidizing bleaching agents that do not contain chlorine are usually based on peroxides such as hydrogen peroxide, sodium percarbonate, and sodium perborate. These bleaches are called 'non-chlorine bleach,' 'oxygen bleach' or 'color-safe bleach.'[2]

Reducing bleaches have niche uses, such as sulfur dioxide used to bleach wool, either as gas or from solutions of sodium dithionite; [3] and sodium borohydride.

Bleaches generally react with many other organic substances besides the intended colored pigments, so they can weaken or damage natural materials like fibers, cloth, and leather, and intentionally applied dyes such as the indigo of denim. For the same reason, ingestion of the products, breathing of the fumes, or contact with skin or eyes can cause health damage.

Summary

- A fabric softener is an after-treatment laundry aid that imparts a softer and fluffier texture.
- Bleach is the generic name for any chemical product that is used industrially and domestically for cleaning and stain removal.

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19.4: All-Purpose and Special Purpose Cleaning Products

Learning Objective

- List various cleaners and their modes of action.

Cleaning agents or **hard-surface cleaners** are substances (usually liquids, powders, sprays, or granules) used to remove dirt, including dust, stains, bad smells, and clutter on surfaces. Purposes of cleaning agents include health, beauty, removing offensive odor, and avoiding the spread of dirt and contaminants to oneself and others. Some cleaning agents can kill bacteria (e.g. door handle bacteria, as well as bacteria on worktops and other metallic surfaces) and clean at the same time. Others, called degreasers, contain organic solvents to help dissolve oils and fats.

Acidic cleaning agents are mainly used for removal of inorganic deposits like scaling. The active ingredients are normally strong mineral acids and chelants. Often, surfactants and corrosion inhibitors are added to the acid.

Hydrochloric acid is a common mineral acid typically used for concrete. Vinegar can also be used to clean hard surfaces and remove calcium deposits that also helps to maintain our environment bacteria free. Sulphuric acid is used in acidic drain cleaners to unblock clogged pipes by dissolving greases, proteins, and even carbohydrate-containing substances such as toilet tissue.

Alkaline cleaning agents contain strong bases like sodium hydroxide or potassium hydroxide. Bleach (pH 12) and ammonia (pH 11) are common alkaline cleaning agents. Often, dispersants, to prevent redeposition of dissolved dirt, and chelants, to attack rust, are added to the alkaline agent.

Alkaline cleaners can dissolve fats (including grease), oils, and protein-based substances.

Neutral washing agents are pH-neutral and based on non-ionic surfactants that disperse different types.

Scouring agents are mixtures of the usual cleaning chemicals (surfactants, water softeners) as well as abrasive powders. The abrasive powder must be of a uniform particle size.

Particles are usually smaller than 0.05 mm. Pumice, calcium carbonate (limestone, chalk, dolomite), kaolinite, quartz, soapstone or talc are often used as abrasives, i.e. polishing agents.

Special bleaching powders contain compounds that release sodium hypochlorite, the classical household bleaching agent. These precursor agents include trichloroisocyanuric acid and mixtures of sodium hypochlorite ("chlorinated orthophosphate").

Examples of notable products include: Ajax, Bar Keepers Friend, Bon Ami, Comet, Vim, Zud, and others.

All-Purpose Cleaners

All-purpose cleansers (Figure **19.4.1**) contain mixtures of anionic and nonionic surfactants, polymeric phosphates or other sequestering agents, solvents, hydrotropic substances, polymeric compounds, corrosion inhibitors, skin-protective agents, and sometimes perfumes and colorants.[7] Aversive agents, such as denatonium, are occasionally added to cleaning products to discourage animals and small children from consuming them.



Figure **19.4.1** *Fabuloso multipurpose cleaner and generic surface cleaners. Source: Wikipedia*

Some cleaners contain water-soluble organic solvents like glycol ethers and fatty alcohols, which ease the removal of oil, fat and paint. Disinfectant additives include quaternary ammonium compounds, phenol derivatives, terpene alcohols (pine oil), aldehydes, and aldehyde-amine condensation products.

All-purpose cleaners are usually concentrated solutions of surfactants and water softeners, which enhance the behavior of surfactant in hard water. Typical surfactants are alkylbenzenesulfonates, an anionic detergent, and modified fatty alcohols. A typical water softener is sodium triphosphate.

All-purpose cleansers are effective with most common kinds of dirt. Their dilute solutions are neutral or weakly alkaline, and are safe for use on most surfaces.

Special Purpose Cleaners

Traditional **oven cleaners** contain sodium hydroxide (lye), solvents, and other ingredients,[3][4][5] and work best when used in a slightly-warm (not hot) oven. If used in a self-cleaning oven, the lye will cause permanent damage to the oven.

New-style oven cleaners are based on ingredients other than lye. These products must be used in a cold oven. Most new-style oven cleaners can be used in self-cleaning ovens.

Oven cleaners are some of the most toxic household cleaning products available on the market.[6] Correct use of an oven cleaner may be reasonably safe, but incorrect use can have harmful effects.

One popular oven cleaner brand in the US is "Easy-Off", sold by Reckitt Benckiser. Popular choices in the UK include "Zep Oven Brite" and "Mr Muscle Oven Cleaner".

Toilet bowl cleaning agents often are aimed at removal of calcium carbonate deposits, which are attacked by acids. Powdered cleaners contain acids that come in the form of solid salts, such as sodium hydrogen sulfate. Liquid toilet bowl cleaners contain other acids, typically dilute hydrochloric, phosphoric, or formic acids. These convert the calcium carbonate into salts that are soluble in water or are easily rinsed away.

Chemical drain cleaners can be in solid or liquid form that are readily available through hardware stores, though some (primarily acidic ones) are intended for use by licensed plumbers.[1]Alkaline drain cleaners are available in either solid or liquid state while the acidic ones are usually in liquid form.



Figure **19.4.2** *Bottles of alkaline drain cleaners containing sodium hydroxide can dissolve greases and hair. Source: Wikipedia*

Metal cleaners are used for cleaning stainless steel sinks, faucets, metal trim, silverware, etc. These products contain abrasives (e.g., siliceous chalk, diatomaceous earth, alumina) with a particle size < 20 μm. Fatty alcohol or alkylphenol polyglycol ethers with 7-12 ethylene oxide (EO) units are used as surfactants.[7]

For ferrous metals, the cleaners contain chelating agents, abrasives, and surfactants. These agents include citric and phosphoric acids, which are nonaggressive. Surfactants are usually modified fatty alcohols. Silver cleaning is a specialty since silver is noble but tends to tarnish via formation of black silver sulfide, which is removable via silver-specific complexants such as thiourea.

Stainless steel, nickel, and chromium cleaners contain lactic, citric, or phosphoric acid. A solvent (mineral spirits) may be added.

Nonferrous metal cleaners contain ammonia, ammonium soaps (ammonium oleate, stearate) and chelating agents (ammonium citrate, oxalate).

For special type of precious metals especially those used for luxury watches and high-end jewelry, special type of cleaning agents are usually used to clean and protect them from the elements.

Glass cleaners. Light duty hard surface cleaners are not intended to handle heavy dirt and grease. Because these products are expected to clean without rinsing and result in a streak-free shine, they contain no salts. Typical window cleaning items consist of alcohols, either ethanol or isopropanol, and surfactants for dissolving grease. Other components include small amounts of ammonia as well as dyes and perfumes.

These are composed of organic,water-miscible solvent such as isopropyl alcohol and an alkaline detergent. Some glass cleaners also contain a fine, mild abrasive. Most glass cleaners are available as sprays or liquid. They are sprayed directly onto windows, mirrors and other glass surfaces or applied on with a soft cloth and rubbed off using a soft ,lint-free duster. A glass cloth ideal for the purpose and soft water to which some methylated spirit or vinegar is added which is an inexpensive glass cleaner.

Silverware can be freed of silver sulfide tarnish with thiourea, and either hydrochloric or sulfuric acid.

Building facade cleaners. For acid-resistant building facades, such as brick, acids are typically used. These include mixtures of phosphoric and hydrofluoric acids as well as surfactants. For acid-sensitive facades such as concrete, strongly alkaline cleaners are used such as sodium hydroxide and thickeners. Both types of cleaners require a rinsing and often special care since the solutions are aggressive toward skin.

Drain Cleaners: Danger and Usage Considerations

Danger arises from chemical drain cleaners' potential to injure eyes, lungs, and skin; and damage to clothing and household materials such as wood, paint, aluminum, and fiberglass. Chemical drain cleaners should be used only according to the manufacturer's instructions, as other use may cause injury.[7] Strongly corrosive and acid drain cleaners are among the most hazardous household products available to the public. Chemical drain cleaners can cause strong reactions—sometimes explosively—with other chemicals that may have been used previously, which can result in serious injury to anyone in the vicinity.[8] In one such incident, a five-year-old boy was left scarred for life after an acidic drain cleaner leaked through his bedroom ceiling as he slept.[9]

Strong Alkali Drain cleaners are equally capable of causing rapid, severe burns, as seen in the cases of a woman doused with concentrated lye in an attack. A small girl was also permanently disfigured by a common lye drain opener.,[10][11] Moreover, because the acidic or basic drain cleaners themselves are washed down the drain, this contributes to pollution in the water supply. The heat generation can also soften plastic PVC pipes, and the pressure buildup by gas generation can cause older pipes to burst. Commercial chemical based solutions can cause corrosion and other damage to your pipes and sewer lines[12]

Oftentimes, individuals may unknowingly mix two different types of drain cleaners, which can even lead to deadly results. For example, consider the mixing of an acidic and basic drain cleaner:

Sulfuric Acid + Sodium Hydroxide → sodium sulfate (a salt) + water

$H_2SO_4 + 2\ NaOH \rightarrow Na_2SO_4 + 2H_2O$

The neutralization reaction of the acid and base may seem harmless, but in reality this reaction is extremely exothermic and can cause pipes to violently explode. Consider another example of mixing, this time between an acid drain cleaner and bleach:

Hydrochloric acid + bleach → water + table salt + chlorine gas

$2HCl + NaClO \rightarrow H_2O + NaCl + Cl_2$

This reaction generates chlorine gas, which is toxic to the lungs.

Green Cleaners

Green cleaning refers to using cleaning methods and products with environmentally friendly ingredients and procedures which are designed to preserve human health and environmental quality.[1] Green cleaning techniques and products avoid the use of products which contain toxic chemicals, some of which emit volatile organic compounds causing respiratory, dermatological and other conditions.[2] Green cleaning can also describe the way residential and industrial cleaning products are manufactured, packaged and distributed. If the manufacturing process is environmentally friendly and the products are biodegradable, then the term "*green*" or "*eco-friendly*" may apply.

Common household ingredients that are safe to use on its own or in combination for a variety of cleaning applications include baking soda, soap, alcohol, cornstarch, lemon juice, white vinegar, citrus solvent, washing soda (SAL soda or sodium carbonate), oxygen bleach, vegetable oil, and hydrogen peroxide.

WEB LINK

The links below provide information on safe ingredients for homemade substitutions and homemade cleaning products.

https://learn.eartheasy.com/guides/non-toxic-home-cleaning/#homecleaning

Summary

- All-purpose cleansers are effective with most common kinds of dirt and are formulated to contain mixtures of surfactants, sequestering agents, solvents, hydrotropic substances, polymeric compounds, corrosion inhibitors, skin-protective agents, and sometimes perfumes and colorants.
- Special purpose cleaners are formulated with specific chemicals to effectively remove dirt, grime or stain from a particular surface (e.g. glass cleaner, metal cleaner, etc.) or appliance (e.g. oven cleaner).
- Green cleaners are gaining popularity among environmentalists who are interested in using cleaners that are made of biodegradable and eco-friendly ingredients.

Contributors

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19.5: Solvents, Paints, and Waxes

Learning Objective

- List the properties and uses of solvents, paints, and, waxes.

Solvents

A **solvent** is a substance that dissolves a solute, resulting in a solution. A solvent is usually a liquid but can also be a solid, a gas, or a supercritical fluid. The quantity of solute that can dissolve in a specific volume of solvent varies with temperature. Common uses for organic solvents are in dry cleaning (e.g. tetrachloroethylene), as paint thinners (e.g. toluene, turpentine), as nail polish removers and glue solvents (acetone, methyl acetate, ethyl acetate), in spot removers (e.g. hexane, petrol ether), in detergents (citrus terpenes) and in perfumes (ethanol). Water is a solvent for polar molecules and the most common solvent used by living things; all the ions and proteins in a cell are dissolved in water within a cell. Solvents find various applications in chemical, pharmaceutical, oil, and gas industries, including in chemical syntheses and purification processes.

Most organic solvents are flammable or highly flammable, depending on their volatility. Exceptions are some chlorinated solvents like dichloromethane and chloroform. Mixtures of solvent vapors and air can explode. Solvent vapors are heavier than air; they will sink to the bottom and can travel large distances nearly undiluted. Solvent vapors can also be found in supposedly empty drums and cans, posing a flash fire hazard; hence empty containers of volatile solvents should be stored open and upside down.

Paints

Paint is any pigmented liquid, liquefiable, or solid mastic composition that, after application to a substrate in a thin layer, converts to a solid film. It is most commonly used to protect, color, or provide texture to objects.

Paint was one of the earliest inventions of humanity. Some cave paintings drawn with red or yellow ochre, hematite, manganese oxide, and charcoal may have been made by early *Homo sapiens* as long as 40,000 years ago.[3] Paint may be even older. In 2003 and 2004, South African archeologists reported finds in Blombos Cave of a 100,000-year-old human-made ochre-based mixture that could have been used like paint.[4][5] Further excavation in the same cave resulted in the 2011 report of a complete toolkit for grinding pigments and making a primitive paint-like substance.[5][6]

By the proper onset of the Industrial Revolution, in the mid-18th century, paint was being ground in steam-powered mills, and an alternative to lead-based pigments had been found in a white derivative of zinc oxide. Interior house painting increasingly became the norm as the 19th century progressed, both for decorative reasons and because the paint was effective in preventing the walls rotting from damp. Linseed oil was also increasingly used as an inexpensive binder.

In 1866, Sherwin-Williams Figure **19.5.1** in the United States opened as a large paint-maker and invented a paint that could be used from the tin without preparation.



Figure **19.5.1** Sherwin Williams company store in Hillsboro, Oregon

The **binder** is the film-forming component of paint.[10] It is the only component that is always present among all the various types of formulations. Many binders are too thick to be applied and must be thinned. The type of thinner, if present, varies with the binder. The binder imparts properties such as gloss, durability, flexibility, and toughness.[11] Binders include synthetic or natural resins such as alkyds, acrylics, vinyl-acrylics, vinyl acetate/ethylene (VAE), polyurethanes, polyesters, melamine resins, epoxy, silanes or siloxanes or oils.

The main purposes of the **diluent** are to dissolve the polymer and adjust the viscosity of the paint. It is volatile and does not become part of the paint film. It also controls flow and application properties, and in some cases can affect the stability of the paint while in liquid state. Its main function is as the carrier for the non volatile components. To spread heavier oils (for example, linseed) as in oil-based interior house paint, a thinner oil is required. These volatile substances impart their properties temporarily —once the solvent has evaporated, the remaining paint is fixed to the surface. Some paints have no diluent. Water is the main diluent for water-borne paints, even the co-solvent types.

Solvent-borne, also called oil-based, paints can have various combinations of organic solvents as the diluent, including aliphatics, aromatics, alcohols, ketones and white spirit. Specific examples are organic solvents such as petroleum distillate, esters, glycol ethers, and the like. Sometimes volatile low-molecular weight synthetic resins also serve as diluents.

Pigments are granular solids incorporated in the paint to contribute color. **Dyes** are colorants that dissolve in the paint. **Fillers** are granular solids incorporated to impart toughness, texture, give the paint special properties,[16] or to reduce the cost of the paint. During production, the size of such particles can be measured with a Hegman gauge. Rather than using only solid particles, some paints contain dyes instead of or in combination with pigments.

Pigments can be classified as either natural or synthetic. Natural pigments include various clays, calcium carbonate, mica, silicas, and talcs. Synthetics would include engineered molecules, calcined clays, blanc fixe, precipitated calcium carbonate, and synthetic pyrogenic silicas.

Some pigments are toxic, such as the lead pigments that are used in lead paint. Paint manufacturers began replacing white lead pigments with titanium white (titanium dioxide), before lead was banned in paint for residential use in 1978 by the US Consumer Product Safety Commission. The titanium dioxide used in most paints today is often coated with silica/alumina/zirconium for various reasons, such as better exterior durability, or better hiding performance (opacity) promoted by more optimal spacing within the paint film.[17]

Waxes

Waxes are organic compounds, hydrocarbons that characteristically consist of long aliphatic alkyl chains, although aromatic compounds may also be present. Natural waxes may contain unsaturated bonds and include various functional groups such as fatty acids, primary and secondary alcohols, ketones, aldehydes and fatty acid esters. **Synthetic waxes** (e.g. polyethylene and polypropylene waxes) often consist of homologous series of long-chain aliphatic hydrocarbons (alkanes or paraffins) that lack functional groups.[1]

The best known animal wax is **beeswax** used in constructing the honeycombs of honeybees, but other insects secrete waxes. A major component of the beeswax is myricyl palmitate which is an ester of triacontanol and palmitic acid. Its melting point is 62-65 °C. **Spermaceti** occurs in large amounts in the head oil of the sperm whale. One of its main constituents is cetyl palmitate, another ester of a fatty acid and a fatty alcohol. **Lanolin** is a wax obtained from wool, consisting of esters of sterols.[1]

Plants secrete waxes into and on the surface of their cuticles as a way to control evaporation, wettability and hydration.[3] The epicuticular waxes of plants are mixtures of substituted long-chain aliphatic hydrocarbons, containing alkanes, alkyl esters, fatty acids, primary and secondary alcohols, diols, ketones and aldehydes.[2] From the commercial perspective, the most important plant wax is **carnauba wax**, a hard wax obtained from the Brazilian palm *Copernicia prunifera*. Containing the ester myricyl cerotate, it has many applications, such as confectionery and other food coatings, car and furniture polish, floss coating, and surfboard wax. Other more specialized vegetable waxes include **jojoba oil**, **candelilla wax** and **ouricury wax**.

Paraffin wax (or **petroleum wax**) is a soft colorless solid derived from petroleum, coal or shale oil that consists of a mixture of hydrocarbon molecules containing between twenty and forty carbon atoms.Waxes are mainly consumed industrially as components of complex formulations, often for coatings.The main use of polyethylene and polypropylene waxes is in the formulation of colourants for plastics. Waxes confer matting effects and wear resistance to paints. Polyethylene waxes are incorporated into inks in

the form of dispersions to decrease friction. They are employed as release agents, find use as slip agents in furniture, and confer corrosion resistance.



Figure **19.5.2** Paraffin candle.

Waxes such as paraffin wax or beeswax, and hard fats such as tallow are used to make candles (Figure **19.5.2**). used for lighting and decoration. Waxes are used as finishes and coatings for wood products.[10] Beeswax is frequently used as a lubricant on drawer slides where wood to wood contact occurs. Waxes are used to make wax paper, impregnating and coating paper and card to waterproof it or make it resistant to staining, or to modify its surface properties. Waxes are also used in shoe polishes, wood polishes, and automotive polishes, as mold release agents in mold making, as a coating for many cheeses, and to waterproof leather and fabric. Wax has been used since antiquity as a temporary, removable model in lost-wax casting of gold, silver and other materials.

Wax with colorful pigments added has been used as a medium in encaustic painting, and is used today in the manufacture of crayons, china markers and colored pencils. Carbon paper, used for making duplicate typewritten documents was coated with carbon black suspended in wax, typically montan wax, but has largely been superseded by photocopiers and computer printers. In another context, lipstick and mascara are blends of various fats and waxes colored with pigments, and both beeswax and lanolin are used in other cosmetics. Ski wax is used in skiing and snowboarding. Also, the sports of surfing and skateboarding often use wax to enhance the performance.

Some waxes are considered food-safe and are used to coat wooden cutting boards and other items that come into contact with food. Beeswax or coloured synthetic wax is used to decorate Easter eggs in Romania, Ukraine, Poland, Lithuania and the Czech Republic. Paraffin wax is used in making chocolate covered sweets.

Summary

- A solvent is a liquid, solid, a gas, or a supercritical fluid that dissolves a solute to form a solution. Solvents are found in various personal and household items, and also used in chemical, pharmaceutical, oil, and gas industries, including in chemical syntheses and purification processes.
- Paint is any pigmented liquid, liquefiable, or solid mastic composition that, after application to a substrate in a thin layer, converts to a solid film. It is most commonly used to protect, color, or provide texture to objects.
- Natural and synthetic waxes are used for lighting, for surface coating and polishing, for waterproofing leather and fabric. Waxes are also key ingredients in cosmetics and personal care products.

Contributors and Attributions

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19.6: Cosmetics - Personal Care Chemicals

Learning Objectives

- List the main ingredients in different personal care products and their functions.
- Describe the steps in formation of temporary and permanent waves.

In the United States, the Food and Drug Administration (FDA), which regulates cosmetics, defines cosmetics as products "intended to be applied to the human body for cleansing, beautifying, promoting attractiveness, or altering the appearance without affecting the body's structure or functions". This broad definition includes any material intended for use as an ingredient of a cosmetic product, with the FDA specifically excluding pure soap from this category.



Figure **19.6.1** Assorted cosmetics and tools.

Cosmetics (Figure **19.6.1**) have been in use for thousands of years. Egyptian men and women used makeup to enhance their appearance. They were very fond of eyeliner and eye-shadows in dark colors including blue, red, and black. Ancient Sumerian men and women were possibly the first to invent and wear lipstick, about 5,000 years ago. They crushed gemstones and used them to decorate their faces, mainly on the lips and around the eyes.

According to one source, early major developments include:

- Kohl used by ancient Egypt as a protectant of the eye (Figure **19.6.2**).
- Castor oil used by ancient Egypt as a protective balm.
- Skin creams made of beeswax, olive oil, and rose water, described by Romans.
- Vaseline and lanolin in the nineteenth century.

Although modern makeup has been traditionally used mainly by women, an increasing number of men are using cosmetics usually associated with women to enhance or cover their own facial features such as blemishes and dark circles, as well the use of eyeshadow, mascara and lipstick by some. Cosmetics brands have increasingly also targeted men in the sale of cosmetics, with some products targeted specifically at men.

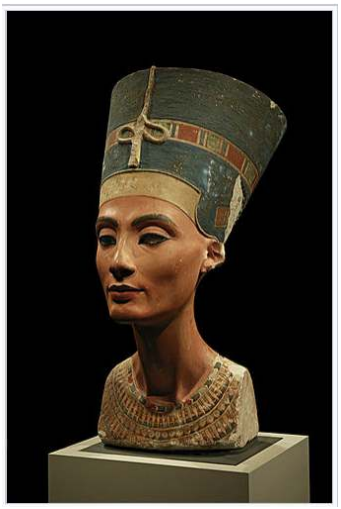


Figure **19.6.2** Nefertiti Bust showing the use of eye liner made of kohl.

The Skin

The cutaneous membrane is the technical term for our skin. The skin's primary role is to help protect the rest of the body's tissues and organs from physical damage such as abrasions, chemical damage such as detergents, and biological damage from microorganisms. For example, while the skin harbors many permanent and transient bacteria, these bacteria are unable to enter the body when healthy, intact skin is present.

Our skin is made of three general layers (Figure **19.6.3**). In order from most superficial to deepest they are the epidermis, dermis, and subcutaneous tissue (hypodermis).

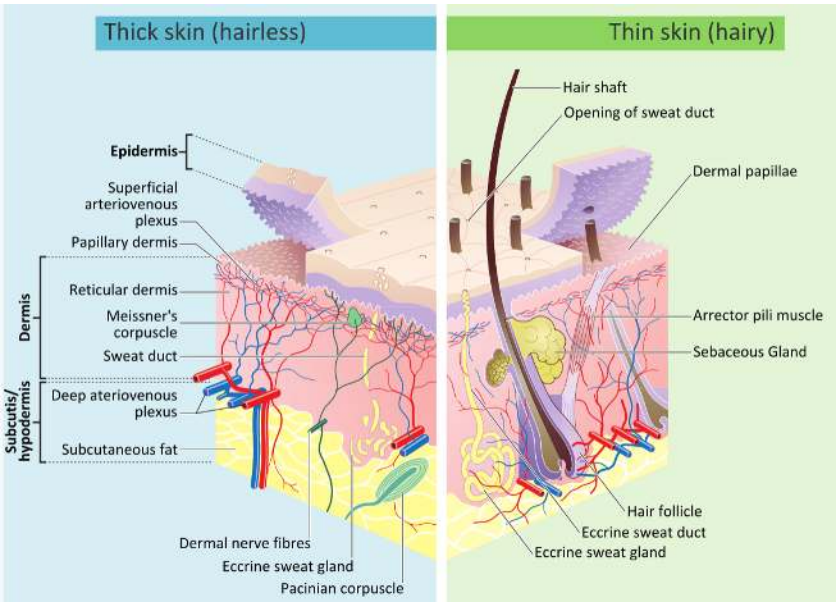


Figure **19.6.3** Skin layers, of both the hairy and hairless skin.

There are several different types of cells in the **epidermis**. All of the cells are necessary for the important functions of the epidermis.

- The epidermis consists mainly of stacks of keratin-producing epithelial cells called keratinocytes. These cells make up at least 90 percent of the epidermis. Near the top of the epidermis, these cells are also called squamous cells.
- Another 8 percent of epidermal cells are melanocytes. These cells produce the pigment melanin that protects the dermis from UV light.

- About 1 percent of epidermal cells are Langerhans cells. These are immune system cells that detect and fight pathogens entering the skin.
- Less than 1 percent of epidermal cells are Merkel cells, which respond to light touch and connect to nerve endings in the dermis.

The epidermis has several crucial functions in the body. These functions include protection, water retention, and vitamin D synthesis. The epidermis provides protection to underlying tissues from physical damage, pathogens, and UV light.

Skin Creams and Lotions

A **lotion** is a low-viscosity topical preparation intended for application to the skin. By contrast, creams and gels have higher viscosity, typically due to lower water content. Lotions are applied to external skin with bare hands, a brush, a clean cloth, or cotton wool.

While a lotion may be used as a medicine delivery system, many lotions, especially **hand lotions** and **body lotions** are meant instead to simply smooth, moisturize, soften and perhaps perfume the skin.

Most cosmetic lotions are moisturizing lotions, although other forms, such as tanning lotion, also exist.

Cosmetic lotions may be marketed as anti-aging lotions, which can also be classified as a cosmetic in many cases, and may contain fragrances. The Food and Drug Administration voiced concern about lotions not classified as drugs that advertise anti-aging or anti-wrinkle properties.

Most lotions are oil-in-water emulsions using a substance such as cetearyl alcohol to keep the emulsion together, but water-in-oil lotions are also formulated.

A **cream** is a preparation usually for application to the skin. Creams for application to mucous membranes such as those of the rectum or vagina are also used. Creams may be considered pharmaceutical products as even cosmetic creams are based on techniques developed by pharmacy and unmedicated creams are highly used in a variety of skin conditions (dermatoses). The use of the finger tip unit concept may be helpful in guiding how much topical cream is required to cover different areas.

Creams are semi-solid emulsions of oil and water. They are divided into two types: oil-in-water (O/W) creams which are composed of small droplets of oil dispersed in a continuous water phase, and water-in-oil (W/O) creams which are composed of small droplets of water dispersed in a continuous oily phase. Oil-in-water creams are more comfortable and cosmetically acceptable as they are less greasy and more easily washed off using water. Water-in-oil creams are more difficult to handle but many drugs which are incorporated into creams are hydrophobic and will be released more readily from a water-in-oil cream than an oil-in-water cream. Water-in-oil creams are also more moisturizing as they provide an oily barrier which reduces water loss from the stratum corneum, the outermost layer of the skin.

Ointment is a semisolid dosage form it is used for topical application to the medication

Water, oil, emulsifier, and thickening agent are four main ingredients of cold creams and lotions.

Moisturizer or **moisturiser** is a cosmetic preparation used for protecting, moisturizing, and lubricating the skin. These functions are normally performed by sebum produced by healthy skin.

Moisturizers modify the rate of water loss, with active ingredients of moisturizers falling into one of two categories: occlusives and humectants

Occlusives form a coating on the surface of the skin, keeping moisture from escaping.

Humectants absorb water. They can absorb this water from the air and moisturize the skin when the humidity is greater than 70%, but more commonly they draw water from the dermis into the epidermis, making skin dryer. A study published in Skin Research and Technology in 2001 found no link between humectants and moisturizing effect. When used in practical applications, they are almost always combined with occlusives.

Moisturizers often contain water, which acts as a temporary hydration agent and as a way for the absorption of some components and evaporation of the moisturizer.

There are many different types of moisturizers. Petrolatum is one of the most effective moisturizers, although it can be unpopular due to its oily consistency. Other popular moisturizers are cetyl alcohol, cetearyl alcohol, cocoa butter, isopropyl myristate, isopropyl palmitate, lanolin, liquid paraffin, polyethylene glycols, shea butter, silicone oils, stearic acid, stearyl alcohol and castor oil, as well as other oils.

Moisturizers may also be available as lotions, creams, ointments, bath oils, or soap substitutes.

Mineral oils and waxes are insensitive to oxidation or rancidity. For this reason, they have essentially replaced vegetable oils in emollients and topical medication.

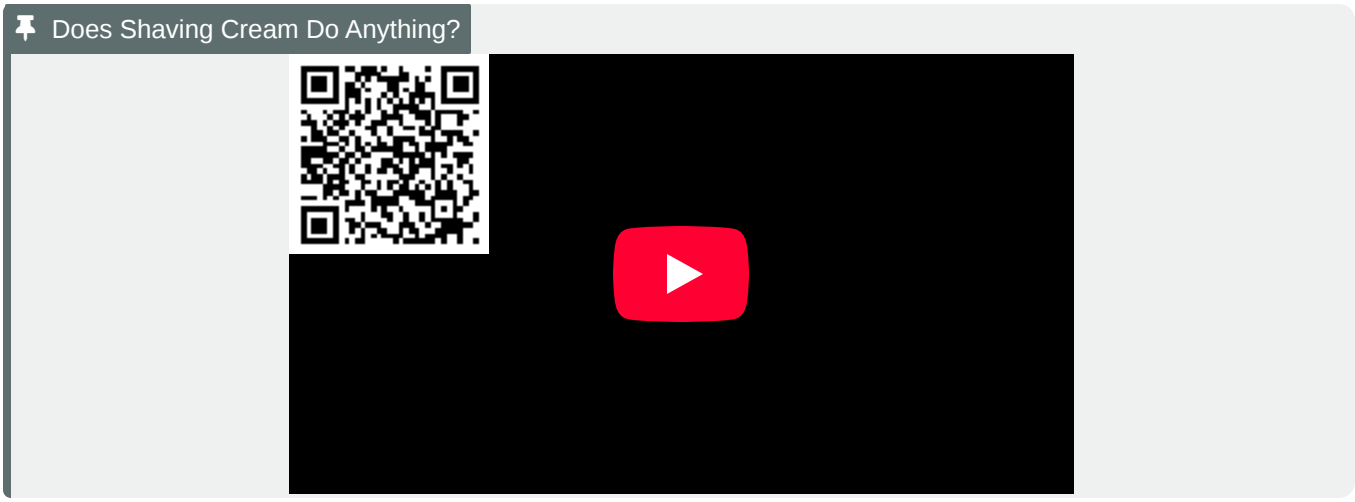
Moisturizer cosmetics may additionally contain antioxidants, ceramides, emulsifiers, fragrances, penetration enhancers, preservatives, and solvents. Some products are marketed as having anti-wrinkle and skin enhancement effects. Many plant and animal extracts have been claimed to impart skin benefits, with little scientific evidence.

Shaving Creams

Shaving cream or **shave cream** is a category of cosmetics used for shaving preparation. The purpose of shaving cream is to soften the hair by providing lubrication.

Different types of shaving creams include aerosol shaving cream (also known as shaving foam), latherless shaving cream (also called brushless shaving cream and non-aerosol shaving cream), and lather shaving cream or lathering shaving cream. The term shaving cream can also refer to the lather produced with a shaving brush from shaving soap or a lather shaving cream.

Shaving creams commonly consist of an emulsion of oils, soaps or surfactants (e.g. triethanolamine steatrate), and water. In addition to soap, lather shaving creams include a humectant for softer consistency and keeping the lather moisturised. Brushless shaving creams, on the other hand, don't contain soap and so don't produce lather. They are an oil-in-water mixture to which humectants, wetting agents, and other ingredients are added. Aerosol shaving creams are basically lather shaving cream in liquid form with propellants, vegetable waxes, and various oils added.



***Video* 19.6.1** *What is shaving cream?*

Sunscreen and Sunblock

UVB radiation in sunlight allows the skin to produce vitamin D. This vitamin prevents bone disorders like rickets and osteoporosis (brittle bone disease). The American Academy of Dermatology suggests vitamin D be obtained through foods or nutritional supplements. Excessive exposure to UV can be damaging and the pigment **melanin**, deposited in cells at the base of the epidermis, helps to protect the underlying layers of the skin from this damage. Melanin also colors the skin and variations in the amount of melanin produces colors from pale yellow to black. The darker the skin tone, the more melanin one has, and the less likely skin cancer will occur.

Excess exposure to the sun can cause sunburn. This is common in humans, but light skinned animals like cats and pigs can also be sunburned, especially on the ears. Skin cancer can also result from excessive exposure to the sun. As holes in the ozone layer

increase exposure to the sun's UV rays, so too does the rate of skin cancer in humans and animals.

Sunscreens and sunblocks are designed to protect skin from ultraviolet rays. *Sunblocks* contain inorganic ingredients like zinc oxide or titanium dioxide. These chemicals act as UV filters by reflecting the sun's UV rays. Sunblocks can have grainy textures due to the inorganic components. The thick nature of a sunblock can make it difficult to spread evenly on the skin. *Sunscreens* contain organic compounds like oxybenzone, avobenzone, homosalate, and octinoxate (Figure **19.6.4**). By absorbing ultraviolet rays, these compounds decompose and give off heat. Sunscreens apply smoother than sunblocks. Often, manufacturers will combine sunscreen and sunblock ingredients to make their products.



Figure **19.6.4** Chemistry of Sunscreen.

Sun protection factor (SPF) measures a product's protection from UVB rays. SPF does not quantify protection from UVA radiation. The American Academy of Dermatology recommends you select a sunscreen or sunblock with a minimum SPF factor of 30. This SPF value means a lotion can filter out 97% of UVB rays. Moving to a SPF of 50 will only filter out 1 more percentage of UVB rays. Increasing a SPF factor past 30 really does very little in shielding skin from UVB radiation.

Products that protect skin from UVA must be labeled as being a broad spectrum. Sunblocks provide UVA and UVB protection, but sunscreens can vary on what they can screen. Every two hours, sunscreens/sunblocks should be reapplied to the skin. Sweating and swimming can remove sunscreen/sunblock products. No sun products are waterproof, but some are labeled as being water-resistant. Consumers are encouraged to reapply these products every two hours as well.

Sunscreen Label

***Figure* 19.6.5** *Sunscreen label. Source: Badger: Healthy Body Care*

Is Sunscreen Safe?

Check the link below on FAQs regarding sunscreen.

https://www.aad.org/public/everyday-care/sun-protection/sunscreen/understand-sunscreen-labels

Lipsticks and Lip Balms

Lipstick, lip gloss, lip liner, lip plumper, lip balm, lip stain, lip conditioner, lip primer, lip boosters, and lip butters: Lipsticks are intended to add color and texture to the lips and often come in a wide range of colors, as well as finishes such as matte, satin, gloss and lustre.

Lipstick contains wax, oils, antioxidants, and emollients. Wax provides the structure to the solid lipstick. Lipsticks may be made from several waxes such as beeswax, ozokerite and candelilla wax. Because of its high melting point, carnauba wax is a key ingredient in terms of strengthening the lipstick. Various oils and fats are used in lipsticks, such as olive oil, mineral oil, cocoa butter, lanolin, and petrolatum.

Lipsticks get their colors from a variety of pigments and lake dyes including, but not limited to bromo acid, D&C Red No. 21, Calcium Lake such as D&C Red 7 and D&C Red 34, and D&C Orange No. 17. Pink lipsticks are made by mixing white titanium dioxide and red shades. Both organic and inorganic pigments are employed.

Lip stains have a water or gel base and may contain alcohol to help the product stay on leaving a matte look. They temporarily saturate the lips with a dye. Usually designed to be waterproof, the product may come with an applicator brush, directly through the applicator, rollerball, or could be applied with a finger. Lip glosses are intended to add shine to the lips and may add a tint of color, as well as being scented or flavored. Lip balms are most often used to moisturize, tint, and protect the lips. Some brands contain sunscreen. Using a priming lip product such as lip balm or chapstick can prevent chapped lips.

Eye Make-up

- **Mascara** is a cosmetic commonly used to enhance the eyelashes. It may darken, thicken, lengthen, and/or define the eyelashes. Normally in one of three forms—liquid, powder, or cream—the modern mascara product has various formulas; however, most contain the same basic components of pigments, oils, waxes, and preservatives. The most common form of mascara is a liquid in a tube.
- **Eye shadow** (or **eyeshadow**) is a cosmetic applied primarily to the eyelids to make the wearer's eyes stand out or look more attractive. Eye shadow can also be applied under eyes or to brow bones.

  Eye shadow can add depth and dimension to one's eyes, complement one's eye color, make one's eyes appear larger, or simply draw attention to the eyes. Eye shadow comes in many different colors and textures. It is usually made from a powder but can also be found in liquid, pencil, cream or mousse form. Just like other trends, eyeshadow looks also have trends.

  Eye shadows typically consist of four types of ingredients: base fillers, binders, slip and preservatives. In order to make eye shadow, there must be a balance between the fillers and binders.

  Base fillers are usually minerals such as mica, talc or kaolin clay, which add bulk and texture to eye shadow. They make up about 30% of eye shadow powders and 25% of cream eye shadows. Mica absorbs moisture, gives the eye shadow shine and luster, and makes it opaque. Mica powders, iron oxides and clays can give color pigments to eye shadows.

  Binders help eye shadow adhere and stay attached to skin. Eye shadows can have dry or liquid binders. Zinc and magnesium, which are both white powders, are commonly used as dry binders. Zinc also adds color and can be used to increase the thickness of the eyeshadow. Silicone, paraffin wax, mineral oil or vegetable oils may be used as liquid binders.

  Slip allows eye shadow to glide across the skin smoothly. Products may use silica or nylon, which are fine, colorless powders. Other types of slip include dimethicone, boron nitride or bismuth oxychloride.

Preservatives help products stay bacteria free and extend their lifespan. Common preservatives in eye shadow are glycol and tocopherol.



Figure **19.6.6** Eyes with heavy gold eye shadow. Source: Wikipedia

Eye liner or **eyeliner** is a cosmetic used to define the eyes. It is applied around the contours of the eye(s) to create a variety of aesthetic effects. It can come in the form of a pencil, a gel, or a liquid and can be found in almost any color. Traditional wax-based eye liners are made from about 20 components. About 50% by weight are waxes (e.g., Japan wax, fats, or related soft materials that easily glide on to the skin. Stearyl heptanoate is found in most cosmetic eyeliner. Typical pigments include black iron oxides, as well as smaller amounts of titanium dioxide and Prussian blue.

Eyebrow shaders, and pencils are often used to define the eyebrow or make it appear fuller. These can create an outline for the brows or mimic hairs where there are sparse areas. Brow gels are also used in creating a thicker brow; they allow for the hairs to be more textured, which gives the appearance of thicker, fuller brows. Lastly, brow powders or even eye shadows are used for those who want a fuller and more natural look, by placing the brow powder or eye shadow (closest to the natural hair color) in areas where there is less hair.

Deodorants and Antiperspirants

A **deodorant** is a substance applied to the body to prevent or mask body odor due to bacterial breakdown of perspiration in the armpits, groin, and feet, and in some cases vaginal secretions. A subclass of deodorants, called **antiperspirants**, prevents sweating itself, typically by blocking sweat glands. Antiperspirants are used on a wider range of body parts, at any place where sweat would be inconvenient or unsafe, since unwanted sweating can interfere with comfort, vision, and grip (due to slipping). Other types of deodorant allow sweating but prevent bacterial action on sweat, since human sweat only has a noticeable smell when it is decomposed by bacteria.

In the United States, the Food and Drug Administration classifies and regulates most deodorants as cosmetics but classifies antiperspirants as over-the-counter drugs.

In the United States, deodorants are classified and regulated as cosmetics by the U.S. Food and Drug Administration (FDA) and are designed to eliminate odor. Deodorants are often alcohol based. Alcohol initially stimulates sweating but may also temporarily kill bacteria. Other active ingredients in deodorants include sodium stearate, sodium chloride, and stearyl alcohol. Deodorants can be formulated with other, more persistent antimicrobials such as triclosan that slow bacterial growth or with metal chelant compounds such as EDTA. Deodorants may contain perfume fragrances or natural essential oils intended to mask the odor of perspiration. In the past, deodorants included chemicals such as zinc oxide, acids, ammonium chloride, sodium bicarbonate, and formaldehyde, but some of these ingredients were messy, irritating to the skin, or even carcinogenic.

Over-the-counter products, often labeled as "natural deodorant crystal", contain the chemical rock crystals potassium alum or ammonium alum, which prevents bacterial action on sweat. These have gained popularity as an alternative health product, in spite of concerns about possible risks related to aluminum (see below – all alum salts contain aluminum in the form of aluminum sulphate salts) and contact dermatitis.

In the United States, deodorants combined with antiperspirant agents are classified as drugs by the FDA. Antiperspirants attempt to stop or significantly reduce perspiration and thus reduce the moist climate in which bacteria thrive. Aluminium chloride, aluminium chlorohydrate, and aluminium-zirconium compounds, most notably aluminium zirconium tetrachlorohydrex gly and aluminium zirconium trichlorohydrex gly, are frequently used in antiperspirants. Aluminium chlorohydrate and aluminium-zirconium tetrachlorohydrate gly are the most frequent active ingredients in commercial antiperspirants. Aluminium-based complexes react with the electrolytes in the sweat to form a gel plug in the duct of the sweat gland. The plugs prevent the gland from excreting

liquid and are removed over time by the natural sloughing of the skin. The metal salts work in another way to prevent sweat from reaching the surface of the skin: the aluminium salts interact with the keratin fibrils in the sweat ducts and form a physical plug that prevents sweat from reaching the skin's surface. Aluminium salts also have a slight astringent effect on the pores; causing them to contract, further preventing sweat from reaching the surface of the skin. The blockage of a large number of sweat glands reduces the amount of sweat produced in the underarms, though this may vary from person to person. Methenamine (Figure **19.6.7**) in the form of cream or spray is effective in the treatment of excessive sweating and attendant odor. Antiperspirants are usually best applied before bed.

Figure **19.6.7** *Methenamine-based antiperspirant for treatment of excessive sweating.*

Toothpaste: Soap with Grit and Flavor

Toothpaste (Figure **19.6.8**) is a paste or gel dentifrice used with a toothbrush to clean and maintain the aesthetics and health of teeth. Toothpaste is used to promote oral hygiene: it is an abrasive that aids in removing dental plaque and food from the teeth, assists in suppressing halitosis, and delivers active ingredients (most commonly fluoride) to help prevent tooth decay (dental caries) and gum disease (gingivitis). Salt and sodium bicarbonate (baking soda) are among materials that can be substituted for commercial toothpaste. Large amounts of swallowed toothpaste can be toxic.



Figure **19.6.8** A variety of brands of toothpaste.

In addition to 20%–42% water, toothpastes are derived from a variety of components, the three main ones being abrasives, fluoride, and detergents.

Abrasives constitute at least 50% of a typical toothpaste. These insoluble particles are designed to help remove plaque from the teeth. The removal of plaque and calculus prevents the accumulation of tartar and is widely claimed to help minimize cavities and periodontal disease, although the clinical significance of this benefit is debated. Representative abrasives include particles of aluminum hydroxide ($Al(OH)_3$), calcium carbonate ($CaCO_3$), various calcium hydrogen phosphates, various silicas and zeolites, and hydroxyapatite ($Ca_5(PO_4)_3OH$).

Abrasives, like the dental polishing agents used in dentists' offices, also cause a small amount of enamel erosion which is termed "polishing" action. Some brands contain powdered white mica, which acts as a mild abrasive, and also adds a cosmetically pleasing glittery shimmer to the paste. The polishing of teeth removes stains from tooth surfaces, but has not been shown to improve dental health over and above the effects of the removal of plaque and calculus.

The abrasive effect of toothpaste is indicated by its RDA value. Too high RDA values are deleterious. Some dentists recommend toothpaste with an RDA value no higher than 50 for daily use.

Fluoride in various forms is the most popular active ingredient in toothpaste to prevent cavities. Fluoride is present in small amounts in plants, animals, and some natural water sources. The additional fluoride in toothpaste has beneficial effects on the

formation of dental enamel and bones. Sodium fluoride (NaF) is the most common source of fluoride, but stannous fluoride (SnF_2), olaflur (an organic salt of fluoride), and sodium monofluorophosphate (Na_2PO_3F) are also used. Stannous fluoride has been shown to be more effective than sodium fluoride in reducing the incidence of dental caries and controlling gingivitis, but causes somewhat more surface stains.

Much of the toothpaste sold in the United States has 1,000 to 1,100 parts per million fluoride. In European countries, such as the UK or Greece, the fluoride content is often higher; a NaF content of 0.312% w/w (1,450 ppm fluoride) is common. All of these concentrations are likely to prevent tooth decay, according to a 2019 Cochrane review. Concentrations below 1,000 ppm are not likely to be preventive, and the preventive effect increases with concentration. Clinical trials support the use of high fluoride dentifrices, as it was found to reduce the amount of plaque accumulated, decrease the number of mutans streptococci and lactobacilli and possibly promote calcium fluoride deposits to a higher degree than after the use of traditional fluoride containing dentifrices. However, these effects must be balanced with the increased risk of harm at higher concentrations.

Many, although not all, toothpastes contain sodium lauryl sulfate (SLS) or related **surfactants (detergents)**. SLS is found in many other personal care products as well, such as shampoo, and is mainly a foaming agent, which enables uniform distribution of toothpaste, improving its cleansing power.

Other Components in toothpaste formulations include:

- Antibacterial agents. Triclosan or zinc chloride prevent gingivitis and, according to the American Dental Association, helps reduce tartar and bad breath.
- Flavorants. Toothpaste comes in a variety of colors and flavors intended to encourage use of the product. The three most common flavorants are peppermint, spearmint, and wintergreen.
- Reminalizers. Hydroxyapatite nanocrystals and a variety of calcium phosphates are included in formulations for remineralization, i.e. the reformation of enamel.

Agents are added to suppress the tendency of toothpaste to dry into a powder. Included are various sugar alcohols, such as glycerol, sorbitol, or xylitol, or related derivatives, such as 1,2-propylene glycol and polyethyleneglycol

Strontium chloride or potassium nitrate is included in some toothpastes to reduce sensitivity. Two systemic meta-analysis reviews reported that arginine, and calcium sodium phosphosilicate - CSPS containing toothpastes are also effective in alleviating dentinal hypersensitivity respectively. Another randomized clinical trial found superior effects when both formulas were combined together.

Sodium polyphosphate is added to minimize the formation of tartar. Other example to components in toothpastes is the Biotene, which has proved its efficiency in relieving the symptoms of dry mouth in people who suffer from xerostomia according to the results of two randomized clinical trials.

Chlorohexidine mouthwash has been popular for its positive effect on controlling plaque and gingivitis, however, a systemic review studied the effects of chlorohexidine toothpastes and found insufficient evidence to support its use, tooth surface discoloration was observed as a side effect upon using it, which is considered a negative side effect that can affect patients' compliance.

Sodium hydroxide, also known as lye or caustic soda, is listed as an inactive ingredient in some toothpaste, for example Colgate Total.

Some studies have demonstrated that toothpastes with xylitol as an ingredient are more effective at preventing dental caries in permanent teeth of children than toothpastes containing fluoride alone.

Perfumes, Colognes, and Aftershaves

Perfume (Figure **19.6.9**) is a mixture of fragrant essential oils or aroma compounds, fixatives and solvents, used to give the human body, animals, food, objects, and living-spaces an agreeable scent. Perfume types reflect the concentration of aromatic compounds in a solvent, which in fine fragrance is typically ethanol or a mix of water and ethanol. Various sources differ considerably in the definitions of perfume types. The intensity and longevity of a perfume is based on the concentration, intensity, and longevity of the aromatic compounds, or perfume oils, used. Specific terms are used to describe a fragrance's approximate concentration by the percent of perfume oil in the volume of the final product. The most widespread terms are:

- **parfum** or **extrait**, in English known as perfume extract, pure perfume, or simply perfume: 15–40% aromatic compounds (IFRA: typically ~20%);

- **esprit de parfum** (ESdP): 15–30% aromatic compounds, a seldom used strength concentration in between EdP and perfume;
- **eau de parfum** (EdP) or **parfum de toilette** (PdT) (The strength usually sold as "perfume"): 10–20% aromatic compounds (typically ~15%); sometimes called "eau de perfume" or "millésime"; parfum de toilette is a less common term, most popular in the 1980s, that is generally analogous to eau de parfum;
- **eau de toilette** (EdT): 5–15% aromatic compounds (typically ~10%); This is the staple for most masculine perfumes.
- **eau de Cologne** (EdC): often simply called cologne: 3–8% aromatic compounds (typically ~5%);
- **eau fraiche**: products sold as "splashes", "mists", "veils" and other imprecise terms. Generally these products contain 3% or less aromatic compounds and are diluted with water rather than oil or alcohol.



Figure **19.6.9** A bottle of perfume by Yves Saint Laurent

Perfume is described in a musical metaphor as having three sets of *notes*, making the harmonious scent *accord*. The notes unfold over time, with the immediate impression of the top note leading to the deeper middle notes, and the base notes gradually appearing as the final stage. These notes are created carefully with knowledge of the evaporation process of the perfume.

- **Top notes**: Also called the ***head notes***. The scents that are perceived immediately on application of a perfume. Top notes consist of small, light molecules that evaporate quickly. They form a person's initial impression of a perfume and thus are very important in the selling of a perfume. Examples of top notes include mint, lavender and coriander.
- **Middle notes**: Also referred to as ***heart notes***. The scent of a perfume that emerges just prior to the dissipation of the top note. The middle note compounds form the "*heart*" or main body of a perfume and act to mask the often unpleasant initial impression of base notes, which become more pleasant with time. Examples of middle notes include seawater, sandalwood and jasmine.
- **Base notes**: The scent of a perfume that appears close to the departure of the middle notes. The base and middle notes together are the main theme of a perfume. Base notes bring depth and solidity to a perfume. Compounds of this class of scents are typically rich and "deep" and are usually not perceived until 30 minutes after application. Examples of base notes include tobacco, amber and musk.

The scents in the top and middle notes are influenced by the base notes; conversely, the scents of the base notes will be altered by the types of fragrance materials used as middle notes. Manufacturers who publish perfume notes typically do so with the fragrance components presented as a *fragrance pyramid*, using imaginative and abstract terms for the components listed.

Aftershave is a product applied to skin after shaving. Traditionally it is an alcohol based liquid (splash), but it can be a lotion, gel, or even a paste.

It often contains an antiseptic agent such as denatured alcohol, stearate citrate or witch hazel to prevent infection of cuts, as well as to act as an astringent to reduce skin irritation. Menthol is used in some varieties as well to numb irritated skin.

An alcohol-based aftershave usually causes an immediate stinging sensation after applying it post-shave, with effects sometimes lasting several minutes, but most commonly only for seconds. For this reason, a market consisting of highly differentiated products has been created—some using alcohols, some not.

Aftershave balms are frequently recommended for winter use as they tend to be alcohol free and lotion-like, moisturizing the skin.

Some aftershaves use fragrance or essential oil to enhance scent. Moisturizers—natural and artificial, are often touted as able to soften the skin.

Aftershave is sometimes mistakenly referred to as Eau de Cologne due to the very similar nature of the two products. Some aftershave manufacturers encourage using their fragranced aftershave as if it were cologne, in order to increase sales by encouraging consumers to use it in a more versatile manner, rather than just after a shaving session. Some aftershaves were inspired by a cologne.

Early aftershaves included witch-hazel and bay rum, and have been documented in shaving guides. Both still are sold as aftershaves.

Hairy Chemistry

Hair keratin consists of many protein alpha-helices (Figure **19.6.10**). Three alpha-helices are interwoven into a left-handed coil called a protofibril. Eleven protofibrils are bonded and coiled together to make a microfibril. Hundreds of these microfibrils are cemented into an irregular bundle called a macrofibril. These in turn are mixed with dead and living cells to make a complete strand of hair.

The alpha-helices are extensively cross-linked with disulfide bonds from cysteine. These bonds enable keratin to have a somewhat elastic nature. If the alpha -helices stretch unevenly past each other, the disulfide cross-links return them to the original position when the tension is released.

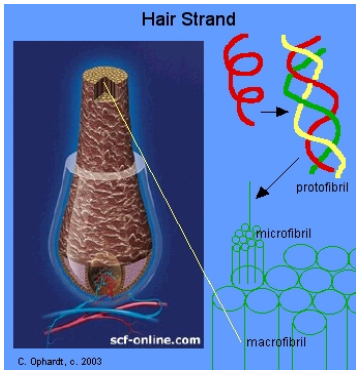


Figure **19.6.10** Protein alpha-helices in a hair strand.

Shampoo

Shampoo (/ʃæm'puː/) is a hair care product, typically in the form of a viscous liquid, that is used for cleaning hair. Less commonly, shampoo is available in bar form, like a bar of soap. Shampoo is used by applying it to wet hair, massaging the product into the scalp, and then rinsing it out. Some users may follow a shampooing with the use of hair conditioner.

The typical reason of using shampoo is to remove the unwanted build-up of sebum in the hair without stripping out so much as to make hair unmanageable. Shampoo is generally made by combining a surfactant, most often sodium lauryl sulfate or sodium laureth sulfate, with a co-surfactant, most often cocamidopropyl betaine in water. The sulphate ingredient acts as a surfactant, essentially heavy duty soap that makes it easier to trap oil and grease.

Specialty shampoos are marketed to people with dandruff, color-treated hair, gluten or wheat allergies, an interest in using an organic product, and infants and young children ("baby shampoo" is less irritating). There are also shampoos intended for animals that may contain insecticides or other medications to treat skin conditions or parasite infestations such as fleas.

Shampoo is generally made by combining a surfactant, most often sodium lauryl sulfate or sodium laureth sulfate, with a co-surfactant, most often cocamidopropyl betaine in water to form a thick, viscous liquid. Other essential ingredients include salt (sodium chloride), which is used to adjust the viscosity, a preservative and fragrance. Other ingredients are generally included in shampoo formulations to maximize the following qualities:

- pleasing foam
- ease of rinsing

- minimal skin and eye irritation
- thick or creamy feeling
- pleasant fragrance
- low toxicity
- good biodegradability
- slight acidity (pH less than 7)
- no damage to hair
- repair of damage already done to hair

Many shampoos are pearlescent. This effect is achieved by the addition of tiny flakes of suitable materials, e.g. glycol distearate, chemically derived from stearic acid, which may have either animal or vegetable origins. Glycol distearate is a wax. Many shampoos also include silicone to provide conditioning benefits.

How Does Shampoo Work?



***Video* 19.6.2** *Shampoo applied to wet hair.*

Hair Coloring

Hair color is the pigmentation of hair follicles due to two types of melanin: eumelanin and pheomelanin. Generally, if more eumelanin is present, the color of the hair is darker; if less eumelanin is present, the hair is lighter. Levels of melanin can vary over time causing a person's hair color to change, and it is possible to have hair follicles of more than one color on the same person. Particular hair colors are often associated with ethnic groups, while gray or white hair is associated with age.

Hair coloring, or **hair dyeing**, is the practice of changing the hair color. The main reasons for this are cosmetic: to cover gray or white hair, to change to a color regarded as more fashionable or desirable, or to restore the original hair color after it has been discolored by hairdressing processes or sun bleaching.

Hair coloring can be done professionally by a hairdresser or independently at home. Today, hair coloring is very popular, with 75% of women and 18% of men living in Copenhagen having reported using hair dye (according to a study by the University of Copenhagen). At-home coloring in the United States reached $1.9 billion in 2011 and was expected to rise to $2.2 billion by 2016.

Hair color can be changed by a chemical process. Hair coloring is classed as "permanent" or "semi-permanent".

Permanent hair color means that the hair's structure has been chemically altered until it is eventually cut away. This does not mean that the synthetic color will remain permanently. During the process, the natural color is removed, one or more shades, and synthetic color has been put in its place. All pigments wash out of the cuticle. Natural color stays in much longer and artificial will fade the fastest (depending on the color molecules and the form of the dye pigments).

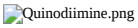
Permanent hair coloring requires three components: (1) 1,4-diaminobenzene (historically) or 2,5-diaminotoluene (currently), (2) a coupling agent, and (3) an oxidant. The process is typically performed under basic conditions. The mechanism of oxidation dyes involves three steps: 1) Oxidation of 1,4-diaminobenzene derivative to the quinone state. 2) Reaction of this diimine with a coupler compound (more detail below). 3) Oxidation of the resulting compound to give the final dye.



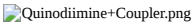
Figure 19.6.11 *Shown here are three red couplers (A, B, C), two yellow-green couplers (D, E) and a blue coupler (F). Couplers are chemical compounds that define the color of the hair dye.*

Steps in Permanent Hair Coloring

The first step shows the oxidation of p-phenylenediamine to the quinonediimine ($C_6H_4(NH)_2$):



The second step involves the attack of this quinonediimine on the coupler.



In the third and final step, the product from the quinonediimine-coupler reaction oxidizes to the final hair dye.



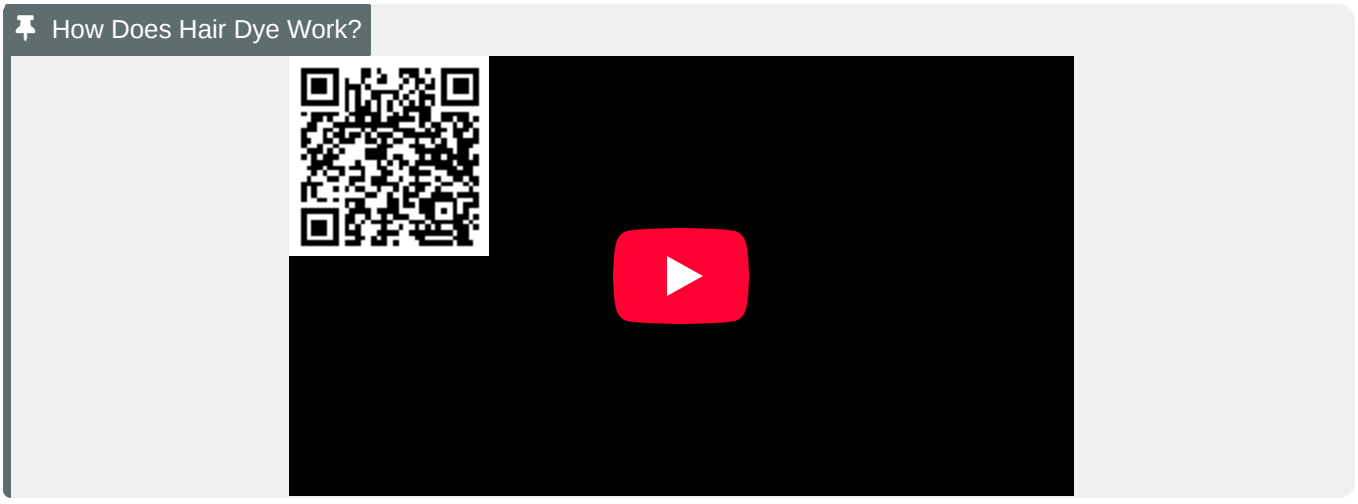
It was once believed that the dye forms in the above reaction bonds to hair permanently. It was later shown that the main reason that this reaction imparts a permanent color on hair by producing larger dye molecules, which is locked inside the hair.

Semi-permanent color washes out over a period of time—typically four to six weeks, so root regrowth is less noticeable. The final color of each strand is affected by its original color and porosity, so there will be subtle variations in color across the head—more natural and less harsh than a permanent dye. However, this means that gray and white hair will not dye to the same color as the rest of the head (in fact, some white hair will not absorb the color at all). A few gray and white hairs will blend in sufficiently not to be noticeable, but as they become more widespread, there will come a point where a semi-permanent alone will not be enough. The move to 100% permanent color can be delayed by using a semi-permanent as a base color, with permanent highlights.

Semi-permanent hair color cannot lighten hair. Hair can only be lightened using chemical lighteners, such as bleach. Bleaching is always permanent because it removes the natural pigment.

"Rinses" are a form of temporary hair color, usually applied to hair during a shampoo and washed out again the next time the hair is wash.

Plant based dyes include henna, indigo and anthocyanin pigments extracted form blackcurrant skin waste.



***Video* 19.6.3** *Applying hair dye.*

Permanent and Temporary Waving

Temporary Wave. When the hair gets wet, water molecules intrude into the keratin strands. The sheer numbers of water molecules are able to disrupt some of the hydrogen bonds which also help to keep the alpha-helices aligned. The helices are able to slip past

each other and will retain a new shape in the hair drying process as new hydrogen bonds are formed. The hair strands are able for a short time to maintain the new curl in the hair.

A **permanent hairstyle**, commonly called a **perm** or "**permanent**" (sometimes called a "perm" to distinguish it from a "straight perm"), is a hairstyle consisting of styles set into the hair. The hairstyle may last a number of months, hence the name.

Perms may be applied using thermal or chemical means. In the latter method, chemicals are applied to the hair, which is then wrapped around forms to produce hairstyles. The same process is used for chemical straightening or relaxing, with the hair being flattened instead of curled during the chemical reaction.

The formation of disulfide bonds has a direct application in producing curls in hair by the permanent wave process. Disulfide bonds Figure **19.6.12** are formed by oxidation of the sulfhydryl groups on cysteine. Different protein chains or loops within a single chain are held together by the strong covalent disulfide bonds. The alpha-helices in the hair strands are bonded by disulfide links.



Figure **19.6.12** Disulfide bonds in hair.

In the permanent wave process, a basic reducing substance (usually ammonium thioglycolate) is first added to reduce and rupture some of the disulfide cross-links, see Figure **19.6.13** below.

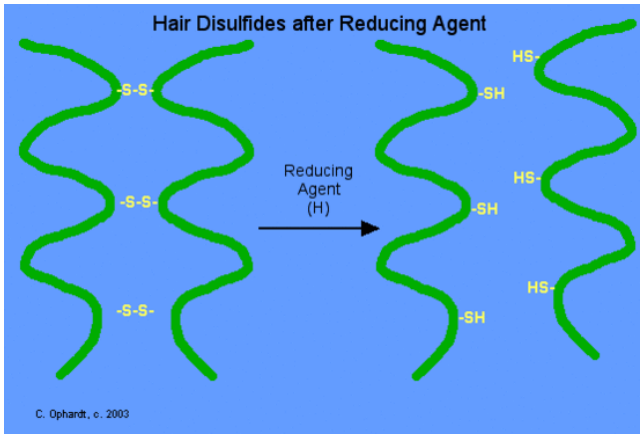


Figure **19.6.13** Addition of a reducing agent to disrupt the disulfide bonds.

The hair is put on rollers or curlers. Since the alpha-helices are no longer tightly cross-linked to each other, the alpha-helices can shift positions in relation to each other. An oxidizing agent, usually a dilute solution of hydrogen peroxide, (also called the neutralizer) is added to reform the disulfide bonds in their new positions (Figure **19.6.14**). The permanent will hold these new disulfide bond positions until the hair grows out, since new hair growth is of course not treated.

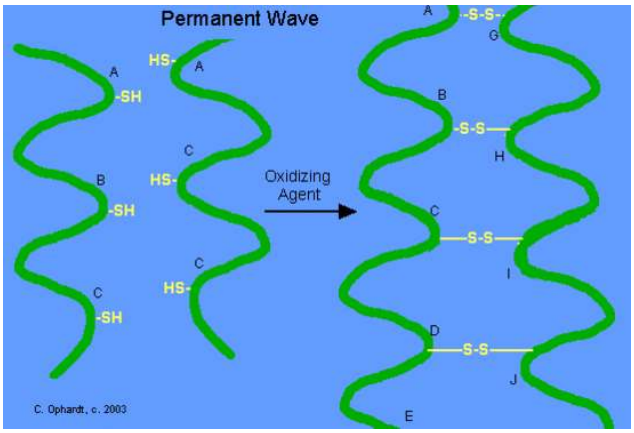


Figure **19.6.14** Addition of a oxidizing agent to reform disulfide bonds.

Hair spray

Hair spray is a common household aqueous solution which is used to stiffen hair into a certain style. It was first developed and manufactured in 1948 by Chase Products, based in Broadview, Illinois. Weaker than hair gel or hair wax, it is sprayed directly onto the hair to hold styles for long periods of time. It sprays evenly over the hair using a pump or aerosol spray nozzle. The product may leave hair feeling 'crunchy' unless brushed out.

The active ingredients in hair spray are called polymers, which keep the hair stiff and firm without snapping. Solvents, which make up most of the content of the hairspray, are responsible for carrying these polymers in a solution.

Originally, the solvent found in hair spray was a chlorofluorocarbon (CFC). CFCs are nontoxic, nonflammable, and make almost ideal aerosol propellants. However, when research concluded that CFCs cause destruction of stratospheric ozone, they were replaced with other solvents, such as alcohols and hydrocarbons.

Hair sprays consist of the following components: concentrate, plasticizers, luster agents, and fragrances, as well as propellants.

One of the polymers used in hair spray is polyvinylpyrrolidone (Figure **19.6.15**) , which is water-soluble. The non-water-soluble polymer polydimethylsiloxane is added to make the hold last a bit longer. Some less common polymers found in hair spray include copolymers with vinyl acetate and copolymers with maleic anhydride.

Figure **19.6.15** Polyvinylpyrrolidone *is a common component of hair spray that confers stiffness to hair.*

Some hair sprays use natural polymers and solvents like vegetable gums dissolved in alcohol. One popular ingredient in natural hair sprays is gum arabic, which is made from the sap of various species of the acacia tree. Gum tragacanth is another herbal gum that is used to stiffen calico and crepe, as well as hair.

Hair Removers

Depilation is the removal of the part of the hair above the surface of the skin. The most common form of depilation is shaving or trimming. Another option is the use of chemical depilatories, which work by breaking the disulfide bonds that link the protein chains that give hair its strength.

A **chemical depilatory** is a cosmetic preparation used to remove hair from the skin. Common active ingredients are salts of thioglycolic acid and thiolactic acids. These compounds break the disulfide bonds in keratin and also hydrolyze the hair so that it is easily removed. Formerly, sulfides such as strontium sulfide were used, but due to their unpleasant odor, they have been replaced by thiols.

The main chemical reaction effected by the thioglycolate is:

$2\ HSCH_2CO_2H$ (thioglycolic acid) + R-S-S-R (cystine) → HO_2CCH_2-S-S-CH_2CO_2H (dithiodiglycolic acid) + 2 RSH (cysteine)

Chemical depilatories contain 5–6% calcium thioglycolate in a cream base (to avoid runoff). Calcium hydroxide or strontium hydroxide maintain a pH of about 12. Hair destruction requires about 10 minutes. Depilation is followed by careful rinsing with

water, and various conditioners are applied to restore the skin's pH to normal. Depilation does not destroy the dermal papilla, and the hair grows back.

Chemical depilatories are available in gel, cream, lotion, aerosol, roll-on, and powder forms. Common brands include Nair, Magic Shave and Veet.

Depilatory ointments, or plasters, were known to Greek and Roman authors as *psilothrum*. In Jewish lore, King Solomon is said to have discovered a chemical depilatory made from a mixture of lime and water and orpiment (arsenic trisulfide).

Hair Restorers

Treatments for the various forms of hair loss have only moderate success. Three medications have evidence to support their use in male pattern hair loss: finasteride, dutasteride and minoxidil. They typically work better to prevent further hair loss than to regrow lost hair.

They may be used together when hair loss is progressive or further regrowth is desired after 12 months. Other medications include ketoconazole, and in female androgenic alopecia spironolactone and flutamide. Combinations of finasteride, minoxidil and ketoconazole are more effective than individual use.

Minoxidil is applied topically, is widely used for the treatment of hair loss. It may be effective in helping promote hair growth in both men and women with androgenic alopecia. About 40% of men experience hair regrowth after 3–6 months. It is the only topical product that is FDA approved in America for androgenic hair loss. However, increased hair loss has been reported.

Finasteride is used to treat male pattern hair loss. Treatment provides about 30% improvement in hair loss after six months of treatment, and effectiveness only persists as long as the drug is taken. There is no good evidence for its use in women. It may cause gynecomastia, erectile dysfunction and depression.

Dutasteride is used off label for male pattern hair loss.

There is tentative support for **spironolactopne** in women. Due to its feminising side effects and risk of infertility it is not often used by men. It can also cause low blood pressure, high blood potassium, and abnormal heart rhythms. Also, women who are pregnant or trying to become pregnant generally cannot use the medication as it is a teratogen, and can cause ambiguous genitalia in newborn children.

There is tentative evidence for **flutamide** in women; however, it is associated with relatively high rates of liver problems. Like spironolactone, it is typically only used by women.

Ketoconazole shampoo in conjunction with an oral 5α-reductase inhibitor such as finasteride or dutasteride has been used off label to treat androgenic alopecia.

Summary

- Various personal care products contain ingredients to protect the skin, protect the hair, promote hygiene, for aesthetic purposes etc.
- Temporary and permanent waves are formed due to the disruption and reformation of disulfide bonds in hair strands.

Contributors

- US FDA
- Elizabeth R. Gordon (Furman University)
- American Academy of Dermatology Association
- Libretext: Anatomy and Physiology 1 (Lumen)
- Libretext: Human Biology (Wakim and Grewal)
- Libretext: Supplemental Module (Biological Chemistry)
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- **5.5: The Basics of Skin Cancer** by Elizabeth Gordon is licensed CC BY-NC-SA 4.0.

CHAPTER OVERVIEW

20: Hazardous Materials

20.1: Natural Poisons and Food Poisoning
20.2: Poisons and How They Act
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20.4: The Lethal Dose
20.5: The Liver as a Detox Facility
20.6: Carcinogens and Teratogens
20.7: Hazardous Wastes

What is Toxicology?

Toxicology is traditionally defined as "the science of poisons." Over time, our understanding of how various agents can cause harm to humans and other organisms has increased, resulting in a more descriptive definition of toxicology as "the *study of the adverse effects of chemical, physical, or biological agents on living organisms and the ecosystem, including the prevention and amelioration of such adverse effects."*

These adverse effects can take many forms, ranging from immediate death to subtle changes not appreciated until months or years later. They may occur at various levels within the body, such as an organ, a type of cell, or a specific biochemical. Our understanding of how toxic agents damage the body has progressed along with medical knowledge. We now know that various observable changes in anatomic or bodily functions actually result from previously unrecognized changes in specific biochemicals in the body.

A poison is any substance that is harmful to your body. You might swallow it, inhale it, inject it, or absorb it through your skin. Any substance can be poisonous if too much is taken. Poisons can include

- Prescription or over-the-counter medicines taken in doses that are too high
- Overdoses of illegal drugs
- Carbon monoxide from gas appliances
- Household products, such as laundry powder or furniture polish
- Pesticides
- Indoor or outdoor plants
- Metals such as lead and mercury

The effects of poisoning range from short-term illness to brain damage, coma, and death. To prevent poisoning it is important to use and store products exactly as their labels say. Keep dangerous products where children can't get to them. Treatment for poisoning depends on the type of poison.

Sources

National Institute of Health (NIH) US National Library of Medicine

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20.1: Natural Poisons and Food Poisoning

Learning Objectives

- List different plant and animal poisons and their properties.
- List various causes of food poisoning.

In biology, **poisons** are substances that cause death, injury or harm to organs, usually by chemical reactions or other activity on the molecular scales, when an organism absorbs a sufficient quantity. The fields of medicine (particularly veterinary) and zoology often distinguish a poison from a toxin, and from a venom. Toxins are poisons produced by organisms in nature, and venoms are toxins injected by a bite or sting (this is exclusive to animals). The difference between venom and other poisons is the delivery method.

The **history of poison** stretches from before 4500 BCE to the present day. Poisons have been used for many purposes across the span of human existence, most commonly as weapons, anti-venoms, and medicines. Poison has allowed much progress in branches, toxicology, and technology, among other sciences.

Over the centuries, the variety of harmful uses of poisons continued to increase. The means for curing these poisons also advanced in parallel. In the modern world, intentional poisoning is less common than the Middle Ages. Rather, the more common concern is the risk of accidental poisoning from everyday substances and products.

Constructive uses for poisons have increased considerably in the modern world. Poisons are now used as pesticides, disinfectants, cleaning solutions, and preservatives. Nonetheless, poison continues to be used as a hunting tool in remote parts of developing countries, including Africa, South America, and Asia.

Poisonous Plants

Poisonous plants are plants that produce toxins that deter herbivores from consuming them. Plants cannot move to escape their predators, so they must have other means of protecting themselves from herbivorous animals. Some plants have physical defenses such as thorns, spines and prickles, but by far the most common type of protection is chemical. Over millennia, through the process of natural selection, plants have evolved the means to produce a vast and complicated array of chemical compounds in order to deter herbivores. Tannin, for example, is a defensive compound that emerged relatively early in the evolutionary history of plants, while more complex molecules such as polyacetylenes are found in younger groups of plants such as the Asterales. Many of the known plant defense compounds primarily defend against consumption by insects, though other animals, including humans, that consume such plants may also experience negative effects, ranging from mild discomfort to death. Several poisonous plants, the specific toxins and the poisonous effects are listed below.

Poison ivy (Figure **20.1.1**) - The poison Urushiol is an oily mixture of organic compounds with allergic properties. Symptoms of a reaction include itching, redness, swelling, and blisters. It is important to note that the blisters are not contagious.



Figure **20.1.1** Poison Ivy.

Western water hemlock (Figure **20.1.2**) - The toxin, cicutoxin and oenanthotoxin, are conjugated polyacetylenes. These unsaturated alcohols have a strong carrot-like odor and are noncompetitive antagonists for the gamma-aminocutyric acid (GABA) neural transmitter in the central nervous system. GABA role is to inhibit neuron excitability; essentially it has a relaxing function. Blocking this results in convulsing and grand mal seizures and eventually death can occur.



Figure **20.1.2** Western water hemlock.

Autumn skullcap - The toxin amatoxin in the form of γ-amanitin, β-amanitin, and α-amanitin causes severe abdominal pain, vomiting, and diarrhea may last for six-nine hours. The toxins affect the liver, results in gastrointestinal bleeding, coma, kidney failure, or even death, within seven days of consumption

Henbane - The toxins in this plant are atropine and scopolamine, found in leaves. Apoatropine and cuscohygrine are the main alkaloids of the root. The main alkaloid in seeds is hyoscyamine, little hyoscine and little atropine. the plant is toxic to cattle, wild animals, fish, and birds. Pigs are immune. In humans, it could cause hallucinations, dilated pupils, restlessness, fast heart, seizure, vomiting, high blood pressure, and ataxia. Initial effects last for 3-4 hours, after effects last up to three days.

Oak - Tannic acid, binds and precipitates proteins. Cattle, sheep, horses and goats are most affected while pigs are immune. In humans, Tannic acid poisoning could cause anorexia, depression, constipation, diarrhea, blood in urine. Signs typically occur around 3-7 days after consumption, with

The links below are an extensive, if incomplete, list of plants containing one or more poisonous parts that pose a serious risk of illness, injury, or death to humans or domestic animals. There is significant overlap between plants considered poisonous and those with psychotropic properties, some of which are toxic enough to present serious health risks at recreational doses. There is a distinction between plants that are poisonous because they naturally produce dangerous phytochemicals, and those that may become dangerous for other reasons, including but not limited to infection by bacterial, viral, or fungal parasites; the uptake of toxic compounds through contaminated soil or groundwater; and/or the ordinary processes of decay after the plant has died; this list deals exclusively with plants that produce phytochemicals. Many plants, such as peanuts, produce compounds that are only dangerous to people who have developed an allergic reaction to them, and with a few exceptions, those plants are not included here (see list of allergens instead). Despite the wide variety of plants considered poisonous, human fatalities caused by poisonous plants – especially resulting from accidental ingestion – are rare in the developed world.

WEB LINK

A more extensive list of poisonous plants can be found on the link below.

https://en.Wikipedia.org/wiki/List_o...isonous_plants

Poisonous Animals

Several deadly poisons are from snakes and spiders. Several poisonous animals, the specific toxins and the poisonous effects are listed below.

Timber rattlesnake - There are 4 types of toxin. Type A : A neurotoxin known as canebrake. Type B : A hemorrhagic and proteolytic toxin. Type A + B: Intergrade between snakes with Type A and Type B. Type C : relatively weak. The toxins could cause myokymia, defibrination syndrome, numbness, lightheadedness, weakness, vomiting, blurred vision, sweating, salivating. It can be treated with CroFab Antivenom.

Eastern coral snake (Figure **20.1.3**).- Phospholipase A2 and three-finger toxins (abbreviated as 3FTx). 3FTx proteins are neurotoxins, attacking nerve tissue. Phospholipase A2 can cause inflammation and pain at the site of the bite, though this is uncommon. The toxins could also cause slurred speech, double vision, muscle paralysis, and can lead to cardiac arrest if left untreated.



Figure **20.1.3** *The eastern coral snake*

Cotton mouth snake - Cotton mouth toxins mainly consist of three protein families: phospholipase A2 (PLA2), metalloproteases (SVMP), and serine proteases (SVSP). PLA2s are responsible for inflammation and pain, while SVMPs are responsible for hemorrhage and SVSPs affect the coagulation of blood. The poison could lead to low blood pressure, weakness, change in skin color at site of bite, trouble breathing, nausea, increase in heart rate.

Black widow spider (Figure **20.1.4**) - Latrotoxins are the main component of the venom, but other compounds such as polypeptides, adenosine, and guanosine are active as well. Only the bite of the female is dangerous to humans, as their venom glands are very large. The toxin can cause pain and sweating at the site of the bite, muscle cramps, headache, nausea, vomiting, weakness. Typically only localized pain is felt, but in some cases the pain can spread. Symptoms typically last from 3-7 days after the bite takes place.

Brown recluse spider - Brown recluse venom possesses potentially deadly hemotoxins and cytotoxins that affect the red blood cells and their ability to clot. It is a mixture of enzymes such as collagenase, protease, and phospholipase. Symptoms include redness, fever, weakness, pain and nausea. In around 10% of victims necrosis can occur at the site of the bite, and in even fewer cases hemolysis (bursting of red blood cells) can occur.



Figure **20.1.4** *Western black widow.*

Other Poisonous Animals

The list below is a partial list of animals that are poisonous to humans (and other animals), or put another way, their flesh is toxic if consumed, or in some cases touched:

Birds: Pitohui, Blue-capped ifrit, Little shrikethrush, Spur-winged goose[1] (diet-dependent), and Common quail (diet-dependent)

Snakes: Rhabdophis keelback snakes and Garter snake (diet-dependent, when feeding on Pacific newts)[2]

Frogs and toads: American toad, Asiatic toad, Cane toad, Colorado River toad, Common toad, Corroboree frog, European green toad, Fowler's toad, Mantella, and poison dart frog (Figure **20.1.5**).



Figure 20.1.5 *Poison dart frogs are well known for their brightly colored skin, which serves as a warning to predators of their toxicity.*

Salamanders: Pacific newts

Fish: Tetraodontidae (Blowfish, Pufferfish), Greenland shark, and Barracuda (age and diet dependent)

Cephalophods: Blue-ringed octopus and Pfeffer's flamboyant cuttlefish

Insects: Blister beetle, Birdwings, Milkweed butterfly, Battus (butterfly), Diamphidia, and Monarch (butterfly)

Food Poisoning

Foodborne illness (also **foodborne disease** and colloquially referred to as **food poisoning**)[1] is any illness resulting from the spoilage of contaminated food, pathogenic bacteria, viruses, or parasites that contaminate food,[2] as well as toxins such as poisonous mushrooms and various species of beans that have not been boiled for at least 10 minutes.

Many different disease-causing germs (Figure 20.1.6 below) can contaminate foods, so there are many different foodborne infections. The US CDC estimates that each year 48 million people get sick from a foodborne illness, 128,000 are hospitalized, and 3,000 die. Researchers have identified more than 250 foodborne diseases. Most of them are infections, caused by a variety of bacteria, viruses, and parasites. Harmful toxins and chemicals also can contaminate foods and cause foodborne illness.

Although anyone can get a foodborne illness, some people are more likely to develop one. Those groups include Pregnant women, Young children, Older adults, People with immune systems weakened from medical conditions, such as diabetes, liver disease, kidney disease, organ transplants, HIV/AIDS, or from receiving chemotherapy or radiation treatment. Most people with a foodborne illness get better without medical treatment, but people with severe symptoms should see their doctor.

Food Poisoning Symptoms

Common symptoms of foodborne diseases are nausea, vomiting, stomach cramps, and diarrhea. However, symptoms may differ among the different types of foodborne diseases. Symptoms can sometimes be severe and some foodborne illnesses can even be life-threatening. Most people have only mild illnesses, lasting a few hours to several days. However, some people need to be hospitalized, and some illnesses result in long-term health problems or even death. Infections transmitted by food can result in chronic arthritis, brain and nerve damage, and hemolytic uremic syndrome (HUS), which causes kidney failure.

Food poisoning symptoms may range from mild to severe and may differ depending on the germ you swallowed (see Table 20.1.1 below). After you consume a contaminated food or drink, it may take hours or days before you develop symptoms. See your doctor or healthcare provider if you have symptoms that are severe, including:

- High fever (temperature over 101.5°F, measured orally)
- Blood in stools
- Frequent vomiting that prevents keeping liquids down (which can lead to dehydration)
- Signs of dehydration, including a marked decrease in urination, a very dry mouth and throat, or feeling dizzy when standing up.
- Diarrhea that lasts more than 3 days

The top five germs that cause illnesses from food eaten in the United States are *Norovirus, Salmonella, Clostridium perfringens, Campylobacter, and Staphylococcus aureus (Staph).*

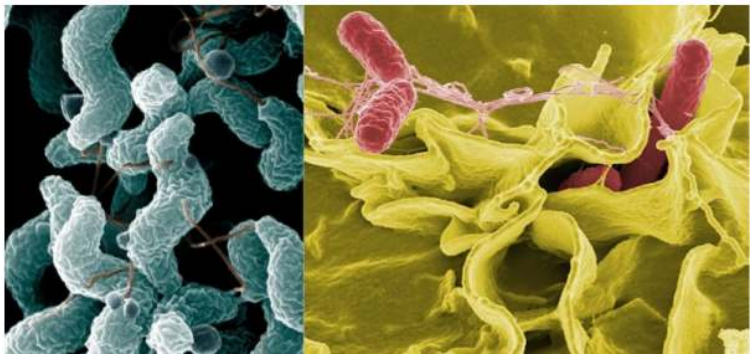
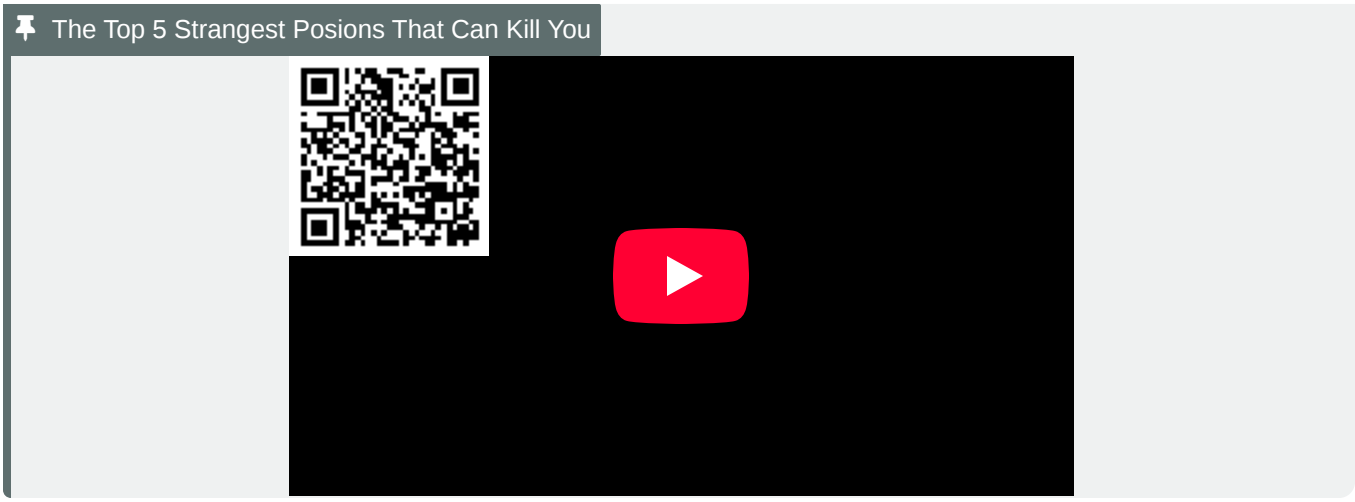


Figure **20.1.6** Campylobacter (left) , a bacteria that is a major cause of food poisoning and Salmonella (right). Images used with permission (Public Domain; De Wood, Pooley, USDA (left) and Rocky Mountain Laboratories, NIAID, NIH).

Some other germs don't cause as many illnesses, but when they do, the **illnesses are more likely to lead to hospitalizatio**n. Those germs include *Clostridium botulinum* (botulism), *Listeria, Escherichia coli (E. coli), and Vibrio.*

Table **20.1.1** Symptoms and Sources of 10 Foodborne Germs

Germ and Typical Time for Symptoms to Appear	Typical Signs and Symptoms	Common Food Sources
Campylobacter 2 – 5 days	Diarrhea (often bloody), stomach cramps/pain, fever	Raw or undercooked poultry, raw (unpasteurized) milk, and contaminated water
Clostridium botulinum 18 – 36 hours	Double or blurred vision, drooping eyelids, slurred speech. Difficulty swallowing, breathing and dry mouth. Muscle weakness and paralysis. Symptoms start in the head and move down as severity increases	Improperly canned or fermented foods, usually homemade. Prison-made illicit alcohol.
Clostridium perfringens 6 – 24 hours	Diarrhea, stomach cramps. Vomiting and fever are uncommon. Usually begins suddenly and lasts for less than 24 hours	Beef or poultry, especially large roasts; gravies; dried or precooked foods
Cyclospora 1 week	Watery diarrhea, loss of appetite and weight loss. Stomach cramps/pain, bloating, increased gas, nausea, and fatigue.	Raw fruits or vegetables, and herbs
Escherichia coli 3 – 4 days	Severe stomach cramps, diarrhea (often bloody), and vomiting. Around 5-10% of people diagnosed with this infection develop a life-threatening complication.	Raw or undercooked ground beef, raw (unpasteurized) milk and juice, raw vegetables (such as lettuce), and raw sprouts, contaminated water
Listeria 1 – 4 weeks	Pregnant women typically experience fever and other flu-like symptoms, such as fatigue and muscle aches. Infections during pregnancy can lead to serious illness or even death in newborns. Other people (most often older adults): headache, stiff neck, confusion, loss of balance and convulsions in addition to fever and muscle aches.	Raw (unpasteurized) milk, soft cheeses made with raw milk, raw sprouts, melons, hot dogs, pâtés, lunch meats, and cold cuts, smoked seafood
Norovirus 12 – 48 hours	Diarrhea, nausea/stomach pain, vomiting	Infected person, contaminated food like leafy greens, fresh fruits, shellfish (such as oysters), or water, or by touching contaminated surfaces
Salmonella 12 – 72 hours	Diarrhea, fever, stomach cramps, vomiting	Eggs, raw or undercooked poultry or meat, unpasteurized milk or juice, cheese, raw fruits and vegetables
Staphylococcus aureus (Staph) 30 minutes – 6 hours	Diarrhea, nausea, stomach cramps, vomiting	Foods that are handled by people and not cooked (sliced meat, puddings, pastries, and sandwiches). Raw (unpasteurized) milk and cheese made from it.
Vibrio 1 – 4 days	Watery diarrhea, nausea. stomach cramps, vomiting, fever, chills	Raw or undercooked shellfish, particularly oysters



***Video* 20.1.1** *Strange poisons.*

Summary

- Various plants produce toxins that could be lethal or cause allergic reactions in herbivores. A few examples of poisonous plants include poison ivy, western water hemlock, autumn skullcap, henbane, oak, etc.
- Several deadly poisons come from snakes and spiders. Various birds, fishes, frogs, insects, etc. are deadly when consumed or touched due to their toxic flesh.
- The top five germs that cause illnesses from food eaten in the United States are *Norovirus, Salmonella, Clostridium perfringens, Campylobacter, and Staphylococcus aureus (Staph).*

Contributors

- Wikipedia
- Scioly.org
- USDA Agricultural Service
- US Center for Disease Control
- Libretexts: Nutrition (Coppola)
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20.2: Poisons and How They Act

Learning Objective

- Describe the modes of action and treatments for different poisons.

Corrosive Substances

A **corrosive substance** is one that will damage or destroy other substances with which it comes into contact by means of a chemical reaction. Corrosives are different from ***poisons*** in that corrosives are immediately dangerous to the tissues they contact, whereas poisons may have systemic toxic effects that require time to become evident. Colloquially, corrosives may be called *poisons* but the concepts are technically distinct. However, there is nothing which precludes a corrosive from being a poison; there are substances that are both corrosives and poisons.

There are several household products that contain chemical substances which are considered highly reactive and thus are very dangerous upon ingestion or skin contact. Chemical poisoning with corrosive agents occurs by ingestion of: acids (hydrochloric, nitric, sulfuric, perchloric, chloric), alkalis (sodium and potassium, soaps, detergents), heavy metal salts (sublimate), strong oxidizing agents, formalin, iodine tincture and many other chemical substances. Strong acids or bases, readily decomposes proteins and lipids through amide and ester hydrolysis upon contact with living tissues, such as skin and flesh.

Oxidizing Agents as Poisons

Household cleaning products with strong oxidizing agents like **sodium hypochlorite** (NaOCl) and **hydrogen peroxide** (H_2O_2) are dangerous when ingested. Generally speaking, the ingestion of bleaches (Figure **20.2.2**) will cause damage to the esophagus and stomach, possibly leading to death. On contact with the skin or eyes, it causes irritation, drying, and potentially burns. Inhalation of bleach fumes can damage the lungs. Personal protective equipment should always be used when using bleach. Bleach should never be mixed with vinegar or other acids as this will create highly toxic chlorine gas and can cause severe burns internally and externally. Mixing bleach with ammonia similarly produces toxic chloramine gas, which can burn the lungs. Mixing bleach with hydrogen peroxide results in an exothermic chemical reaction that releases oxygen, and may cause the contents to splatter and cause skin and eye injury. Heating bleach and boiling it may produce chlorates, a strong oxidizer which may lead to a fire or explosion.



Figure **20.2.1** Clorox bleach. Source: Wikipedia.

Ozone. For the last few decades, scientists studied the effects of acute and chronic ozone exposure on human health. Hundreds of studies suggest that ozone is harmful to people at levels currently found in urban areas. Ozone has been shown to affect the respiratory, cardiovascular and central nervous system. Early death and problems in reproductive health and development are also shown to be associated with ozone exposure.

Acute ozone exposure ranges from hours to a few days. Because ozone is gas, it directly affects the lungs and the entire respiratory system. Inhaled ozone causes inflammation and acute -but reversible- changes in lung function, as well as airway hyperresponsiveness. These changes lead to shortness of breath, wheezing, and coughing which may exacerbate lung diseases, like asthma or chronic obstructive pulmonary disease (COPD) resulting in the need to receive medical treatment. Acute and chronic exposure to ozone has been shown to cause an increased risk of respiratory infections, due to the following mechanism.

Multiple studies have been conducted to determine the mechanism behind ozone's harmful effects, particularly in the lungs. These studies have shown that exposure to ozone causes changes in the immune response within the lung tissue, resulting in disruption of both the innate and adaptive immune response, as well as altering the protective function of lung epithelial cells. It is thought that these changes in immune response and the related inflammatory response are factors that likely contribute to the increased risk of lung infections, and worsening or triggering of asthma and reactive airways after exposure to ground-level ozone pollution.

Inhaling ozone not only affects the immune system and lungs, but it may also affect the heart as well. Ozone causes short-term autonomic imbalance leading to changes in heart rate and reduction in heart rate variability; and high levels exposure for as little as one-hour results in a supraventricular arrhythmia in the elderly, both increase the risk of premature death and stroke. Ozone may also lead to vasoconstriction resulting in increased systemic arterial pressure contributing to increased risk of cardiac morbidity and mortality in patients with pre-existing cardiac diseases.

Metabolic Poisons

Carbon monoxide and cyanide are chemical substances that interfere with the normal bodily functions i.e. during the delivery of oxygen to bodily tissues and cellular respiration.

Carbon Monoxide Poisoning

Carbon monoxide poisoning typically occurs from breathing in carbon monoxide (CO) at excessive levels. Symptoms (Figure **20.2.2**) are often described as "flu-like" and commonly include headache, dizziness, weakness, vomiting, chest pain, and confusion. Large exposures can result in loss of consciousness, arrhythmias, seizures, or death. The classically described "cherry red skin" rarely occurs. Long-term complications may include chronic fatigue, trouble with memory, and movement problems.

CO is a colorless and odorless gas which is initially non-irritating. It is produced during incomplete burning of organic matter. This can occur from motor vehicles, heaters, or cooking equipment that run on carbon-based fuels. Carbon monoxide primarily causes adverse effects by combining with hemoglobin to form carboxyhemoglobin (HbCO) preventing the blood from carrying oxygen and expelling carbon dioxide as carbaminohemoglobin. Additionally, many other hemoproteins such as myoglobin, Cytochrome P450, and mitochondrial cytochrome oxidase are affected, along with other metallic and non-metallic cellular targets.

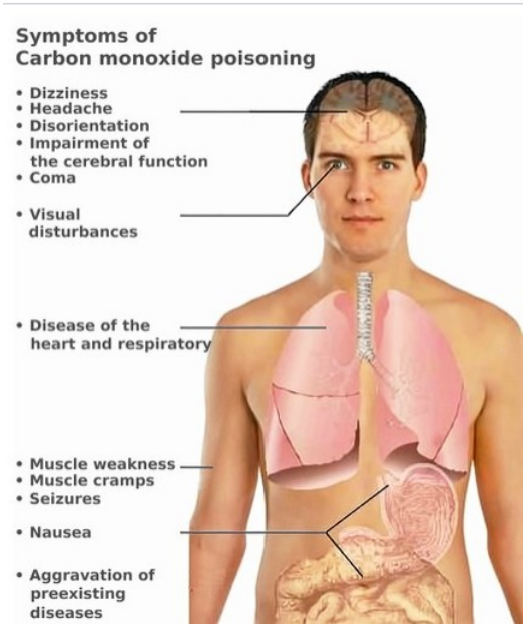


Figure **20.2.2** CO toxicity symptoms. Source: Wikipedia.

Initial treatment for carbon monoxide poisoning is to immediately remove the person from the exposure without endangering further people. Those who are unconscious may require CPR on site. Administering oxygen via non-rebreather mask shortens the half-life of carbon monoxide from 320 minutes, when breathing normal air, to only 80 minutes. Oxygen hastens the dissociation of carbon monoxide from carboxyhemoglobin, thus turning it back into hemoglobin. Due to the possible severe effects in the baby, pregnant women are treated with oxygen for longer periods of time than non-pregnant people.

Cyanide Poisoning

Cyanide poisoning is poisoning that results from exposure to a number of forms of cyanide. Early symptoms include headache, dizziness, fast heart rate, shortness of breath, and vomiting. This may then be followed by seizures, slow heart rate, low blood pressure, loss of consciousness, and cardiac arrest. Onset of symptoms is usually within a few minutes. If a person survives, there may be long-term neurological problems.

Toxic cyanide-containing compounds include hydrogen cyanide gas and a number of cyanide salts. Poisoning is relatively common following breathing in smoke from a house fire. Other potential routes of exposure include workplaces involved in metal polishing, certain insecticides, and the medication nitroprusside. Liquid forms of cyanide can be absorbed through the skin. Cyanide ions interfere with cellular respiration, resulting in the body's tissues being unable to use oxygen.

In addition to its uses as a pesticide and insecticide, cyanide is contained in tobacco smoke and smoke from building fires, and is present in many seeds or kernels such as those of almonds, apricots, apples, oranges, and in foods including cassava (also known as tapioca, yuca or manioc), and bamboo shoots. Vitamin B12, in the form of hydroxocobalamin (also spelled hydroxycobalamin), may reduce the negative effects of chronic exposure, and a deficiency can lead to negative health effects following exposure. Flaxseed also contains cyanogenic glycosides.

Cyanide is a potent cytochrome *c* oxidase (COX, a.k.a Complex IV) inhibitor. As such, cyanide poisoning is a form of histotoxic hypoxia, because it interferes with an essential step in aerobic metabolism called oxidative phosphorylation.

The United States standard cyanide antidote kit first uses a small inhaled dose of amyl nitrite, followed by intravenous sodium nitrite, followed by intravenous sodium thiosulfate. Hydroxocobalamin is newly approved in the US and is available in Cyanokit antidote kits. Sulfanegen TEA, which could be delivered to the body through an intra-muscular (IM) injection, detoxifies cyanide and converts the cyanide into thiocyanate, a less toxic substance. Alternative methods of treating cyanide intoxication are used in other countries.

Arsenic Poisoning

Arsenic poisoning is a medical condition that occurs due to elevated levels of arsenic in the body. If arsenic poisoning occurs over a brief period of time, symptoms may include vomiting, abdominal pain, encephalopathy, and watery diarrhea that contains blood. Long-term exposure can result in thickening of the skin, darker skin, abdominal pain, diarrhea, heart disease, numbness, and cancer.

The most common reason for long-term exposure is contaminated drinking water. Groundwater most often becomes contaminated naturally; however, contamination may also occur from mining or agriculture. It may also be found in the soil and air. Recommended levels in water are less than 10–50 µg/L (10–50 parts per billion). Other routes of exposure include toxic waste sites and traditional medicines. Most cases of poisoning are accidental. Arsenic acts by changing the functioning of around 200 enzymes. Diagnosis is by testing the urine, blood, or hair.

Prevention is by using water that does not contain high levels of arsenic. This may be achieved by the use of special filters or using rainwater. There is not good evidence to support specific treatments for long-term poisoning. For acute poisonings treating dehydration is important. Dimercaptosuccinic acid (DMSA) or dimercaptopropane sulfonate (DMPS) may be used while dimercaprol (BAL) is not recommended. Hemodialysis may also be used.

WEBLINK

More Information on arsenic can be found on the link below

https://www.niehs.nih.gov/health/topics/agents/arsenic/index.cfm

Heavy Metal Poisoning

Lead poisoning, also known as **plumbism** and **saturnism**, is a type of metal poisoning caused by lead in the body. The brain is the most sensitive. Symptoms may include abdominal pain, constipation, headaches, irritability, memory problems, infertility, and tingling in the hands and feet. It causes almost 10% of intellectual disability of otherwise unknown cause and can result in behavioral problems. Some of the effects are permanent. In severe cases, anemia, seizures, coma, or death may occur.

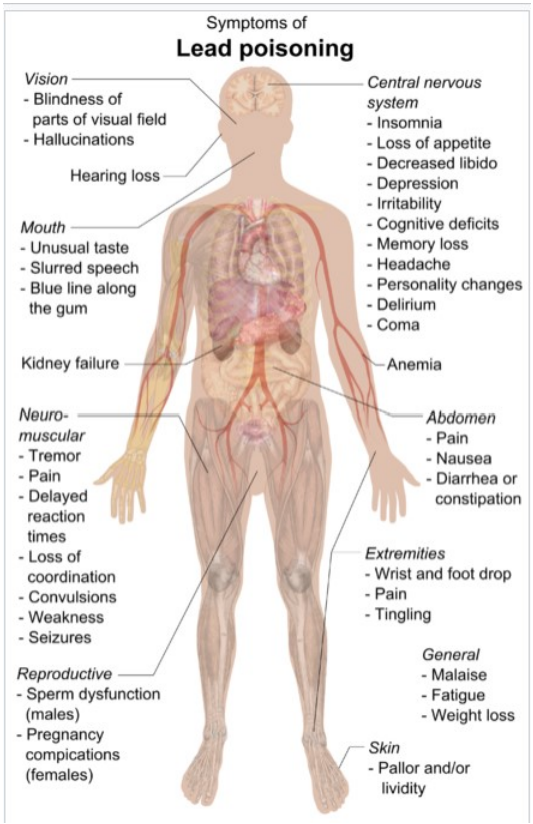


Figure **20.2.3**. Symptoms of lead poisoning. SOurce: Wikipedia.

Exposure to lead can occur by contaminated air, water, dust, food, or consumer products. Children are at greater risk as they are more likely to put objects in their mouth such as those that contain lead paint and absorb a greater proportion of the lead that they eat. Exposure at work is a common cause of lead poisoning in adults with certain occupations at particular risk. Diagnosis is typically by measurement of the blood lead level. The Centers for Disease Control (US) has set the upper limit for blood lead for adults at 10 µg/dl (10 µg/100 g) and for children at 5 µg/dl. Elevated lead may also be detected by changes in red blood cells or dense lines in the bones of children as seen on X-ray.

Lead has no known physiologically relevant role in the body, and its harmful effects are myriad. Lead and other heavy metals create reactive radicals which damage cell structures including DNA and cell membranes. Lead also interferes with DNA transcription, enzymes that help in the synthesis of vitamin D, and enzymes that maintain the integrity of the cell membrane. Anemia may result when the cell membranes of red blood cells become more fragile as the result of damage to their membranes. Lead interferes with metabolism of bones and teeth and alters the permeability of blood vessels and collagen synthesis. Lead may also be harmful to the developing immune system, causing production of excessive inflammatory proteins; this mechanism may mean that lead exposure is a risk factor for asthma in children. Lead exposure has also been associated with a decrease in activity of immune cells such as polymorphonuclear leukocytes. Lead also interferes with the normal metabolism of calcium in cells and causes it to build up within them.

Lead poisoning is preventable. This includes individual efforts such as removing lead-containing items from the home, workplace efforts such as improved ventilation and monitoring, state laws that ban the use of and national policies such as laws that ban lead in products such as paint, gasoline, ammunition, wheel weights, and fishing weights reduce allowable levels in water or soil, and provide for cleanup of contaminated soil. Workers' education could be helpful as well. The major treatments are removal of the source of lead and the use of medications that bind lead so it can be eliminated from the body, known as chelation therapy. Chelation therapy in children is recommended when blood levels are greater than 40–45 µg/dl. Medications used include dimercaprol, edetate calcium disodium, and succimer.

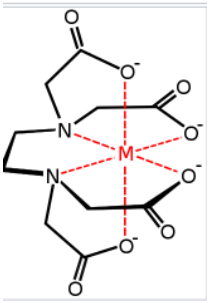


Figure **20.2.4** EDTA, a chelating agent, binds a heavy metal, sequestering it.

WEBLINKS

Links to various lead and mercury related topics can be found below

https://medlineplus.gov/leadpoisoning.html

https://medlineplus.gov/mercury.html

Mercury poisoning is a type of metal poisoning due to exposure to mercury. Symptoms depend upon the type, dose, method, and duration of exposure. They may include muscle weakness, poor coordination, numbness in the hands and feet, skin rashes, anxiety, memory problems, trouble speaking, trouble hearing, or trouble seeing. High-level exposure to methylmercury is known as Minamata disease. Methylmercury exposure in children may result in acrodynia (pink disease) in which the skin becomes pink and peels. Long-term complications may include kidney problems and decreased intelligence. The effects of long-term low-dose exposure to methylmercury are unclear.

Forms of mercury exposure include metal, vapor, salt, and organic compound. Most exposure is from eating fish, amalgam based dental fillings, or exposure at work. In fish, those higher up in the food chain generally have higher levels of mercury. Less commonly, poisoning may occur as a method of attempted suicide. Human activities that release mercury into the environment include the burning of coal and mining of gold. Tests of the blood, urine, and hair for mercury are available but do not relate well to the amount in the body.

The primary mechanism of mercury toxicity involves its irreversible inhibition of selenoenzymes, such as thioredoxin reductase. High mercury exposures deplete the amount of cellular selenium available for the biosynthesis of thioredoxin reductase and other selenoenzymes that prevent and reverse oxidative damage, which, if the depletion is severe and long lasting, results in brain cell dysfunctions that can ultimately cause death.

Prevention includes eating a diet low in mercury, removing mercury from medical and other devices, proper disposal of mercury, and not mining further mercury. In those with acute poisoning from inorganic mercury salts, chelation with either dimercaptosuccinic acid (DMSA) or dimercaptopropane sulfonate (DMPS) appears to improve outcomes if given within a few hours of exposure. Chelation for those with long-term exposure is of unclear benefit.

Cadmium poisoning. Cadmium is a naturally occurring toxic metal with common exposure in industrial workplaces, plant soils, and from smoking. Due to its low permissible exposure in humans, overexposure may occur even in situations where trace quantities of cadmium are found. Cadmium is used extensively in electroplating, although the nature of the operation does not generally lead to overexposure. Cadmium is also found in some industrial paints and may represent a hazard when sprayed. Operations involving removal of cadmium paints by scraping or blasting may pose a significant hazard. The primary use of cadmium is in the manufacturing of NiCd rechargeable batteries. The primary source for cadmium is as a byproduct of refining zinc metal. Exposures to cadmium are addressed in specific standards for the general industry, shipyard employment, the construction industry, and the agricultural industry.

Acute exposure to cadmium fumes may cause flu-like symptoms including chills, fever, and muscle ache sometimes referred to as "the cadmium blues." Symptoms may resolve after a week if there is no respiratory damage. More severe exposures can cause tracheo-bronchitis, pneumonitis, and pulmonary edema. Symptoms of inflammation may start hours after the exposure and include cough, dryness and irritation of the nose and throat, headache, dizziness, weakness, fever, chills, and chest pain.

Inhaling cadmium-laden dust quickly leads to respiratory tract and kidney problems which can be fatal (often from kidney failure). Ingestion of any significant amount of cadmium causes immediate poisoning and damage to the liver, bones, and the kidneys. Compounds containing cadmium are also carcinogenic.

Summary

- Corrosive poisons are chemicals (that can be found in many household products) that are considered highly reactive and thus are very dangerous upon ingestion or skin contact.
- Metabolic poisons such as carbon monoxide and cyanide interfere with the bodily functions.
- Human exposure to lead, mercury, and cadmium have affected the nervous system, respiratory system, brain, and other various organs.

Contributors

- Marisa Alviar-Agnew (Sacramento City College)

- Wikipedia
- US NIH MedlinePlus
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- Robert J. Lancashire (University of West Indies-Mona)

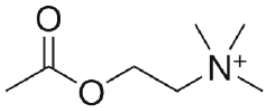
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20.3: More Chemistry of the Nervous System

Learning Objectives

- Describe the overall mechanism of neurotransmission.
- Describe how various nerve agents interrupt the neurotransmission process.

Acetylcholine is an organic chemical that functions in the brain and body of many types of animals, including humans, as a neurotransmitter—a chemical released by nerve cells to send signals to other cells. Its name is derived from its chemical structure: it is an ester of acetic acid and choline. Parts in the body that use or are affected by acetylcholine are referred to as cholinergic. Substances that interfere with acetylcholine activity are called anticholinergics.



Acetylcholine: The chemical structure of acetylcholine is depicted.

Acetylcholine is the neurotransmitter used at the neuromuscular junction—in other words, it is the chemical that motor neurons of the nervous system release in order to activate muscles. This property means that drugs that affect cholinergic systems can have very dangerous effects ranging from paralysis to convulsions. Acetylcholine is also used as a neurotransmitter in the autonomic nervous system, both as an internal transmitter for the sympathetic nervous system and as the final product released by the parasympathetic nervous system.

In the brain, acetylcholine functions as a neurotransmitter and as a neuromodulator. The brain contains a number of cholinergic areas, each with distinct functions. They play an important role in arousal, attention, memory and motivation.

Mechanism of Action

When a normally functioning motor nerve is stimulated, it releases the neurotransmitter acetylcholine, which transmits the impulse to a muscle or organ.

1. During neurotransmission (Figure **20.3.1**), ACh is released from the presynaptic neuron into the synaptic cleft and binds to ACh receptors on the post-synaptic membrane, relaying the signal from the nerve.

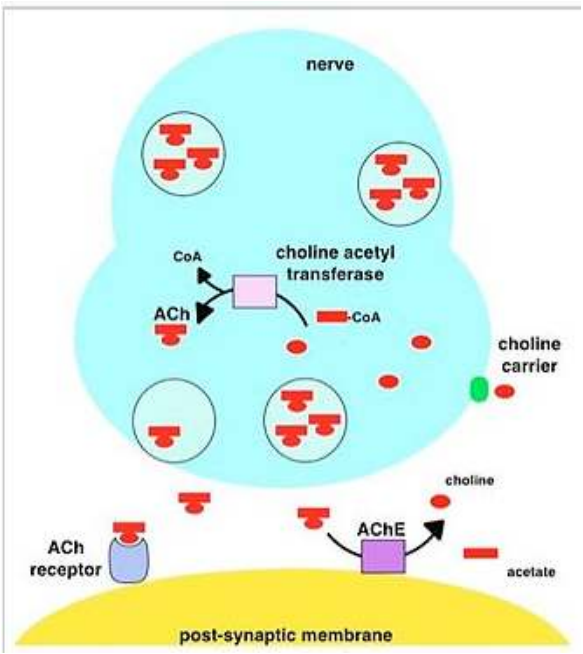


Figure **20.3.1** Different steps during neurotransmission.

2. AChE, also located on the post-synaptic membrane, terminates the signal transmission by hydrolyzing ACh (Figure **20.3.2**). Source: Wikipedia.

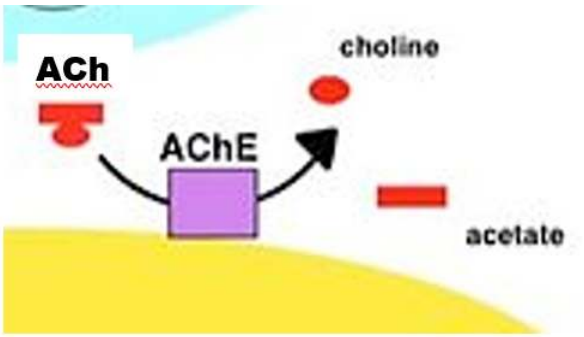


Figure **20.3.2** Acetylcholinesterase (AChe) breaks down acetylcholine (ACh) to choline and acetate (acetic acid). Source: Wikipedia.

3. The liberated choline is taken up again by the pre-synaptic neuron and ACh is synthesized by combining with acetyl-CoA through the action of choline acetyltransferase.[19][20]

Nerve Poisons and the Acetylcholine Cycle

Botulinum toxin (**Botox**) is a neurotoxic protein produced by the bacterium *Clostridium botulinum* and related species.[1] It prevents the release of the neurotransmitter acetylcholine from axon endings at the neuromuscular junction and thus causes flaccid paralysis.[2]The toxin causes the disease botulism. The toxin is also used commercially for medical and cosmetic purposes.

Foodborne botulism can be transmitted through food that has not been heated correctly prior to being canned, or food from a can that has not been cooked correctly. Most infant botulism cases cannot be prevented because the bacteria that cause this disease are in soil and dust. The bacteria can also be found inside homes on floors, carpet, and countertops, even after cleaning. Honey can contain the bacteria that cause infant botulism, so children less than 12 months old should not be fed honey.

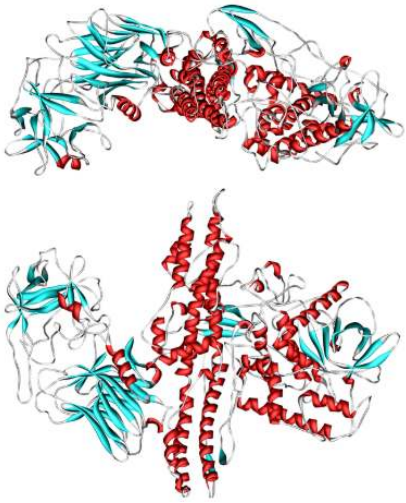


Figure **20.3.3** *Structure of Botulinum toxin.*

Curare is a generic term for various South American arrow poisons. The main active ingredient in curare is d-tubocurarine (Figure **20.3.4**), which has the chemical structure shown below.

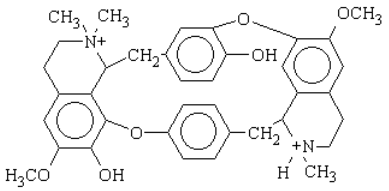


Figure 20.3.4 *Structure of d-tubocurarine.*

In brief, d-tubocurarine, blocks competitively the transmitter action of acetylcholine. When the drug is applied directly to the end-plate of a single isolated muscle fiber under microscopic control, the muscle cell becomes insensitive to motor-nerve impulses and to direct applied acetylcholine; however, the end -plate region and the remainder of the muscle fiber membrane retain their normal sensitivity to the application of potassium ions, and the muscle fiber still responds to direct electrical stimulation. Because acetylcholine release into the neuromuscular junction muscle is what initiates contraction, curare causes muscle relaxation and paralysis.

Nerve agents, sometimes also called **nerve gases**, are a class of organic chemicals that disrupt the mechanisms by which nerves transfer messages to organs. The disruption is caused by the blocking of acetylcholinesterase (AChE), an enzyme that catalyzes the breakdown of acetylcholine, a neurotransmitter. Nerve agents are acetylcholinesterase inhibitors used as poison.

Poisoning by a nerve agent leads to constriction of pupils, profuse salivation, convulsions, and involuntary urination and defecation, with the first symptoms appearing in seconds after exposure. Death by asphyxiation or cardiac arrest may follow in minutes due to the loss of the body's control over respiratory and other muscles. Some nerve agents are readily vaporized or aerosolized, and the primary portal of entry into the body is the respiratory system. Nerve agents can also be absorbed through the skin, requiring that those likely to be subjected to such agents wear a full body suit in addition to a respirator.

Nerve agents are generally colorless to amber-colored, tasteless liquids that may evaporate to a gas. Agents Sarin and VX are odorless; Tabun has a slightly fruity odor and Soman has a slight camphor odor.

Organophosphorous Compounds as Insecticides and Weapons of War

This first class of nerve agents, the G-series, was accidentally discovered in Germany on December 23, 1936, by a research team headed by Gerhard Schrader working for IG Farben. Since 1934, Schrader had been working in a laboratory in Leverkusen to develop new types of insecticides for IG Farben. While working toward his goal of improved insecticide, Schrader experimented with numerous compounds, eventually leading to the preparation of tabun (GA).

In experiments, tabun was extremely potent against insects: as little as 5 ppm of tabun killed all the leaf lice he used in his initial experiment. In January 1937, Schrader observed the effects of nerve agents on human beings first-hand when a drop of tabun spilled onto a lab bench. Within minutes he and his laboratory assistant began to experience miosis (constriction of the pupils of the eyes), dizziness and severe shortness of breath. It took them three weeks to recover fully. The G-series naming system was created by the United States when it uncovered the German activities, labeling (Figure 20.3.5.

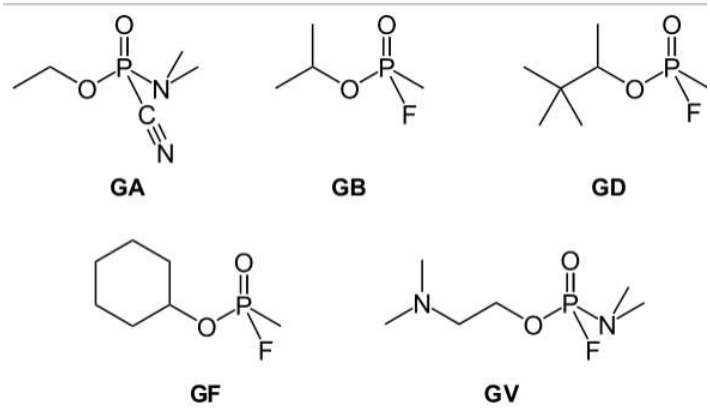


Figure 20.3.5 The G-series of nerve agents. Tabun as GA (German Agent A), sarin as GB and soman as GD. Ethyl sarin was tagged GE and cyclosarin as GF. *Source: Wikipedia.*

In 1935 the Nazi government had passed a decree that required all inventions of possible military significance to be reported to the Ministry of War, so in May 1937 Schrader sent a sample of tabun to the chemical warfare (CW) section of the Army Weapons Office in Berlin-Spandau. Schrader was summoned to the Wehrmacht chemical lab in Berlin to give a demonstration, after which Schrader's patent application and all related research was classified as secret. Colonel Rüdiger, head of the CW section, ordered the construction of new laboratories for the further investigation of tabun and other organophosphate compounds and Schrader soon moved to a new laboratory at Wuppertal-Elberfeld in the Ruhr valley to continue his research in secret throughout World War II. The compound was initially codenamed Le-100 and later Trilon-83.

Sarin was discovered by Schrader and his team in 1938 and named in honor of its discoverers: **S**chrader, **A**mbros, Gerhard **R**itter, and von der L**in**de.[26] It was codenamed T-144 or Trilon-46. It was found to be more than ten times as potent as tabun.

Soman was discovered by Richard Kuhn in 1944 as he worked with the existing compounds; the name is derived from either the Greek 'to sleep' or the Latin 'to bludgeon'. It was codenamed T-300.

Cyclosarin was also discovered during WWII but the details were lost and it was rediscovered in 1949.

Some **insecticides**, including carbamates and organophosphates such as dichlorvos, malathion and parathion, are nerve agents (Figure **20.3.6**). The metabolism of insects is sufficiently different from mammals that these compounds have little effect on humans and other mammals at proper doses, but there is considerable concern

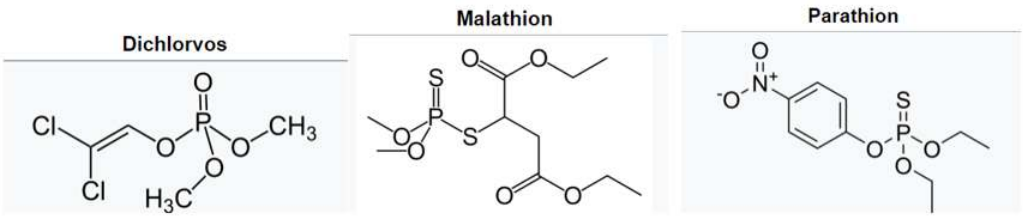


Figure **20.3.6** Organophosphate insecticides. Source: Wikipedia

about the long-term exposure to these chemicals by farm workers and animals alike. At high enough doses, acute toxicity and death can occur through the same mechanism as other nerve agents. Some insecticides such as demeton, dimefox and paraoxon are sufficiently toxic to humans that they have been withdrawn from agricultural use, and were at one stage investigated for potential military applications. Paraoxon was allegedly used as an assassination weapon by the apartheid South African government as part of Project Coast. Organophosphate pesticide poisoning is a major cause of disability in many developing countries and is often the preferred method of suicide.[24]

Treatment

Standard treatment for nerve agent poisoning is a combination of an anticholinergic to manage the symptoms, and an oxime as an antidote. Anticholinergics treat the symptoms by reducing the effects of acetylcholine, while oximes displaces phosphate molecules from the active site of the cholinesterase enzymes, allowing the breakdown of acetylcholine. Military personnel are issued the combination in an autoinjector (e.g. ATNAA), for ease of use in stressful conditions.

Atropine (Figure **20.3.7** is the standard anticholinergic drug used to manage the symptoms of nerve agent poisoning. It acts as an antagonist to muscarinic acetylcholine receptors, blocking the effects of excess acetylcholine. Some synthetic anticholinergics, such as biperiden, may counteract the central symptoms of nerve agent poisoning more effectively than atropine, since they pass the blood–brain barrier better than atropine. While these drugs will save the life of a person affected by nerve agents, that person may be incapacitated briefly or for an extended period, depending on the extent of exposure. The endpoint of atropine administration is the clearing of bronchial secretions.

Pralidoxime chloride (also known as *2-PAMCl*) is the standard oxime used to treat nerve agent poisoning. Rather than counteracting the initial effects of the nerve agent on the nervous system as does atropine, pralidoxime chloride reactivates the poisoned enzyme (acetylcholinesterase) by scavenging the phosphoryl group attached on the functional hydroxyl group of the

enzyme, counteracting the nerve agent itself. Revival of acetylcholinesterase with pralidoxime chloride works more effectively on nicotinic receptors while blocking acetylcholine receptors with atropine is more effective on muscarinic receptors.

Anticonvulsants, such as diazepam, may be administered to manage seizures, improving long term prognosis and reducing risk of brain damage. This is not usually self-administered as its use is for actively seizing patients.

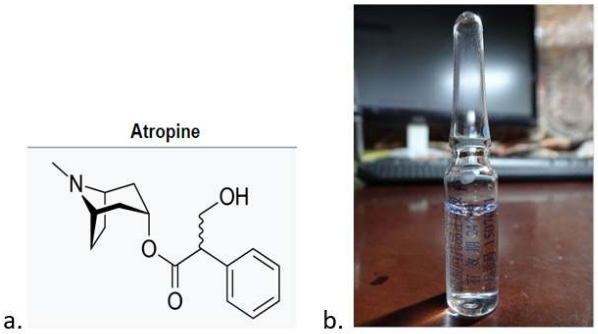


Figure **20.3.7** a. Atrophine molecule and b. an ampoule containing atropine injection 1mL/0.5mg.

Summary

- Upon stimulation, a normally functioning motor nerve releases the neurotransmitter acetylcholine, which transmits the impulse to a muscle or organ.
- Nerve poisons (i.e. carbamates and organophosphorus compounds) disrupt the nervous system by inhibiting the function of the enzyme acetylcholinesterase. Acetylcholine thus builds up and continues to act so that any nerve impulses are continually transmitted and muscle contractions do not stop.
- The botulin toxin and curare interfere with nerve impulses (by preventing the release of acetylcholine) and causes flaccid (sagging) paralysis of muscles.
- Atropine (Figure **20.3.7** is the standard anticholinergic drug used to manage the symptoms of nerve agent poisoning.

Contributors and Attributions

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20.4: The Lethal Dose

Learning Objectives

- Describe the LD_{50} value and its limitations.
- Know the LD_{50} value of various substances.

The LD_{50} is a standardized measure for expressing and comparing the toxicity of chemicals. The LD_{50} is the dose that kills half (50%) of the animals tested (LD = "lethal dose"). The animals are usually rats or mice, although rabbits, guinea pigs, hamsters, and so on are sometimes used. In all these tests, the dose must be calculated relative to the size of the animal. The most common units are milligrams of chemical per kilogram of test animal (mg/kg or ppm). (Table **20.4.1**) provides examples of LD_{50} values for various substances.

As a measure of toxicity, lethal dose is somewhat unreliable and results may vary greatly between testing facilities due to factors such as the genetic characteristics of the sample population, animal species tested, environmental factors and mode of administration.

There can be wide variability between species as well; what is relatively safe for rats may very well be extremely toxic for humans (*cf.* paracetamol toxicity), and vice versa. For example, chocolate, comparatively harmless to humans, is known to be toxic to many animals. When used to test venom from venomous creatures, such as snakes, LD_{50} results may be misleading due to the physiological differences between mice, rats, and humans. Many venomous snakes are specialized predators of mice, and their venom may be adapted specifically to incapacitate mice; and mongooses may be exceptionally resistant. While most mammals have a very similar physiology, LD_{50} results may or may not have equal bearing upon every mammal species, including humans.

Table **20.4.1**: LD_{50} *Values of Various Substances. Source: Wikipedia*

Substance	Animal Route	LD_{50} (mg/kg)
Water	rat, oral	90,000
Sucrose (table sugar)	rat, oral	29,700
Glucose (blood sugar)	rat, oral	25,800
Monosodium glutamate (MSG)	rat, oral	16,600
Cadmium sulfide	rat, oral	7,080
Ethanol (grain alcohol)	rat, oral	7,060
Methanol	human, oral	810
Sodium chloride (table salt)	rat, oral	3,000
Metallic arsenic	rat, oral	763
Arsenic trisulfide	rat, oral	185-6400
Sodium cyanide	rat, oral	6.4
Hydrogen cyanide	mouse, oral	3.7
Ibuprofen	rat, oral	636
Aspirin	rat, oral	200
Caffeine	rat, oral	192
Cocaine	mouse, oral	96
Nicotine	rat, oral	50
Heroin (diamorphine)	mouse, intravenous	21.8
Methamphetamine	rat, intraperitoneal	57
Mercury(II) chloride	rat, oral	1
Strychnine	human, oral	1-2
Sarin	mouse, subcutaneous injection	172 microgram/kg
Ricin (from castor oil plant)	rat, oral	20-30
Botulinum toxin (Botox)	human, oral injection, inhalation	1 ng/kg

(Table **20.4.2**) gives the LD_{50} values of some insecticides. In each case, the chemical was fed to laboratory rats. Note that the lower the LD_{50}, the more toxic the chemical. Even adjusting for the test animal's weight, the LD_{50} for one species is often quite different from that for another. Thus any LD_{50} value gives only a rough estimate of the risk to humans. The way in which the chemical is administered also has a marked effect on LD_{50} values. The chemical may be fed, injected, applied to the animal's skin, etc., and each method usually generates a different LD_{50}.

Table **20.4.2**: LD_{50} Values of Pesticides.

Chemical	Category	Oral LD_{50} in Rats (mg/kg)
Aldicarb ("Temik")	Carbamate	1
Carbaryl ("Sevin")	Carbamate	307
DDT	Chlorinated hydrocarbon	87
Dieldrin	Chlorinated hydrocarbon	40
Diflubenzuron ("Dimilin")	Chitin inhibitor	10,000
Malathion	Organophosphate	885
Methoprene	JH mimic	34,600
Methoxychlor	Chlorinated hydrocarbon	5,000
Parathion	Organophosphate	3
Piperonyl butoxide	Synergist	7,500
Pyrethrin	Plant extract	200
Rotenone	Plant extract	60

Summary

- The LD_{50} is the dose that kills half (50%) of the animals tested (LD = "lethal dose"). It is a standardized measure for expressing and comparing the toxicity of chemicals.
- LD_{50} values are given for common drugs (e.g. ibuprofen and aspirin), common household ingredients including water, table sugar (sucrose), salt (sodium chloride), insecticides (e.g. DDT and pyrethrin), and harmful drugs (e.g. cocaine and heroin).

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20.5: The Liver as a Detox Facility

Learning Objective

- Describe the different mechanisms of drug detoxification in the liver.

The human liver is thought to be responsible for up to 500 separate functions, usually in combination with other systems and organs. The liver breaks down or modifies toxic substance, such as alcohol and most medicial products, in a process called drug metabolism. This sometimes results in toxication, when the metabolite is more toxic than its precursor.

Alcohol Metabolism

Giving the liver enough time to fully metabolize the ingested alcohol is the only effective way to avoid alcohol toxicity. Drinking coffee or taking a shower will not help. The legal limit for intoxication is a BAC of 0.08. Taking into account the rate at which the liver metabolizes alcohol after drinking stops, and the alcohol excretion rate, it takes at least five hours for a legally intoxicated person to achieve sobriety.

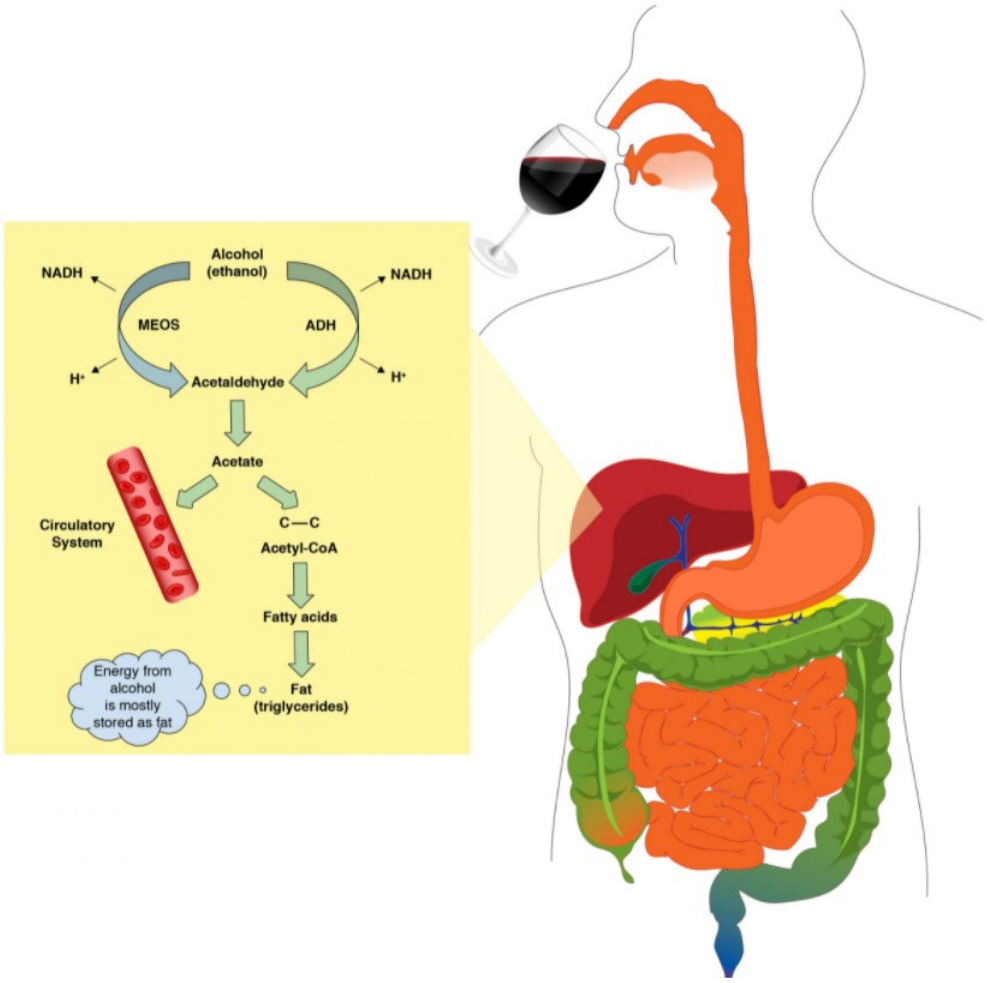


Figure **20.5.1**: Alcohol Metabolism Summary.

The liver metabolizes up to 85% – 98% of the circulatory ethanol. The liver uses two metabolic processes to get rid of this circulatory ethanol as quickly and safely as possible.

1. Alcohol dehydrogenase system
2. Microsomal ethanol oxidizing system (MEOS)

Alcohol Dehydrogenase System

About 80 to 90% of the total hepatic ethanol uptake is processed via the alcohol dehydrogenase system.The degradation of ethanol begins in the liver. The enzyme that catalyzes this reaction is called alcohol dehydrogenase. The products from this reaction are acetaldehyde, NADH (a reduced coenzyme that carries electrons from one reaction to another) and H+ ion. Acetaldehyde is very toxic to the liver and the body's cells. The moment acetaldehyde is produced; it must be degraded to protect the liver cells. The enzyme that will carry this type of degradation reaction is acetaldehyde dehydrogenase (ALDH). Acetaldehyde dehydrogenase converts acetaldehyde into acetate, a non-toxic molecule.

Microsomal Ethanol Oxidizing System (MEOS)

In a moderate drinker, about 10 to 20% of the total liver ethanol uptake is processed via the microsomal ethanol oxidizing system (MEOS). During periods of heavy drinking, the MEOS system will metabolize most of the excess ethanol ingested. Heavy drinking stimulates the human body to include the MEOS system enzymes to clear ethanol faster from the body.

The MEOS system is also located in the liver. Similar to the Alcohol dehydrogenase system, acetaldehyde dehydrogenase will immediately convert acetaldehyde into acetate, a non-toxic molecule. Other products from this reaction are NADH and H+ ion.

Fate of Acetate

The acetate produced (from the alcohol dehydrogenase system and microsomal ethanol oxidizing system) is either released into circulation or retained inside the liver cells. In the liver cells, acetate is converted to acetyl CoA where it is used to produce other molecules like CO2 or used in the synthesis of fatty acids and cholesterol.

Nicotine and Ammonia

In humans, **nicotine i**s extensively metabolized in the liver into various metabolites. About 70-80% of nicotine is broken down to cotinine, the predominant metabolite. Other primary metabolites include nicotine *N*′-oxide, nornicotine, nicotine isomethonium ion, 2-hydroxynicotine and nicotine glucuronide. Under some conditions, other substances may be formed such as myosmine.

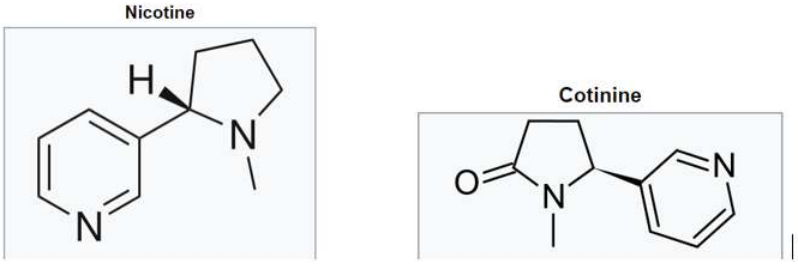


Figure **20.5.1** Nicotine and cotinine.

The liver converts ammonia into urea as part of the ornithine cycle or the urea cycle, and the urea is excreted in the urine.

Summary

- The liver is involved in the breakdown or modification of various substances in a process called drug metabolism, but the metabolites are not directly removed from the body.
- Ethanol is broken down through a series of steps (involving various liver enzymes) to carbon dioxide and water.
- Ethanol therapy is the traditional treatment for methanol and ethylene glycol poisoning.
- Nicotine is extensively metabolized in the liver into a variety of breakdown products whereas toxic ammonia is converted to non toxic urea.

Contributors and Attributions

- Wikipedia
- Benowitz, N. L., Hujjanen, J., Peyton III, J. Nicotine Chemistry, Metabolism, Kinetics, and Biomarkers. Hand Exp Pharmacol. 2009. (192): 29-60.
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20.6: Carcinogens and Teratogens

Learning Objectives

- Explain the process of cancer development.
- List the factors that may increase and lower the risk of cancer.
- Define teratogens and describe the birth defects that result from them.

A **carcinogen** is any agent that directly increases the incidence of cancer. Most, but not all carcinogens are mutagens. Carcinogens that do not directly damage DNA include substances that accelerate cell division, thereby leaving less opportunity for cell to repair induced mutations, or errors in replication. Carcinogens that act as mutagens may be biological, physical, or chemical in nature, although the term is most often used in relation to chemical substances.

Defining Cancer

Cancer is actually a group of more than 100 diseases, all of which involve abnormal cell growth with the potential to invade or spread to other parts of the body. In general terms, cancer occurs when the cell cycle is no longer regulated due to DNA damage. The number of potential underlying causes of this DNA damage is great, so there are many different risk factors for cancer. Any cells that become cancerous divide more quickly than normal cells. They may form a mass of abnormal cells called a tumor. The rapidly dividing cells take up nutrients and space, damaging the normal cells around them. If the cancer cells spread to other parts of the body, they invade and damage other tissues and organs. They may eventually lead to death.

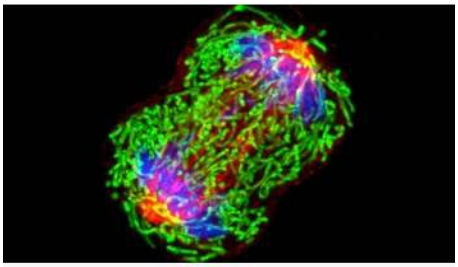


Figure **20.6.1** A dividing breast cancer cell. Source: National Cancer Institute/Univ. of Pittsburgh Cancer Institute

By far, the most common of the 100-plus types of human cancer is basal cell carcinoma, the type of skin cancer Bernie Sanders had removed in 2016. Basal cell carcinoma makes up 40 percent of all new cancers each year in the United States. Other common types of cancer include lung, colorectal, prostate (in males), and breast (in females) cancers. These cancers are not as common as skin cancer, but they cause the majority of cancer deaths.

How Cancer Develops

Carcinogenesis, also called **oncogenesis** or **tumorigenesis,** is the formation of a cancer, whereby normal cells are transformed into cancer cells. The transformation of a normal cell into a cancer cell is a multi-step process that involves initiation, promotion, progression and finally malignancy (see Figure **20.6.2**). This process takes years and starts with a single cell in which the right genes are mutated so the cell does not appropriately die and begins to proliferate abnormally. Then, additional mutations occur that select for more rapidly growing cells within this population leading to a tumor with rapid growth and malignancy. By the time the cells are cancerous, proto-oncogenes have been activated and tumor suppressor genes inactivated. Even within the same tumor type, like colon cancer, the specific genes mutated can vary from person to person making cancer a unique disease for each individual.

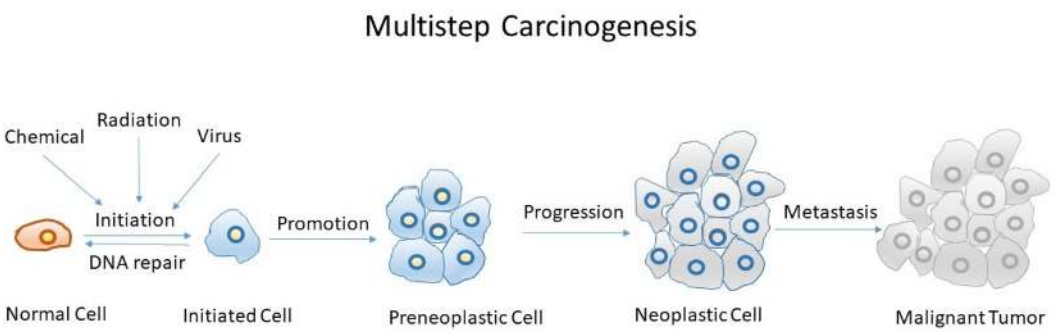


Figure 20.6.2: Multistep process involved in carcinogenesis that transforms a normal cell into a malignant tumor.

How Cancer Spreads

Once a normal cell transforms into a cancer cell and starts dividing out of control, cancer cells can spread from the original site (called the primary tumor) to other tissues. This can occur in three different ways. One way is local spread, in which aggressively dividing cancer cells directly invade nearby tissues. Another way involves the lymphatic system. Cancer cells can spread to regional lymph nodes through lymph vessels that pass by the primary tumor.

The third way cancer cells can spread is through the blood to distant sites. This is called metastasis, and the new cancers that form are called **metastases.** Although the blood can carry cancer cells to tissues everywhere in the body, cancer cells generally grow only in certain sites (Figure 20.6.3). Different types of cancers tend to metastasize to particular organs. The most common places for metastases to occur are the brain, lungs, bones, and liver. Almost all cancers can metastasize, especially during the late stages of the disease. Cancer that has metastasized generally has the worst prognosis and is associated with most cancer deaths.

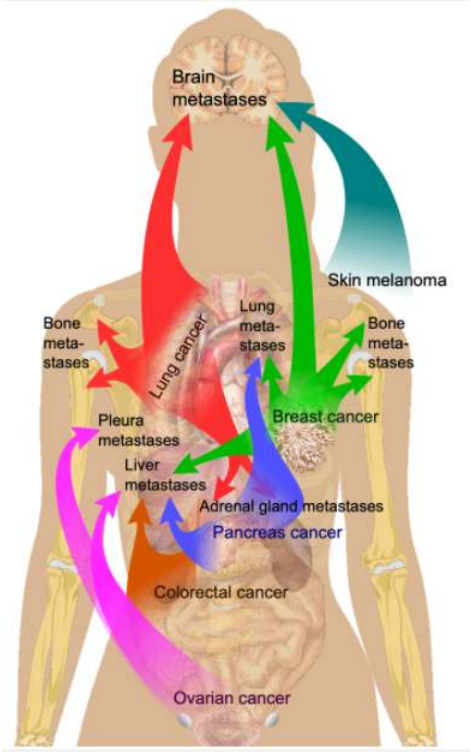


Figure 20.6.3: Cancer cells that originate in one organ may metastasize by traveling in the blood to distant sites (metastases). Metastasized lung cancer grows in the brain, bone, and adrenal gland. Metastasized pancreas cancer grows in the liver and lungs. Metastasized breast cancer can grow in the bone, brain, and liver. Metastasized Colon and Ovarian cancer grow in the liver.

Chemical Carcinogens

Chemical carcinogens (Table 20.6.1) can be either natural or synthetic compounds that, based on animal feeding trials or **epidemiological** (i.e. human population) studies, increase the incidence of cancer. The definition of a chemical as a carcinogen is problematic for several reasons. Some chemicals become carcinogenic only after they are metabolized into another compound in the body; not all species or individuals may metabolize chemicals in the same way. Also, the carcinogenic properties of a compound are usually dependent on its dose. It can be difficult to define a relevant dose for both lab animals and humans. Nevertheless, when a correlation between cancer incidence and chemical exposure is observed, it is usually possible to find ways to reduce exposure to that chemical.

Table 20.6.1: Some Classes of Chemical Carcinogens.

Class	Examples and/or Sources
PAHs (polycyclic aromatic hydrocarbons)	benzo[a]pyrene and several other components of the smoke of cigarettes, wood, and fossil fuels
Aromatic amines	compounds formed in food when meat (including fish, poultry) are cooked at high temperature
Nitrosamines and nitrosamides	found in tobacco and in some smoked meat and fish
Azo dyes	various dyes and pigments used in textiles, leather, paints.
Carbamates	ethyl carbamate (urethane) found in some distilled beverages and fermented foods
Halogenated compounds	e.g. pentachlorophenol used in some wood preservatives and pesticides.
Inorganic compounds	asbestos; may induce chronic inflammation and reactive oxygen species
Miscellaneous compounds	e.g. alkylating agents, phenolics

WEB LINK

A detailed list of occupational carcinogens can be found on the link below

https://bio.libretexts.org/Bookshelves/Human_Biology/Book:_Human_Biology_(Wakim_and_Grewal)/21:_Disease/21.7:_Cancer

The carcinogens implicated as the main causative agents of the four most common cancers worldwide are given in the table below. These four cancers are lung, breast, colon, and stomach cancers. Together they account for about 41% of worldwide cancer incidence and 42% of cancer deaths.

Table 20.6.2: Major Carcinogens Implicated In The Four Most Common Cancers Worldwide.

Type of Cancer	Carcinogen
Lung Cancer	Tobacco smoke
Breast Cancer	Estrogen
Colon Cancer	Tobacco smoke and bile acids: deoxycholic acid (DCA) or lithocholic acid (LCA)
Stomach Cancer	Heliobacter pylori

WEB LINK

Note: A more detailed description for each major carcinogen listed in Table **20.6.2** can be found on the link below

https://en.Wikipedia.org/wiki/Carcin...cers_worldwide

Anticarcinogens

Dietary fiber and calorie restriction are two anti-carcinogen or anti-promoters that decrease the risk of tumor formation. Dietary fiber is both and is inversely associated with cancer, particularly colon cancer. So the more fiber you eat, the less risk you have of developing colon cancer. One mechanism by which fiber acts is hastening bile acid excretion. Fiber also increases the rate of passage of materials through the colon resulting in decreased production and exposure of the colon to cancer-causing agents, ie dilutes the concentration of carcinogens.

Animal studies have shown that restricting caloric intake by 30% reduces tumor growth and increases life span. The mechanism is not known but may be due to less oxidation thus damage to DNA.

Antioxidants can help block the action of initiators or promoters if their mode of action is to damage DNA by oxidation. Vitamin A, C, E, beta-carotene, and selenium are antioxidant nutrients. Some work locally, like vitamin E in the colon, while other work more globally like selenium and vitamin C. Vitamin A appears to work by keeping cells differentiated which slows the growth rate.

Other compounds in food, particularly fruits and vegetables, have been shown to slow tumor formation. Cruciferous vegetables (eg broccoli, cauliflower, cabbage, and Brussel sprouts to name a few) are rich in nutrients, fiber, glucosinolates which are sulfur-containing chemicals, indoles, and isothiocyanates. Animal studies have found these substances inhibit the development of cancer in several organs in rats and mice (Hecht SS. Inhibition of carcinogenesis by isothiocyanates. *Drug Metabolism Reviews* 2000;32(3-4):395-411; Murillo G, Mehta RG. Cruciferous vegetables and cancer prevention. *Nutrition and Cancer* 2001;41(1-2):17-28). Indoles and isothiocyanates help protect cells from DNA damage; help inactivate carcinogens; have antiviral and antibacterial effects; have anti-inflammatory effects; induce cell death (apoptosis); and inhibit tumor blood vessel formation (angiogenesis) and tumor cell migration (needed for metastasis) (National Cancer Institute, Cruciferous Vegetables and Cancer Prevention, 2012, https://www.cancer.gov/about-cancer/...les-fact-sheet). Studies in humans, however, have shown mixed results.

Test for Carcinogens

In genetics, a **mutagen** is a physical or chemical agent that permanently changes genetic material, usually DNA, in an organism and thus increases the frequency of mutations above the natural background level. As many mutations can cause cancer, such mutagens are therefore carcinogens, although not all necessarily are. Many different systems for detecting mutagen have been developed. Animal systems may more accurately reflect the metabolism of human, however, they are expensive and time-consuming (may take around three years to complete), they are therefore not used as a first screen for mutagenicity or carcinogenicity.

The **Ames test** is a widely employed method that uses bacteria to test whether a given chemical can cause mutations in the DNA of the test organism. More formally, it is a biological assay to assess the mutagenic potential of chemical compounds. A positive test indicates that the chemical is mutagenic and therefore may act as a carcinogen, because cancer is often linked to mutation. The test serves as a quick and convenient assay to estimate the carcinogenic potential of a compound because standard carcinogen assays on mice and rats are time-consuming (taking two to three years to complete) and expensive. However, false-positives and false-negatives are known. Other tests, similar to the Ames tests have also been developed using yeast and other bacteria.

Drosophila, plants, and cell cultures have been used in various test assays for mutagenecity of chemicals.

In **animal test systems,** rodents are usually used in animal test. The chemicals under test are usually administered in the food and in the drinking water, but sometimes by dermal application, by gavage, or by inhalation, and carried out over the major part of the life span for rodents. **Transgenic mouse assay** using a mouse strain infected with a viral shuttle vector is another method for testing mutagens. Animals are first treated with suspected mutagen, the mouse DNA is then isolated and the phage segment recovered and used to infect *E. coli*.

Did You Know?



***Video* 20.6.1** *Risk factors for cancer.*

WEB LINKS - American Cancer Society and NIH:MedlinePlus & National Cancer Institute

Risk factors for Cancer

https://www.cancer.gov/about-cancer/causes-prevention/patient-prevention-overview-pdq#_199

Common Cancer Myths and Misconceptions

https://www.cancer.gov/about-cancer/causes-prevention/risk/myths

List of Probable Carcinogens

https://www.cancer.org/cancer/cancer-causes/general-info/known-and-probable-human-carcinogens.html?sitearea=who

Cancer Prevention: Take Charge of Your Lifestyle

https://medlineplus.gov/ency/patientinstructions/000825.htm

Cruciferous Vegetables and Cancer Prevention

https://www.cancer.gov/about-cancer/causes-prevention/risk/diet/cruciferous-vegetables-fact-sheet

Birth Defects:Teratogens

A teratogen is a compound that permanently deforms the function or structure of a developing embryo or fetus in utero. In general, the degree of teratogenicity depends on:

- The potency of the drug as a mutagen.
- The susceptibility of the fetus to teratogenesis.
- The dose of the teratogen.
- The duration of teratogen exposure.
- The time of exposure.
- The degree of transfer from maternal to fetal circulation.

The global average of all live births complicated by malformation is 6% (Environmental Health Perspectives, (NIH), October 2009). The majority of these complications are due to unknown factors. The vast majority of recognized etiologies are genetic, with only 10% being attributed to environmental etiologies such as maternal health, infection, and toxicants. In general, the central nervous and skeletal systems are the most affected.

Thalidomide (a sedative previously marketed in Europe to prevent morning sickness) see Figure **20.6.4**is a classic teratogen that caused limb defects in babies born to women who took this drug in the 1960s (see Figure **20.6.5**). Thalidomide was first marketed in 1957 in West Germany, where it was available over the counter.[5][6] When first released, thalidomide was promoted for anxiety,

trouble sleeping, "tension", and morning sickness.[6][7] While initially deemed to be safe in pregnancy, concerns regarding birth defects were noted in 1961 and the medication was removed from the market in Europe that year.[6][5] The total number of people affected by use during pregnancy is estimated at 10,000, of which about 40% died around the time of birth.[6][3] Those who survived had limb, eye, urinary tract, and heart problems.[5]

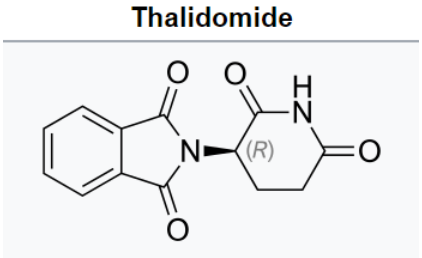


Figure **20.6.4**. Chemical structure of Thalidomide.

Its initial entry into the US market was prevented by Frances Kelsey at the FDA.[7] The birth defects of thalidomide led to the development of greater drug regulation and monitoring in many countries. in 2006 the U.S. Food and Drug Administration granted accelerated approval for thalidomide in combination with dexamethasone for the treatment of newly diagnosed multiple myeloma patients.



Figure **20.6.5**. *Thalidomide effects: A photograph of the limbs ofbaby born to a mother who took thalidomide while pregnant.*

Women may encounter a number of other teratogens. **Smoking** is most likely to cause growth retardation, but has also been implicated in the prelabor rupture of the membranes, preterm labor, abruption of the placenta, spontaneous abortion, perinatal morbidity and mortality, and sudden infant death syndrome. Smoking may exert its effects through competitive binding of carbon monoxide with hemoglobin and/or through the various other components found in cigarettes that cause adverse biological effects.

Alcohol use in pregnancy may result in fetal alcohol syndrome (FAS) see Figure **20.6.6**, which occurs in approximately 1% of all births. Children with FAS present with a flattened and thin upper lip, small palpebral fissures, epicanthal folds, flattened nasal bridge, and a short nose. They may also exhibit microcephaly, mental retardation, and have learning disabilities. It is not clear if there is any safe amount of alcohol consumption in pregnancy.

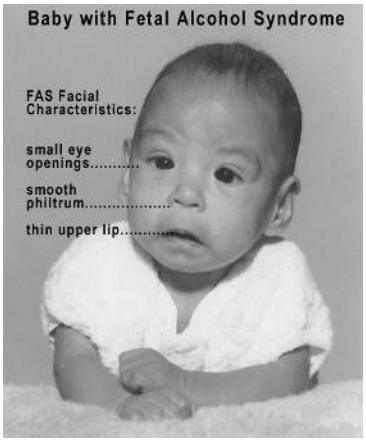


Figure **20.6.6**. Fetal alcohol syndrome: Alcohol is a teratogen. When consumed in pregnancy, it can result in mothers giving birth to children with fetal alcohol syndrome. The facial characteristics highlighted in the photograph are small eye opening, smooth philtrum, and a thin upper lip.

Cocaine generally produces growth restriction, preterm delivery, microcephaly, spontaneous abortion, placental abruption, limb anomalies, and central nervous system abnormalities. Cocaine appear to exert a number of its effects through peripheral vasoconstriction that leads to fetal hypoxia.

Women with indications for **warfarin** therapy should either abstain from pregnancy or switch to low molecular weight heparins. Warfarin typically produces mental retardation, growth restriction, nasal hypoplasia, and opthalmic abnormalities.

Angiotensin converting enzyme (ACE) inhibitors will cause fetal renal failure and oligohydramnios that lead to pulmonary hypoplasia and limb contracture. Fetal cranial bone abnormalities are also common.

Isotretinoin (Accutane), used to treat acne, may cause cardiac, oral, otological, thymic, and central nervous system abnormalities. In one quarter of cases, it causes mental retardation.

Other teratogenic substance classes and conditions include

- Various prescription drugs and nutrient deficiencies (e.g., insufficient folic acid).
- Chemical compounds such as methyl iodide (used in pesticides) and bisphenol A (used in plastics) are suspected teratogens.

Summary

- A carcinogen is any agent that directly increases the incidence of cancer.
- Cancer is caused by changes to the DNA which could be inherited or acquired.
- Various tests have been developed to test for carcinogens.
- The American Cancer Society provides an extensive list of probable chemical carcinogens including those found in processed foods and beverages, various household products, pesticides etc.
- The effects of a teratogen on the fetus depend on several factors: the potency of the teratogen, the susceptibility of the fetus to the teratogen, the dose and duration of teratogen exposure, the degree of transfer from maternal to fetal circulation, and when during development the exposure occurs.
- Approximately 10% of congenital malformations are attributed to environmental factors, and 20% are due to genetic or hereditary factors. The rest have unknown causes or are due to a mix of different factors.
- Cigarette components, alcohol, cocaine, warfarin, ACE inhibitors, and Accutane are all teratogens that affect fetal development.

Contributors and Attributions

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American Cancer Society

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20.7: Hazardous Wastes

Learning Objectives

- List the different types of hazardous wastes based on their classification.
- Describe the handling of hazardous waste.

Hazardous waste is waste that has substantial or potential threats to public health or the environment. Hazardous wastes may be found in different physical states such as gaseous, liquids, or solids. A hazardous waste is a special type of waste because it cannot be disposed of by common means like other by-products of our everyday lives. Depending on the physical state of the waste, treatment and solidification processes might be required.

Statutory Definition of Hazardous Waste

A discussion of the definition of hazardous waste should begin with Congress' original statutory definition of the term. RCRA (Resource Recovery and Conservation Act) §1004(5) defines hazardous waste as: A solid waste, or combination of solid waste, which because of its quantity, concentration, or physical, chemical, or infectious characteristics may (a) cause, or significantly contribute to, an increase in mortality or an increase in serious irreversible, or incapacitating reversible, illness; or (b) pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, transported, or disposed of, or otherwise managed.

Listed, Characteristic, and Mixed Wastes

Listed hazardous wastes (see Table **20.7.1**) are materials specifically listed as hazardous wastes which are from non-specific sources, specific sources, or discarded chemical products. Title 40 of the Code of Federal Regulations (CFR) in section 261 provides four lists (the F, K, P and U lists) of hazardous materials.

Table 20.7.1 List Hazardous Wastes. Source US EPA.

List Type	Section	Description of Waste
F List	40 CFR section 261.31	Wastes from common manufacturing and industrial processes • Spent solvent wastes, • Electroplating and other metal finishing wastes, • Dioxin-bearing wastes, • Chlorinated aliphatic hydrocarbons production, • Wood preserving wastes, • Petroleum refinery wastewater treatment sludges, and • Multisource leachate.
K List	40 CFR section 261.32	Source specific wastes from 13 various industries and manufacturers namely: • Wood preservation, • Organic chemicals manufacturing, • Pesticides manufacturing, • Petroleum refining, • Veterinary pharmaceuticals manufacturing, • Inorganic pigment manufacturing, • Inorganic chemicals manufacturing, • Explosives manufacturing, • Iron and steel production, • Primary aluminum production, • Secondary lead processing, • Ink formulation, and • Coking (processing of coal to produce coke).
P List	40 CFR section 261.33	Acute hazardous wastes from discarded commercial chemical products. • The chemical in the waste must be unused; and • The chemical in the waste must be in the form of a commercial chemical product.
U List	40 CFR section 261.33	Hazardous wastes from discarded commercial chemical products • The chemical in the waste must be unused; and • The chemical in the waste must be in the form of a commercial chemical product.

- **Characteristic hazardous wastes** are materials that are dangerous because it is toxic, corrosive, flammable, or reactive. Detailed information provided by the US Environmental Agency (US EPA) is summarized in Table 20.7.2.

Table 20.7.2 Characteristic Hazardous Wastes. Source US EPA.

Waste Characteristic	EPA Waste Code	Section	Description of Waste
Ignitability	D001	40 CFR section 261.21	Liquids with flash points below 60 °C (e.g. used solvents and waste oils), non-liquids that cause fire through specific conditions, ignitable compressed gases and oxidizers
Corrosivity	D002	40 CFR section 261.22	Aqueous wastes with a pH of less than or equal to 2 (acids), a pH greater than or equal to 12.5 (bases) or based on the liquids ability to corrode steel. Example: battery acid
Reactivity	D003	40 CFR section 261.23	Wastes that are unstable under normal conditions, may react with water, may give off toxic gases and may be capable of detonation or explosion under normal conditions or when heated. Examples: lithium–sulfur batteries and explosives.
Toxicity	D004 through D043	40 CFR section 261.24	Wastes that are harmful when ingested or absorbed. Toxic waste can be reactive, ignitable, and corrosive. Examples: old batteries, pesticides, paint, and car oil

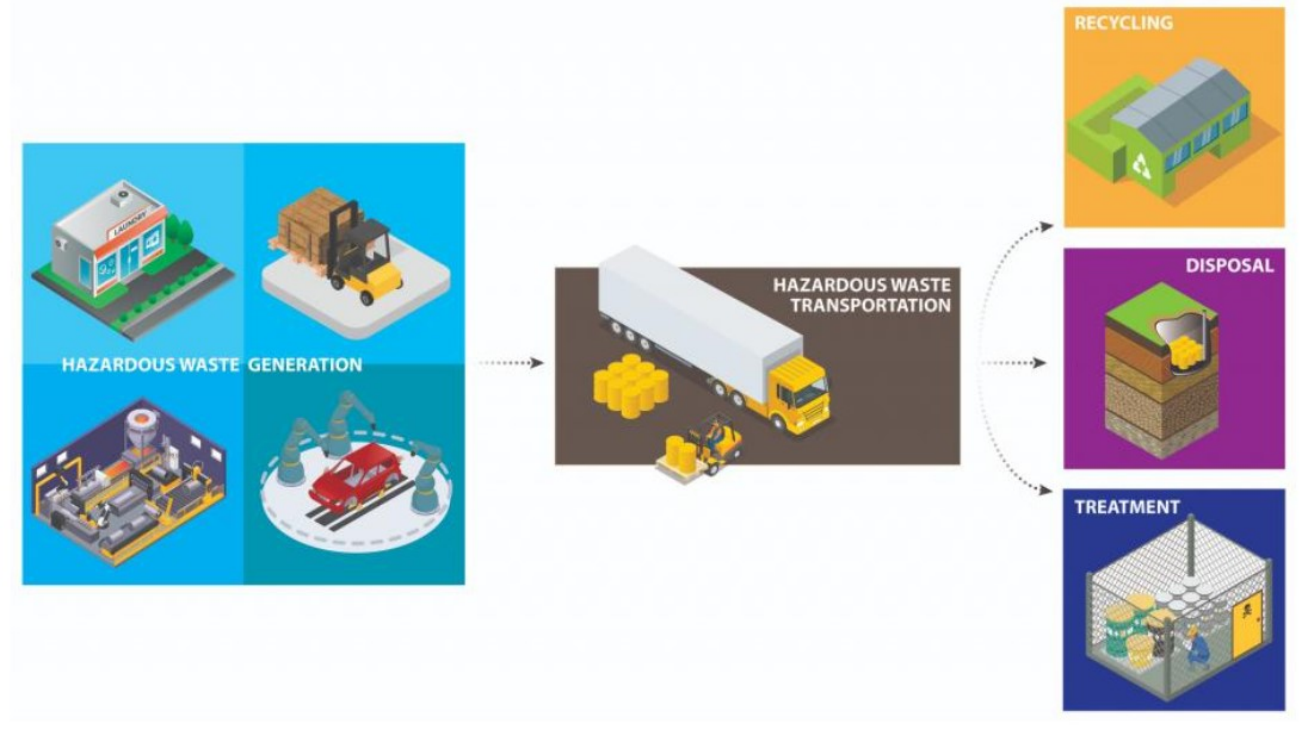
Mixed wastes is the term for hazardous wastes that also contain radioactive material and is regulated under the EPAs Resource Conservation and Recovery Act (RCRA) and the Department of Energy's Atomic Energy Act.

EPA's Cradle-to-Grave Hazardous Waste Management Program

https://www.epa.gov/hw/learn-basics-...ous-waste#hwid

In the mid-twentieth century, solid waste management issues rose to new heights of public concern in many areas of the United States because of increasing solid waste generation, shrinking disposal capacity, rising disposal costs, and public opposition to the siting of new disposal facilities. These solid waste management challenges continue today, as many communities are struggling to develop cost-effective, environmentally protective solutions. The growing amount of waste generated has made it increasingly important for solid waste management officials to develop strategies to manage wastes safely and cost effectively.

RCRA set up a framework for the proper management of hazardous waste . From this authority, EPA established a comprehensive regulatory program to ensure that hazardous waste is managed safely from "cradle to grave" meaning from the time it is created, while it is transported, treated, and stored, and until it is disposed:



Hazardous Waste Generation

Under RCRA, hazardous waste generators are the first link in the hazardous waste management system. All generators must determine if their waste is hazardous and must oversee the ultimate fate of the waste. Furthermore, generators must ensure and fully document that the hazardous waste that they produce is properly identified, managed, and treated prior to recycling or disposal. The degree of regulation that applies to each generator depends on the amount of waste that a generator produces.

Hazardous Waste Transportation

After generators produce a hazardous waste, transporters may move the waste to a facility that can recycle, treat, store or dispose of the waste. Since such transporters are moving regulated wastes on public roads, highways, rails and waterways, United States Department of Transportation hazardous materials regulations, as well as EPA's hazardous waste regulations, apply.

Hazardous Waste Recycling, Treatment, Storage and Disposal

To the extent possible, EPA tried to develop hazardous waste regulations that balance the conservation of resources, while ensuring the protection of human health and environment. Many hazardous wastes can be recycled safely and effectively, while other wastes will be treated and disposed of in landfills or incinerators.

Recycling hazardous waste has a variety of benefits including reducing the consumption of raw materials and the volume of waste materials that must be treated and disposed. However, improper storage of those materials might cause spills, leaks, fires, and contamination of soil and drinking water. To encourage hazardous waste recycling while protecting health and the environment, EPA developed regulations to ensure recycling would be performed in a safe manner.

Treatment Storage and Disposal Facilities (TSDFs) provide temporary storage and final treatment or disposal for hazardous wastes. Since they manage large volumes of waste and conduct activities that may present a higher degree of risk, TSDFs are stringently regulated. The TSDF requirements establish generic facility management standards, specific provisions governing hazardous waste management units and additional precautions designed to protect soil, ground water and air resources.

Comprehensive information on the final steps in EPA’s hazardous waste management program is available online, including Web pages and resources related to:

- Hazardous waste recycling,
- Regulations that apply to treatment, storage and disposal facilities, and
- Descriptions of land disposal restrictions.

Summary

- Hazardous waste is defined as solid waste, or combination of solid waste, which because of its quantity, concentration, or physical, chemical, or infectious characteristics may (a) cause, or significantly contribute to, an increase in mortality or an increase in serious irreversible, or incapacitating reversible, illness; or (b) pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, transported, or disposed of, or otherwise managed.
- Listed wastes are wastes from common manufacturing and industrial processes, specific industries and can be generated from discarded commercial products.
- Characteristic wastes are wastes that exhibit any one or more of the following characteristic properties: ignitability, corrosivity, reactivity or toxicity.
- A waste that has a hazardous component and a radioactive component is called a **mixed waste** and is regulated under both the Resource Conservation and Recovery Act (RCRA) and the Atomic Energy Act.
- The Environmental Protection Agency (EPA) has developed a hazardous waste management program to ensure proper handling of hazardous waste from recycling, treatment, storage, and disposal.

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