THE BASICS OF GOB CHEMISTRY

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TABLE OF CONTENTS

1: Chemistry, Matter, and Measurement

2: Elements, Atoms, and the Periodic Table

3: Ionic Bonding and Simple Ionic Compounds

4: Covalent Bonding and Simple Molecular Compounds

5: Introduction to Chemical Reactions

6: Quantities in Chemical Reactions

7: Energy and Chemical Processes

8: Solids, Liquids, and Gases

9: Solutions

10: Acids and Bases

11: Nuclear Chemistry

12: Organic Chemistry - Alkanes and Halogenated Hydrocarbons

13: Unsaturated and Aromatic Hydrocarbons

14: Organic Compounds of Oxygen

15: Organic Acids and Bases and Some of Their Derivatives

16: Carbohydrates

17: Lipids

18: Amino Acids, Proteins, and Enzymes

19: Nucleic Acids

20: Energy Metabolism

Index

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CHAPTER OVERVIEW

1: Chemistry, Matter, and Measurement

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

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1.0: Prelude to Chemistry, Matter, and Measurement

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

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

1.1: What is Chemistry?

Learning Objectives

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

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

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

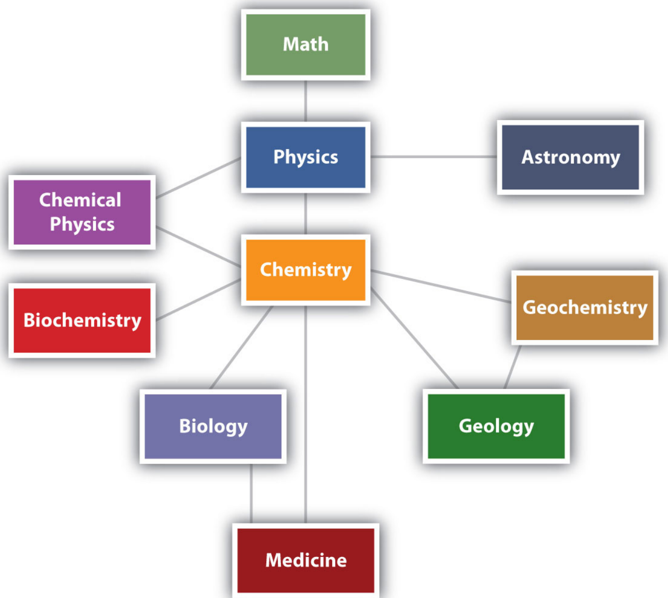


Figure 1.1.1: The Relationships between Some of the Major Branches of Science. Chemistry lies more or less in the middle, which emphasizes its importance to many branches of science.

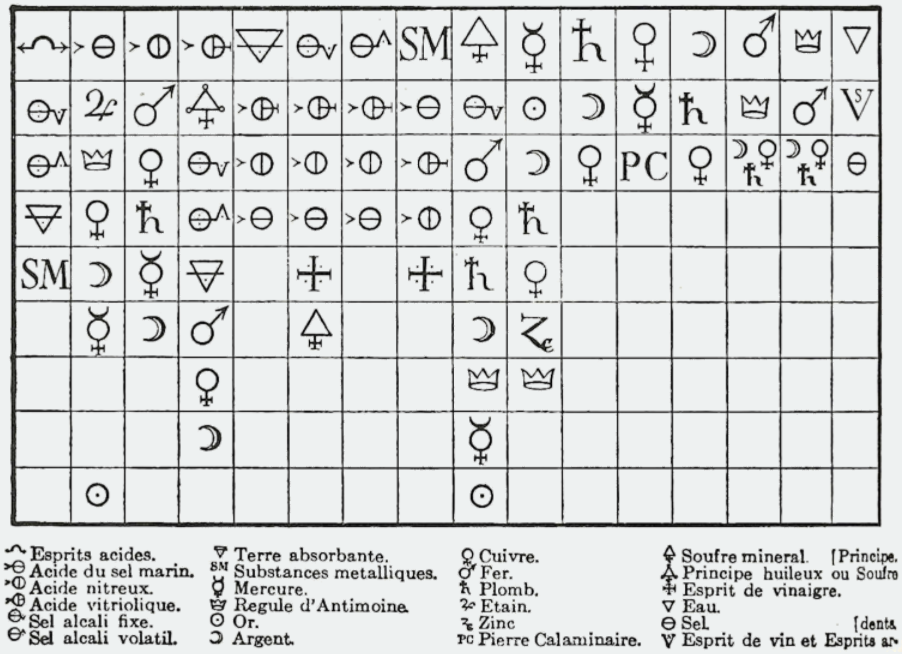
Although we divide science into different fields, there is much overlap among them. For example, some biologists and chemists work in both fields so much that their work is called biochemistry. Similarly, geology and chemistry overlap in the field called geochemistry. Figure 1.1.1 shows how many of the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

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

Alchemy

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

Alchemy was a somewhat mystical and secretive approach to learning how to manipulate matter. Practitioners, called alchemists, thought that all matter was composed of different proportions of the four basic elements—fire, water, earth, and air—and believed that if you changed the relative proportions of these elements in a substance, you could change the substance. The long-standing attempts to "transmute" common metals into gold represented one goal of alchemy. Alchemy's other major goal was to synthesize the philosopher's stone, a material that could impart long life—even immortality. Alchemists used symbols to represent substances, some of which are shown in the accompanying figure. This was not done to better communicate ideas, as chemists do today, but to maintain the secrecy of alchemical knowledge, keeping others from sharing in it.



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

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

✓ Exercise 1.1.1

Which fields of study are branches of science? Explain.

a. sculpture
b. astronomy

Answer a

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

Answer b

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

? Exercise 1.1.2

Which fields of study are branches of science?

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

Answer

a, b and c only

How do scientists work? Generally, they follow a process called the scientific method. The scientific method is an organized procedure for learning answers to questions and making explanations for observations. To find the answer to a question (for example, “Why do birds fly toward Earth’s equator during the cold months?”), a scientist goes through the following steps, which are also illustrated in Figure 1.1.2:

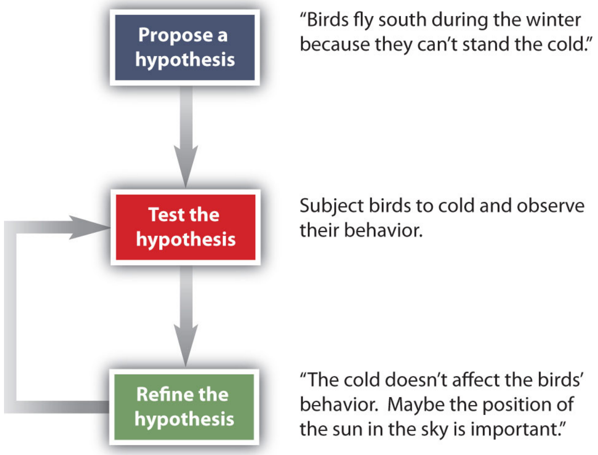


Figure 1.1.2: The General Steps of the Scientific Method. After an observation is made or a question is identified, a hypothesis is made and experiments are designed to test the hypothesis.

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

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

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

rcise

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.

rcise

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.

1.2: The Classification of Matter

Learning Objectives

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

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

Physical and Chemical Properties

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

Figure 1.2.1: (left) Ice Melting is a physical change. When liquid water (H_2O) freezes into a solid state (ice), it appears changed; However, this change is only physical as the the composition of the constituent molecules is the same: 11.19% hydrogen and 88.81% oxygen by mass. (right) Burning of wax to generate water and carbon dioxide is a chemical reaction. (CC-SA-BY-3.0; Andrikkos)

Elements and Compounds

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

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

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

However, scientists can also describe chemical events on the level of individual atoms or molecules, which is referred to as the *microscopic viewpoint*. We will see examples of both macroscopic and microscopic viewpoints throughout this book (Figure 1.2.2).

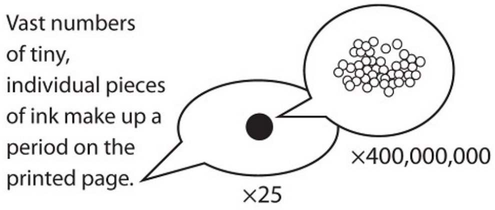


Figure 1.2.2: How Many Particles Are Needed for a Period in a Sentence? Although we do not notice it from a macroscopic perspective, matter is composed of microscopic particles so tiny that billions of them are needed to make a speck we can see with the naked eye. The ×25 and ×400,000,000 indicate the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

Mixtures

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

✓ Example 1.2.1

How would a chemist categorize each example of matter?

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

Answer a

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

Answer b

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

Answer c

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

Answer d

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

? Exercise 1.2.2

How would a chemist categorize each example of matter?

a. breakfast coffee
b. hydrogen
c. an egg

Answer a

homogeneous mixture or solution

Answer b

element

Answer c

heterogeneous mixture

Phases or Physical States of Matter

All matter can be further classified by one of three physical **states** or **phases**, solid, liquid or gas. These three descriptions each imply that the matter has certain physical properties when in these states. A solid has a definite shape and a definite volume. Liquids ordinarily have a definite volume but not a definite shape; they take the shape of their containers. Gases have neither a definite shape nor a definite volume, and they expand to fill their containers.

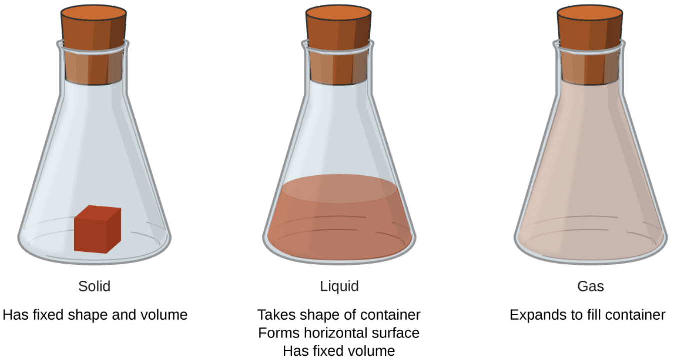


Figure 1.2.3: The three most common states or phases of matter are solid, liquid, and gas. (CC BY-4.0; OpenStax)

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

We encounter matter in each phase every day; in fact, we regularly encounter water in all three phases: ice (solid), water (liquid), and steam (gas) (Figure 1.2.2).

Figure 1.2.5: Boiling Water. When liquid water boils to make gaseous water, it undergoes a phase change. (CC BY-SA 3.0 Unported; Markus Schweiss via Wikipedia)

We know from our experience with water that substances can change from one phase to another if the conditions are right. Typically, varying the temperature of a substance (and, less commonly, the pressure exerted on it) can cause a **phase change**, a physical process in which a substance changes from one phase to another (Figure 1.2.5). Phase changes are identified by particular names depending on what phases are involved, as summarized in Table 1.2.1.

Table 1.2.1: Phase Changes

Change	Name
solid to liquid	melting, fusion
solid to gas	sublimation

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

Figure $1.2.3$ illustrates the relationships between the different ways matter can be classified.

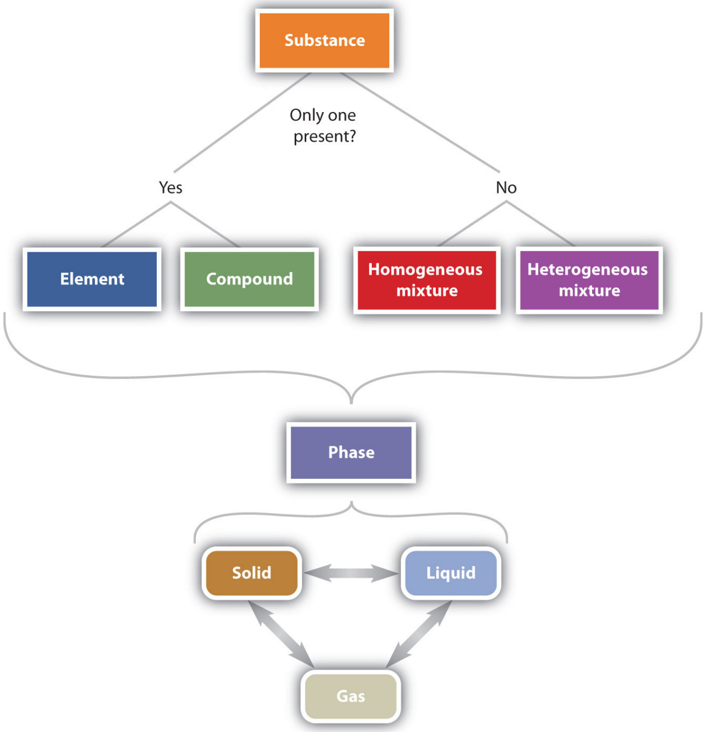


Figure $1.2.6$: The Classification of Matter. Matter can be classified in a variety of ways, depending on its properties. This table starts with a substance. If there is only one present, it can either be an element or a compound. If there is more than one present, it can either be a homogeneous mixture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

Concept Review Exercises

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

Answers

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

Key Takeaways

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

Exercise 1.2.3

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

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

Answer

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

Exercise 1.2.4

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

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

Answer

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

Exercise 1.2.5

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

Answer

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

Exercise 1.2.6

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

Answer

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

Exercise 1.2.7

Give two examples of a heterogeneous mixture.

Answer

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

? Exercise 1.2.8

Give two examples of a homogeneous mixture.

Answer

vinegar and rubbing alcohol (answers will vary)

? Exercise 1.2.9

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

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

Answer

1. element
2. heterogeneous mixture
3. compound

? Exercise 1.2.10

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

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

Answer

1. compound
2. element
3. heterogeneous mixture

? Exercise 1.2.11

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

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

Answer

1. heterogeneous mixture
2. solution
3. compound

? Exercise 1.2.12

What word describes each phase change?

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

Answer

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

? Exercise 1.2.13

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

Answer

1. freezing
2. condensation
3. deposition

1.3: Measurements

Learning Objectives

- Express quantities properly using a number and a unit.

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

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

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

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

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

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

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

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

✓ Exercise 1.3.1

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

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

Answer a

The number is one, and the unit is dozen.

Answer b

The number is 2.54, and the unit is centimeter.

Answer c

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

Answer d

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

? Exercise 1.3.2

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

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

Answer a

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

Answer b

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

Answer c

The number 32, and the unit is fluid ounces

Answer d

The number is 98.6, and the unit is degrees Fahrenheit

? Exercise 1.3.2

What are the two necessary parts of a quantity?

Answer

The two necessary parts are the number and the unit.

Key Takeaway

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

1.4: 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*:

$$1,\underset{\curvearrowleft}{5}\underset{\curvearrowleft}{0}\underset{\curvearrowleft}{0},\underset{\curvearrowleft}{0}\underset{\curvearrowleft}{0}\underset{\curvearrowleft}{0} = 1.5 \times 10^6$$

Example 1.4.1: 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 1.4.1

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.

$$1.5 \times 10^6 = 1.\underbrace{500000}. = 1{,}500{,}000$$

✓ Example 1.4.2

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 1.4.2

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:

$$0.\underset{\curvearrowright}{0}\underset{\curvearrowright}{0}\underset{\curvearrowright}{6} = 6 \times 10^{-3}$$

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. $1,\underset{\curvearrowleft}{5}\underset{\curvearrowleft}{0}\underset{\curvearrowleft}{0},\underset{\curvearrowleft}{0}\underset{\curvearrowleft}{0}\underset{\curvearrowleft}{0} = 1.5 \times 10^{6}$
- 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. $0.\underset{\curvearrowright}{0}\underset{\curvearrowright}{0}\underset{\curvearrowright}{6} = 6 \times 10^{-3}$

Example 1.4.3

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 1.4.3

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

Example 1.4.4

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 1.4.4

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.

Concept Review Exercises

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

Answers

1. Scientific notation is more convenient than listing a large number of zeros.
2. 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.

1.5: 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 1.5.1).

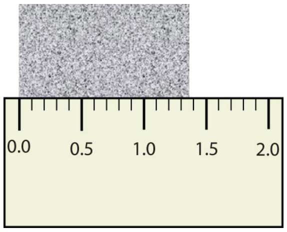


Figure 1.5.1: Measuring an Object to the Correct Number of Digits. How many digits should be reported for the length of this object?

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 1.5.1

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 1.5.1

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:

$$\begin{array}{rr@{.}l}
 & 56 & 789 \\
+ & 102 & 2 \\
+ & 1{,}300 & 099 \\
\hline
= & 1{,}459 & 088 \\
 & & \!\!\uparrow \text{Limit to this column}
\end{array}$$

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 1.5.2

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 1.5.2

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

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

Answer a

$0.240 = 2.40 \text{ x } 10^{-1}$

Answer b

$1437 = 1.437 \text{ x } 10^3$

Answer c

$156 = 1.56 \text{ x } 10^2$

Answer d

$2.14 = 2.14 \text{ x } 10^0$

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.

Concept Review Exercises

1. Explain why the concept of significant figures is important in scientific measurements.
2. State the rules for determining the significant figures in a measurement.
3. When do you round a number up, and when do you not round a number up?

Answers

1. 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.
2. 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.
3. 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.

1.6: 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 $1.6.1$, 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:

$$K = {}^{\circ}C + 273 \tag{1.6.1}$$

Table $1.6.1$: 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 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.

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 $1.6.1$). 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.

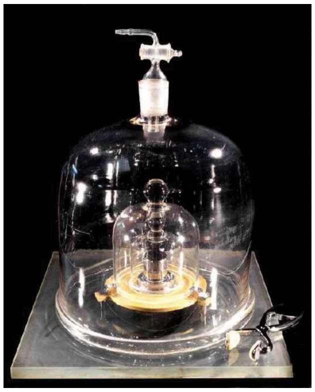


Figure 1.6.1: The Kilogram. The standard for the kilogram is a platinum-iridium cylinder kept in a special vault in France. Source: Photo reproduced by permission of the Bureau International des Poids et Mesures, who retain full internationally protected copyright.

Common prefixes and their multiplicative factors are listed in Table 1.6.2. (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 1.6.2: 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.

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.

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

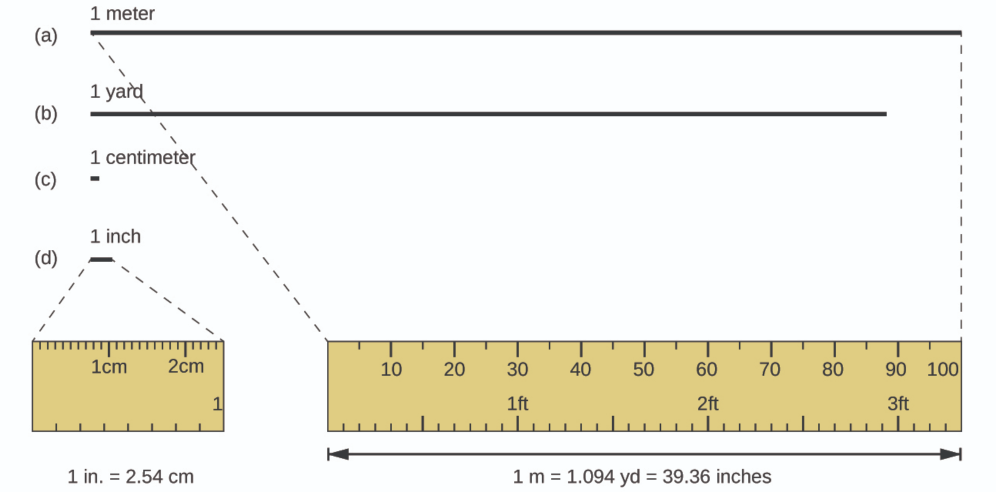


Figure 1.6.2: The relative lengths of 1 m, 1 yd, 1 cm, and 1 in. are shown (not actual size), as well as comparisons of 2.54 cm and 1 in., and of 1 m and 1.094 yd. (CC BY 4.0; OpenStax)

As shown in Figure 1.6.3, 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.

$$1\ mL = 1\ cm^3 \tag{1.6.2}$$

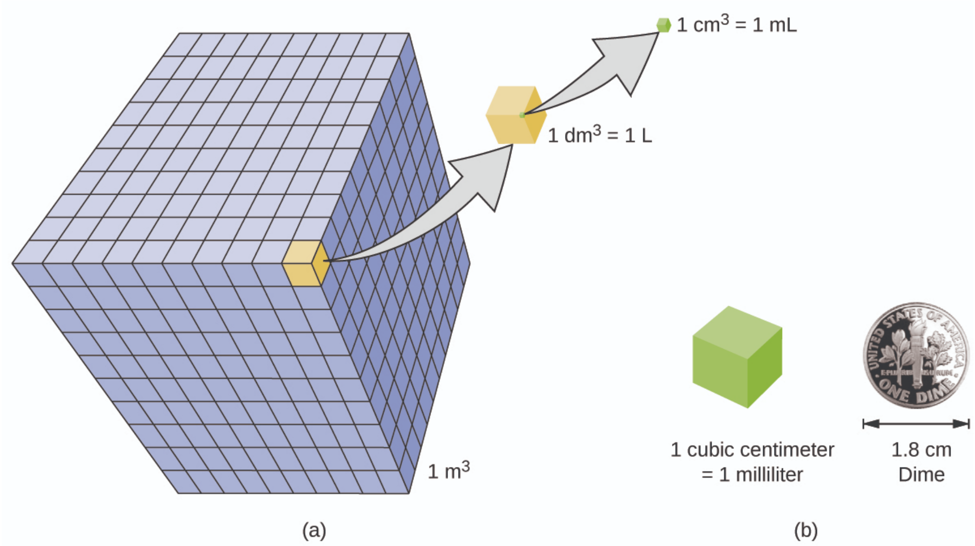


Figure 1.6.3: Units of Volume. (a) The relative volumes are shown for cubes of 1 m^3, 1 dm^3 (1 L), and 1 cm^3 (1 mL) (not to scale). A liter (L) is defined as a cube 1 dm (1/10th of a meter) on a side. A milliliter (mL), 1/1,000th of a liter, is equal to 1 cubic centimeter. (b) The diameter of a dime is compared relative to the edge length of a 1-cm^3 (1-mL) cube. (CC BY 4.0; OpenStax)

✓ Example 1.6.1

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 1.6.1

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)

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.

$$\text{density} = \frac{\text{mass}}{\text{volume}} \tag{1.6.3}$$

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 1.6.2: 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 1.6.2: 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 1.6.2: Density of Oxygen

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

Answer

1.45 g/L

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

Concept Review Exercises

1. What is the difference between a base unit and a derived unit? Give two examples of each type of unit.

2. Do units follow the same mathematical rules as numbers do? Give an example to support your answer.

3. What is density?

Answers

1. Base units are the seven fundamental units of SI; derived units are constructed by making combinations of the base units; Two examples of base units: kilograms and meters (answers will vary); Two examples of derived units: grams per milliliter and joules (answers will vary).

2. yes; $\text{mL} \times \frac{\text{g}}{\text{mL}} = \text{g}$ (answers will vary)

3. Density is defined as the mass of an object divided by its volume

Key Takeaways

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

1.7: Converting Units

Learning Objectives

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

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

Conversion Factors

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

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

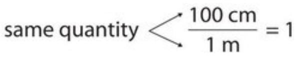
or

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

Suppose we divide both sides of the equation by 1 m (both the number *and* the unit):

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

As long as we perform the same operation on both sides of the equals sign, the expression remains an equality. Look at the right side of the equation; it now has the same quantity in the numerator (the top) as it has in the denominator (the bottom). Any fraction that has the same quantity in the numerator and the denominator has a value of 1:



We know that 100 cm *is* 1 m, so we have the same quantity on the top and the bottom of our fraction, although it is expressed in different units. A fraction that has equivalent quantities in the numerator and the denominator but expressed in *different units* is called a **conversion factor**.

Here is a simple example. How many centimeters are there in 3.55 m? Perhaps you can determine the answer in your head. If there are 100 cm in every meter, then 3.55 m equals 355 cm. To solve the problem more formally with a conversion factor, we first write the quantity we are given, 3.55 m. Then we multiply this quantity by a conversion factor, which is the same as multiplying it by 1. We can write 1 as $\frac{100\text{ cm}}{1\text{ m}}$ and multiply:

$$3.55\text{ m} \times \frac{100\text{ cm}}{1\text{ m}}$$

The 3.55 m can be thought of as a fraction with a 1 in the denominator. Because m, the abbreviation for meters, occurs in both the numerator *and* the denominator of our expression, they cancel out:

$$\frac{3.55\ \cancel{\text{m}}}{1} \times \frac{100\text{ cm}}{1\ \cancel{\text{m}}}$$

The final step is to perform the calculation that remains once the units have been canceled:

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

In the final answer, we omit the 1 in the denominator. Thus, by a more formal procedure, we find that 3.55 m equals 355 cm. A generalized description of this process is as follows:

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

You may be wondering why we use a seemingly complicated procedure for a straightforward conversion. In later studies, the conversion problems you will encounter *will not always be so simple*. If you can master the technique of applying conversion factors, you will be able to solve a large variety of problems.

In the previous example (Equation 1.7.1), we used the fraction $\frac{100\text{ cm}}{1\text{ m}}$ as a conversion factor. Does the conversion factor $\frac{1\text{ m}}{100\text{ cm}}$ also equal 1? Yes, it does; it has the same quantity in the numerator as in the denominator (except that they are expressed in different units). Why did we not use *that* conversion factor? If we had used the second conversion factor, the original unit would not have canceled, and the result would have been meaningless. Here is what we would have gotten:

$$3.55\text{ m}\times\frac{1\text{ m}}{100\text{ cm}}=0.0355\frac{\text{m}^2}{\text{cm}}$$

For the answer to be meaningful, we have to *construct the conversion factor in a form that causes the original unit to cancel out*. Figure $1.7.1$ shows a **concept map** for constructing a proper conversion.

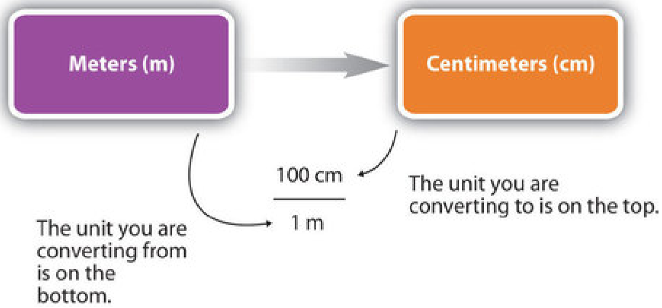


Figure $1.7.1$: A Concept Map for Conversions. This is how you construct a conversion factor to convert from one unit to another.

Meters converted to centimeters. A fraction showing 100 cm over 1 m. The unit you convert to is on top, and the unit you convert from is on bottom.

Significant Figures in Conversions

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

✓ Example 1.7.1

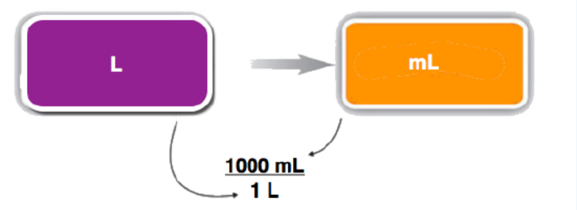
a. The average volume of blood in an adult male is 4.7 L. What is this volume in milliliters?
b. A hummingbird can flap its wings once in 18 ms. How many seconds are in 18 ms?

Solution

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

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

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



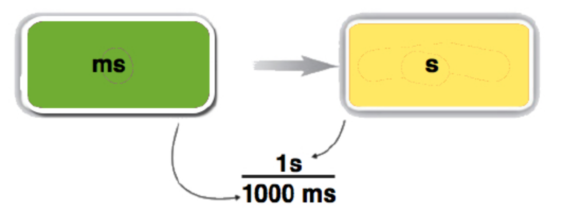
$$4.7\ \cancel{\text{L}} \times \frac{1,000\ \text{mL}}{1\ \cancel{\text{L}}} = 4,700\ \text{mL}$$

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

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

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

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



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

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

? Exercise 1.7.1

Perform each conversion.

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

Answer a

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

Answer b

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

Conversion Factors From Different Units

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

13.6 g mercury = 1 mL mercury

This relationship can be used to construct two conversion factors:

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

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

$$\begin{aligned} 16\ \cancel{\text{mL}} \times \frac{13.6\ \text{g}}{1\ \cancel{\text{mL}}} &= 217.6\ \text{g} \\ &\approx 220\ \text{g} \end{aligned}$$

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

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

Example 1.7.2: Mercury Thermometer

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

Solution

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

$$\begin{aligned} 0.750\ \cancel{\text{g}} \times \frac{1\ \text{mL}}{13.6\ \cancel{\text{g}}} &= 0.055147\ldots\ \text{mL} \\ &\approx 0.0551\ \text{mL} \end{aligned}$$

We have limited the final answer to three significant figures.

Exercise 1.7.2

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

Answer

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

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

Looking Closer: Density and the Body

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

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

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

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

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

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

Problem Solving With Multiple Conversions

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

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

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

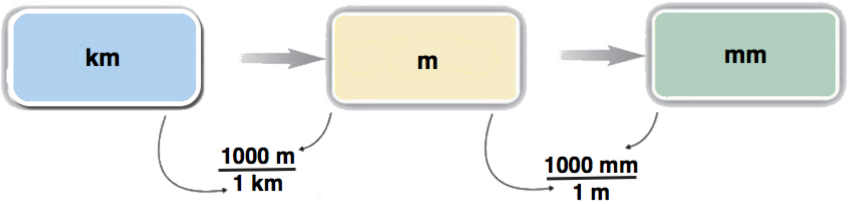
Then we take the result (54,700 m) and convert it to millimeters, remembering that there are $1,000\ \text{mm}$ for every $1\ \text{m}$:

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

We have expressed the final answer in scientific notation.

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

Concept Map



Calculation

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

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

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

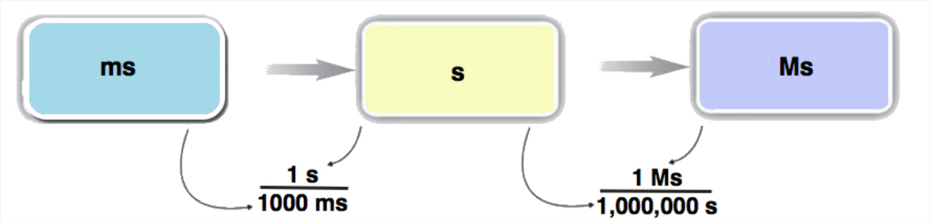
✓ Example 1.7.3

Convert 58.2 ms to megaseconds in one multistep calculation.

Solution

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

Concept Map



Calculation

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

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

? Exercise 1.7.3

Convert 43.007 mg to kilograms in one multistep calculation.

Answer

$$\begin{aligned} 43.007\ \cancel{\text{mg}} \times \frac{1\cancel{\text{g}}}{1,000\ \cancel{\text{mg}}} \times \frac{1\ \text{kg}}{1,000\ \cancel{\text{g}}} &= 0.000043007\ \text{kg} \\ &= 4.3007 \times 10^{-5}\ \text{kg} \end{aligned}$$

.

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

Career Focus: Pharmacist

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

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

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

Key Takeaway

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

Concept Review Exercises

1. How do you determine which quantity in a conversion factor goes in the denominator of the fraction?
2. State the guidelines for determining significant figures when using a conversion factor.

3. Write a concept map (a plan) for how you would convert 1.0×10^{12} *nano*liters (nL) to *kilo*liters (kL).

Answers

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

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

1.8: Dosage Calculations

Learning Objectives

- Calculate drug dosages using conversion factors.

To Your Health: Dosages

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

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

Effects are dose-dependent

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

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

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

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

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

Calculation of dose

Calculating drug dosages for humans based on the doses used in animal studies can be based on weight (e.g., mg/kg) or surface area (e.g., mg/m2) based on weight2/3.[1]

Drug dosage calculations

Drug dosage calculation is required if the physician's order is different from what is available.

✓ Example 1.8.1

a. A physician ordered 100 mg of Demerol. Demerol is available as 50 mg per tablet. How many tablets should the nurse administer?
b. The doctor's order is 1.2 g of Folic Acid. Folic Acid is available as 800 mg per tablet. How many tablets should be taken?

Solution

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

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

Hence, the nurse should administer 2 tablets.

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

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

Hence, 1.5 tablets should be taken.

? Exercise 1.8.1

Calculate each of the following.

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

Answer a

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

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

Answer b

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

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

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

✓ Example 1.8.2

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

Solution

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

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

Hence, the nurse administers 3 tablets.

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

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

Hence, the nurse administers 2 tablets.

Exercise 1.8.2

Calculate each of the following.

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

Answer a

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

Answer b

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

References

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

Contributors and Attributions

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- Leticia Colmenares (UH-WCC)

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

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

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

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

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

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

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

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.

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

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

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

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

2.1: The Elements

Learning Objectives

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

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

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

Abundance

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

Table 2.1.1: Elemental Composition of Earth

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

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

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

Table 2.1.2: Elemental Composition of a Human Body

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

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

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

LOOKING CLOSER: PHOSPHOROUS, THE CHEMICAL BOTTLENECK

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

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

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

Names and Symbols

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

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

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

Table 2.1.3: Element Names and Symbols

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

*The symbol comes from the Latin name of element.

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

lithium	Li	zirconium	Zr
*The symbol comes from the Latin name of element.			
[†]The symbol for tungsten comes from its German name—*wolfram*.			

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

✓ Example 2.1.1

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

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

Answer a

Br

Answer b

B

Answer c

C

Answer d

Ca

Answer e

Au

? Exercise 2.1.1

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

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

Answer a

Mn

Answer b

Mg

Answer c

Ne

Answer d

N

Answer e

Ag

✓ Example 2.1.2

What element is represented by each chemical symbol?

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

Answer a

sodium

Answer b

mercury

Answer c

phosphorus

Answer d

potassium

Answer e

iodine

? Exercise 2.1.2

What element is represented by each chemical symbol?

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

Answer a

lead

Answer b

tin

Answer c

uranium

Answer d

oxygen

Answer e

fluorine

Concept Review Exercises

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

Answers

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

Key Takeaways

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

2.2: 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 $2.2.1$), 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).

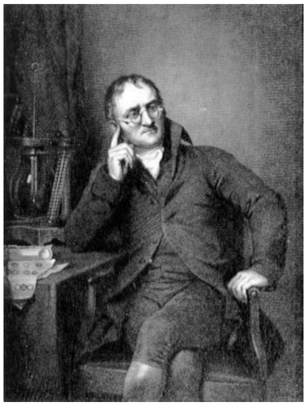


Figure 2.2.1 John Dalton was an English scientist who enunciated the modern atomic theory.

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 $2.2.2$).

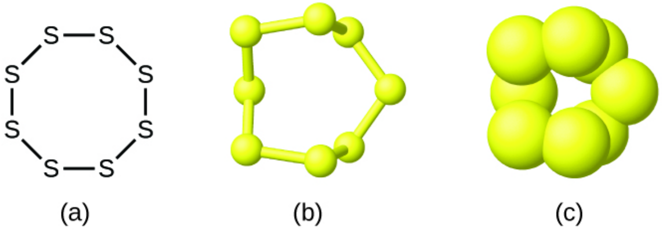


Figure 2.2.2: A molecule of sulfur is composed of eight sulfur atoms and is therefore written as S_8. It can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. Sulfur atoms are represented by yellow spheres.

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 2.2.3).

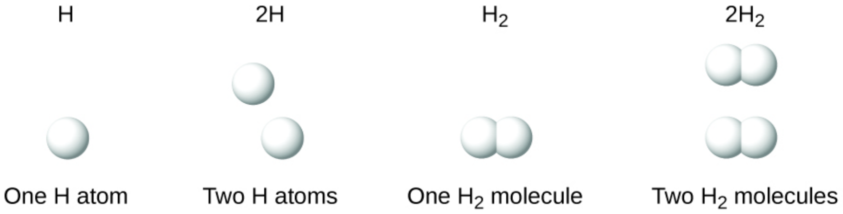


Figure 2.2.3: The symbols H, 2H, H_2, and $2H_2$ represent very different entities.

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 2.2.1

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.

rcise

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.

2.3: 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 $2.3.1$ lists some of their important characteristics and the symbols used to represent each particle.

Table $2.3.1$: 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 $2.3.1$ shows a diagram of the experimental setup.

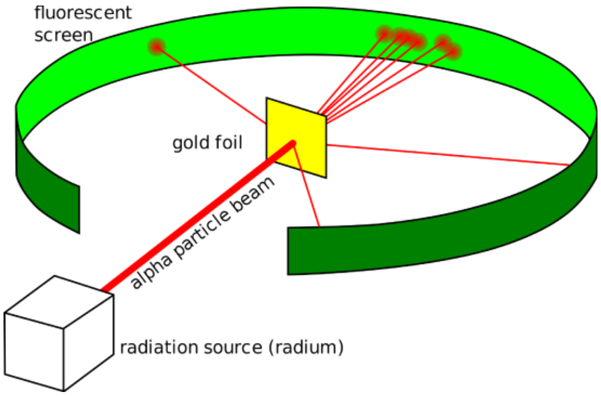


Figure 2.3.1: The Geiger-Marsden Experimental Setup. Experiments using this setup were used to investigate the structure of atoms. In this experiment, most of the particles traveled straight through the foil, but some alpha particles were deflected off to one side. Some were even deflected back toward 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 2.3.2 shows how this model explains the experimental results.

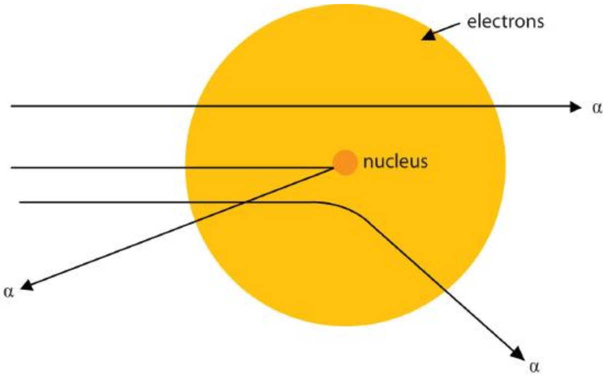


Figure 2.3.2: Rutherford’s Metal Foil Experiments. Rutherford explained the results of the metal foil experiments by proposing that most of the mass and the positive charge of an atom are located in its nucleus, while the relatively low-mass electrons orbit about the nucleus. Most alpha particles go 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 2.3.3 shows a more modern version of our understanding of atomic structure.

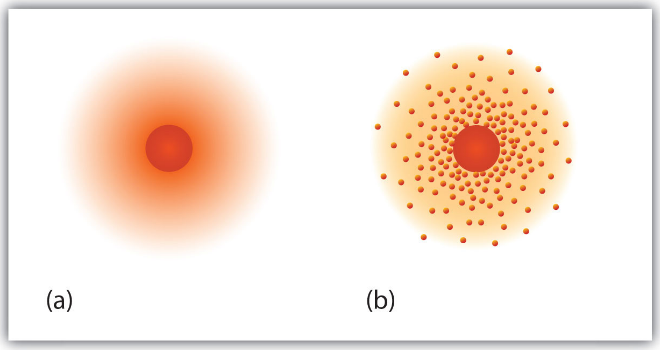


Figure 2.3.3: A Modern Depiction of Atomic Structure. A more modern understanding of atoms, reflected in these representations of the electron in a hydrogen atom, is that electrons occupy regions of space about the nucleus; they are not in discrete orbits like planets around the sun. (a) The darker the 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.

2.4: 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 2.4.1 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.

Table 2.4.1: 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

Element	Atomic Number	Element	Atomic Nmbers
iron (Fe)	26	tungsten (W)	74
iodine (I)	53	uranium (U)	92
lead (Pb)	82	zinc (Zn)	30
lithium (Li)	3	zirconium (Zr)	40

✓ Example 2.4.1

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 2.4.1

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 2.4.2

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 2.4.2

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.

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.

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 2.4.1 compares the three isotopes of hydrogen.

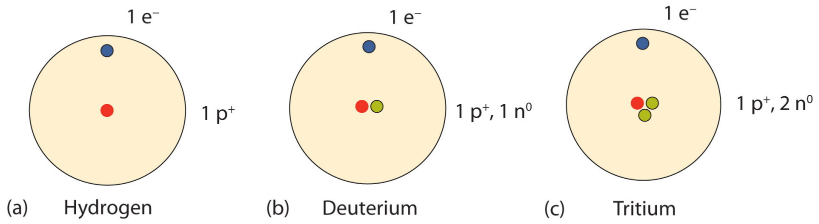


Figure 2.4.1: Isotopes of Hydrogen. Most hydrogen atoms have only a proton in the nucleus (a). A small amount of hydrogen exists as the isotope deuterium, which has one proton and one neutron in its nucleus (b). A tiny amount of the hydrogen isotope tritium, with one proton and two neutrons in its nucleus, also exists on Earth (c). The nuclei and electrons are proportionately much smaller than depicted here.

> 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

$$\begin{matrix} \text{mass number} \longrightarrow \\ \text{atomic number} \longrightarrow \end{matrix} {}^{56}_{26}\text{Fe} \tag{2.4.1}$$

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 2.4.3

How many protons and neutrons are in each atom?

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

Answer a

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

Answer b

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

? Exercise 2.4.3

How many protons and neutrons are in each atom?

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

Answer a

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

Answer b

In ${}^{23}_{11}\text{Na}$ 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 ${}^{13}\text{C}$ or ${}^{235}\text{U}$. 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 2.4.2.

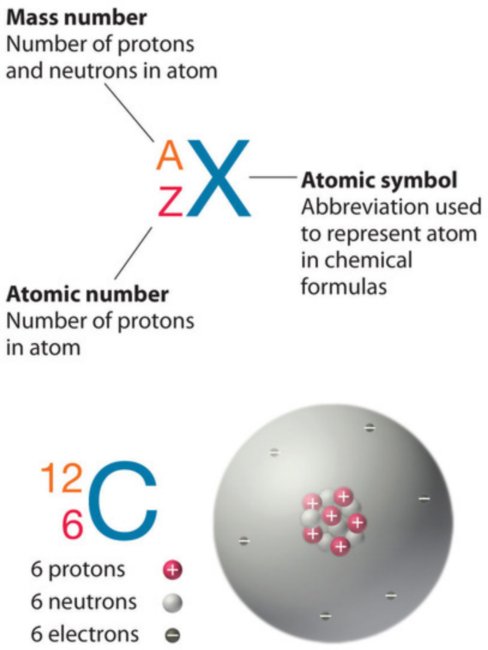


Figure 2.4.2: Formalism used for identifying specific nuclide (any particular kind of nucleus)

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.

2.5: 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:

$$1\ \text{u} = \frac{1}{12}\ \text{the mass of}\ ^{12}\text{C atom} \tag{2.5.1}$$

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 2.5.1) are the naturally occurring isotopes of selected elements along with the percent natural abundance of each.

Table 2.5.1: 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.

$$\text{Atomic mass} = (\%1)(\text{mass } 1) + (\%2)(\text{mass } 2) + \cdots$$

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:

$$\text{Atomic mass} = (\%1)(\text{mass } 1) + (\%2)(\text{mass } 2) + (\%3)(\text{mass } 3)$$

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

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

✓ Example 2.5.1

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.

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

rcise

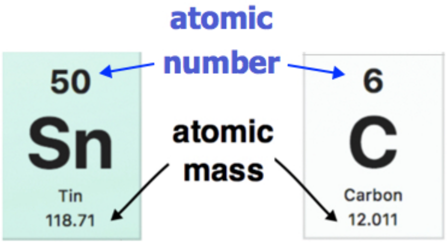
Calculate the atomic mass of copper. Copper exists as a mixture of 2 isotopes. Their respective masses and natural abundance are shown below.

- ^{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 2.5.2: 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 2.5.2: 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.

2.6: 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 2.6.1: Shells and Subshells

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

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

Table 2.6.2: Number of Electrons

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

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

We use numbers to indicate which shell an electron is in. As shown in Table 2.6.1, 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 $\mathbf{1s^1}$ 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 $\mathbf{1s^2}$ (spoken as “one-ess-two”).

The 1s 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 1s 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 2s subshell holds a maximum of 2 electrons, and the 2p subshell holds a maximum of 6 electrons. Because lithium's final electron goes into the 2s subshell, we write the electron configuration of a lithium atom as **1$s^2$2s^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.

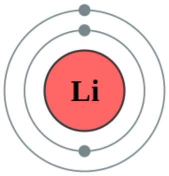


Figure 2.6.1: Shell diagram of lithium (Li) atom.

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

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

With neon, the 2p 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 1$s^2$2$s^2$2$p^6$3$s^2$3p^1. However, a curious thing happens after the 3p subshell is filled: the 4s subshell begins to fill before the 3d 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 2.6.2. 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.

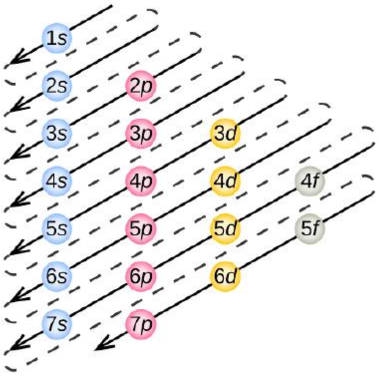


Figure 2.6.2: The order of electron filling in an atom.

✔ Example 2.6.1: Electronic Configuration of Phosphorus Atoms

Using Figure 2.6.2 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 $1s^22s^22p^63s^23p^3$.

? Exercise 2.6.1: Electronic Configuration of Chlorine Atoms

Using Figure $2.6.2$ 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 $1s^22s^22p^63s^23p^5$.

Since the arrangement of the periodic table is based on the electron configurations, Figure $2.6.3$ 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.

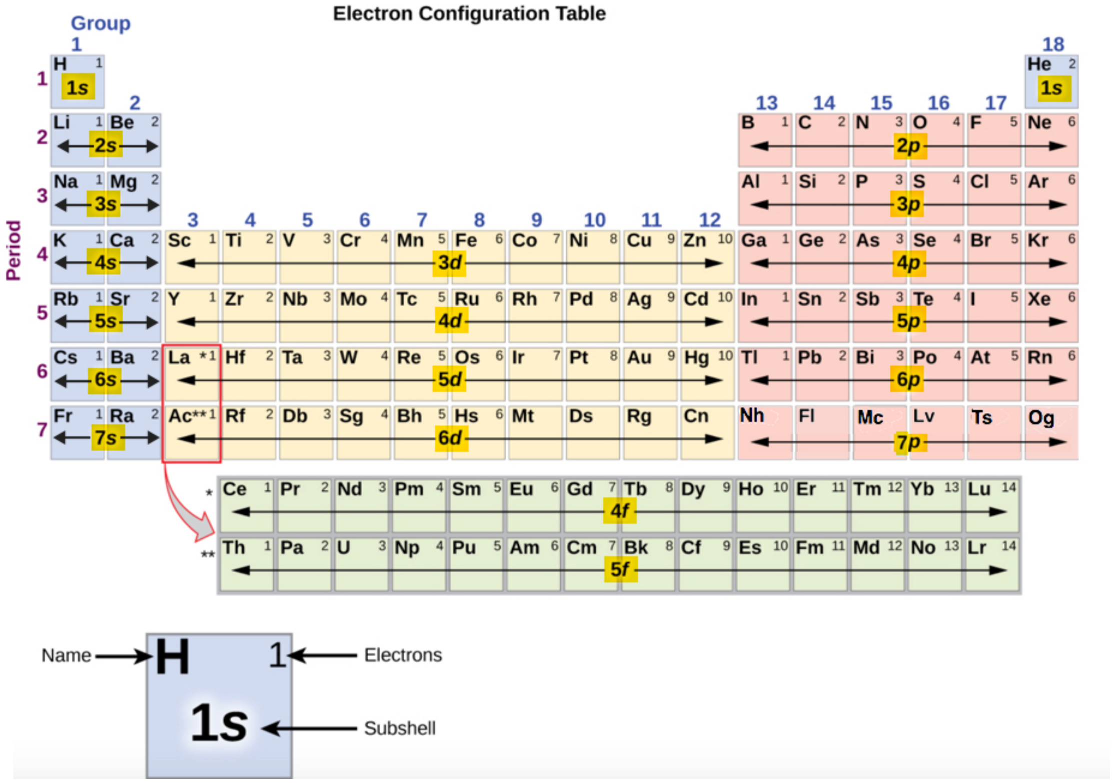


Figure $2.6.3$: This periodic table shows the electron configuration for each subshell. By “building up” from hydrogen, this table can be used to determine the electron configuration for any atom on the periodic table.

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 $2.6.3$ 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 2.6.2: Aluminum

Using Figure $2.6.3$ 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 $2.6.3$. 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 **$1s^22s^22p^63s^23p^1$**

rcise

Using Figure $2.6.3$ as your guide, write the electron configuration of the atom that has 20 electrons

Answer

Start at Period 1 of Figure $2.6.3$ 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 **$1s^22s^22p^63s^23p^64s^2$**

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 $1s$ 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 $2s$ and the $2p$ 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 $2s^22p^6$, has eight valence electrons.

The alkali metal sodium (atomic number 11) has one more electron than the neon atom. This electron must go into the lowest-energy subshell available, the 3*s* orbital, giving a $1s^22s^22p^63s^1$ configuration. The electrons occupying the outermost shell orbital(s) (highest value of *n*) are called valence electrons, and those occupying the inner shell orbitals are called **core electrons** (Figure \PageIndex4). Since the core electron shells correspond to noble gas electron configurations, we can abbreviate electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. For our sodium example, the symbol [Ne] represents core electrons, ($1s^22s^22p^6$) and our abbreviated or condensed configuration is [Ne]$3s^1$.

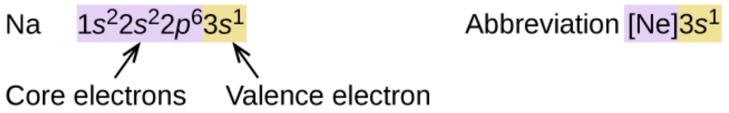


Figure 2.6.4: A core-abbreviated electron configuration (right) replaces the core electrons with the noble gas symbol whose configuration matches the core electron configuration of the other element.

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.

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

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 2.6.3

Examine the electron configuration of neutral phosphorus atoms in Example 2.6.1, $1s^2 2s^2 2p^6 3s^2 3p^3$ 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 2.6.3). Abbreviated notation is : [Ne]$3s^2 3p^3$

? Exercise 2.6.3

Examine the electron configuration of neutral calcium atom (Exercise 2.6.2), $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$, and write the abbreviated notation.

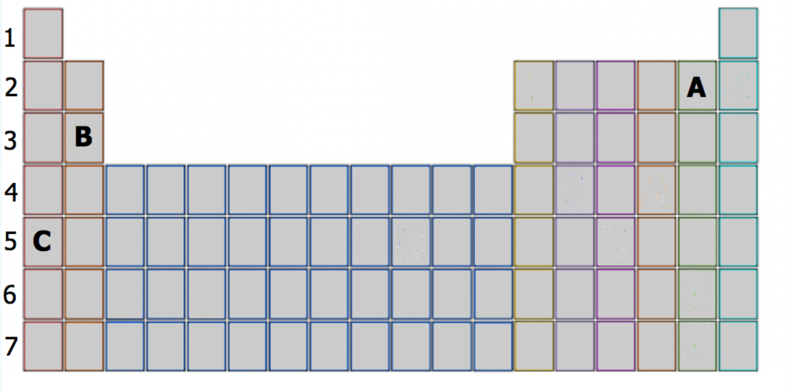
Answer

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 2.6.3 The abbreviated notation is: [Ar]$4s^2$

✓ Example 2.6.4

Based on their respective locations in the periodic table (use Figure 2.6.3), 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: **$5s^1$**.

rcise

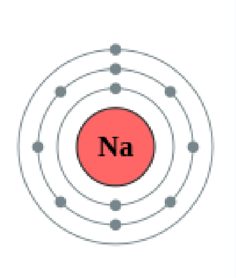
Using the location of Na is the periodic table (Figure 2.6.3), draw the shell diagram of sodium atom.

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

2.7: 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 $2.7.1$. 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.

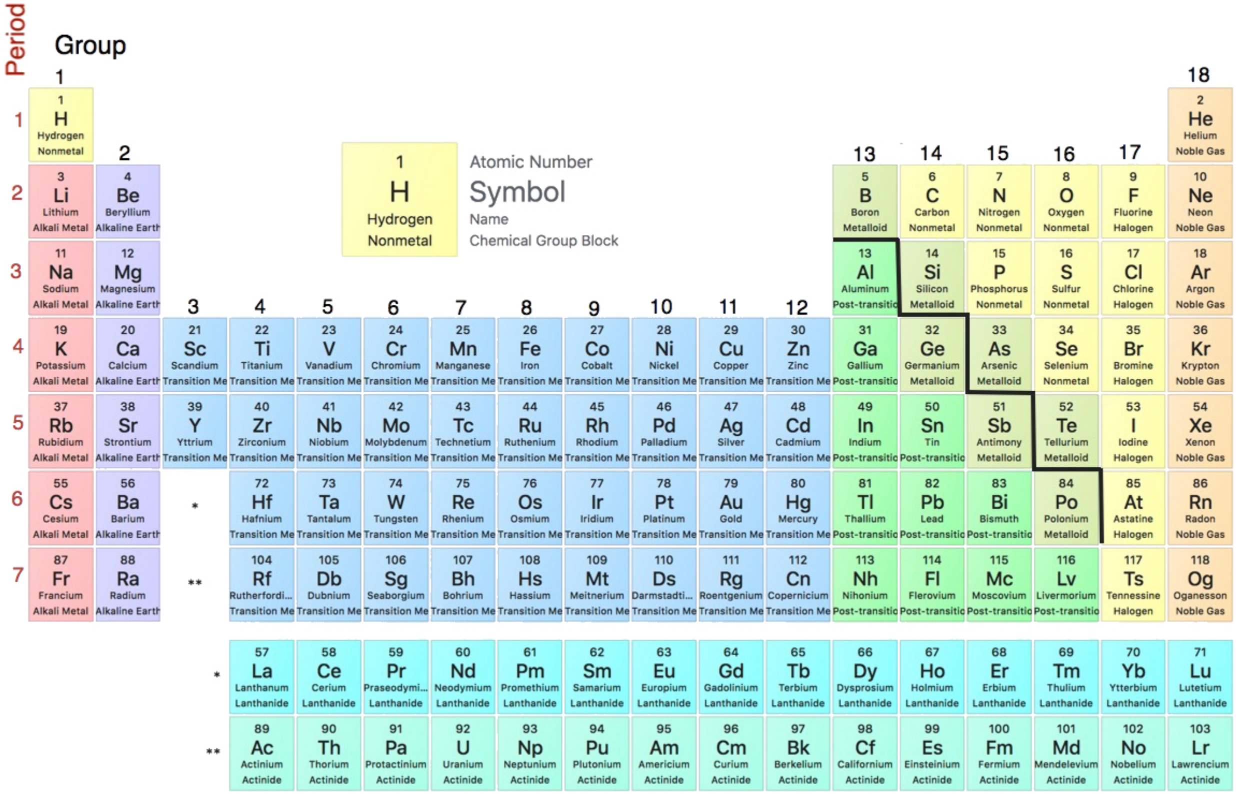


Figure $2.7.1$: Modern Periodic Table. (Public Domain; PubChem modified Leticia Colmenares).

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 2.7.2. 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 2.7.2, **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.

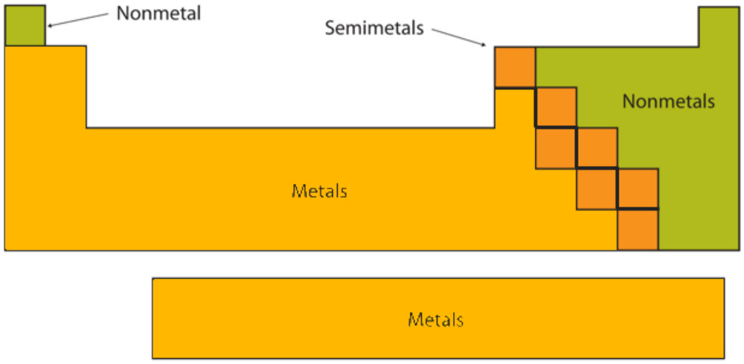


Figure 2.7.2: Types of Elements. Elements are either metals, nonmetals, or semimetals. Each group is located in a different part of the periodic table.

✓ Example 2.7.1

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.

rcise

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 2.7.3. 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**.

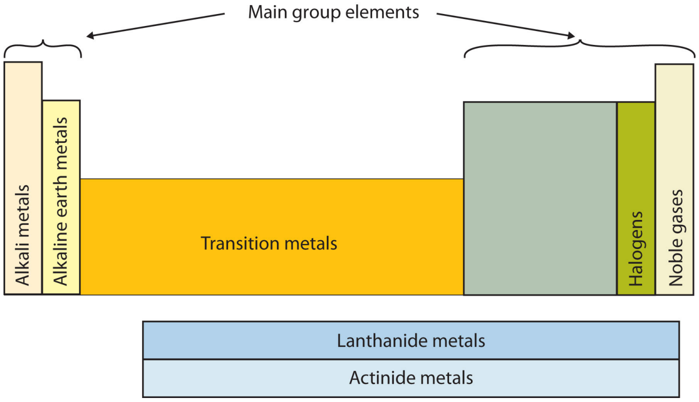


Figure 2.7.3: Special Names for Sections of the Periodic Table. Some sections of the periodic table have special names. The elements lithium, sodium, potassium, rubidium, cesium, and francium are collectively known as alkali metals.

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 2.7.4. 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.**

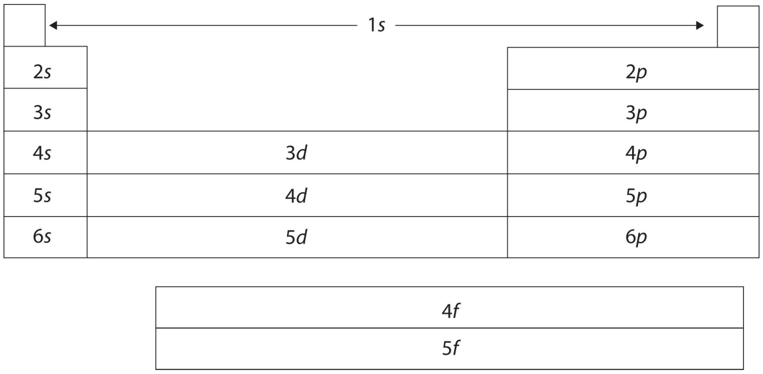


Figure 2.7.4 The Shape of the Periodic Table. The shape of the periodic table reflects the order in which electron shells and subshells fill with electrons.

✓ Example 2.7.1

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 2.7.1

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 2.7.1. 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 2.7.5). The atomic radius is defined as one-half the distance between the nuclei of identical atoms that are bonded together. The units for atomic radii are picometers, equal to 10^{-12} meters. As an example, the internuclear distance between the two hydrogen atoms in an H_2 molecule is measured to be $74\ pm$. Therefore, the atomic radius of a hydrogen atom is $\frac{74}{2} = 37\ pm$.

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 2.7.5

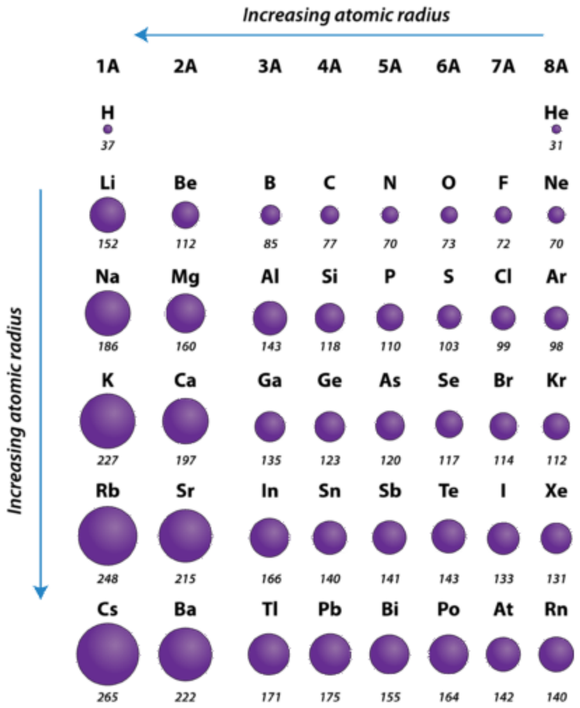


Figure 2.7.5 Trends on the Periodic Table. Atomic radii of the representative elements measured in picometers. The relative sizes of the atoms show several trends with regard to the structure of the periodic table. Atoms become larger going down a group and going from right to left across a period.

✓ Example 2.7.2

Using the periodic table (rather than Figure 2.7.5), 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 2.7.2

Using the periodic table (rather than Figure 2.7.5), 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.

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

02.E: Exercises II

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

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

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

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

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

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

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

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

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

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

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.

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3.0: Prelude to Ionic Bonding and Simple Ionic Compounds

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

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

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

3.1: Two Types of Bonding

Learning Objectives

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

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

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

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

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

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

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

Example 3.1.1

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

Solution

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

Table explaining the solution to the example.

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

? Exercise 3.1.1

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

Answer

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

Key Takeaways

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

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.

3.2: Ions

Learning Objectives

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

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

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

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

Electron Transfer

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

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

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

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

Figure $3.2.1$ is a graphical depiction of this process.

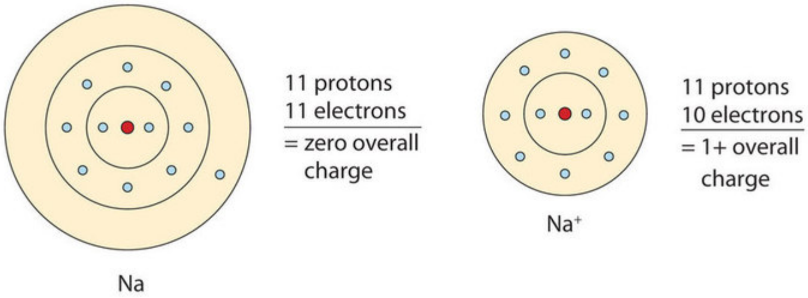

Figure $3.2.1$: The Formation of a Sodium Ion. On the left, a sodium atom has 11 electrons. On the right, the sodium ion only has 10 electrons and a 1+ charge.

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

Only one more electron is needed to achieve an octet in chlorine's valence shell. When a chlorine atom gains an electron, its outermost principal energy level achieves an octet. In this case, the ion has the same outermost shell as the original atom, but now that shell has eight electrons in it. Once again, the octet rule has been satisfied. The resulting anion, Cl^-, is called the chloride ion; note the slight change in the suffix (*-ide* instead of *-ine*) to create the name of this anion. This process is illustrated below. (In table salt, this electron comes from the sodium atom.)

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

Figure $3.2.2$ is a graphical depiction of this process.

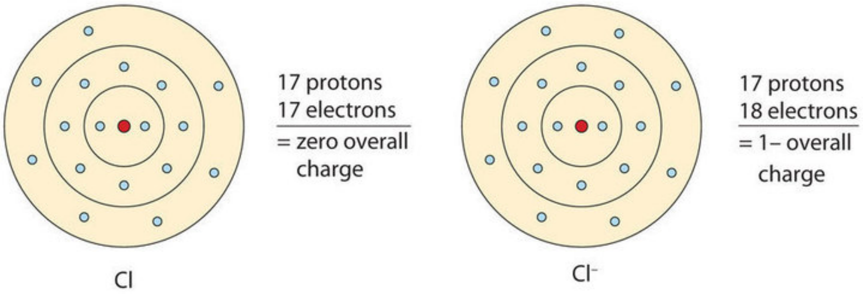

Figure $3.2.2$: The Formation of a Chlorine Ion. On the left, the chlorine atom has 17 electrons. On the right, the chloride ion has 18 electrons and has a 1− charge.

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

✓ Example 3.2.1

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

Solution

The electron configuration of Al atom is $1s^22s^22p^63s^23p^1$. The second shell has octet ($2s^22p^6$) while the valence shell has 3 electrons ($3s^23p^1$). Mg can achieve octet by losing the 3 valence electrons. The resulting cation is Al^{3+} with electron configuration, $1s^22s^22p^6$.

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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 $1s^22s^22p^4$. The second shell has six electrons ($2s^22p^4$) and needs two electrons to achieve octet. Oxygen will gain 2 electrons. The resulting anion is O^{2-} with electron configuration, $1s^22s^22p^6$.

In many cases, elements that belong to the same group (vertical column) on the periodic table form ions with the same charge because they have the same number of valence electrons. Thus, the periodic table becomes a tool for remembering the charges on many ions. For example, all ions made from alkali metals, the first column on the periodic table, have a 1+ charge. Ions made from alkaline earth metals, the second group on the periodic table, have a 2+ charge. On the other side of the periodic table, the next-to-last column, the halogens, form ions having a 1− charge. Figure $3.2.3$ shows how the charge on many ions can be predicted by the location of an element on the periodic table. Note the convention of first writing the number and then the sign on a multiply charged ion. The barium cation is written Ba^{2+}, not Ba^{+2}.

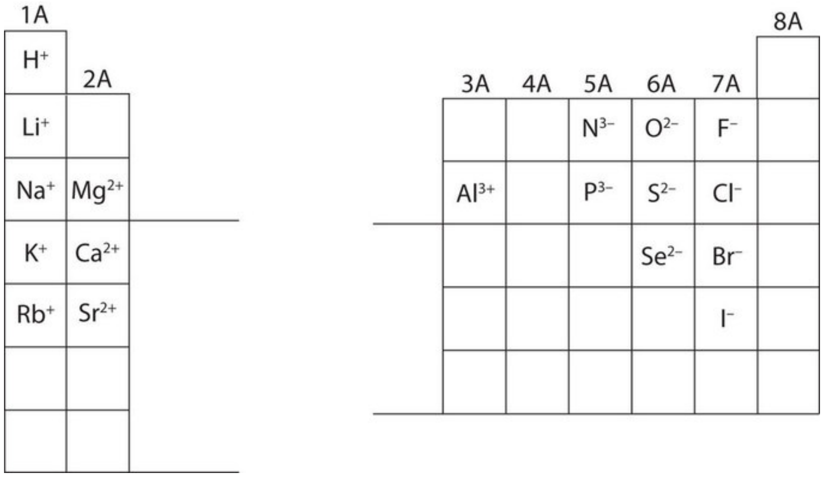

Figure 3.2.3: Predicting Ionic Charges. The charge that an atom acquires when it becomes an ion is related to the structure of the periodic table. Within a group (family) of elements, atoms form ions of a certain charge.

✓ Example 3.2.2

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

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

Solution

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

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

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

Answer

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

Lewis Diagrams

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

and the representation for chlorine is as follows:

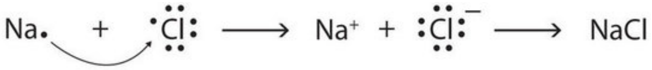
> For the above diagrams, it does not matter what sides the dots are placed on in Lewis diagrams as long as each side has a maximum of two dots.

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

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

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

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



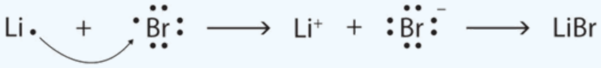
In representing the final formula, the dots are omitted.

Example 3.2.3

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

Solution

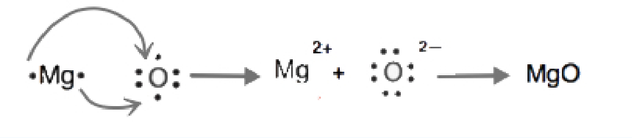
From the periodic table, we see that lithium is in the same column as sodium, so it will have the same valence shell electron configuration. That means that the neutral lithium atom will have the same Lewis diagram that the sodium atom has. Similarly, bromine is in the same column as chlorine, so it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



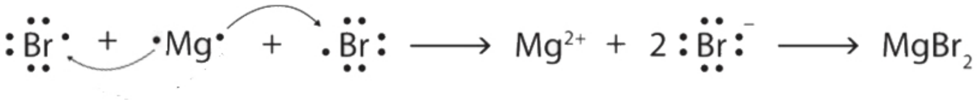
Exercise 3.2.3

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

Answer



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



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

Most of the elements that make ionic compounds form an ion that has a characteristic charge. For example, sodium makes ionic compounds in which the sodium ion always has a 1+ charge. Chlorine makes ionic compounds in which the chloride ion always has a 1− charge. Some elements, especially transition metals, can form ions of multiple charges. Figure $3.2.5$ shows the characteristic charges for some of these ions. As we saw in Figure $3.2.1$, there is a pattern to the charges on many of the main group ions, but there is no simple pattern for transition metal ions (or for the larger main group elements).

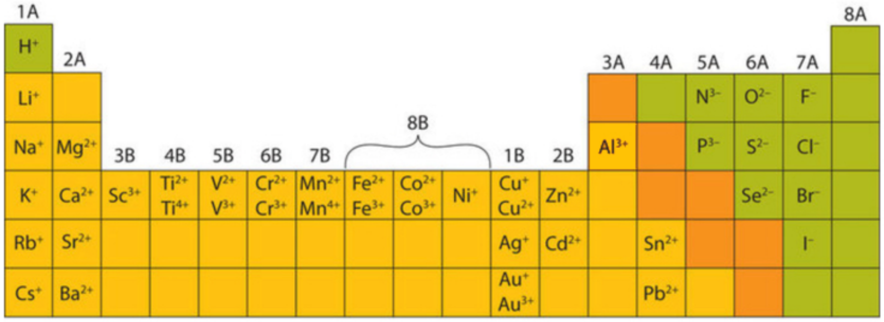


Figure $3.2.5$: Charges of the Monatomic Ions. Note that some atoms commonly form ions of variable charges.

Key Takeaways

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

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

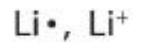
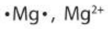
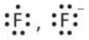
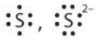
6.
   a. $1s^2$
   b. $1s^2 2s^2 2p^6$

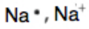
   c. $1s^2 2s^2 2p^6$
   d. $1s^2 2s^2 2p^6 3s^2 3p^6$

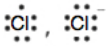
7.

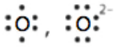
   a. $1s^2 2s^2 2p^6$
   b. $1s^2$
   c. $1s^2 2s^2 2p^6 3s^2 3p^6$
   d. $1s^2 2s^2 2p^6$

8.

   a. 
   b. 
   c. 
   d. 







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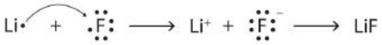
10. 

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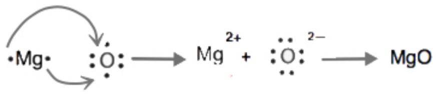
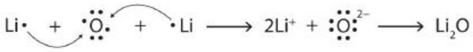
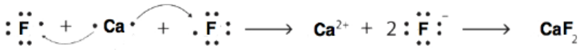


12. 

13.



14. 1+

15. 2+

16. 2−

17. 1−

3.3: 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 $3.3.1$). 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 $3.3.1$ shows that no single ion is exclusively associated with any other single ion. Each ion is surrounded by ions of opposite charge.

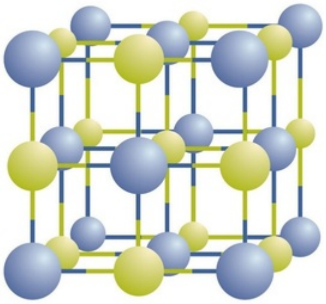


Figure $3.3.1$: A Sodium Chloride Crystal. A crystal contains a three-dimensional array of alternating positive and negative ions. The precise pattern depends on the compound. A crystal of sodium chloride, shown here, is a collection of alternating sodium and chlorine ions.

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:

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

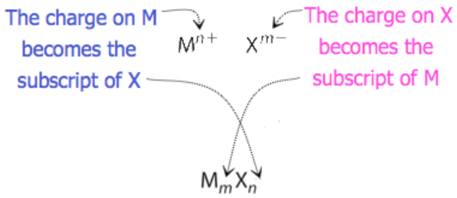
Combining one ion of each does not completely balance the positive and negative charges. The easiest way to balance these charges is to assume the presence of *two* chloride ions for each magnesium ion:

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

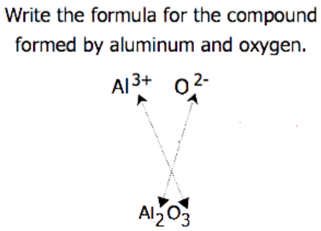
Now the positive and negative charges are balanced. We could write the chemical formula for this ionic compound as $MgClCl$, but the convention is to use a numerical subscript when there is more than one ion of a given type—$MgCl_2$. This chemical formula says that there are one magnesium ion and *two* 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 3.3.2: 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 3.3.1

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

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

Solution

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

? Exercise 3.3.1

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:

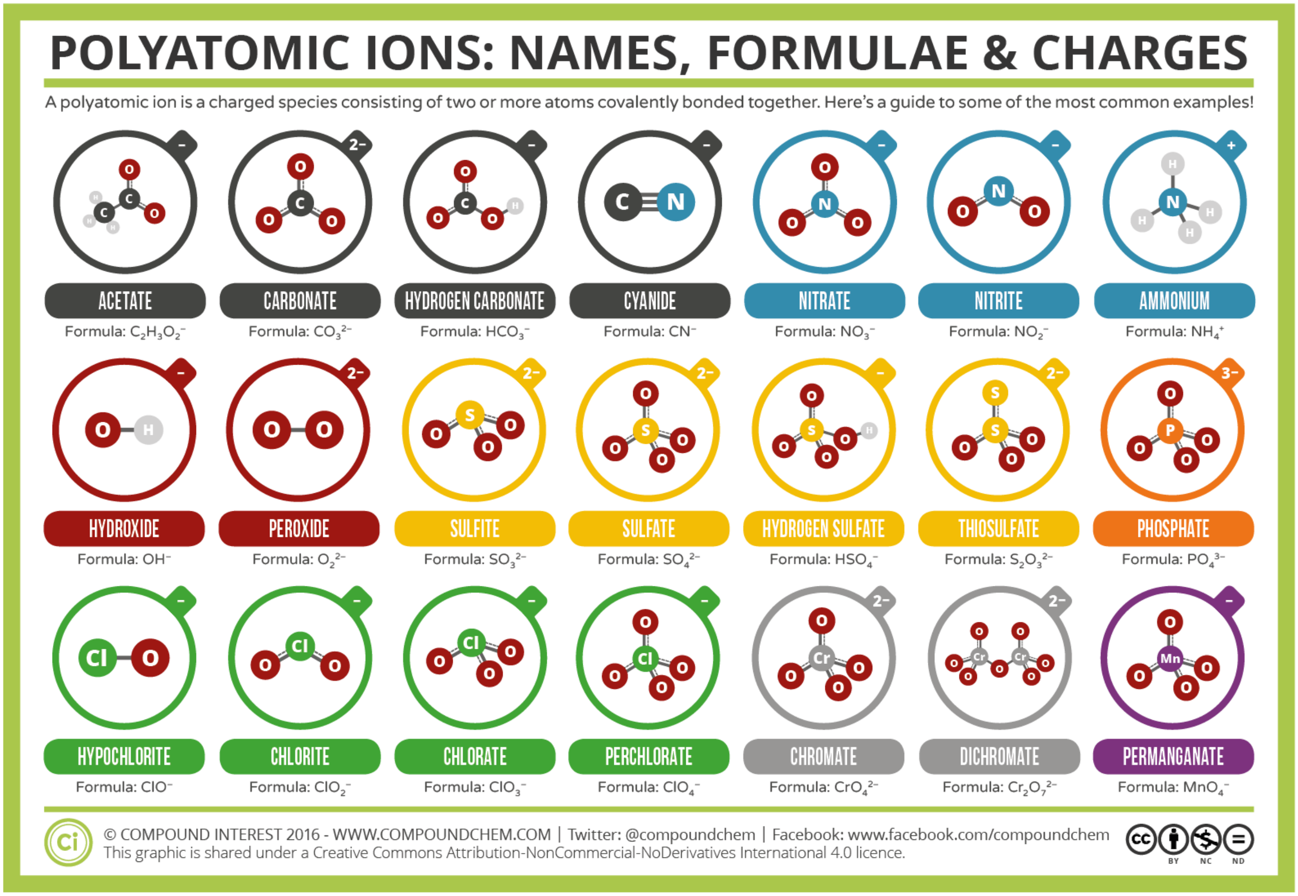
CuS

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.


POLYATOMIC IONS: NAMES, FORMULAE & CHARGES

A polyatomic ion is a charged species consisting of two or more atoms covalently bonded together. Here's a guide to some of the most common examples!

Table 3.3.1: Some Polyatomic Ions

Polyatomic ions have defined formulas, names, and charges that cannot be modified in any way. Table 3.3.2 lists the ion names and ion formulas of the most common polyatomic ions. For example, NO_3^- is the nitrate ion; it has one nitrogen atom and three oxygen atoms and an overall 1− charge. Figure 3.3.2 lists the most common polyatomic ions.

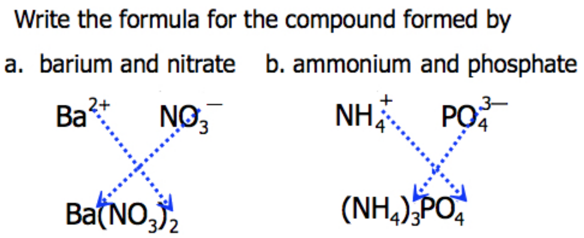
Table 3.3.2: Ion Names and Ion Formulas of Common Polyatomic Ions

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}

Ion Name	Ion Formula
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 3.3.2

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 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 $Ca(NO_3)_2$ as the formula for this ionic compound.

? Exercise 3.3.2

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

✓ Example 3.3.3

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 3.3.3

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

Key Takeaways

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

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

3.4: 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 3.4.1: 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 3.4.1 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 3.4.2 lists the names of some common monatomic ions.

Table 3.4.2: 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 3.4.1

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 3.4.2)

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 3.4.1

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 3.4.2

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 3.4.2

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

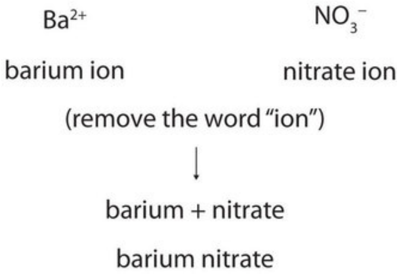
Fe^{2+}

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 $\mathrm{Ba(NO_3)_2}$?



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 $\mathrm{FeCl_2}$ and $\mathrm{FeCl_3}$. In the first compound, the iron ion has a 2+ charge because there are two $\mathrm{Cl^-}$ ions in the formula (1− charge on each chloride ion). In the second compound, the iron ion has a 3+ charge, as indicated by the three $\mathrm{Cl^-}$ ions in the formula. These are two different compounds that need two different names. By the Stock system, the names are iron(II) chloride and iron(III) chloride. If we were to use the stems and suffixes of the common system, the names would be ferrous chloride and ferric chloride, respectively.

✓ Example 3.4.3

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

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

Answer a

calcium phosphate

Answer b

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

Answer c

potassium chloride

Answer d

copper(I) chloride or cuprous chloride

Answer e

tin(II) fluoride or stannous fluoride

? Exercise 3.4.3

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

a. $ZnBr_2$
b. $Fe(NO_3)_3$
c. Al_2O_3

d. CuF_2
e. AgF

Answer a

zinc bromide

Answer b

iron (III) nitrate or ferric nitrate

Answer c

aluminum oxide

Answer d

copper (II) fluoride or cupric fluoride

Answer e

silver fluoride

Figure $3.4.1$ is a synopsis of how to name simple ionic compounds.

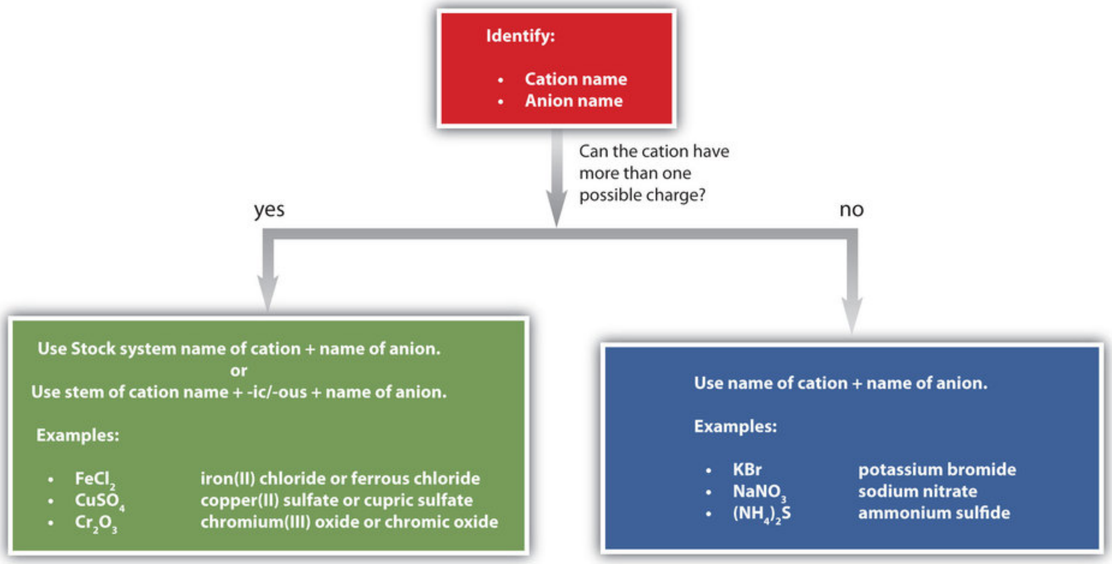


Figure $3.4.1$: A Guide to Naming Simple Ionic Compounds. Follow these steps to name a simple ionic compound. Identify the cation name and the anion name. If the cation can have more than one possible charge, either use the Stock system name of the cation and name of the anion, or use the stem of the cation name and -ic/-ous and the name of the anion. Examples of this would be $FeCl_2$, 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

3.5: Formula Mass

Learning Objectives

- To determine the formula mass of an ionic compound.

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

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

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

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

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

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

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

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

The formula mass of CaF_2 is 78.08 amu.

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

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

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

The formula mass of KNO_3 is 101.11 amu.

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

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

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

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

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

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

Example 3.5.1

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

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

Solution

a.

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

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

The formula mass of $FeCl_3$ is 162.19 amu.

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

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

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

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

Exercise 3.5.1

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

a. TiO_2
b. AgBr
c. $Au(NO_3)_3$
d. $Fe_3(PO_4)_2$

Answer a:

47.87 + 2 (16.00) = 79.87 amu

Answer b:

107.87 + 79.90 = 187.77 amu

Answer c:

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

Answer d:

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

To Your Health: Hydrates

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

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

Magnesium sulfate heptahydrate. (Public Domain; Chemicalinterest).

Hydrates have various uses in the health industry. Calcium sulfate hemihydrate ($CaSO_4 \bullet ½H_2O$), known as plaster of Paris, is used to make casts for broken bones. Epsom salt ($MgSO_4 \bullet 7\,H_2O$) is used as a bathing salt and a laxative. Aluminum chloride hexahydrate is an active ingredient in antiperspirants. The accompanying table lists some useful hydrates.

Table 3.5.1: Names and Formulas of Some Widely Used Hydrates

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

3.6: 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.

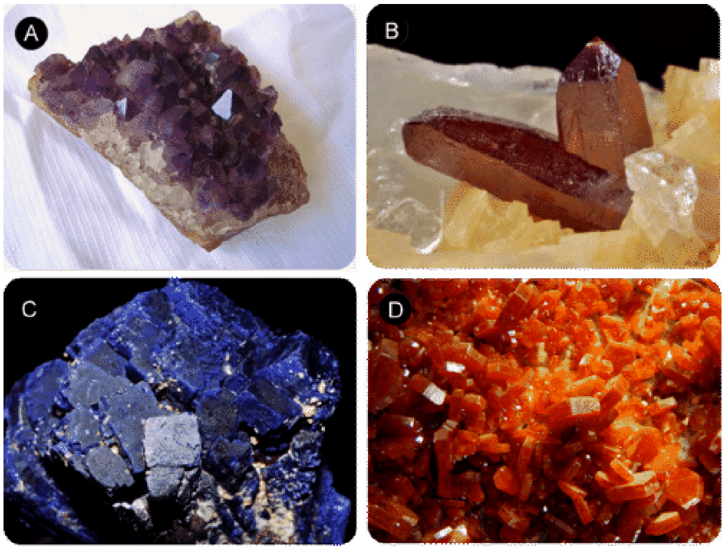


Figure 3.6.1: *In nature, the ordered arrangement of ionic solids gives rise to beautiful crystals. (A) Amethyst - a form of quartz,* SiO_2*, whose purple color comes from iron ions. (B) Cinnabar - the primary ore of mercury is mercury (II) sulfide, HgS (C) Azurite - a copper mineral,* $Cu_3(CO_3)_2(OH)_2$*.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

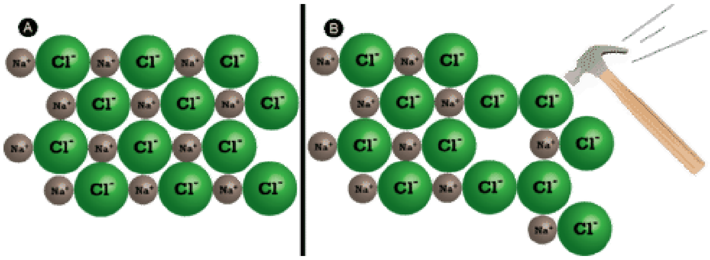
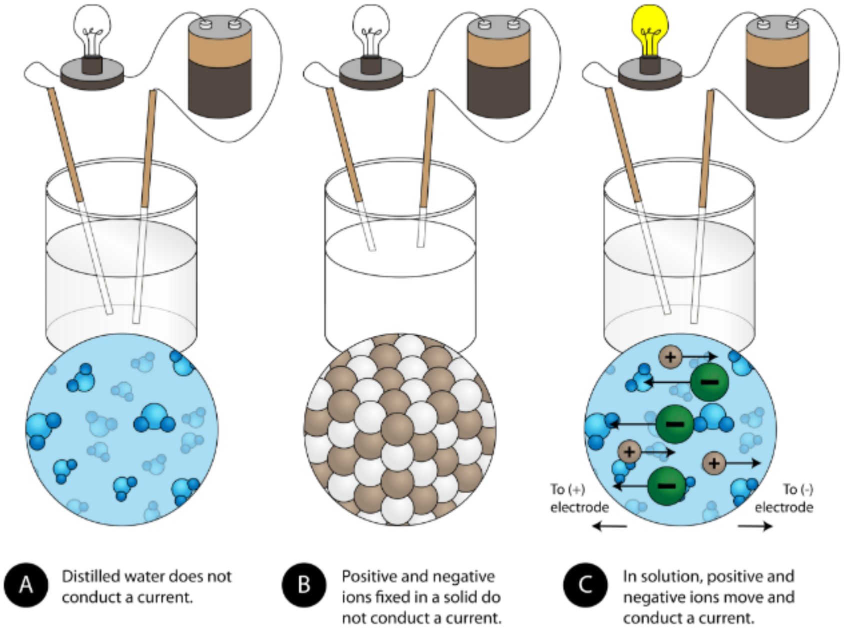


Figure 3.6.2: *(A) The sodium chloride crystal is shown in two dimensions. (B) When struck by a hammer, the negatively-charged chloride ions are forced near each other and the repulsive force causes the crystal to shatter.*

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.



Distilled water does not conduct a current.

Positive and negative ions fixed in a solid do not conduct a current.

In solution, positive and negative ions move and conduct a current.

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.

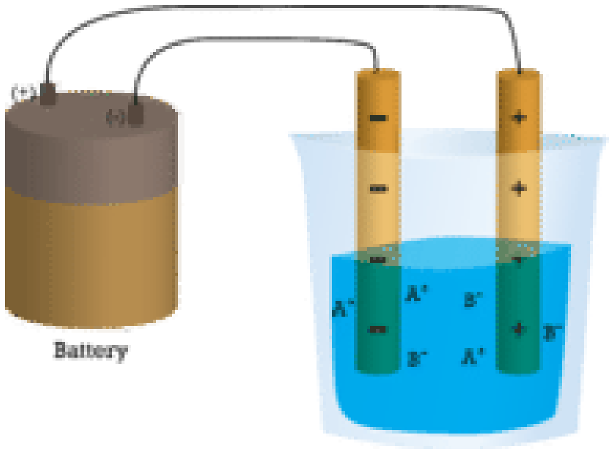


Figure 3.6.4: *In an ionic solution, the A^+ ions migrate toward the negative electrode, while the B^- ions migrate toward the positive electrode.*

Example 3.6.1

Write the dissociation equation of solid NaCl in water.

Solution

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

rcise

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. $Ba(NO_3)_2$

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

Additional Exercises

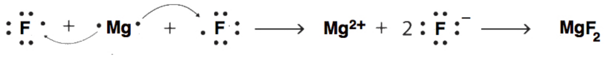
1. What number shell is the valence electron shell of a sodium atom? What number shell is the valence shell of a sodium ion? Explain the difference.
2. What number shell is the valence electron shell of a bromine atom? What number shell is the valence shell of a bromide ion? Explain the difference between 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? $1s^22s^22p^6$
23. Which ion with a 3− charge has the following electron configuration? $1s^22s^22p^6$

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. $1s^22s^22p^63s^23p^6$
   2. $1s^22s^22p^6$
   3. $1s^22s^22p^6$
   4. $1s^22s^22p^63s^23p^6$
4.
   1. $1s^2$
   2. $1s^22s^22p^63s^23p^6$
   3. $1s^22s^22p^63s^23p^6$
   4. $1s^22s^22p^6$
5.
   1. $1s^22s^22p^5$
   2. It probably requires too much energy to form.
6. 1. $1s^22s^22p^63s^23p^64s^1$

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

7.



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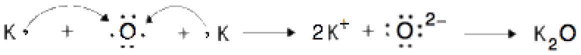

9. 1. mercuric and mercurous, respectively

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-}

3.S: Ionic Bonding and Simple Ionic Compounds (Summary)

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

Atoms combine into compounds by forming **chemical bonds**. A survey of stable atoms and molecules leads to the **octet rule**, which says that stable atoms tend to have eight electrons in their outermost, or valence, shell. One way atoms obtain eight electrons in the valence shell is for some atoms to lose electrons while other atoms gain them. When this happens, the atoms take on an electrical charge. Charged atoms are called **ions**. Ions having opposite charges attract each other. This attraction is called **ionic bonding**, and the compounds formed are called **ionic compounds**.

Positively charged ions are called **cations**, while negatively charged ions are called **anions**. The formation of both cations and anions can be illustrated using electron configurations. Because elements in a column of the periodic table have the same valence shell electron configuration, atoms in the same column of the periodic table tend to form ions having the same charge. **Electron dot diagrams**, or **Lewis diagrams**, can also be used to illustrate the formation of cations and anions.

Ionic compounds are represented in writing by a **chemical formula**, which gives the lowest ratio of cations and anions present in the compound. In a formula, the symbol of the cation is written first, followed by the symbol of the anion. **Formula unit** is considered the basic unit of an ionic compound because ionic compounds do not exist as discrete units. Instead, they exist as **crystals**, three-dimensional arrays of ions, with cations surrounded by anions and anions surrounded by cations. Chemical formulas for ionic compounds are determined by balancing the positive charge from the cation(s) with the negative charge from the anion(s). A subscript to the right of the ion indicates that more than one of that ion is present in the chemical formula.

Some ions are groups of atoms bonded together and having an overall electrical charge. These are called **polyatomic ions**. Writing formulas with polyatomic ions follows the same rules as with monatomic ions, except that when more than one polyatomic ion is present in a chemical formula, the polyatomic ion is enclosed in parentheses and the subscript is outside the right parenthesis. Ionic compounds typically form between metals and nonmetals or between polyatomic ions.

Names of ionic compounds are derived from the names of the ions, with the name of the cation coming first, followed by the name of the anion. If an element can form cations of different charges, there are two alternate systems for indicating the compound’s name. In the **Stock system**, a roman numeral in parentheses indicates the charge on the cation. An example is the name for $FeCl_2$, which is iron(II) chloride. In the common system, the suffixes *-ous* and *-ic* are used to stand for the lower and higher possible charge of the cation, respectively. These suffixes are attached to a stem representing the element (which frequently comes from the Latin form of the element name). An example is the common name for $FeCl_2$, which is ferrous chloride.

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

Ionic compounds are hard, brittle and have very high melting points. When in solution, the ions separate and form **electrolyte** solutions.

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.

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4.0: Prelude to Covalent Bonding and Simple Molecular Compounds

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

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

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

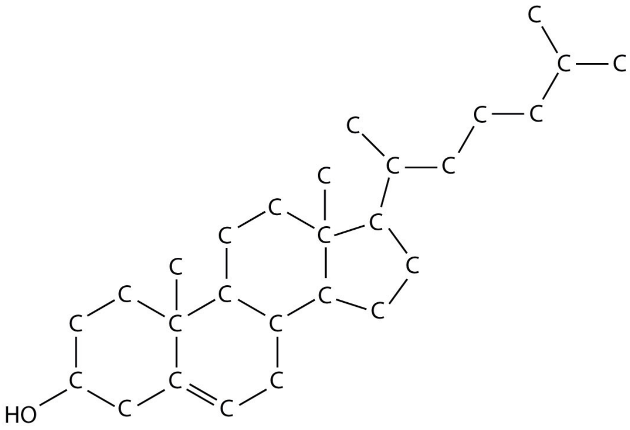


Figure 4.0.1: A Molecular Model of Cholesterol

4.1: Covalent Bonds

Learning Objectives

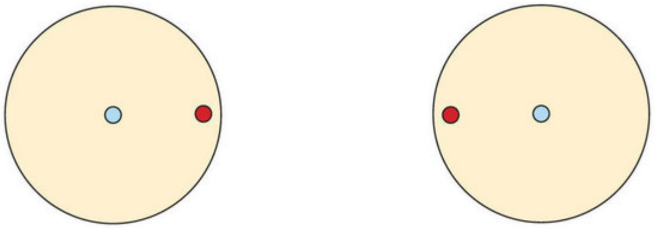
- To describe how a covalent bond forms.
- To apply the octet rule to covalent compounds

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

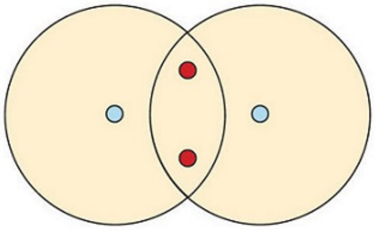
Electron Sharing

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

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



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



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

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

H•   •H

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

H:H

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

H—H

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

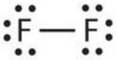
The bond in a hydrogen molecule, measured as the distance between the two nuclei, is about 7.4×10^{-11} m, or 74 picometers (pm; 1 pm = 1×10^{-12} m). This particular bond length represents a balance between several forces: the attractions between oppositely charged electrons and nuclei, the repulsion between two negatively charged electrons, and the repulsion between two positively charged nuclei. If the nuclei were closer together, they would repel each other more strongly; if the nuclei were farther apart, there would be less attraction between the positive and negative particles.

Fluorine is another element whose atoms bond together in pairs to form *diatomic* (two-atom) molecules. Two separate fluorine atoms have the following electron dot diagrams:

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

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

The circles show that each fluorine atom has eight electrons around it. As with hydrogen, we can represent the fluorine molecule with a dash in place of the bonding electrons:



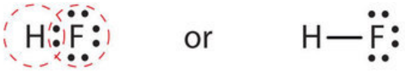
Two F's with a long dash in between them, and two dots on the top, left/right side, and bottoms of each F.

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

Covalent Bonds between Different Atoms

Now that we have looked at electron sharing between atoms of the same element, let us look at covalent bond formation between atoms of different elements. Consider a molecule composed of one hydrogen atom and one fluorine atom:

Each atom needs one additional electron to complete its valence shell. By each contributing one electron, they make the following molecule:



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

In this molecule, the hydrogen atom does not have nonbonding electrons, while the fluorine atom has six nonbonding electrons (three lone electron pairs). The circles show how the valence electron shells are filled for both atoms.

✓ Example 4.1.1

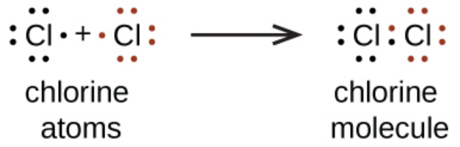
Use Lewis diagrams to indicate the formation of the following:

a. Cl_2
b. HBr

Solution

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

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



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

b. When a hydrogen atom and a bromine atom form HBr, they share one pair of electrons. In the HBr molecule, H achieves a full valence of two electrons (**duet**) while Br achieves an **octet**. The Lewis diagram for HBr is similar to that for HF shown above.

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

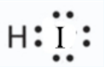
Exercise 4.1.1

Draw the Lewis diagram for each compound.

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

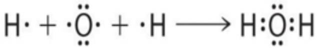
Answer a:

Answer b:



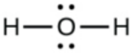
Covalent Bonds in Larger Molecules

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



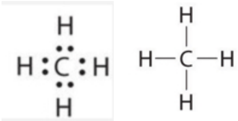
H with one dot + O with 6 dots + H with one dot turns into H connected to O with two dots connected to H with two dots. O also has two dots on top and top dots on bottom.

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



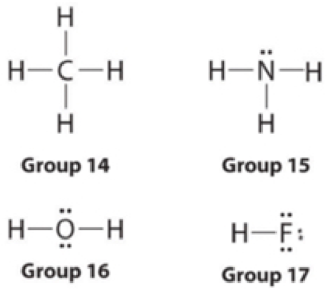
Water

Other large molecules are constructed in a similar fashion, with some atoms participating in more than one covalent bond. For example, methane (CH_4), the central carbon atom bonded to four hydrogen atoms, can be represented using either of the Lewis structures below. Again, sharing electrons between C and H atoms results in C achieving and octet while H achieving a duet number of electrons.



How Many Covalent Bonds Are Formed?

The number of bonds that an atom can form can often be predicted from the number of electrons needed to reach an octet (eight valence electrons). In the Lewis structure, the number of bonds formed by an element in a neutral compound is the same as the number of unpaired electrons it must share with other atoms to complete its octet of electrons. For example, each atom of a **group 4A** (14) element has four electrons in its outermost shell and therefore requires four more electrons to reach an octet. These four electrons can be gained by forming **four covalent bonds**, as illustrated here for carbon in CH_4 (methane). **Group 5A** (15) elements such as nitrogen have five valence electrons in the atomic Lewis symbol: one lone pair and three unpaired electrons. To obtain an octet, these atoms form **three covalent bonds**, as in NH_3 (ammonia). Oxygen and other atoms in **group 6A** (16) obtain an octet by forming **two covalent bonds**. Fluorine and the other halogens in **group 7A** (17) have seven valence electrons and can obtain an octet by forming **one covalent bond**.



Typically, the atoms of group 4A form 4 covalent bonds; group 5A form 3 bonds; group 6A form 2 bonds; and group 7A form one bond. The number of electrons required to obtain an octet determines the number of covalent bonds an atom can form. This is summarized in the table below. In each case, the sum of the number of bonds and the number of lone pairs is 4, which is equivalent to eight (octet) electrons.

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

Atom (Group number)	Number of Bonds	Number of Lone Pairs
Carbon (Group 14 or 4A)	4	0
Nitrogen (Group 15 or 5A)	3	1
Oxygen (Group 16 or 6A)	2	2
Fluorine (Group 17 or 7A)	1	3

Because hydrogen only needs two electrons to fill its valence shell, it follows the duet rule. It is an **exception to the octet rule.** Hydrogen only needs to form one bond. This is the reason why H is always a terminal atom and never a central atom. Figure 4.1.1 shows the number of covalent bonds various atoms typically form.

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

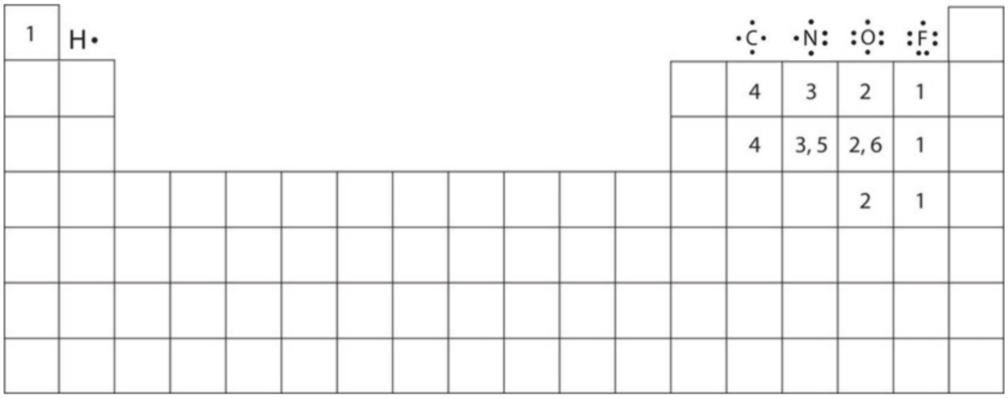
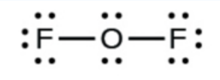


Figure 4.1.1: How Many Covalent Bonds Are Formed? In molecules, there is a pattern to the number of covalent bonds that different atoms can form. Each block with a number indicates the number of covalent bonds formed by that atom in neutral compounds.

✓ Example 4.1.2

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



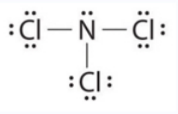
F surrounded by 6 dots, connected to O with a long dash. O surrounded by 4 dots and connects to another F with a long dash. F surrounded by 6 dots.

Solution

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

rcise

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.

4.2: Covalent Compounds - Formulas and Names

Learning Objectives

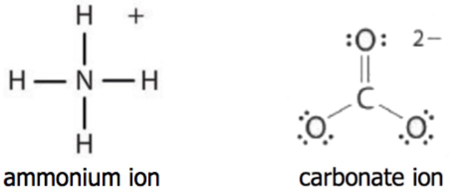
- Identify covalent and ionic compounds.
- Determine the chemical formula of a simple covalent compound from its name.
- Determine the name of a simple covalent compound from its chemical formula.

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-}.



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

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

Characteristics of Covalent (Molecular) Compounds

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

Example 4.2.1

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 4.2.1

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:

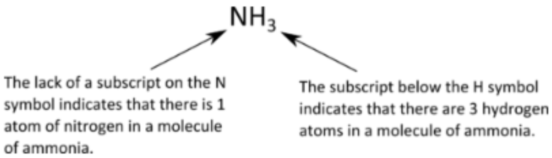
covalent

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 4.2.1 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 4.2.1: Numerical Prefixes for Naming Binary Covalent Compounds

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

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

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

✓ Example 4.2.2

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 4.2.2

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 4.2.3

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 4.2.3

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.

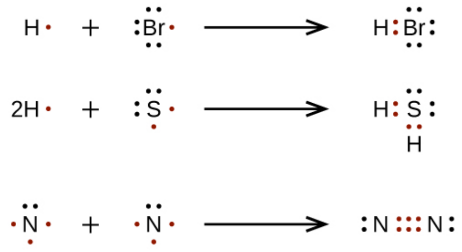
4.3: Drawing Lewis Structures

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.

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

$$6e^- + (2 \text{ x } 7e^-) = 20e^-$$

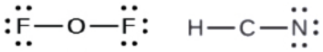
$$H + C + N = HCN$$

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

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.

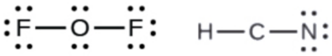
3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen) to complete their valence shells with an octet of electrons.

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



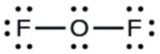
4. Place all remaining electrons on the central atom.

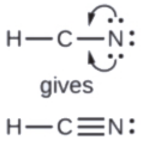
- In OF_2, 4 electrons are placed on O.
- In HCN: no electrons remain (the total valence of 10e$^-$is reached) so nothing changes.



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



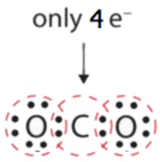


H dash C dash N with 6 dots around the N. 4 of the dots are pointing to the dash connecting the C and the N. This turns the formula into H dash C and three lines connecting the C and N together, with two dots on the outside of the N.

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.

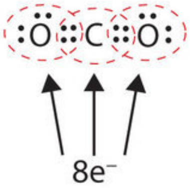
MULTIPLE BONDS

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 x 6e$^-$) = 16e$^-$. Following steps 1 to 4, we draw the following:

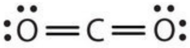


This does not give the carbon atom a complete octet; only four electrons are in its valence shell. This arrangement of shared electrons is far from satisfactory.

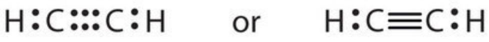
In this case, more than one pair of electrons must be shared between two atoms for both atoms to have an octet. A second electron pair from each oxygen atom must be shared with the central carbon atom shown by the arrows above. A lone pair from each O must be converted into a bonding pair of electrons.



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 4.3.1

Draw the Lewis diagram for each molecule.

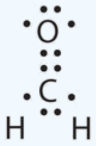
1. N_2
2. CH_2O (The carbon atom is the central atom.) One application of CH_2O, also called formaldehyde, is the preservation of biological specimens. Aqueous solutions of CH_2O are called formalin and have a sharp, characteristic (pungent) odor.

Solution

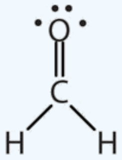
1. The total number of electrons is 2 x 5 = 10 electrons. The bond between the two nitrogen atoms is a triple bond. The Lewis diagram for $N_2$is as follows:

or

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:



or

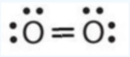


Exercise 4.3.1

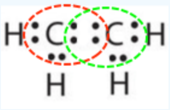
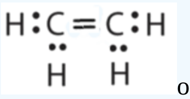
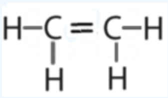
Draw the Lewis diagram for each molecule.

a. O_2
b. C_2H_4

Answer a:

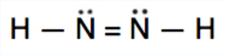

or


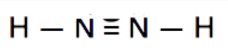
Answer b:

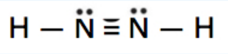

or

or


Example 4.3.2

Which is the correct Lewis structure for N_2H_2?

A. 

B. 

C. 

Solution

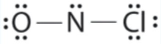
Lewis structure A is the correct answer. It has a total of (2 x $5e^-$) + (2 x $1e^-$) = $12e^-$. Each of the N atoms satisfy the octet requirement and the H atoms follow the duet rule.

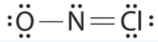
Structure B is electron deficient. It has only $10e^-$ instead of 12.

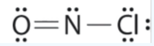
Structure C has 14 (2 extra) electrons. The N atoms do not satisfy the octet.

rcise

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.

4.4: 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 4.4.1 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 4.4.1: 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 4.4.2 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 4.4.2: 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

Bond	Length ($\times 10^{-12}\ m$)
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 $4.4.1$. A covalent bond that has an equal sharing of electrons (Figure $4.4.1a$) is called a **nonpolar covalent bond**. A covalent bond that has an unequal sharing of electrons, as in Figure $4.4.1b$, is called a **polar covalent bond**.

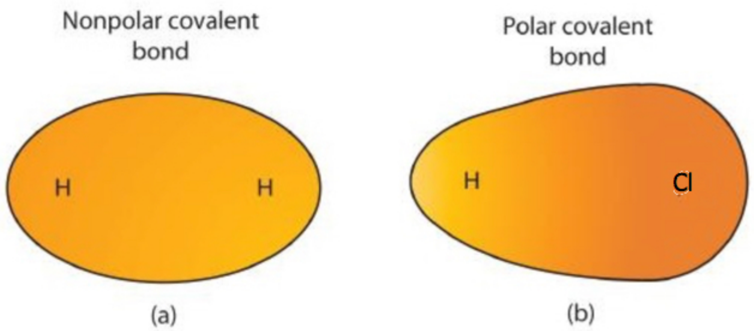


Figure $4.4.1$ Polar versus Nonpolar Covalent Bonds. (a) The electrons in the covalent bond are equally shared by both hydrogen atoms. This is a nonpolar covalent bond. (b) The chlorine atom attracts the electrons in the bond more than the hydrogen atom does, leading to an imbalance in the electron distribution. 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 $4.4.1b$ is much larger than it is around H.

This imbalance in electron density results in a buildup of partial negative charge (designated as δ−) on one side of the bond (Cl) and a partial positive charge (designated δ+) on the other side of the bond (H). This is seen in Figure $4.4.2a$. The separation of charge in a polar covalent bond results in an electric dipole (two poles), represented by the arrow in Figure $4.4.2b$. The direction of the arrow is pointed toward the δ− end while the + tail of the arrow indicates the δ+ end of the bond.

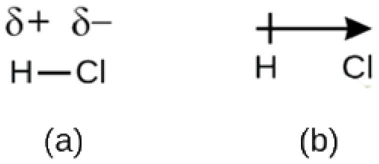


Figure $4.4.2$: (a) Unequal sharing of the bonding pair of electrons between H and Cl leads to partial positive charge on the H atom and partial negative charge on the Cl. Symbols δ+ and δ– indicate the polarity of the H–Cl bond. (b) The dipole is represented by an arrow with a cross at the tail. The 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 $4.4.3$ shows one of the most popular—the Pauling scale.

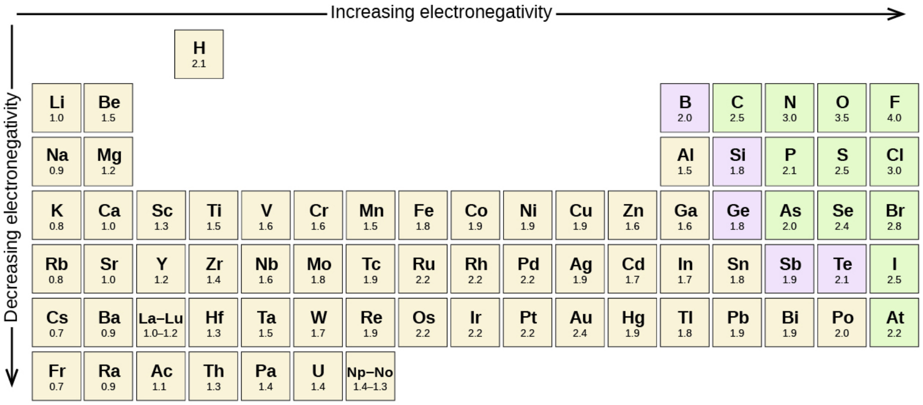
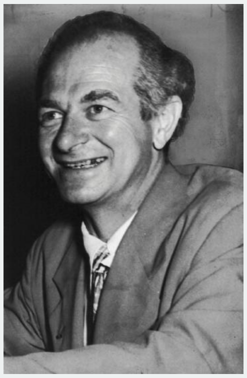


Figure 4.4.3 The electronegativity values derived by Pauling follow predictable periodic trends with the higher electronegativities toward the upper right of the periodic table. Fluorine has the highest value (4.0).

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.

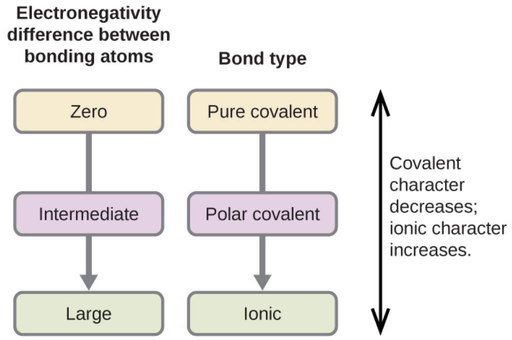
By 1935, Pauling’s interest turned to biological molecules, and he was awarded the 1954 Nobel Prize in Chemistry for his work on protein structure. (He was very close to discovering the double helix structure of DNA when James Watson and James Crick announced their own discovery of its structure in 1953.) 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 4.4.4: As the electronegativity difference increases between two atoms, the bond becomes more ionic.

✓ Example 4.4.1

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 4.4.1

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).

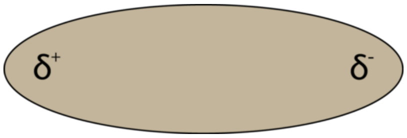


Figure 4.4.5: A molecular dipole results from the unequal distribution of electron density throughout a molecule.

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).

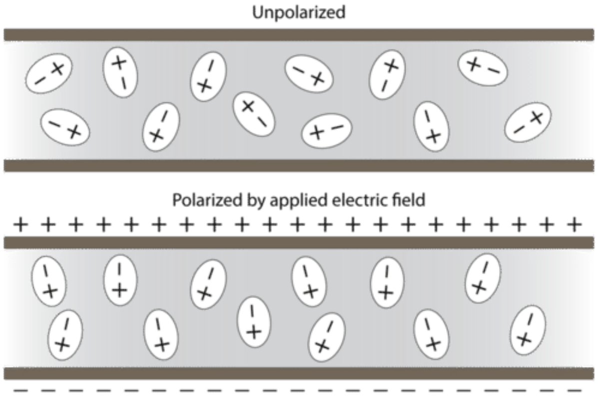


Figure 4.4.6: Polar molecules are randomly oriented in the absence of an applied electric field (top). In an electric field, the molecules orient themselves to maximize the attraction between opposite charges (bottom).

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 4.4.7) 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 4.4.7 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.

4.5: 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 4.5.1

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 4.5.1

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:

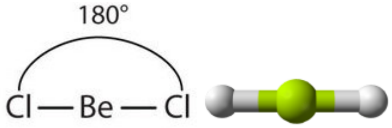
44.01 amu

Answer d:

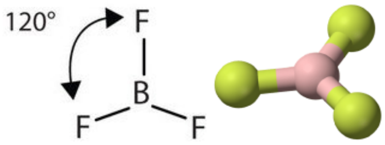
67.81 amu

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.

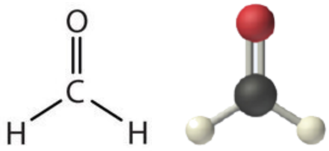
> Try sticking three toothpicks into a marshmallow or a gumdrop and see if you can find different positions where your “bonds” are farther apart than the planar 120° orientation.

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.

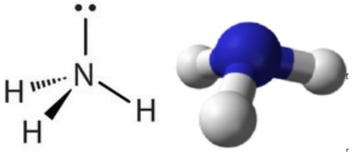
Atoms Around Central Atom	Geometry	Example
2 AB_2	Linear	$BeCl_2$
3 AB_3	Trigonal Planar	BF_3
4 AB_4	Tetrahedral	CCl_4

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***.

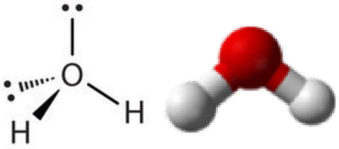


Molecules With Lone Pairs Around Central Atom

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.

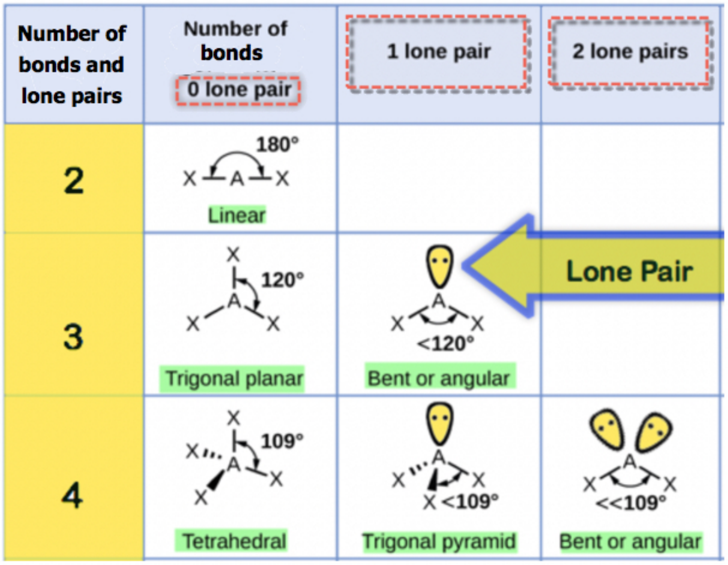


In summary, to determine the molecular geometry:

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.



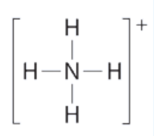
Number of bonds and lone pairs	Number of bonds 0 lone pair	1 lone pair	2 lone pairs
2	180° Linear		
3	120° Trigonal planar	<120° Bent or angular	
4	109° Tetrahedral	<109° Trigonal pyramid	<<109° Bent or angular

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.**

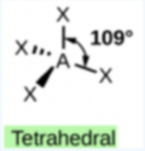
Example 4.5.1

What is the geometry of the ammonium ion, NH_4^+? Its Lewis structure is shown below. How is this different from ammonia, NH_3?

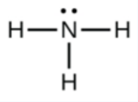


Solution

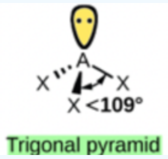
In ammonium ion, the central atom N has 4 bonds and no lone pair. It is equivalent to the below in Table 4.5.1. Hence, this is *tetrahedral*.



In ammonia (NH_3), shown below, N has 3 bonds and one lone pair.

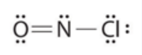


It is equivalent to the below in Table 4.5.1. Hence, the shape of this molecule is *trigonal pyramid*.



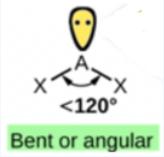
rcise

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***.

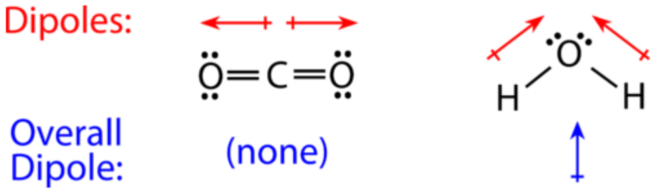


Figure 4.5.1: The molecular geometry of a molecule (linear vs. bent) affects its polarity.

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.

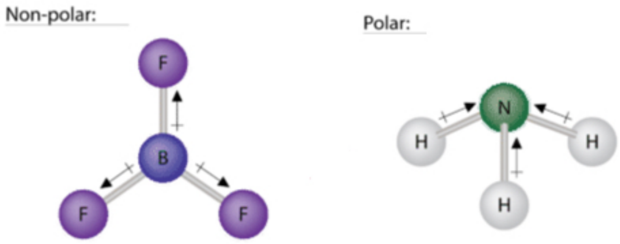


Figure 4.5.2: The molecular geometry of a molecule (trigonal planar vs. trigonal pyramid) affects its polarity.

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.

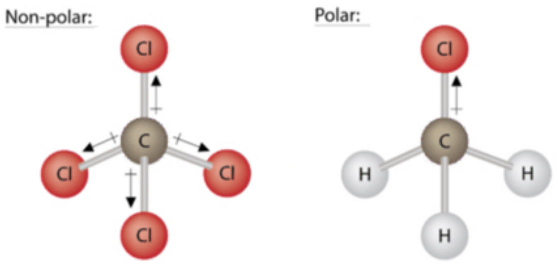


Figure 4.5.3: *The same molecular geometry but peripheral bonds are of different electronegativity.* *CCl_4 is nonpolar but CH_3Cl is polar.*

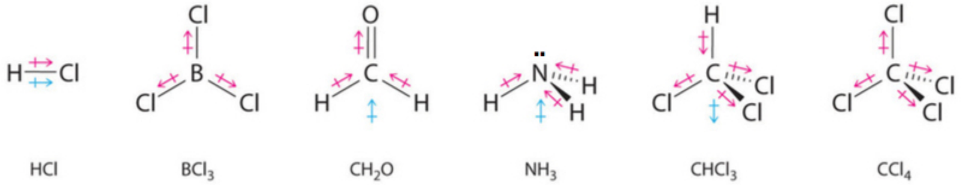


Figure 4.5.4: Molecules with Polar Bonds. Individual bond dipole moments are indicated in red. Due to their different three-dimensional geometry, some molecules with polar bonds have a net dipole moment (HCl, CH_2O, NH_3, and $CHCl_3$), indicated in blue, whereas others do not because the bond dipoles 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.

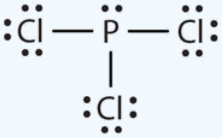
✓ Example 4.5.2

Describe the shape of each molecule. Is it polar or nonpolar?

a. PCl_3
b. CO_2

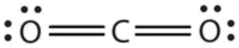
Solution

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:



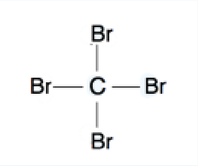
Focus on the central atom, C. The multiple bonds are treated as one group, hence C has 2 bonds and zero lone pair. CO_2 has only two groups of electrons that repel each other. They will direct themselves 180° apart from each other, so CO_2 molecules are *linear*. This is highly symmetrical, with the two opposite dipoles cancelling each other. The CO_2 molecule is *nonpolar*.

? Exercise 4.5.2

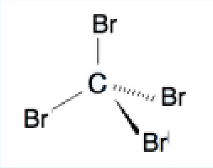
Describe the shape of each molecule. Is it polar or nonpolar?

a. CBr_4
b. BCl_3

Answer a:

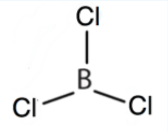


or



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.

4.6: Organic Chemistry

Learning Objectives

- Define *organic chemistry*.
- Identify organic molecules as alkanes, alkenes, alkynes, alcohols, or carboxylic acids.

When methane was mentioned previously, we described it as the simplest organic compound. In this section, we introduce organic chemistry more formally. Organic chemistry is the study of the chemistry of carbon compounds. Carbon is singled out because it has a chemical diversity unrivaled by any other chemical element. Its diversity is based on the following:

- Carbon atoms bond reasonably strongly with other carbon atoms.
- Carbon atoms bond reasonably strongly with atoms of other elements.
- Carbon atoms make a large number of covalent bonds (four).

Curiously, elemental carbon is not particularly abundant. It does not even appear in the list of the most common elements in Earth's crust. Nevertheless, all living things consist of organic compounds. Most organic chemicals are covalent compounds, which is why we introduce organic chemistry here. By convention, compounds containing carbonate ions and bicarbonate ions, as well as carbon dioxide and carbon monoxide, are not considered part of organic chemistry, even though they contain carbon.

Alkanes

The simplest organic compounds are the **hydrocarbons**, compounds composed of carbon and hydrogen atoms only. Some hydrocarbons have only single bonds and appear as a chain (which can be a straight chain or can have branches) of carbon atoms also bonded to hydrogen atoms. These hydrocarbons are called **alkanes (saturated hydrocarbons)**. Each alkane has a characteristic, systematic name depending on the number of carbon atoms in the molecule. These names consist of a stem that indicates the number of carbon atoms in the chain plus the ending -ane. The stem meth- means one carbon atom, so methane is an alkane with one carbon atom. Similarly, the stem eth- means two carbon atoms; ethane is an alkane with two carbon atoms. Continuing, the stem prop- means three carbon atoms, so propane is an alkane with three carbon atoms. The stem but- means four carbon atoms; butane is an alkane with four carbon atoms. Figure $4.6.1$ gives the Lewis structures, condensed structural formulas and molecular formulas of the four simplest alkanes. In the **condensed structural formula**, the covalent bonds are understood to exist between each carbon and the hydrogens associated with it, as well as between carbon atoms.

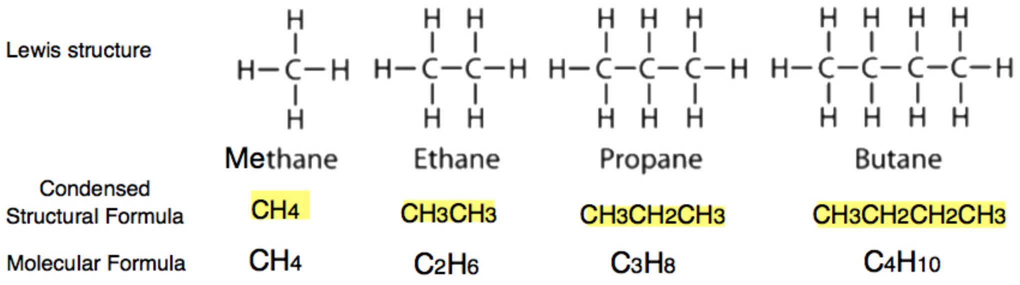


Figure $4.6.1$: Formulas and Molecular Models of the Four Simplest Alkanes. The four smallest alkanes are methane, ethane, propane and butane.

Alkenes

Some hydrocarbons have one or more carbon–carbon double bonds (denoted C=C). These hydrocarbons are called alkenes. Figure $4.6.2$ shows the formulas and the molecular models of the two simplest alkenes. Note that the names of alkenes have the same stem as the alkane with the same number of carbon atoms in its chain but have the ending *-ene*. Thus, ethene is an alkene with two carbon atoms per molecule, and propene is a compound with three carbon atoms and one double bond.

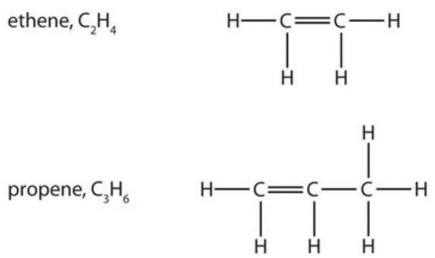


Figure 4.6.2: Formulas and Molecular Models of the Two Simplest Alkenes. Ethene is commonly called ethylene, while propene is commonly called propylene.

Alkynes

Alkynes are hydrocarbons with a carbon–carbon triple bond (denoted C≡C) as part of their carbon skeleton. Below is the formula and the molecular model of the simplest alkyne and its systematic name. Its common name is acetylene. Its chemical formula is $\mathbf{C_2H_2}$.

$$H-C\equiv C-H$$

Ethyne

The names for alkynes have the same stems as for alkanes but with the ending *-yne*.

To Your Health: Saturated and Unsaturated Fats

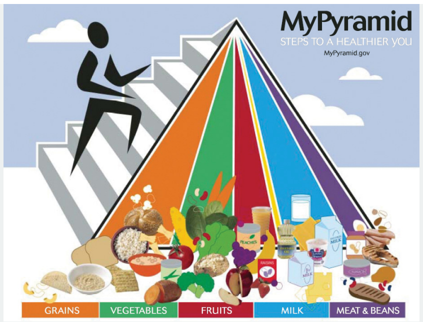
Hydrocarbons are not the only compounds that can have carbon–carbon double bonds. A group of compounds called fats can have them as well, and their presence or absence in the human diet is becoming increasingly correlated with health issues.

Fats are combinations of long-chain organic compounds (fatty acids) and glycerol ($C_3H_8O_3$). (For more information on fats, see Chapter 17) The long carbon chains can have either all single bonds, in which case the fat is classified as *saturated*, or one or more double bonds, in which case it is a *monounsaturated* or a *polyunsaturated* fat, respectively. Saturated fats are typically solids at room temperature; beef fat (tallow) is one example. Mono- or polyunsaturated fats are likely to be liquids at room temperature and are often called oils. Olive oil, flaxseed oil, and many fish oils are mono- or polyunsaturated fats.

Studies have linked higher amounts of saturated fats in people’s diets with a greater likelihood of developing heart disease, high cholesterol, and other diet-related diseases. In contrast, increases in unsaturated fats (either mono- or polyunsaturated) have been linked to a lower incidence of certain diseases. Thus, there have been an increasing number of recommendations by government bodies and health associations to decrease the proportion of saturated fat and increase the proportion of unsaturated fat in the diet. Most of these organizations also recommend decreasing the total amount of fat in the diet.

Recently, certain fats called trans fats have been implicated in the presence of heart disease. These are fats from animal sources and are also produced when liquid oils are exposed to partial hydrogenation, an industrial process that increases their saturation. Trans fats are used in many prepared and fried foods. Because they bring with them the health risks that naturally occurring saturated fats do, there has been some effort to better quantify the presence of trans fats in food products. US law now requires that food labels list the amount of trans fat in each serving.

Since the early 1900's, the US Department of Agriculture has been providing science-based dietary guidelines for the public. The most current version is the MyPlate illustration that gives a simple, visual picture of how much of what kind of foods make up a good, balanced diet. It recommends minimizing daily intake of sugars, the "bad fats", trans and saturated fat, and sodium. "Good fats", unsaturated fats or oils, are not considered a food group but do contain essential nutrients and therefore are included as part of a healthy eating pattern. The difference as simple as the difference between a single and double carbon–carbon bond, good and bad fats, can have a significant impact on health.



MyPlate is a reminder that everything you eat and drink matters. Source: Image courtesy of the USDA, www.mypyramid.gov/downloads/MiniPoster.pdf.

Functional Groups

The carbon–carbon double and triple bonds are examples of functional groups in organic chemistry. A functional group is a specific structural arrangement of atoms or bonds that imparts a characteristic chemical reactivity to a molecule. Alkanes have no functional group. A carbon–carbon double bond is considered a functional group because carbon–carbon double bonds chemically react in specific ways that differ from reactions of alkanes (for example, under certain circumstances, alkenes react with water); a carbon–carbon triple bond also undergoes certain specific chemical reactions. In the remainder of this section, we introduce two other common functional groups.

If an OH group (also called a hydroxyl group) is substituted for a hydrogen atom in a hydrocarbon molecule, the compound is an alcohol. Alcohols are named using the parent hydrocarbon name but with the final *-e* dropped and the suffix *-ol* attached. The two simplest alcohols are methanol and ethanol. Figure $4.6.4$ shows their formulas along with a molecular model of each.

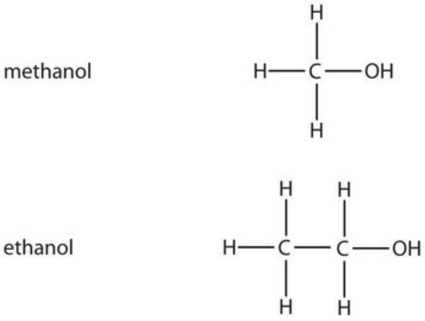


Figure $4.6.4$: The Two Simplest Organic Alcohol Compounds. Alcohols have an OH functional group in the molecule.

Cholesterol, described in the chapter-opening essay, has an alcohol functional group, as its name implies.

Alcohol

Ethanol (also called ethyl alcohol) is the alcohol in alcoholic beverages. Other alcohols include methanol (or methyl alcohol), which is used as a solvent and a cleaner, and isopropyl alcohol (or rubbing alcohol), which is used as a medicinal disinfectant. Neither methanol nor isopropyl alcohol should be ingested, as they are toxic even in small quantities.

Another important family of organic compounds has a carboxyl group, in which a carbon atom is double-bonded to an oxygen atom and to an OH group. Compounds with a carboxyl functional group are called carboxylic acids, and their names end in *-oic acid*. Figure $4.6.5$ shows the formulas and the molecular models of the two simplest carboxylic acids, perhaps best known by the common names formic acid and acetic acid. The carboxyl group is sometimes written in molecules as COOH.

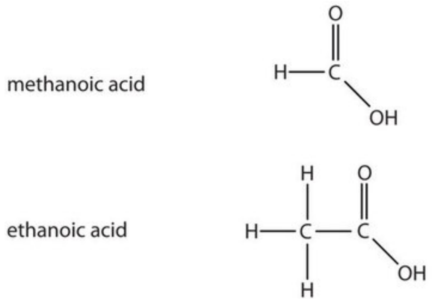


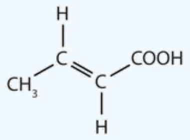
Figure 4.6.5: The Two Smallest Organic Acids. The two smallest carboxylic acids are formic acid (found in the stingers of ants) and acetic acid (found in vinegar).

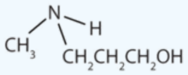
The condensed structures of methanoic acid and ethanoic acid are **HCOOH** and **CH_3COOH**, respectively.

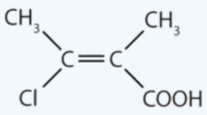
Many organic compounds are considerably more complex than the examples described here. Many compounds, such as cholesterol discussed in the chapter-opening essay, contain more than one functional group. The formal names can also be quite complex.

✓ Example 4.6.1

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

a. 

b. 

c. 

d. $CH_3CH_2CH_2CH_2OH$

Answer a

This molecule has a double bond and a carboxyl functional group.

Answer b

This molecule has an alcohol functional group.

Answer c

This molecule has a carbon-carbon double bond and a carboxyl functional group.

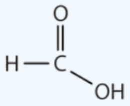
Answer d

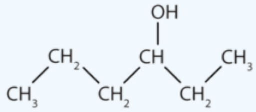
This molecule has an alcohol functional group.

? Exercise 4.6.1

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

a. $CH_3C\equiv CCH3$

b. 

c. 

d. $CH_2{=}CH{-}COOH$

Answer a:

triple bond (alkyne)

Answer b:

carboxyl group

Answer c:

alcohol group

Answer d:

double bond (alkene) and carboxyl group

Career Focus: Forensic Chemist

The main job of a forensic chemist is to identify unknown materials and their origins. Although forensic chemists are most closely associated in the public mind with crime labs, they are employed in pursuits as diverse as tracing evolutionary patterns in living organisms, identifying environmental contaminants, and determining the origin of manufactured chemicals.

In a crime lab, the forensic chemist has the job of identifying the evidence so that a crime can be solved. The unknown samples may consist of almost anything—for example, paint chips, blood, glass, cloth fibers, drugs, or human remains. The forensic chemist subjects them to a variety of chemical and instrumental tests to discover what the samples are. Sometimes these samples are extremely small, but sophisticated forensic labs have state-of-the-art equipment capable of identifying the smallest amount of unknown sample.

Another aspect of a forensic chemist's job is testifying in court. Judges and juries need to be informed about the results of forensic analyses, and it is the forensic chemist's job to explain those results. Good public-speaking skills, along with a broad background in chemistry, are necessary to be a successful forensic chemist.

Key Takeaways

- Organic chemistry is the study of the chemistry of carbon compounds.
- Organic molecules can be classified according to the types of elements and bonds in the molecules.

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.

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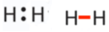

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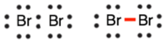

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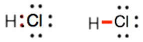
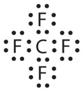


6. A molecule is a discrete combination of atoms; a formula unit is the lowest ratio of ions in a crystal. 7. Hydrogen atoms follow the duet rule (not the octet rule). This is because it has only one shell and this shell can only hold 2 electrons.

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.

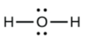
   - a. N_2
   - b. CO
   - c. HCN (The carbon atom is the central atom.)
   - d. POCl (The phosphorus atom is the central atom.)

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.



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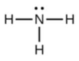

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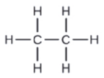

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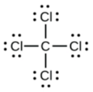
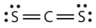


3. a.



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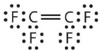

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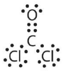
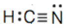


4. a. 

b. 

c. 

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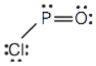
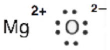


5. Hydrogen can accept only one more electron; multiple bonds require more than one electron pair to be shared.

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.

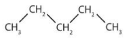
Answers

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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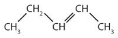

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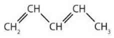

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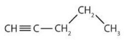
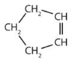


4. Identify the type of hydrocarbon in each structure.

a.



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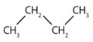
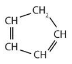
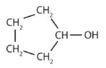


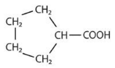
c. $CH\equiv C-CH_2-CH_3$

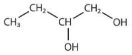
d.

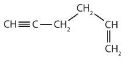


5. Identify the functional group(s) in each molecule.

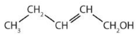
a. 

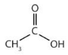
b. 

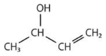
c. 

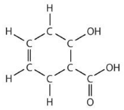
d. 

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

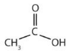
7. two; carbon-carbon double bonds and carbon-carbon triple bonds

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.

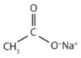
Additional Exercises

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:

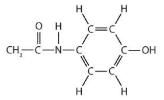


This molecule can lose a hydrogen ion (H^+) and the resulting anion can combine with other cations, such as Na^+:



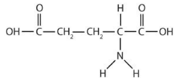
Name this ionic compound.

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

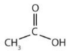
b. $Ca(HCOO)_2$

c. $Fe(HCOO)_3$

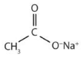
7. :N≡C–C≡N:
8. 6.49×10^7 C-C bonds
9. 7.46×10^7 C=C bonds
10. Hydrogen atoms make relatively nonpolar bonds with carbon atoms.
11. The greatest electronegativity difference is 3.2, between F and Rb.
12. alcohol; the ring with double bonds, and the O=C-NH are also likely functional groups.
13. carboxyl and $-NH_2$ functional groups

Additional Questions

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.

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7. Cyanogen has the formula C_2N_2. Propose a bonding scheme that gives each atom the correct number of covalent bonds. (Hint: the two carbon atoms are in the center of a linear molecule.)

8. The molecular formula C_3H_6 represents not only propene, a compound with a carbon–carbon double bond, but also a molecule that has all single bonds. Draw the molecule with formula C_3H_6 that has all single bonds.
9. How many carbon–carbon single bonds, linked together, are needed to make a carbon chain that is 1.000 cm long?
10. How many carbon–carbon double bonds, linked together, are needed to make a carbon chain that is 1.000 cm long?
11. In addition to themselves, what other atoms can carbon atoms bond with and make covalent bonds that are nonpolar (or as nonpolar as possible)?
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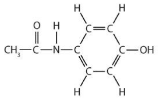

Name the recognizable functional groups in this molecule. Do you think there are other groups of atoms in this molecule that might qualify as functional groups?

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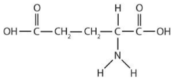

Name the functional groups you recognize in this molecule. Do you think there are other groups of atoms in this molecule that might qualify as functional groups?

Answers

1. 1a: 5.75×10^{-23} g; 1b: 1.53×10^{-22} g; 1c: 3.88×10^{-22} g; 1d: 6.06×10^{-23} g

3. 14.96 g

5. sodium acetate

7. N≡C–C≡N

9. 6.49×10^7 bonds

11. Hydrogen atoms make relatively nonpolar bonds with carbon atoms.

13. alcohol; the N–H group, the ring with double bonds, and the C=O are also likely functional groups.

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4.S: Covalent Bonding and Simple Molecular Compounds (Summary)

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

Atoms can share pairs of valence electrons to obtain a valence shell octet. This sharing of electrons is a **covalent bond**. A species formed from covalently bonded atoms is a **molecule** and is represented by a **molecular formula**, which gives the number of atoms of each type in the molecule. The two electrons shared in a covalent bond are called a **bonding pair of electrons**. The electrons that do not participate in covalent bonds are called **nonbonding pairs** (or **lone pairs**) **of electrons**. A covalent bond consisting of one pair of shared electrons is called a **single bond**.

Covalent bonds occur between nonmetal atoms. Naming simple covalent compounds follows simple rules similar to those for ionic compounds. However, for covalent compounds, numerical prefixes are used as necessary to specify the number of atoms of each element in the compound.

In some cases, more than one pair of electrons is shared to satisfy the octet rule. Two pairs of electrons are shared by two atoms to make a **double bond**. Three pairs of atoms are shared to make a **triple bond**. Single, double, and triple covalent bonds may be represented by one, two, or three dashes, respectively, between the symbols of the atoms.

The distance between two covalently bonded atoms is the **bond length**. Bond lengths depend on the types of atoms participating in the bond as well as the number of electron pairs being shared. A covalent bond can be a **polar covalent bond** if the electron sharing between the two atoms is unequal. If the sharing is equal, the bond is a **nonpolar covalent bond**. Because the strength of an atom’s attraction for electrons in a bond is rated by the atom’s **electronegativity**, the difference in the two atoms’ electronegativities indicates how polar a covalent bond between those atoms will be.

The mass of a molecule is called its **molecular mass** and is the sum of the masses of the atoms in the molecule. The shape of a molecule can be predicted using **valence shell electron pair repulsion (VSEPR)**, which uses the fact that the negative electrons in covalent bonds repel each other as much as possible. Molecules with polar bonds are **polar** except when the bond polarities cancel due to symmetry.

Organic chemistry is the chemistry of carbon compounds. Carbon forms covalent bonds with other carbon atoms and with the atoms of many other elements. The simplest organic compounds are **hydrocarbons**, which consist solely of carbon and hydrogen. Hydrocarbons containing only single bonds are called **alkanes (saturated hydrocarbons)**. Hydrocarbons containing carbon–carbon double bonds are **alkenes**, while hydrocarbons with carbon–carbon triple bonds are **alkynes**. Carbon-carbon double and triple bonds are examples of **functional groups**, atoms or bonds that impart a characteristic chemical function to the molecule. Other functional groups include the alcohol functional group (OH) and the **carboxyl functional group** (COOH). They are the characteristic functional group in organic compounds called **alcohols** and **carboxylic acids**.

CHAPTER OVERVIEW

5: Introduction to Chemical Reactions

Chemical change is a central concept in chemistry. The goal of chemists is to know how and why a substance changes in the presence of another substance or even by itself. Because there are tens of millions of known substances, there are a huge number of possible chemical reactions. In this chapter, we will find that many of these reactions can be classified into a small number of categories according to certain shared characteristics.

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http://en.Wikipedia.org/wiki/Exother...teReaction.jpg

5.0: Prelude to Introduction to Chemical Reactions

Although yeast has been used for thousands of years, its true nature has been known only for the last two centuries. Yeasts are single-celled fungi. About 1,000 species are recognized, but the most common species is *Saccharomyces cerevisiae*, which is used in bread making. Other species are used for the fermentation of alcoholic beverages. Some species can cause infections in humans.

Yeasts live primarily on sugars, such as glucose $(C_6H_{12}O_6)$. They convert glucose into carbon dioxide (CO_2) and ethanol (C_2H_5OH) in a chemical transformation that is represented as follows:

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

Bread making depends on the production of carbon dioxide. The gas, which is produced in tiny pockets in bread dough, acts as a leavening agent: it expands during baking and makes the bread rise. Leavened bread is softer, lighter, and easier to eat and chew than unleavened bread. The other major use of yeast, fermentation, depends on the production of ethanol, which results from the same chemical transformation. Some alcoholic beverages, such as champagne, can also be carbonated using the carbon dioxide produced by the yeast.

Yeast is among the simplest life forms on Earth, yet it is absolutely necessary for at least two major food industries. Without yeast to turn dough into bread and juice into wine, these foods and food industries would not exist today.

5.1: The Law of Conservation of Matter

Learning Objectives

- Correctly define a law as it pertains to science.
- State the law of conservation of matter.

In science, a law is a general statement that explains a large number of observations. Before being accepted, a law must be verified many times under many conditions. Laws are therefore considered the highest form of scientific knowledge and are generally thought to be inviolable. Scientific laws form the core of scientific knowledge. One scientific law that provides the foundation for understanding in chemistry is the law of conservation of matter. It states that in any given system that is closed to the transfer of matter (in and out), the amount of matter in the system stays constant. A concise way of expressing this law is to say that the amount of matter in a system is *conserved*.

With the development of more precise ideas on elements, compounds and mixtures, scientists began to investigate how and why substances react. French chemist A. Lavoisier laid the foundation to the scientific investigation of matter by describing that substances react by following certain laws. These laws are called the laws of chemical combination. These eventually formed the basis of Dalton's Atomic Theory of Matter.

Law of Conservation of Mass

According to this law, during any physical or chemical change, the total mass of the products remains equal to the total mass of the reactants.

$$\underbrace{\overbrace{\mathrm{HgO(s)}}^{\text{Mercuric oxide}}}_{100\ \mathrm{g}} \rightarrow \underbrace{\overbrace{\mathrm{Hg(l)}}^{\text{Mercury}}}_{92.6\ \mathrm{g}} + \underbrace{\overbrace{\mathrm{O_2(g)}}^{\text{Oxygen}}}_{7.4\ \mathrm{g}}$$

Another way of stating this is, "In a chemical reaction, matter is neither created nor destroyed." The law of conservation of mass is also known as the "law of indestructibility of matter."

✓ Example 5.1.1

If heating 10 grams of $\mathrm{CaCO_3}$ produces 4.4 g of $\mathrm{CO_2}$ and 5.6 g of CaO, show that these observations are in agreement with the law of conservation of mass.

A sample of calcium carbonate (CaCO3). (Public Domain; Walkerma).

Solution

- Mass of the reactants, $\mathrm{CaCO_3}$: $10\ g$
- Mass of the products, $\mathrm{CO_2}$ and CaO: $4.4\ g + 5.6\ g = 10\ g$.

Because the mass of the reactants = the mass of the products, the observations are in agreement with the law of conservation of mass.

What does this mean for chemistry? In any chemical change, one or more initial substances change into a different substance or substances. Both the initial and final substances are composed of atoms because all matter is composed of atoms. According to the law of conservation of matter, matter is neither created nor destroyed, so we must have the **same number and kind of atoms** after the chemical change as were present before the chemical change.

It may seem as though burning destroys matter, but the same amount, or mass, of matter still exists after a campfire as before. Figure 5.1.1 shows that when wood burns, it combines with oxygen and changes not only to ashes, but also to carbon dioxide and water vapor. The gases float off into the air, leaving behind just the ashes. Suppose we had measured the mass of the wood before it burned and the mass of the ashes after it burned. Also suppose we had been able to measure the oxygen used by the fire and the gases produced by the fire. What would we find? The total mass of matter after the fire would be the same as the total mass of matter before the fire.

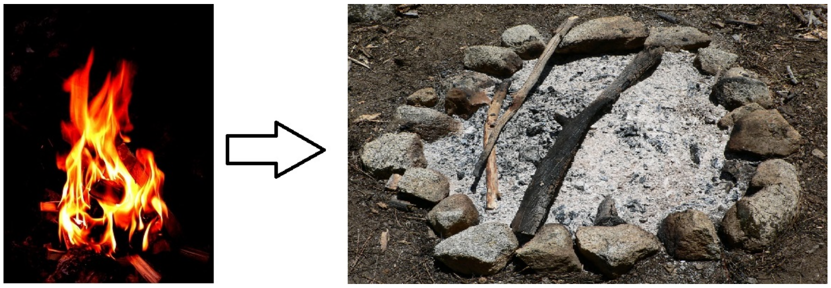


Figure 5.1.1: Burning is a chemical process. The flames are caused as a result of a fuel undergoing combustion (burning). Images used with permission (CC BY-SA 2.5; Einar Helland Berger for fire and for ash).

Exercise 5.1.1

a. What is the law of conservation of matter?
b. How does the law of conservation of matter apply to chemistry?

Answer a:

The law of conservation of matter states that in any given system that is closed to the transfer of matter, the amount of matter in the system stays constant

Answer b:

The law of conservation of matter says that in chemical reactions, the total mass of the products must equal the total mass of the reactants.

Key Takeaway

The amount of matter in a closed system is conserved.

5.2: Chemical Equations

Learning Objectives

- Define *chemical reaction*.
- Use a balanced chemical equation to represent a chemical reaction.

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

"hydrogen and oxygen react to make water"

is one way to represent that process, which is called a chemical reaction. Figure 5.2.1 shows a rather dramatic example of this very reaction.

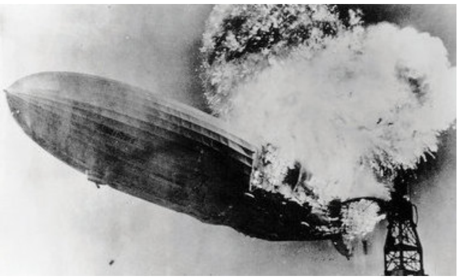


Figure 5.2.1: The Formation of Water. Hydrogen and oxygen combine to form water. Here, the hydrogen gas in the zeppelin *SS Hindenburg* reacts with oxygen in the air to make water. Source: Photo courtesy of the US Navy. For a video of this see www.youtube.com/watch?v=CgWHbpMVQ1U.

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

$$H_2 + O_2 \rightarrow H_2O \tag{5.2.1}$$

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

$$H_2(g) + O_2(g) \rightarrow H_2O(\ell) \tag{5.2.2}$$

> Chemical equations can also be used to describe physical changes. We will see examples of this soon.

This equation is still not complete because *it does not satisfy the **law of conservation of matter***. Count the **number of atoms of each element** on each side of the arrow. On the reactant side, there are two H atoms and two O atoms; on the product side, there are two H atoms and only one oxygen atom. The equation is **not balanced** because the number of oxygen atoms on each side is not the same (Figure 5.2.2).

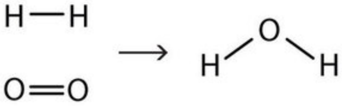


Figure 5.2.2: Balanced—Yes or No?. By counting the atoms of each element, we can see that the reaction is not balanced as written.

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

$$\mathrm{H_2(g) + O_2(g) \rightarrow 2\,H_2O(\ell)} \tag{5.2.3}$$

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

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

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

$$\mathrm{2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(\ell)} \tag{5.2.4}$$

Now we have four hydrogen atoms and two oxygen atoms on each side of the equation. The **law of conservation of matter is satisfied** because we now have the same number of atoms of each element in the reactants and in the products. We say that the reaction is **balanced** (Figure 5.2.3). The diatomic oxygen has a coefficient of 1, which typically is not written but assumed in balanced chemical equations.

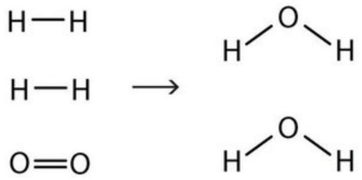


Figure 5.2.3: Balanced—Yes or No?. By counting the atoms of each element, we can see that the reaction is now balanced.

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

✓ Example 5.2.1

Is each chemical equation balanced?

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

Solution

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

? Exercise 5.2.1

Is each chemical equation balanced?

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

Answer a:

balanced

Answer b:

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

Answer c:

balanced

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

Below are guidelines for writing and balancing chemical equations.

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

For example, to balance the equation

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

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

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

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

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

$$\mathrm{CH_4 + Cl_2 \rightarrow CCl_4 + 4\,HCl} \tag{5.2.6}$$

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

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

$$\mathrm{CH_4 + 4\,Cl_2 \rightarrow CCl_4 + 4\,HCl} \tag{5.2.7}$$

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

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

Example 5.2.2

Aqueous solutions of lead (II) nitrate and sodium chloride are mixed. The products of the reaction are an aqueous solution of sodium nitrate and a solid precipitate of lead (II) chloride. Write the balanced chemical equation for this reaction.

Solution

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

$$Pb(NO_3)_2\,(aq) + NaCl\,(aq) \rightarrow NaNO_3\,(aq) + PbCl_2\,(s)$$

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

Reactants	Products
1 Pb atom	1 Pb atom
2 NO_3^- ions	1 NO_3^- ions
1 Na atom	1 Na atom
1 Cl atom	2 Cl atoms

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

$$Pb(NO_3)_2\,(aq) + 2NaCl\,(aq) \rightarrow 2NaNO_3\,(aq) + PbCl_2\,(s)$$

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

Reactants	Products
1 Pb atom	1 Pb atom
2 NO_3^- ions	2 NO_3^- ions
2 Na atom	2 Na atom
2 Cl atom	2 Cl atoms

Step 5: Think about the result.

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

Exercise 5.2.2

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

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

Answer

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

Key Takeaway

Chemical reactions are represented by chemical equations that list reactants and products. Proper chemical equations are balanced; the same number of each element's atoms appears on each side of the equation.

5.3: Quantitative Relationships Based on Chemical Equations

Learning Objectives

- To calculate the amount of one substance that will react with or be produced from a given amount of another substance.

A balanced chemical equation not only describes some of the chemical properties of substances—by showing us what substances react with what other substances to make what products—but also shows numerical relationships between the reactants and the products. The study of these numerical relationships is called stoichiometry. The stoichiometry of chemical equations revolves around the coefficients in the balanced chemical equation because these coefficients determine the molecular ratio in which reactants react and products are made.

> *The word stoichiometry is pronounced "stow-eh-key-OM-et-tree." It is of mixed Greek and English origins, meaning roughly "measure of an element."*

Looking Closer: Stoichiometry in Cooking

Let us consider a stoichiometry analogy from the kitchen. A recipe that makes 1 dozen biscuits needs 2 cups of flour, 1 egg, 4 tablespoons of shortening, 1 teaspoon of salt, 1 teaspoon of baking soda, and 1 cup of milk. If we were to write this as a chemical equation, we would write

2 c flour + 1 egg + 4 tbsp shortening + 1 tsp salt + 1 tsp baking soda + 1 c milk → 12 biscuits

(Unlike true chemical reactions, this one has all 1 coefficients written explicitly—partly because of the many different units here.) This equation gives us ratios of how much of what reactants are needed to make how much of what product. Two cups of flour, when combined with the proper amounts of the other ingredients, will yield 12 biscuits. One teaspoon of baking soda (when also combined with the right amounts of the other ingredients) will make 12 biscuits. One egg must be combined with 1 cup of milk to yield the product food. Other relationships can also be expressed.

We can use the ratios we derive from the equation for predictive purposes. For instance, if we have 4 cups of flour, how many biscuits can we make if we have enough of the other ingredients? It should be apparent that we can make a double recipe of 24 biscuits.

But how would we find this answer formally, that is, mathematically? We would set up a conversion factor, much like we did in Chapter 1. Because 2 cups of flour make 12 biscuits, we can set up an equivalency ratio:

$$\frac{12\text{ biscuits}}{2\text{ c flour}}$$

We then can use this ratio in a formal conversion of flour to biscuits:

$$4\text{ c flour}\times\frac{12\text{ biscuits}}{2\text{ c flour}}=24\text{ biscuits}$$

Similarly, by constructing similar ratios, we can determine how many biscuits we can make from any amount of ingredient. When you are doubling or halving a recipe, you are doing a type of stoichiometry. Applying these ideas to chemical reactions should not be difficult if you use recipes when you cook.

A recipe shows how much of each ingredient is needed for the proper reaction to take place. from Wikipedia.

Consider the following balanced chemical equation:

$$2\,C_2H_2 + 5\,O_2 \rightarrow 4\,CO_2 + 2\,H_2O \tag{5.3.1}$$

The coefficients on the chemical formulas give the ratios in which the reactants combine and the products form. Thus, we can make the following statements and construct the following ratios:

Table uses a statement from the balanced chemical reaction to show ratios and inverse ratios.

Statement from the Balanced Chemical Reaction	Ratio	Inverse Ratio
two C_2H_2 molecules react with five O_2 molecules	$\frac{2C_2H_2}{5O_2}$	$\frac{5O_2}{2C_2H_2}$
two C_2H_2 molecules react to make four CO_2 molecules	$\frac{2C_2H_2}{4CO_2}$	$\frac{4CO_2}{2C_2H_2}$
five O_2 molecules react to make two H_2O molecules	$\frac{5O_2}{2H_2O}$	$\frac{2H_2O}{5O_2}$
four CO_2 molecules are made at the same time as two H_2O molecules	$\frac{2H_2O}{4CO_2}$	$\frac{4CO_2}{2H_2O}$

Other relationships are possible; in fact, 12 different conversion factors can be constructed from this balanced chemical equation. In each ratio, the unit is assumed to be molecules because that is how we are interpreting the chemical equation.

Any of these fractions can be used as a conversion factor to relate an amount of one substance to an amount of another substance. For example, suppose we want to know how many CO_2 molecules are formed when 26 molecules of C_2H_2 are reacted. As usual with a conversion problem, we start with the amount we are given—$26C_2H_2$—and multiply it by a conversion factor that cancels out our original unit and introduces the unit we are converting to—in this case, CO_2. That conversion factor is $\frac{4CO_2}{2C_2H_2}$, which is composed of terms that come directly from the balanced chemical equation. Thus, we have

$$26C_2H_2 \times \frac{4CO_2}{2C_2H_2}$$

The molecules of C_2H_2 cancel, and we are left with molecules of CO_2. Multiplying through, we get

$$26C_2H_2 \times \frac{4CO_2}{2C_2H_2} = 52CO_2$$

Thus, 52 molecules of CO_2 are formed.

This application of stoichiometry is extremely powerful in its predictive ability, as long as we begin with a balanced chemical equation. Without a balanced chemical equation, the predictions made by simple stoichiometric calculations will be incorrect.

✓ Example 5.3.1

Start with this balanced chemical equation.

$$\mathrm{KMnO_4 + 8\,HCl + 5\,FeCl_2 \rightarrow 5\,FeCl_3 + MnCl_2 + 4\,H_2O + KCl}$$

1. Verify that the equation is indeed balanced.
2. Give 2 ratios that give the relationship between HCl and $FeCl_3$.

Solution

1. Each side has 1 K atom and 1 Mn atom. The 8 molecules of HCl yield 8 H atoms, and the 4 molecules of H_2O also yield 8 H atoms, so the H atoms are balanced. The Fe atoms are balanced, as we count 5 Fe atoms from 5 $FeCl_2$ reactants and 5 $FeCl_3$ products. As for Cl, on the reactant side, there are 8 Cl atoms from HCl and 10 Cl atoms from the 5 $FeCl_2$ formula units, for a total of 18 Cl atoms. On the product side, there are 15 Cl atoms from the 5 $FeCl_3$ formula units, 2 from the $MnCl_2$ formula unit, and 1 from the KCl formula unit. This is a total of 18 Cl atoms in the products, so the Cl atoms are balanced. All the elements are balanced, so the entire chemical equation is balanced.
2. Because the balanced chemical equation tells us that 8 HCl molecules react to make 5 $FeCl_3$ formula units, we have the following 2 ratios: $\frac{\mathrm{8HCl}}{\mathrm{5FeCl_3}}$ and $\frac{\mathrm{5FeCl_3}}{\mathrm{8HCl}}$. There are a total of 42 possible ratios. Can you find the other 40 relationships?

? Exercise 5.3.1

Start with this balanced chemical equation.

$$\mathrm{2KMnO_4 + 3CH_2{=}CH_2 + 4H_2O \rightarrow 2MnO_2 + 3HOCH_2CH_2OH + 2KOH}$$

a. Verify that the equation is balanced.
b. Give 2 ratios that give the relationship between $KMnO_4$ and CH_2=CH_2. (A total of 30 relationships can be constructed from this chemical equation. Can you find the other 28?)

Answer a:

Each side has 2 K atoms and 2 Mn atoms. On the reactant side, 3 CH_2=CH_2 yield 6 C atoms and on the product side, 3 $HOCH_2CH_2OH$ also yield 6 C atoms, so the C atoms are balanced. There are 20 H atoms on the reactants side: 12 H atoms from 3 CH_2=CH_2 and 8 H atoms from 4 H_2O. On the product side, there are also 20 H atoms: 18 H atoms from 3 $HOCH_2CH_2OH$ and 2 H atoms from 2 KOH. So, the H atoms are balanced. As for O, on the reactant side, there are 8 O atoms from 2 $KMnO_4$ and 4 O atoms from 4 H_2O, for a total of 12 O atoms. On the product side, there are 4 O atoms from the 2 MnO_2 formula units, 6 O atoms from 3 $HOCH_2CH_2OH$, and 2 O atoms from the 2 KOH formula units. This is a total of 12 O atoms in the products, so the O atoms are balanced. All the elements are balanced, so the entire chemical equation is balanced.

Answer b:

Because the balanced chemical equation tells us that 2 $KMnO_4$ formula units react with 3 CH_2=CH_2 molecules, we have the following 2 ratios: $\frac{\mathrm{2KMnO_4}}{\mathrm{3CH_2{=}CH_2}}$ and $\frac{\mathrm{3CH_2{=}CH_2}}{\mathrm{2KMnO_4}}$. There are a total of 30 possible ratios. Can you find the other 28 relationships?

Key Takeaway

The coefficients in a balanced chemical equation give the ratios in which molecules of substances react and are produced in a chemical reaction.

5.4: Some Types of Chemical Reactions

Learning Objectives

- To classify a given chemical reaction into a variety of types.

Although there are untold millions of possible chemical reactions, most can be classified into a small number of general reaction types. Classifying reactions has two purposes: it helps us to recognize similarities among them, and it enables us to predict the products of certain reactions. A particular reaction may fall into more than one of the categories that we will define in this book.

Combination (composition) Reactions

A combination (composition) reaction is a chemical reaction that makes a single substance from two or more reactants. There may be more than one molecule of product in the balanced chemical equation, but there is only one substance produced. For example, the equation

$$4\,Fe + 3\,O_2 \rightarrow 2\,Fe_2O_3$$

is a combination reaction that produces Fe_2O_3 from its constituent elements — Fe and O_2. Combination reactions do not have to combine elements, however. The chemical equation

$$Fe_2O_3 + 3\,SO_3 \rightarrow Fe_2(SO_4)_3$$

shows a combination reaction in which Fe_2O_3 combines with three molecules of SO_3 to make $Fe_2(SO_4)_3$.

Example 5.4.1

Which equations are combination reactions?

a. $Co(s) + Cl_2(g) \rightarrow CoCl_2(s)$
b. $CO(g) + Cl_2(g) \rightarrow COCl_2(g)$
c. $N_2H_4(\ell) + O_2(g) \rightarrow N_2(g) + 2\,H_2O(\ell)$

Solution

a. This is a combination reaction.
b. This is a combination reaction. (The compound $COCl_2$ is called phosgene and, in the past, was used as a gassing agent in chemical warfare.)
c. This is not a combination reaction.

Exercise 5.4.1

Which equations are combination reactions?

a. $P_4(s) + 6\,Cl_2(g) \rightarrow 4\,PCl_3(g)$
b. $SO_3(\ell) + H_2O(\ell) \rightarrow H_2SO_4(\ell)$
c. $NaOH(s) + HCl(g) \rightarrow NaCl(s) + H_2O(\ell)$

Answer

a and b are combination reactions

Decomposition Reactions

A decomposition reaction is the reverse of a combination reaction. In a decomposition reaction, a single substance is converted into two or more products. There may be more than one molecule of the reactant, but there is only one substance initially. For example, the equation

$$2\,NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(\ell)$$

is a decomposition reaction that occurs when $\mathrm{NaHCO_3}$ is exposed to heat. Another example is the decomposition of $\mathrm{KClO_3}$:

$$2\,\mathrm{KClO_3(s)} \rightarrow 2\,\mathrm{KCl(s)} + 3\,\mathrm{O_2(g)}$$

This reaction was once commonly used to generate small amounts of oxygen in the chemistry lab.

> The decomposition reaction of $\mathrm{NaHCO_3}$ is the reaction that occurs when baking soda is poured on a small kitchen fire. The intent is that the $\mathrm{H_2O}$ and $\mathrm{CO_2}$ produced by the decomposition will smother the flames.

Combustion Reactions

A combustion reaction occurs when a substance combines with molecular oxygen to make oxygen-containing compounds of other elements in the reaction. Many combustion reactions occur with a hydrocarbon, a compound made up solely of carbon and hydrogen. The products of the combustion of hydrocarbons are carbon dioxide and water. Many hydrocarbons are used as fuel because their combustion releases very large amounts of heat energy. An example is propane ($\mathrm{C_3H_8}$), a gaseous hydrocarbon that is commonly used as the fuel source in gas grills.

$$\mathrm{C_3H_8(g)} + 5\,\mathrm{O_2(g)} \rightarrow 3\,\mathrm{CO_2(g)} + 4\,\mathrm{H_2O(g)}$$

Another example is the burning of acetylene ($\mathrm{C_2H_2}$) in welding torches:

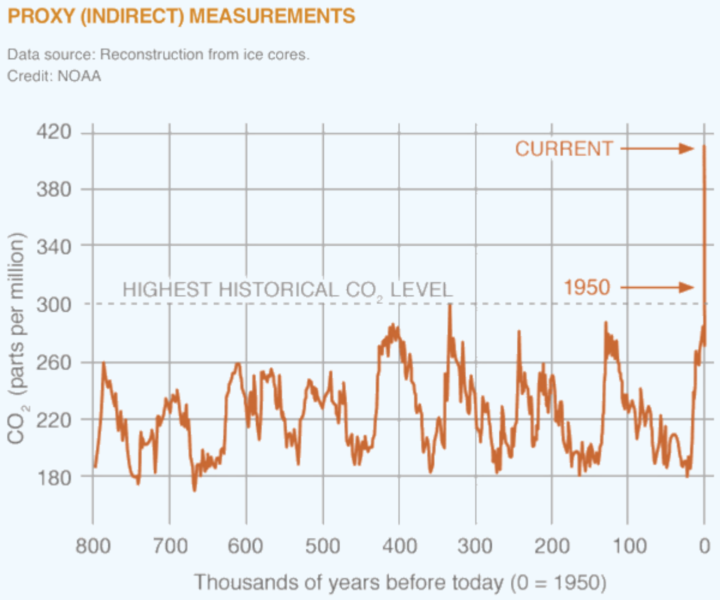
$$2\,\mathrm{C_2H_2} + 5\,\mathrm{O_2} \rightarrow 4\,\mathrm{CO_2} + 2\,\mathrm{H_2O}$$

Oxygen (in its elemental form) is a crucial reactant in combustion reactions.

> *Energy in the form of heat is usually given off as a product in a combustion reaction as well.*

✓ Example 5.4.2

Carbon dioxide ($\mathrm{CO_2}$) is an important heat-trapping (greenhouse) gas, which is released through human activities such as deforestation and burning fossil fuels, as well as natural processes such as respiration and volcanic eruptions. The graph above shows $\mathrm{CO_2}$ levels during the last three glacial cycles, as reconstructed from ice cores.



Carbon dioxide is the primary greenhouse gas emitted through human activities. In 2015, $\mathrm{CO_2}$ accounted for about 82.2% of all U.S. greenhouse gas emissions from human activities. Carbon dioxide is naturally present in the atmosphere as part of the Earth's carbon cycle (the natural circulation of carbon among the atmosphere, oceans, soil, plants, and animals). Human activities are altering the carbon cycle–both by adding more CO_2 to the atmosphere and by influencing the ability of natural sinks, like forests, to remove CO_2 from the atmosphere. While CO_2 emissions come from a variety of natural sources, human-related emissions are responsible for the increase that has occurred in the atmosphere since the industrial revolution.

The main human activity that emits CO_2 is the combustion of fossil fuels (coal, natural gas, and oil) for energy and transportation, although certain industrial processes and land-use changes also emit CO_2. An example of how CO_2 can be generated is the **combustion of octane** (C_8H_{10}), a component of gasoline.

Write the balanced equation to represent the combustion of octane.

Solution

$$2\,C_8H_{18}(l) + 25\,O_2(g) \rightarrow 16\,CO_2(g) + 18\,H_2O(g)$$

The balanced reaction argues that for every two molecules of octane that are burned, 16 molecules of CO_2 are generated.

✓ Example 5.4.2

Identify each type of reaction.

a. $2\,K(s) + S(s) + 2\,O_2(g) \rightarrow K_2SO_4(s)$
b. $(NH_4)_2Cr_2O_7(s) \rightarrow N_2(g) + Cr_2O_3(s) + 4\,H_2O(\ell)$
c. $CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(\ell)$

Solution

a. Multiple reactants are combining to make a single product, so this reaction is a combination reaction.
b. A single substance reacts to make several products, so we have a decomposition reaction.
c. Oxygen reacts with a compound to make carbon dioxide (an oxide of carbon) and water (an oxide of hydrogen). This is a combustion reaction.

? Exercise 5.4.2

Identify each type of reaction.

a. $C_2H_5OH + 3\,O_2 \rightarrow 2\,CO_2 + 3\,H_2O$
b. $2\,Mg(s) + O_2(g) \rightarrow 2\,MgO(s)$
c. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

Answer a

combustion

Answer b

combination (also combustion)

Answer c

decomposition

Key Takeaway

There are several recognizable types of chemical reactions: combination, decomposition, and combustion reactions are examples.

5.5: Oxidation-Reduction (Redox) Reactions

Learning Objectives

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

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

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

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

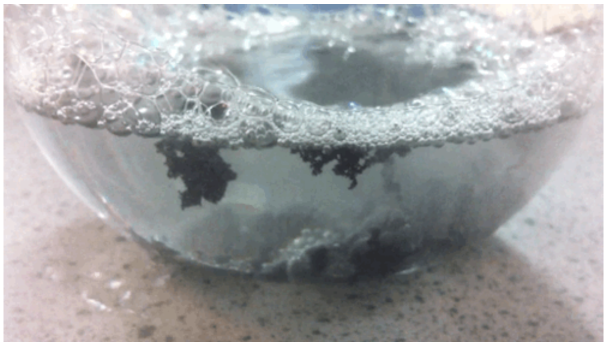


Figure $5.5.1$: Zinc Metal plus Hydrochloric Acid. It is fairly obvious that zinc metal reacts with aqueous hydrochloric acid! The bubbles are hydrogen gas (right side of Equation 5.5.1).

Because some of the substances in this reaction are aqueous, we can separate them into ions:

$$\mathrm{Zn(s)} + 2\,\mathrm{H^+(aq)} + 2\,\mathrm{Cl^-(aq)} \rightarrow \mathrm{H_2(g)} + \mathrm{Zn^{2+}(aq)} + 2\,\mathrm{Cl^-(aq)}$$

Viewed this way, the net reaction seems to be a charge transfer between zinc and hydrogen atoms. (There is no net change experienced by the chloride ion.) In fact, electrons are being transferred from the zinc atoms to the hydrogen atoms (which ultimately make a molecule of diatomic hydrogen), changing the charges on both elements.

To understand electron-transfer reactions like the one between zinc metal and hydrogen ions, chemists separate them into two parts: one part focuses on the loss of electrons, and one part focuses on the gain of electrons. The loss of electrons is called oxidation. The gain of electrons is called reduction. Because any loss of electrons by one substance must be accompanied by a gain in electrons by something else, oxidation and reduction always occur together. As such, electron-transfer reactions are also called oxidation-reduction reactions, or simply **redox reactions**. The atom that loses electrons is **oxidized**, and the atom that gains electrons is **reduced**. Also, because we can think of the species being oxidized as causing the reduction, the species being oxidized is called the **reducing agent**, and the species being reduced is called the **oxidizing agent**.

> *Because batteries are used as sources of electricity (that is, of electrons), all batteries are based on redox reactions.*

Although the two reactions occur together, it can be helpful to write the oxidation and reduction reactions separately as half reactions. In half reactions, we include only the reactant being oxidized or reduced, the corresponding product species, any other species needed to balance the half reaction, and the electrons being transferred. Electrons that are lost are written as products; electrons that are gained are written as reactants. For example, in our earlier equation, now written without the chloride ions,

$$\mathrm{Zn(s)} + 2\,\mathrm{H^+(aq)} \rightarrow \mathrm{Zn^{2+}(aq)} + \mathrm{H_2(g)}$$

zinc atoms are oxidized to $\mathrm{Zn^{2+}}$. The **half reaction for the oxidation** reaction, omitting phase labels, is as follows:

$$\mathrm{Zn} \rightarrow \mathrm{Zn^{2+}} + 2\,\mathrm{e^-}$$

This half reaction is balanced in terms of the number of zinc atoms, and it also shows the two electrons that are needed as products to account for the zinc atom losing two negative charges to become a 2+ ion. With half reactions, there is one more item to balance: the overall charge on each side of the reaction. If you check each side of this reaction, you will note that both sides have a zero net charge.

Hydrogen is reduced in the reaction. The balanced **reduction half reaction** is as follows:

$$2\,H^{+} + 2\,e^{-} \rightarrow H_2$$

There are two hydrogen atoms on each side, and the two electrons written as reactants serve to neutralize the 2+ charge on the reactant hydrogen ions. Again, the overall charge on both sides is zero.

The overall reaction is simply the combination of the two half reactions and is shown by adding them together.

$$\begin{array}{r} Zn \rightarrow Zn^{2+} + \cancel{2e^{-}} \\ 2H^{+} + \cancel{2e^{-}} \rightarrow H_2 \\ \hline Zn + 2H^{+} \rightarrow Zn^{2+} + H_2 \end{array}$$

Because we have two electrons on each side of the equation, they can be canceled. This is the key criterion for a balanced redox reaction: the electrons have to cancel exactly. If we check the charge on both sides of the equation, we see they are the same—2+. (In reality, this positive charge is balanced by the negative charges of the chloride ions, which are not included in this reaction because chlorine does not participate in the charge transfer.)

Redox reactions are often balanced by balancing each individual half reaction and then combining the two balanced half reactions. **Sometimes a half reaction must have all of its coefficients multiplied by some integer for all the electrons to cancel**. The following example demonstrates this process.

✓ Example 5.5.1: Reducing Silver Ions

Write and balance the redox reaction that has silver ions and aluminum metal as reactants and silver metal and aluminum ions as products. Identify the substance oxidized, substance reduced, reducing agent and reducing agent.

Solution

We start by using symbols of the elements and ions to represent the reaction:

$$Ag^{+} + Al \rightarrow Ag + Al^{3\,+}$$

The equation looks balanced as it is written. However, when we compare the overall charges on each side of the equation, we find a charge of +1 on the left but a charge of +3 on the right. This equation is not properly balanced. To balance it, let us write the two half reactions. Silver ions are reduced, and it takes one electron to change Ag^+ to Ag:

Reduction half-reaction:

$$Ag^{+} + e^{-} \rightarrow Ag$$

Aluminum is oxidized, losing three electrons to change from Al to Al^{3+}:

Oxidation half-reaction:

$$Al \rightarrow Al^{3\,+} + 3\,e^{-}$$

To combine these two half reactions and cancel out all the electrons, we need to multiply the silver reduction reaction by 3:

$$\begin{array}{r} 3\left(Ag^{+} + e^{-} \rightarrow Ag\right) \\ Al \rightarrow Al^{3+} + 3e^{-} \\ \hline 3Ag^{+} + Al \rightarrow 3Ag + Al^{3+} \end{array}$$

Now the equation is balanced, not only in terms of elements but also in terms of charge.

- The **substance oxidized** is the reactant that had undergone oxidation: Al
- The **substance reduced** is the reactant that had undergone reduction: Ag^+
- The **reducing agent** is the same as the substance oxidized: Al
- The **oxidizing agent** is the same as the substance reduced: Ag^+

? Exercise 5.5.1

Write and balance the redox reaction that has calcium ions and potassium metal as reactants and calcium metal and potassium ions as products. Identify the substance oxidized, substance reduced, reducing agent and reducing agent.

Answer

Reduction: Ca^{2+} + $2e^{-}$ → Ca

Oxidation: 2 (K → K^{+} + e^{-})

Combined: Ca^{2+} + 2K → Ca + $2K^{+}$

- The **substance oxidized** is the reactant that had undergone oxidation: K
- The **substance reduced** is the reactant that had undergone reduction: Ca^{2+}
- The **reducing agent** is the same as the substance oxidized: K
- The **oxidizing agent** is the same as the substance reduced: Ca^{2+}

Potassium has been used as a reducing agent to obtain various metals in their elemental form.

To Your Health: Redox Reactions and Pacemaker Batteries

All batteries use redox reactions to supply electricity because electricity is basically a stream of electrons being transferred from one substance to another. Pacemakers—surgically implanted devices for regulating a person's heartbeat—are powered by tiny batteries, so the proper operation of a pacemaker depends on a redox reaction.

Pacemakers used to be powered by NiCad batteries, in which nickel and cadmium (hence the name of the battery) react with water according to this redox reaction:

$$\mathrm{Cd(s) + 2\,NiOOH(s) + 2\,H_2O(\ell) \rightarrow Cd(OH)_2(s) + 2\,Ni(OH)2\,(s)}$$

The cadmium is oxidized, while the nickel atoms in NiOOH are reduced. Except for the water, all the substances in this reaction are solids, allowing NiCad batteries to be recharged hundreds of times before they stop operating. Unfortunately, NiCad batteries are fairly heavy batteries to be carrying around in a pacemaker. Today, the lighter lithium/iodine battery is used instead. The iodine is dissolved in a solid polymer support, and the overall redox reaction is as follows:

$$\mathrm{2\,Li(s) + I_2(s) \rightarrow 2\,LiI(s)}$$

Lithium is oxidized, and iodine is reduced. Although the lithium/iodine battery cannot be recharged, one of its advantages is that it lasts up to 10 years. Thus, a person with a pacemaker does not have to worry about periodic recharging; about once per decade a person requires minor surgery to replace the pacemaker/battery unit. Lithium/iodine batteries are also used to power calculators and watches.

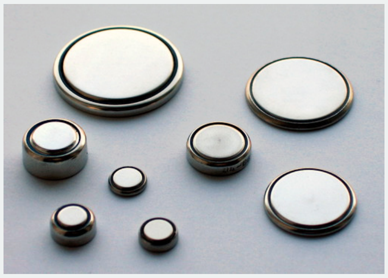


Figure 5.5.1: A small button battery like this is used to power a watch, pacemaker, or calculator. (CC BY-SA; Gerhard H Wrodnigg via Wikipedia)

Oxidation and reduction can also be defined in terms of changes in composition. The original meaning of **oxidation** was "**adding oxygen**," so when oxygen is added to a molecule, the molecule is being oxidized. The reverse is true for **reduction**: if a molecule **loses oxygen** atoms, the molecule is being reduced. For example, the acetaldehyde ($\mathrm{CH_3CHO}$) molecule takes on an oxygen atom to become acetic acid ($\mathrm{CH_3COOH}$).

$$\mathrm{2\,CH_3CHO + O_2 \rightarrow 2\,CH_3COOH}$$

Thus, acetaldehyde is being oxidized.

Similarly, **reduction and oxidation can be defined in terms of the gain or loss of hydrogen atoms**. If a molecule adds hydrogen atoms, it is being reduced. If a molecule loses hydrogen atoms, the molecule is being oxidized. For example, in the conversion of acetaldehyde into ethanol (CH_3CH_2OH), hydrogen atoms are added to acetaldehyde, so the acetaldehyde is being reduced:

$$CH_3CHO + H_2 \rightarrow CH_3CH_2OH$$

Table shows how each process affects the change in oxygen and change in hydrogen.

Process	Change in oxygen (some reactions)	Change in hydrogen (some reactions)
Oxidation	gain	lose
Reduction	lose	gain

✓ Example 5.5.2

In each conversion, indicate whether oxidation or reduction is occurring.

a. N_2 → NH_3
b. $CH_3CH_2OHCH_3$ → CH_3COCH_3
c. HCHO → HCOOH

Solution

a. Hydrogen is being added to the original reactant molecule, so reduction is occurring.
b. Hydrogen is being removed from the original reactant molecule, so oxidation is occurring.
c. Oxygen is being added to the original reactant molecule, so oxidation is occurring.

? Exercise 5.5.2

In each conversion, indicate whether oxidation or reduction is occurring.

a. CH_4 → CO_2 + H_2O
b. NO_2 → N_2
c. CH_2=CH_2 → CH_3CH_3

Answer a:

Oxygen is being added. Oxidation is occurring.

Answer b:

Oxygen is being removed. Reduction is occurring.

Answer a:

Hydrogen is being added. Reduction is occurring.

Key Takeaway

Chemical reactions in which electrons are transferred are called oxidation-reduction, or redox, reactions. Oxidation is the loss of electrons. Reduction is the gain of electrons. Oxidation and reduction always occur together, even though they can be written as separate chemical equations.

5.6: Redox Reactions in Organic Chemistry and Biochemistry

Learning Objectives

- To identify oxidation-reduction reactions with organic compounds.

Oxidation-reduction reactions are of central importance in organic chemistry and biochemistry. The burning of fuels that provides the energy to maintain our civilization and the metabolism of foods that furnish the energy that keeps us alive both involve redox reactions.

Figure 5.6.1: The Burning of Natural Gas. The burning of natural gas is not only a combustion reaction but also a redox reaction. Similar reactions include the burning of gasoline and coal. These are also redox reactions. from Wikipedia.

All combustion reactions are also redox reactions. A typical combustion reaction is the burning of methane, the principal component of natural gas (Figure 5.6.1).

$$\mathrm{CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O} \tag{5.6.1}$$

In respiration, the biochemical process by which the oxygen we inhale in air oxidizes foodstuffs to carbon dioxide and water, redox reactions provide energy to living cells. A typical respiratory reaction is the oxidation of glucose ($C_6H_{12}O_6$), the simple sugar we encountered in the chapter-opening essay that makes up the diet of yeast:

$$\mathrm{C_6H_{12}O_6 + 6\,O_2 \rightarrow 6\,CO_2 + 6\,H_2O} \tag{5.6.2}$$

Organic chemists use a variety of redox reactions. For example, potassium dichromate ($K_2Cr_2O_7$) is a common oxidizing agent that can be used to oxidize alcohols (symbolized by the general formula ROH). The product of the reaction depends on the location of the OH functional group in the alcohol molecule, the relative proportions of alcohol and the dichromate ion, and reaction conditions such as temperature. If the OH group is attached to a terminal carbon atom and the product is distilled off as it forms, the product is an aldehyde, which has a terminal *carbonyl group* (C=O) and is often written as RCHO. One example is the reaction used by the Breathalyzer to detect ethyl alcohol (CH_3CH_2OH) in a person's breath:

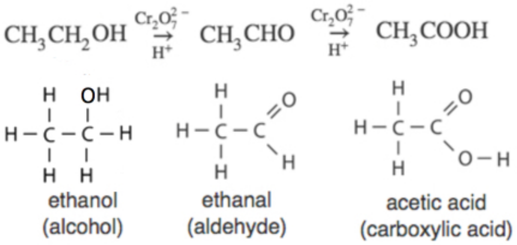
$$\mathrm{3\,CH_3CH_2OH + Cr_2O_7^{2\,-} + 8\,H^+ \rightarrow 3\,CH_3CHO + 2\,Cr^{3\,+} + 7\,H_2O} \tag{5.6.3}$$

If the product acetaldehyde (CH_3CHO) is not removed as it forms, it is further oxidized to acetic acid (CH_3COOH). In this case, the overall reaction is as follows:

$$\mathrm{3\,CH_3CH_2OH + 2\,Cr_2O_7^{2\,-} + 16\,H^+ \rightarrow 3\,CH_3COOH + 4\,Cr^{3\,+} + 11\,H_2O} \tag{5.6.4}$$

In this reaction, the chromium atom is reduced because it lost oxygen atoms from $Cr_2O_7^{2-}$ to Cr^{3+}. On the other hand, the carbon atom in ethanol is oxidized. In the **oxidation** of ethyl alcohol (CH_3CH_2OH, a.k.a. ethanol) to form acetaldehayde (CH_3CHO, a.k.a. ethanal), the **number of bonds to oxygen has increased and the number of hydrogen atoms has decreased** from six to four. Either or both of these indicate that an oxidation has occurred.

In the oxidation of acetaldehyde to acetic acid (a.k.a. ethanoic acid), the carbon atom that gained an additional oxygen is the element oxidized.



When the OH group of the alcohol is bonded to an interior carbon atom, the oxidation of an alcohol will produce a ketone (the formulas of ketones are often written as RCOR, and the carbon–oxygen bond is a double bond). The simplest ketone is derived from 2-propanol ($CH_3CHOHCH_3$). It is the common solvent acetone [$(CH_3)_2CO$], which is used in varnishes, lacquers, rubber cement, and nail polish remover. Acetone can be formed by the following redox reaction:

$$3\,CH_3CHOHCH_3 + Cr_2O_7^{2-} + 8\,H^+ \rightarrow 3\,(CH_3)_2CO + 2\,Cr^{3+} + 7\,H_2O \tag{5.6.5}$$

As we have just seen, aldehydes and ketones can be formed by the oxidation of alcohols. Conversely, aldehydes and ketones can be reduced to alcohols. Reduction of the carbonyl group is important in living organisms. For example, in anaerobic metabolism, in which biochemical processes take place in the absence of oxygen, pyruvic acid ($CH_3COCOOH$) is reduced to lactic acid ($CH_3CHOHCOOH$) in the muscles.

$$CH_3COCOOH \rightarrow CH_3CHOHCOOH \tag{5.6.6}$$

(Pyruvic acid is both a carboxylic acid and a ketone; only the ketone group is reduced.) The buildup of lactic acid during vigorous exercise is responsible in large part for the fatigue that we experience.

In food chemistry, the substances known as antioxidants are reducing agents. Ascorbic acid (vitamin C; $C_6H_8O_6$) is thought to retard potentially damaging oxidation of living cells. In the process, it is oxidized to dehydroascorbic acid ($C_6H_6O_6$). In the stomach, ascorbic acid reduces the nitrite ion (NO_2^-) to nitric oxide (NO):

$$C_6H_8O_6 + 2\,H^+ + 2\,NO_2^- \rightarrow C_6H_6O_6 + 2\,H_2O + 2\,NO \tag{5.6.7}$$

> *If reaction in Equation 5.6.7 did not occur, nitrite ions from foods would oxidize the iron in hemoglobin, destroying its ability to carry oxygen.*

Tocopherol (vitamin E) is also an antioxidant. In the body, **vitamin E** is thought to act by scavenging harmful by-products of metabolism, such as the highly reactive molecular fragments called free radicals. In foods, vitamin E acts to prevent fats from being oxidized and thus becoming rancid. **Vitamin C** is also a good antioxidant (Figure 5.6.2).

Figure 5.6.2: Citrus Fruits. Citrus fruits, such as oranges, lemons, and limes, are good sources of vitamin C, which is an antioxidant. Wedges of pink grapefruit, lime, and lemon, and a half orange (clockwise from top). from Wikipedia.

Finally, and of greatest importance, green plants carry out the redox reaction that makes possible almost all life on Earth. They do this through a process called photosynthesis, in which carbon dioxide and water are converted to glucose ($C_6H_{12}O_6$). The synthesis of glucose requires a variety of proteins called enzymes and a green pigment called chlorophyll that converts sunlight into chemical energy (Figure 5.6.3). The overall change that occurs is as follows:

$$6\,CO_2 + 6\,H_2O \rightarrow C_6H_{12}O_6 + 6\,O_2 \tag{5.6.8}$$

In this reaction, carbon dioxide is reduced to glucose, and water is oxidized to oxygen gas. Other reactions convert the glucose to more complex carbohydrates, plant proteins, and oils.

Figure 5.6.3: Life on Earth. Photosynthesis is the fundamental process by which plants use sunlight to convert carbon dioxide and water into glucose and oxygen. Then plants make more complex carbohydrates. It is the ultimate source of all food on Earth, and it is a redox reaction. (Public Domain; Wikipedia).

Summary

Redox reactions are common in organic and biological chemistry, including the combustion of organic chemicals, respiration, and photosynthesis.

5.E: Introduction to Chemical Reactions (Exercises)

5.1: The Law of Conservation of Matter

1. What is the law of conservation of matter?
2. How does the law of conservation of matter apply to chemistry?

ANSWERS

1. The law of conservation of matter states that in any given system that is closed to the transfer of matter, the amount of matter in the system stays constant
2. The law of conservation of matter says that in chemical reactions, the total mass of the products must equal the total mass of the reactants.

Exercises

1. Express the law of conservation of matter in your own words.

2. Explain why the concept of conservation of matter is considered a scientific law.

3. Potassium hydroxide (KOH) readily reacts with carbon dioxide ($\mathrm{CO_2}$) to produce potassium carbonate ($\mathrm{K_2CO_3}$) and water ($\mathrm{H_2O}$). How many grams of potassium carbonate is produced if 224.4 g of KOH reacted with 88.0 g of $\mathrm{CO_2}$. The reaction also produced 36.0 g of water.

Answers

1. Matter may not be created or destroyed.

2. The concept is a scientific law because it is based on experimentation.

3. 276.4 g

5.2: Chemical Equations

Concept Review Exercises

a. What are the parts of a chemical equation?
b. Explain why chemical equations need to be balanced.

Answers

a. reactants and products

b. Chemical equations need to be balanced to satisfy the law of conservation of matter.

Exercises

1. Write a chemical equation to express the fact that hydrogen gas and solid iodine react to make gaseous hydrogen iodide. Make sure the equation satisfies the law of conservation of matter.

2. Write a chemical equation to express the fact that sodium metal and chlorine gas react to make solid sodium chloride. Make sure the equation satisfies the law of conservation of matter.

3. Write an equation expressing the fact that hydrogen gas and fluorine gas react to make gaseous hydrogen fluoride. Make sure the equation satisfies the law of conservation of matter.

4. Write an equation expressing the fact that solid potassium and fluorine gas react to make solid potassium fluoride. Make sure the equation satisfies the law of conservation of matter.

5. Mercury reacts with oxygen to make mercury(II) oxide. Write a balanced chemical equation that summarizes this reaction.

6. Octane (C_8H_{18}) reacts with oxygen to make carbon dioxide and water. Write a balanced chemical equation that summarizes this reaction.

7. Propyl alcohol (C_3H_7OH) reacts with oxygen to make carbon dioxide and water. Write a balanced chemical equation that summarizes this reaction.
8. Sulfuric acid (H_2SO_4) reacts with iron metal to make iron(III) sulfate and hydrogen gas. Write a balanced chemical equation that summarizes this reaction.
9. Balance each equation.
   a. $MgCl_2 + K \rightarrow KCl + Mg$
   b. $C_6H_{12}O_6 + O_2 \rightarrow CO_2 + H_2O$
   c. $NaN_3 \rightarrow Na + N_2$ (This is the reaction used to inflate airbags in cars.)
10. Balance each equation.
    a. $NH_4NO_3 \rightarrow N_2O + H_2O$
    b. $TiBr_4 + H_2O \rightarrow TiO_2 + HBr$
    c. $C_3H_5N_3O_9 \rightarrow CO_2 + N_2 + O_2 + H_2O$ (This reaction represents the decomposition of nitroglycerine.)
11. Balance each equation.
    a. $NH_3 + O_2 \rightarrow NO + H_2O$
    b. $Li + N_2 \rightarrow Li_3N$
    c. $AuCl \rightarrow Au + AuCl_3$
12. Balance each equation.
    a. $NaOH + H_3PO_4 \rightarrow Na_3PO_4 + H_2O$
    b. $N_2H_4 + Cl_2 \rightarrow N_2 + HCl$
    c. $Na_2S + H_2S \rightarrow NaSH$
13. Chromium(III) oxide reacts with carbon tetrachloride to make chromium(III) chloride and phosgene ($COCl_2$). Write the balanced chemical equation for this reaction.
14. The reaction that occurs when an Alka-Seltzer tablet is dropped into a glass of water has sodium bicarbonate reacting with citric acid ($H_3C_6H_5O_7$) to make carbon dioxide, water, and sodium citrate ($Na_3C_6H_5O_7$). Write the balanced chemical equation for this reaction.
15. When sodium hydrogen carbonate is used to extinguish a kitchen fire, it decomposes into sodium carbonate, carbon dioxide and water. Write a balanced chemical equation for this reaction.
16. Elemental bromine gas can be generated by reacting sodium bromide with elemental chlorine. The other product is sodium chloride. Write a balanced chemical equation for this reaction.

Answers

1. $H_2(g) + I_2(s) \rightarrow 2HI(g)$
2. $2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$
3. $H_2(g) + F_2(g) \rightarrow 2HF(g)$
4. $2K(s) + F_2(g) \rightarrow 2KF(s)$
5. $2Hg + O_2 \rightarrow 2HgO$
6. $2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$
7. $2C_3H_7OH + 9O_2 \rightarrow 6CO_2 + 8H_2O$
8. $3H_2SO_4 + 2Fe \rightarrow Fe_2(SO_4)_3 + 3H_2$
9. a. $MgCl_2 + 2K \rightarrow 2KCl + Mg$
   b. $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

c. $2NaN_3 \rightarrow 2Na + 3N_2$

10.

a. $NH_4NO_3 \rightarrow N_2O + 2H_2O$
b. $TiBr_4 + 2H_2O \rightarrow TiO_2 + 4HBr$
c. $4C_3H_5N_3O_9 \rightarrow 12CO_2 + 6N_2 + O_2 + 10H_2O$

11.

a. $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$
b. $6Li + N_2 \rightarrow 2Li_3N$
c. $3AuCl \rightarrow 2Au + AuCl_3$

12.

a. $3NaOH + H_3PO_4 \rightarrow Na_3PO_4 + 3H_2O$
b. $N_2H_4 + 2Cl_2 \rightarrow N_2 + 4HCl$
c. $Na_2S + H_2S \rightarrow 2NaSH$

13. $Cr_2O_3 + 3CCl_4 \rightarrow 2CrCl_3 + 3COCl_2$

14. $3NaHCO_3 + H_3C_6H_5O_7 \rightarrow 3CO_2 + 3H_2O + Na_3C_6H_5O_7$

15. $2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$

16. $2NaBr + Cl_2 \rightarrow Br_2 + 2NaCl$

5.3: Quantitative Relationships Based on Chemical Equations

Concept Review Exercises

1. Explain how stoichiometric ratios are constructed from a chemical equation.
2. Why is it necessary for a chemical equation to be balanced before it can be used to construct conversion factors?

Answers

1. Stoichiometric ratios are made using the coefficients of the substances in the balanced chemical equation.
2. A balanced chemical equation is necessary so one can construct the proper stoichiometric ratios.

Exercises

1. Balance this equation and write every stoichiometric ratio you can from it.

$$NH_4NO_3 \rightarrow N_2O + H_2O$$

2. Balance this equation.

$$N_2 + H_2 \rightarrow NH_3$$

3. Balance this equation and write every stoichiometric ratio you can from it.

$$Fe_2O_3 + C \rightarrow Fe + CO_2$$

4. Balance this equation.

$$Fe_2O_3 + CO \rightarrow Fe + CO_2$$

5. Balance this equation and determine how many molecules of CO_2 are formed if 15 molecules of C_6H_6 are reacted.

$$C_6H_6 + O_2 \rightarrow CO_2 + H_2O$$

6. Balance this equation and determine how many formula units of $Ag_2CO_3(s)$ are produced if 20 formula units of Na_2CO_3 are reacted.

$$Na_2CO_3(aq) + AgNO_3(aq) \rightarrow NaNO_3(aq) + Ag_2CO_3(s)$$

7. Copper metal reacts with nitric acid according to this equation:

$$3Cu(s) + 8HNO_3(aq) \rightarrow 3Cu(NO_3)_2(aq) + 2NO(g) + 4H_2O(\ell)$$

   a. Verify that this equation is balanced.
   b. How many Cu atoms will react if 488 molecules of aqueous HNO_3 are reacted?

8. Gold metal reacts with a combination of nitric acid and hydrochloric acid according to this equation:

$$Au(s) + 3HNO_3(aq) + 4HCl(aq) \rightarrow HAuCl_4(aq) + 3NO_2(g) + 3H_2O(\ell)$$

   a. Verify that this equation is balanced.
   b. How many Au atoms react with 639 molecules of aqueous HNO_3?

9. Sulfur can be formed by reacting sulfur dioxide with hydrogen sulfide at high temperatures according to this equation:

$$SO_2(g) + 2H_2S(g) \rightarrow 3S(g) + 2H_2O(g)$$

   a. Verify that this equation is balanced.
   b. How many S atoms will be formed from by reacting 1,078 molecules of H_2S?

10. Nitric acid is made by reacting nitrogen dioxide with water:

$$3NO_2(g) + H_2O(\ell) \rightarrow 2HNO_3(aq) + NO(g)$$

   a. Verify that this equation is balanced.
   b. How many molecules of NO will be formed by reacting 2,268 molecules of NO_2?

Answers

1. $NH_4NO_3 \rightarrow N_2O + 2H_2O$; the stoichiometric ratios are $\frac{1NH_4NO_3}{1N_2O}$, $\frac{1NH_4NO_3}{2H_2O}$, $\frac{1N_2O}{2H_2O}$, and their reciprocals.
2. $N_2 + 3H_2 \rightarrow 2NH_3$
3. $2Fe_2O_3 + 3C \rightarrow 4Fe + 3CO_2$; the stoichiometric ratios are $\frac{2Fe_2O_3}{3C}$, $\frac{2Fe_2O_3}{4Fe}$, $\frac{2Fe_2O_3}{3CO_2}$, $\frac{3C}{4Fe}$, $\frac{3C}{3CO_2}$, $\frac{4Fe}{3CO_2}$, and their reciprocals.
4. $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$
5. $2C_6H_6 + 15O_2 \rightarrow 12CO_2 + 6H_2O$; 90 molecules
6. $Na_2CO_3(aq) + 2AgNO_3(aq) \rightarrow 2NaNO_3(aq) + Ag_2CO_3(s)$; 20 formula units
7.
   a. It is balanced.
   b. 183 atoms
8.
   a. It is balanced.
   b. 213 atoms

9.

  a. It is balanced.
  b. 1,617 atoms

10.

  a. It is balanced.
  b. 756 molecules

5.4: Some Types of Chemical Reactions

Concept Review Exercises

1. What is the difference between a combination reaction and a combustion reaction?
2. Give the distinguishing characteristic(s) of a decomposition reaction.
3. How do we recognize a combustion reaction?

Answers

1. A combination reaction produces a certain substance; a combustion reaction is a vigorous reaction, usually a combination with oxygen, that is accompanied by the production of light and/or heat.
2. In a decomposition reaction, a single substance reacts to make multiple substances as products.
3. A combustion reaction is typically a vigorous reaction accompanied by light and/or heat, usually because of reaction with oxygen.

Exercises

1. Identify each type of reaction.
   a. $C_6H_5CH_3 + 9O_2 \rightarrow 7CO_2 + 4H_2O$
   b. $2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$
   c. $C + 2H_2 \rightarrow CH_4$
2. Identify each type of reaction.
   a. $P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$
   b. $FeO + SO_3 \rightarrow FeSO_4$
   c. $CaCO_3(s) \rightarrow CO_2(g) + CaO(s)$
3. Identify each type of reaction.
   a. $2NH_4NO_3(s) \rightarrow 2N_2(g) + 4H_2O(g) + O_2(g)$
   b. $Hg(\ell) + ½O_2\ (g) \rightarrow HgO(s)$
   c. $CH_2CH_2(g) + Br_2(\ell) \rightarrow CH_2BrCH_2Br$
4. Identify each type of reaction.
   a. $Ti(s) + O_2(g) \rightarrow TiO_2(s)$
   b. $H_2SO_3(aq) \rightarrow H_2O(\ell) + SO_2(g)$
   c. $3O_2(g) \rightarrow 2O_3(g)$

Answers

1.

  a. combustion

  b. decomposition

  c. combination

2.

   a. combination
   b. combination
   c. decomposition

3.
   a. decomposition
   b. combustion (also combination)
   c. combination

4.
   a. combination
   b. decomposition
   c. combination

5.5: Oxidation-Reduction (Redox) Reactions

Concept Review Exercises

1. Give two different definitions for oxidation and reduction.
2. Give an example of each definition of oxidation and reduction.

Answers

1. Oxidation is the loss of electrons or the addition of oxygen; reduction is the gain of electrons or the addition of hydrogen.
2. Zn → Zn^{2+} +2e⁻ (oxidation); $C_2H_4 + H_2 \rightarrow C_2H_6$ (reduction) (answers will vary)

Exercises

1. Which reactions are redox reactions? For those that are redox reactions, identify the oxidizing and reducing agents.
   a. $NaOH + HCl \rightarrow H_2O + NaCl$
   b. $3Mg + 2AlCl_3 \rightarrow 2Al + 3MgCl_2$
   c. $H_2O_2 + H_2 \rightarrow 2H_2O$
   d. $KCl + AgNO_3 \rightarrow AgCl + KNO_3$
2. Which reactions are redox reactions? For those that are redox reactions, identify the oxidizing and reducing agents.
   a. $3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$
   b. $2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$
   c. $2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$
   d. $2K + 2H_2O \rightarrow 2KOH + H_2$
3. Balance each redox reaction by writing appropriate half reactions and combining them to cancel the electrons.
   a. $Ca(s) + H^+(aq) \rightarrow Ca^{2+}(aq) + H_2(g)$
   b. $I^-(aq) + Br_2(\ell) \rightarrow Br^-(aq) + I_2(s)$
4. Balance each redox reaction by writing appropriate half reactions and combining them to cancel the electrons.
   a. $Fe(s) + Sn^{4+}(aq) \rightarrow Fe^{3+}(aq) + Sn^{2+}(aq)$
   b. $Pb(s) + Pb^{4+}(aq) \rightarrow Pb^{2+}(aq)$ (Hint: both half reactions will yield the same product.)

Answers

1.

a. no

b. yes; oxidizing agent: $AlCl_3$; reducing agent: Mg

c. yes; oxidizing agent: H_2O_2; reducing agent: H_2

d. no

2.

a. yes; oxidizing agent: HNO_3; reducing agent: Cu
b. yes; oxidizing agent: O_2; reducing agent: C_2H_6
c. no
d. yes; oxidizing agent: H_2O; reducing agent: K

3.

a. Combined: $Ca + 2H^+ \rightarrow Ca^{2+} + H_2$
b. Combined: $Br_2 + 2I^- \rightarrow 2Br^- + I_2$

4.

a. $(Fe \rightarrow Fe^{3+} + 3e^-) \times 2$

$(Sn^{4+} + 2e^- \rightarrow Sn^{2+}) \times 3$

Combined: $2Fe + 3Sn^{4+} \rightarrow 2Fe^{3+} + 3Sn^{2+}$

b. $Pb \rightarrow Pb^{2+} + 2e^-$

$Pb^{4+} + 2e^- \rightarrow Pb^{2+}$

Combined: $Pb + Pb^{4+} \rightarrow 2Pb^{2+}$

5.6: Redox Reactions in Organic Chemistry and Biochemistry

Concept Review Exercise

1. Give some biochemical examples of oxidation and reduction reactions.

Answer

1. photosynthesis and antioxidants in foods (answers will vary)

Exercises

1. A typical respiratory reaction discussed in the text is the oxidation of glucose ($C_6H_{12}O_6$):

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

   Is this a redox reaction? If so, what are the oxidizing and reducing agents?

2. The major net reaction in photosynthesis is as follows:

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$$

   Is this a redox reaction? If so, what are the oxidizing and reducing agents?

3. What would be the ultimate organic product if $CH_3CH_2CH_2OH$ were to react with a solution of $K_2Cr_2O_7$?
4. What would be the ultimate organic product if $CH_3CH_2CH_2CH_2OH$ were to react with a solution of $K_2Cr_2O_7$?

5. What would be the final organic product if $CH_3CH_2CHOHCH_3$ were to react with a solution of $K_2Cr_2O_7$?
6. What would be the major organic product if $CH_3CH_2CHOHCH_2CH_3$ were to react with a solution of $K_2Cr_2O_7$?
7. What alcohol is produced in the reduction of acetone [$(CH_3)_2CO$]?
8. What alcohol is produced in the reduction of propanal (CH_3CH_2CHO)?

Answers

1. yes; oxidizing agent: O_2; reducing agent: $C_6H_{12}O_6$
2. yes; oxidizing agent: CO_2; reducing agent: H_2O
3. CH_3CH_2COOH
4. $CH_3CH_2CH_2COOH$
5. $CH_3CH_2C(O)CH_3$, where the carbon is double bonded to the oxygen
6. $CH_3CH_2C(O)CH_2CH_3$, carbon #3 is double bonded to the oxygen
7. $CH_3CHOHCH_3$, or isopropyl alcohol
8. $CH_3CH_2CH_2OH$
5.

Additional Exercises

1. Isooctane (C_8H_{18}) is used as a standard for comparing gasoline performance. Write a balanced chemical equation for the combustion of isooctane.
2. Heptane (C_7H_{16}), like isooctane (see Exercise 1), is also used as a standard for determining gasoline performance. Write a balanced chemical equation for the combustion of heptane.
3. What is the difference between a combination reaction and a redox reaction? Are all combination reactions also redox reactions? Are all redox reactions also combination reactions?
4. Are combustion reactions always redox reactions as well? Explain.
5. A friend argues that the equation

$$Fe^{2+} + Na \rightarrow Fe + Na^{+}$$

   is balanced because each side has one iron atom and one sodium atom. Explain why your friend is incorrect.
6. Some antacids contain aluminum hydroxide [$Al(OH)_3$]. This compound reacts with excess hydrochloric acid (HCl) in the stomach to neutralize it. If the products of this reaction are water and aluminum chloride, what is the balanced chemical equation for this reaction? What is the stoichiometric ratio between the number of HCl molecules made to the number of H_2O molecules made?
7. Sulfuric acid is made in a three-step process: (1) the combustion of elemental sulfur to produce sulfur dioxide, (2) the continued reaction of sulfur dioxide with oxygen to produce sulfur trioxide, and (3) the reaction of sulfur trioxide with water to make sulfuric acid (H_2SO_4). Write balanced chemical equations for all three reactions.
8. If the products of glucose metabolism are carbon dioxide and water, what is the balanced chemical equation for the overall process? What is the stoichiometric ratio between the number of CO_2 molecules made to the number of H_2O molecules made?
9. Historically, the first true battery was the Leclanché cell, named after its discoverer, Georges Leclanché. It was based on the following reaction:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

   Identify what is being oxidized, what is being reduced, and the respective reducing and oxidizing agents.

Answers

1. $2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$
2. $C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O$
3. A combination reaction makes a new substance from more than one reactant; a redox reaction rearranges electrons. Most (not all) combination reactions are redox reactions. Not all redox reactions are combination reactions.
4. All combustion reactions are redox reactions. In combustion a chemical is combining with oxygen and that chemical is being oxidized. Oxygen, on the other hand, is being reduced.
5. Your friend is incorrect because the number of electrons transferring is not balanced. A balanced equation must not only have the same number of atoms of each element on each side of the equation but must also have the same charge on both sides.
6. $Al(OH)_3 + 3HCl \rightarrow 3H_2O + AlCl_3$; 1:1
7. (1) $S + O_2 \rightarrow SO_2$; (2) $2SO_2 + O_2 \rightarrow 2SO_3$; (3) $SO_3 + H_2O \rightarrow H_2SO_4$
8. $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$; 1:1
9. oxidized and reducing agent: Zn; reduced and oxidizing agent: Cu^{2+}

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5.S: Introduction to Chemical Reactions (Summary)

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

Scientific **laws** are general statements that apply to a wide variety of circumstances. One important law in chemistry is the **law of conservation of matter**, which states that in any closed system, the amount of matter stays constant.

Chemical equations are used to represent **chemical reactions**. **Reactants** change chemically into **products**. The law of conservation of matter requires that a proper chemical equation be **balanced**. **Coefficients** are used to show the relative numbers of reactant and product molecules.

In **stoichiometry**, quantities of reactants and/or products can be related to each other using the balanced chemical equation. The coefficients in a balanced chemical reaction are used to devise the proper ratios that relate the number of molecules of one substance to the number of molecules of another substance.

Chemical reactions can be classified by type. **Combination reactions** (also called **composition reactions**) make a substance from other substances. **Decomposition reactions** break one substance down into multiple substances. **Combustion reactions** combine molecular oxygen with the atoms of another reactant.

Oxidation reactions are reactions in which an atom loses an electron. **Reduction reactions** are reactions in which an atom gains an electron. These two processes always occur together, so they are collectively referred to as **oxidation-reduction** (or **redox**) **reactions**. The species being oxidized it called the **reducing agent**, while the species being reduced is the **oxidizing agent**. Alternate definitions of oxidation and reduction focus on the gain or loss of oxygen atoms, or the loss or gain of hydrogen atoms. Redox reactions are easily balanced if the overall reaction is first separated into **half reactions**, which are individually balanced.

Oxidation-reduction reactions are common in organic and biological chemistry. **Respiration**, the process by which we inhale and metabolize oxygen, is a series of redox reactions. In the absence of oxygen, redox reactions still occur in a process called **anaerobic metabolism**. **Antioxidants** such as ascorbic acid also play a part in the human diet, acting as reducing agents in various biochemical reactions. **Photosynthesis**, the process by which plants convert water and carbon dioxide to glucose, is also based on redox reactions.

CHAPTER OVERVIEW

6: Quantities in Chemical Reactions

So far, we have talked about chemical reactions in terms of individual atoms and molecules. Although this works, most of the reactions occurring around us involve much larger amounts of chemicals. Even a tiny sample of a substance will contain millions, billions, or a hundred billion billions of atoms and molecules. How do we compare amounts of substances to each other in chemical terms when it is so difficult to count to a hundred billion billion? Actually, there are ways to do this, which we will explore in this chapter. In doing so, we will increase our understanding of stoichiometry, which is the study of the numerical relationships between the reactants and the products in a balanced chemical reaction.

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6.0: Prelude to Quantities in Chemical Reactions

When the disengaged gasses are carefully examined, they are found to weigh **113.7 grs.**; these are of two kinds, viz. **144 cubical inches** of carbonic acid gas, weighing **100 grs.** and **380 cubical inches** of a very light gas, weighing only **13.7 grs.**…and, when the water which has passed over into the bottle [labeled] H is carefully examined, it is found to have lost **85.7 grs.** of its weight. Thus, in this experiment, **85.7 grs.** of water, joined to **28 grs.** of charcoal, have combined in such a way as to form **100 grs.** of carbonic acid, and **13.7 grs.** of a particular gas capable of being burnt. (Bold emphasis added.)

In this paragraph from the *Elements of Chemistry*, Antoine Lavoisier (1743–94) is explaining an experiment in which he was trying to demonstrate that water is not an element but instead is composed of hydrogen (the gas "capable of being burnt") and oxygen. This is a historical account of a groundbreaking experiment and illustrates the importance of amounts in chemistry. Lavoisier was pointing out that the initial total mass of water and charcoal, 85.7 g plus 28 g, equals the final total mass of carbonic acid and the particular gas, 100 g plus 13.7 g. In this way, he was illustrating the law of conservation of matter. It is another way of saying that *amounts matter*.

Amounts do matter and in a variety of circumstances. The chapter-opening essay in Chapter 1 tells the story of a nurse who mistakenly read "2–3 mg" as "23 mg" and administered the higher and potentially fatal dose of morphine to a child. Food scientists who work in test kitchens must keep track of specific amounts of ingredients as they develop new products for us to eat. Quality control technicians measure amounts of substances in manufactured products to ensure that the products meet company or government standards. Supermarkets routinely weigh meat and produce and charge consumers by the ounce or the pound.

6.1: The Mole

Learning Objectives

- To define the mole unit.

Figure 6.1.1 shows that we need 2 hydrogen atoms and 1 oxygen atom to make 1 water molecule. If we want to make 2 water molecules, we will need 4 hydrogen atoms and 2 oxygen atoms. If we want to make 5 molecules of water, we need 10 hydrogen atoms and 5 oxygen atoms. The ratio of atoms we will need to make any number of water molecules is the same: 2 hydrogen atoms to 1 oxygen atom.

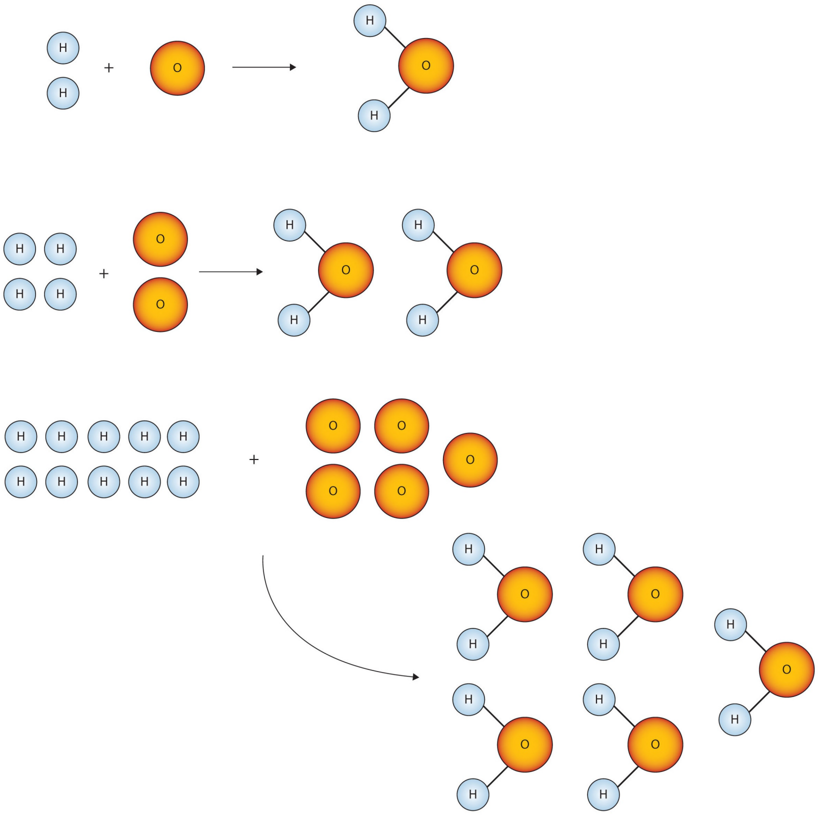


Figure 6.1.1 Water Molecules. The ratio of hydrogen atoms to oxygen atoms used to make water molecules is always 2:1, no matter how many water molecules are being made.

One problem we have, however, is that it is extremely difficult, if not impossible, to organize atoms one at a time. As stated in the introduction, we deal with billions of atoms at a time. How can we keep track of so many atoms (and molecules) at a time? We do it by using mass rather than by counting individual atoms.

A hydrogen atom has a mass of approximately 1 u. An oxygen atom has a mass of approximately 16 u. The ratio of the mass of an oxygen atom to the mass of a hydrogen atom is therefore approximately 16:1.

If we have 2 atoms of each element, the ratio of their masses is approximately 32:2, which reduces to 16:1—the same ratio. If we have 12 atoms of each element, the ratio of their total masses is approximately (12 × 16):(12 × 1), or 192:12, which also reduces to 16:1. If we have 100 atoms of each element, the ratio of the masses is approximately 1,600:100, which again reduces to 16:1. As long as we have equal numbers of hydrogen and oxygen atoms, the ratio of the masses will always be 16:1.

The same consistency is seen when ratios of the masses of other elements are compared. For example, the ratio of the masses of silicon atoms to equal numbers of hydrogen atoms is always approximately 28:1, while the ratio of the masses of calcium atoms to equal numbers of lithium atoms is approximately 40:7.

So we have established that the masses of atoms are constant with respect to each other, as long as we have the same number of each type of atom. Consider a more macroscopic example. If a sample contains 40 g of Ca, this sample has the same number of atoms as there are in a sample of 7 g of Li. What we need, then, is a number that represents a convenient quantity of atoms so we can relate macroscopic quantities of substances. Clearly even 12 atoms are too few because atoms themselves are so small. We need a number that represents billions and billions of atoms.

Chemists use the term **mole** to represent a large number of atoms or molecules. Just as a dozen implies 12 things, a **mole** (abbreviated as ***mol***) represents **6.022×10^{23} things**. The number 6.022×10^{23}, called Avogadro's number after the 19th-century chemist Amedeo Avogadro, is the number we use in chemistry to represent macroscopic amounts of atoms and molecules. Thus, if we have 6.022×10^{23} Na atoms, we say we have 1 mol of Na atoms. If we have 2 mol of Na atoms, we have $2 \times (6.022 \times 10^{23})$ Na atoms, or 1.2044×10^{24} Na atoms. Similarly, if we have 0.5 mol of benzene (C_6H_6) molecules, we have $0.5 \times (6.022 \times 10^{23})$ C_6H_6 molecules, or 3.011×10^{23} C_6H_6 molecules.

> A mole represents a very large number! If 1 mol of quarters were stacked in a column, it could stretch back and forth between Earth and the sun *6.8 billion* times.

Notice that we are applying the mole unit to different types of **chemical entities**. The word *mole* represents a number of things—6.022×10^{23} of them—but does not by itself specify what "they" are. The chemical entities can be ***atoms, molecules***, ***formula units*** and ***ions***. This specific information needs to be specified accurately. Most students find this confusing hence, we need to review the composition of elements, covalent and ionic compounds.

Most elements are made up of individual ***atoms,*** such as helium. However, some elements consist of ***molecules***, such as the diatomic elements, nitrogen, hydrogen, oxygen, etc. One mole of He consists of 6.022×10^{23} He ***atoms*** but one mole of nitrogen contains 6.022×10^{23} N_2 ***molecules***. The basic units of covalent (molecular) compounds are ***molecules*** as well. The molecules of "compounds" consist of different kinds of atoms while the molecules of "elements" consist of only one type of atom. For example, the molecules of ammonia (NH_3) consist of nitrogen and hydrogen atoms while N_2 molecules have N atoms only. Compounds that are ionic, like NaCl, are represented by ionic formulas. One mole of NaCl, for example, refers to 6.022×10^{23} ***formula units*** of NaCl. And, one formula unit of NaCl consists of one sodium ***ion*** and one chloride ***ion***. Figure 6.1.2 summarizes the basic units of elements, covalent and ionic compounds

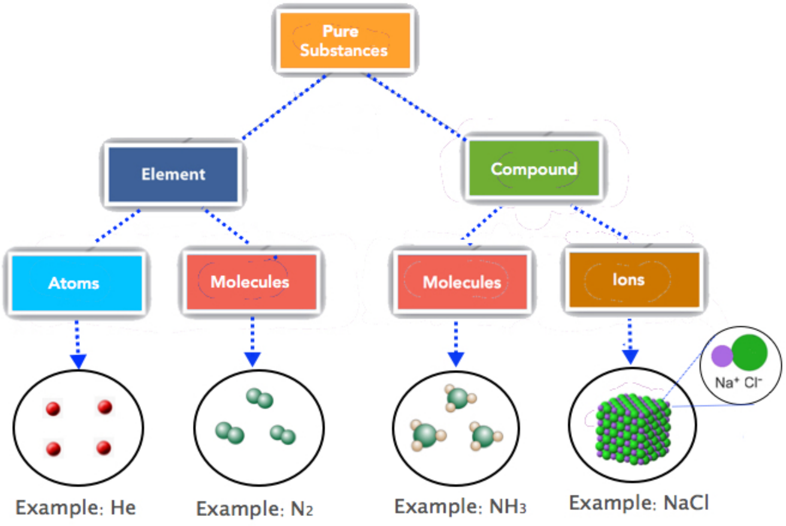


Figure 6.1.2: The basic units of elements (atoms or molecules), covalent compounds (molecules) and ionic compounds (formula units of ions).

Conversion Between Moles and Atoms, Molecules and Ions

Using our unit conversion techniques learned in Chapter 1, we can use the mole relationship and the chemical formula to convert back and forth between the moles and the number of chemical entities (atoms, molecules or ions).

Because 1 N_2 molecule contains 2 N atoms, 1 mol of N_2 molecules (6.022×10^{23} molecules) has 2 mol of N atoms. Using formulas to indicate how many atoms of each element we have in a substance, we can relate the number of moles of molecules to the number of moles of atoms. For example, in 1 mol of ethanol (C_2H_6O), we can construct the following relationships (Table 6.1.1):

Table 6.1.1: Molecular Relationships

1 Molecule of C_2H_6O Has	1 Mol of C_2H_6O Has	Molecular Relationships
2 C atoms	2 mol of C atoms	$\frac{2\text{ mol C atoms}}{1\text{ mol }C_2H_6O\text{ molecules}}$ or $\frac{1\text{ mol }C_2H_6O\text{ molecules}}{2\text{ mol C atoms}}$
6 H atoms	6 mol of H atoms	$\frac{6\text{ mol H atoms}}{1\text{ mol }C_2H_6O\text{ molecules}}$ or $\frac{1\text{ mol }C_2H_6O\text{ molecules}}{6\text{ mol H atoms}}$
1 O atom	1 mol of O atoms	$\frac{1\text{ mol O atoms}}{1\text{ mol }C_2H_6O\text{ molecules}}$ or $\frac{1\text{ mol }C_2H_6O\text{ molecules}}{1\text{ mol O atoms}}$

The following example illustrates how we can use these relationships as conversion factors.

Example 6.1.1

If a sample consists of 2.5 mol of ethanol (C_2H_6O), how many moles of carbon atoms, hydrogen atoms, and oxygen atoms does it have?

Solution

Using the relationships in Table 6.1.1, we apply the appropriate conversion factor for each element:

$$2.5\text{ mol }\cancel{C_2H_6O\text{ molecules}} \times \underbrace{\frac{2\text{ mol C atoms}}{1\text{ mol }\cancel{C_2H_6O\text{ molecules}}}}_{\text{conversion factor}} = 5.0\text{ mol C atoms}$$

Note how the unit *mol C_2H_6O molecules* cancels algebraically. Similar equations can be constructed for determining the number of H and O atoms:

$$2.5\text{ mol }C_2H_6O\text{ molecules} \times \frac{6\text{ mol H atoms}}{1\text{ mol }C_2H_6O\text{ molecules}} = 15\text{ mol H atoms}$$

$$2.5\text{ mol }C_2H_6O\text{ molecules} \times \frac{1\text{ mol O atoms}}{1\text{ mol }C_2H_6O\text{ molecules}} = 2.5\text{ mol O atoms}$$

? Exercise 6.1.1

If a sample contains 6.75 mol of Na_2SO_4, how many moles of sodium atoms, sulfur atoms, and oxygen atoms does it have?

Answer

13.5 mol Na, 6.75 mol S and 27 mol O.

We can use Avogadro's number as a conversion factor, or ratio, in dimensional analysis problems. For example, if we are dealing with element X, the mole relationship is expressed as follows:

$$1\text{ mol X} = 6.022 \times 10^{23}\text{ X atoms}$$

We can convert this relationship into two possible conversion factors shown below:

$$\frac{1\text{ mol X}}{6.022 \times 10^{23}\text{ X atoms}} \text{ or } \frac{6.022 \times 10^{23}\text{ X atoms}}{1\text{ mol X}}$$

If the number of "atoms of element X" is given, we can convert it into "moles of X" by multiplying the given value with the conversion factor at the left. However, if the number of "mol of X" is given, the appropriate conversion factor to use is the one at the right.

If we are dealing with a molecular compound (such as C_4H_{10}), the mole relationship is expressed as follows:

$$1 \text{ mol C4H10} = 6.022 \times 10^{23} \text{ C4H10 molecules}$$

If working with ionic compounds (such as NaCl), the mole relationship is expressed as follows:

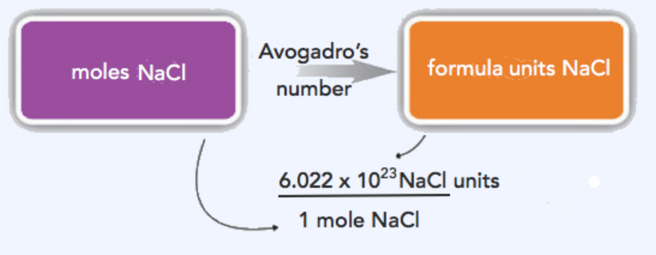
$$1 \text{ mol NaCl} = 6.022 \times 10^{23} \text{ NaCl formula units}$$

✓ Example 6.1.2

How many formula units are present in 2.34 mol of NaCl? How many ions are in 2.34 mol?

Solution

Typically in a problem like this, we start with what we are given and apply the appropriate conversion factor. Here, we are given a quantity of 2.34 mol of NaCl, to which we can apply the definition of a **mole as a conversion factor**:



$$2.34 \text{ mol NaCl} \times \frac{6.022 \times 10^{23} \text{ NaCl units}}{1 \text{ mol NaCl}} = 1.41 \times 10^{24} \text{ NaCl units}$$

Because there are two ions per formula unit, there are

$$1.41 \times 10^{24} \text{ NaCl units} \times \frac{2 \text{ ions}}{\text{NaCl units}} = 2.82 \times 10^{24} \text{ ions}$$

in the sample.

? Exercise 6.1.2

How many molecules are present in 16.02 mol of C_4H_{10}? How many atoms are in 16.02 mol?

Answer

9.647 x 10^{24}molecules, 1.351 x 10^{26} atoms.

Key Takeaway

- A mole is 6.022 × 10^{23} things.

6.2: Atomic and Molar Masses

Learning Objectives

- To learn how the masses of moles of atoms and molecules are expressed.

Now that we have introduced the mole and practiced using it as a conversion factor, we ask the obvious question: why is the mole *that particular* number of things? Why is it 6.022×10^{23} and not 1×10^{23} or even 1×10^{20} ?

The number in a mole, Avogadro's number, is related to the relative sizes of the **atomic mass unit** and **gram mass units**. Whereas one hydrogen atom has a mass of approximately 1 u, **1 mol of H atoms** has a mass of approximately **1 *gram***. And whereas one sodium atom has an approximate mass of 23 u, 1 mol of Na atoms has an approximate mass of 23 *grams*.

One mole of a substance has the same mass in grams that one atom or molecule has in atomic mass units. The numbers in the periodic table that we identified as the atomic masses of the atoms not only tell us the mass of one atom in u but also tell us the mass of 1 mol of atoms in grams.

> One mole of a substance has the same mass in grams that one atom or molecule has in atomic mass units.

✓ Example 6.2.1: Moles to Mass Conversion with Elements

What is the mass of each quantity?

a. 1 mol of Al atoms
b. 2 mol of U atoms

Solution

a. One mole of Al atoms has a mass in grams that is numerically equivalent to the atomic mass of aluminum. The periodic table shows that the atomic mass (rounded to two decimal points) of Al is 26.98, so 1 mol of Al atoms has a mass of 26.98 g.
b. According to the periodic table, 1 mol of U has a mass of 238.0 g, so the mass of 2 mol is twice that, or 476.0 g.

? Exercise 6.2.1: Moles to Mass Conversion with Elements

What is the mass of each quantity?

a. 1 mol of Au atoms
b. 5 mol of Br atoms

Answer a:

197.0 g

Answer b:

5 mol Br atoms x 79.90 g/mol = 399.5 g

The mole concept can be extended to masses of formula units and molecules as well. The mass of 1 mol of molecules (or formula units) in grams is numerically equivalent to the mass of one molecule (or formula unit) in atomic mass units. For example, a single molecule of O_2 has a mass of 32.00 u, and 1 mol of O_2 molecules has a mass of 32.00 g. As with atomic mass unit–based masses, to obtain the mass of 1 mol of a substance, we simply sum the masses of the individual atoms in the formula of that substance. The mass of 1 mol of a substance is referred to as its **molar mass**, whether the substance is an element, an ionic compound, or a covalent compound.

✓ Example 6.2.2: Moles to Mass Conversion with Compounds

What is the mass of 1 mol of each substance?

1. NaCl
2. bilirubin ($C_{33}H_{36}N_4O_6$), the principal pigment present in bile (a liver secretion)

Solution

1. Summing the molar masses of the atoms in the NaCl formula unit gives

Solutions to Example 6.2.2, Summing the molar masses of the atoms in the NaCl formula unit gives

1 Na molar mass:	22.99 g
1 Cl molar mass:	35.45 g
Total:	58.44 g

The mass of 1 mol of NaCl is 58.44 g.

2. Multiplying the molar mass of each atom by the number of atoms of that type in bilirubin’s formula and adding the results, we get

Solutions to Example 6.2.2, Multiplying the molar mass of each atom by the number of atoms of that type in bilirubin’s formula and adding the results, we get

33 C molar mass:	33 × 12.01 g	396.33 g
36 H molar mass:	36 × 1.01 =	36.36 g
4 N molar mass:	4 × 14.01 =	56.04 g
6 O molar mass:	6 × 16.00 =	96.00 g
Total:		584.73 g

The mass of 1 mol of bilirubin is 584.73 g.

? Exercise 6.2.2: Moles to Mass Conversion with Compounds

What is the mass of 1 mol of each substance?

a. barium sulfate ($BaSO_4$), used to take X rays of the gastrointestional tract
b. adenosine ($C_{10}H_{13}N_5O_4$), a component of cell nuclei crucial for cell division

Answer a:

233.36 g

Answer b:

267.28 g

Be careful when counting atoms. In formulas with polyatomic ions in parentheses, the subscript outside the parentheses is applied to every atom inside the parentheses. For example, the molar mass of $Ba(OH)_2$ requires the sum of 1 mass of Ba, 2 masses of O, and 2 masses of H:

The molar mass of Ba(OH)2 requires the sum of 1 mass of Ba, 2 masses of O, and 2 masses of H:

1 Ba molar mass:	1 × 137.3 g =	137.3 g
2 O molar mass:	2 × 16.00 g =	32.00 g
2 H molar mass:	2 × 1.01 g =	2.02 g

1 Ba molar mass:	1 × 137.3 g =	137.3 g
Total:		171.32 g

Because molar mass is defined as the mass for 1 mol of a substance, we can refer to molar mass as grams per mole (g/mol). The division sign (/) implies "per," and "1" is implied in the denominator. Thus, the molar mass of bilirubin can be expressed as 584.73 g/mol, which is read as "five hundred eighty four point seventy three grams per mole."

Key Takeaway

- The mass of moles of atoms and molecules is expressed in units of grams.

6.3: Mole-Mass Conversions

Learning Objectives

- To convert quantities between mass units and mole units.

A previous Example stated that the mass of 2 mol of U is twice the molar mass of uranium. Such a straightforward exercise does not require any formal mathematical treatment. Many questions concerning mass are not so straightforward, however, and require some mathematical manipulations.

The simplest type of manipulation using molar mass as a conversion factor is a mole-mass conversion (or its reverse, a mass-mole conversion). In such a conversion, we use the molar mass of a substance as a conversion factor to convert mole units into mass units (or, conversely, mass units into mole units).

We also established that 1 mol of Al has a mass of 26.98 g (Example $6.3.1$). Stated mathematically,

1 mol Al = 26.98 g Al

We can divide both sides of this expression by either side to get one of two possible conversion factors:

$$\frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \text{ and } \frac{26.98 \text{ g Al}}{1 \text{ mol Al}}$$

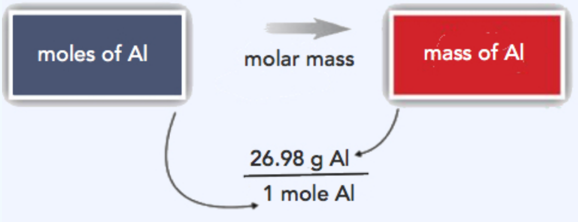
The first conversion factor can be used to convert from mass to moles, and the second converts from moles to mass. Both can be used to solve problems that would be hard to do “by eye.”

Example 6.3.1

What is the mass of 3.987 mol of Al?

Solution

The first step in a conversion problem is to decide what conversion factor to use. Because we are starting with mole units, we want a conversion factor that will cancel the mole unit and introduce the unit for mass in the numerator. Therefore, we should use the $\frac{26.98 \text{ g Al}}{1 \text{ mol Al}}$ conversion factor. We start with the given quantity and multiply by the conversion factor:



$$3.987 \text{ mol Al} \times \frac{26.98 \text{ g Al}}{1 \text{ mol Al}}$$

Note that the mol units cancel algebraically. (The quantity 3.987 mol is understood to be in the numerator of a fraction that has 1 in the unwritten denominator.) Canceling and solving gives

$$3.987 \text{ mol Al} \times \frac{26.98 \text{ g Al}}{1 \text{ mol Al}} = 107.6 \text{ g Al}$$

Our final answer is expressed to four significant figures.

Exercise 6.3.1

How many moles are present in 100.0 g of Al? (Hint: you will have to use the other conversion factor we obtained for aluminum.)

Answer

$$100.0 \text{ g Al} \times \frac{1 \text{ mol Al}}{26.98 \text{ g Al}} = 3.706 \text{ mol Al}$$

Conversions like this are possible for any substance, as long as the proper atomic mass, formula mass, or molar mass is known (or can be determined) and expressed in grams per mole. Figure $6.3.1$ is a chart for determining what conversion factor is needed, and Figure $6.3.2$ is a flow diagram for the steps needed to perform a conversion.

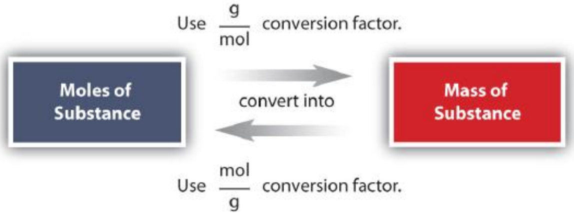


Figure 6.3.1 A Simple Flowchart for Converting between Mass and Moles of a Substance. It takes one mathematical step to convert from moles to mass or from mass to moles.

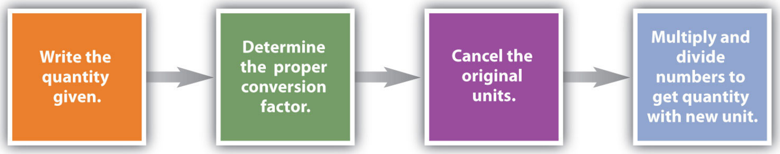


Figure 6.3.2 A Flowchart Illustrating the Steps in Performing a Unit Conversion. When performing many unit conversions, the same logical steps can be taken.

✓ Example 6.3.2

A biochemist needs 0.00655 mol of bilirubin ($C_{33}H_{36}N_4O_6$) for an experiment. How many grams of bilirubin will that be?

Solution

To convert from moles to mass, we need the molar mass of bilirubin, which we can determine from its chemical formula:

Solutions to Example 6.3.2

33 C molar mass:	33 × 12.01 g =	396.33 g
36 H molar mass:	36 × 1.01 g =	36.36 g
4 N molar mass:	4 × 14.01 g =	56.04 g
6 O molar mass:	6 × 16.00 g =	96.00 g
Total:		584.73 g

The molar mass of bilirubin is 584.73 g. Using the relationship

1 mol bilirubin = 584.73 g bilirubin

we can construct the appropriate conversion factor for determining how many grams there are in 0.00655 mol. Following the steps from Figure $6.3.2$:

$$0.00655 \text{ mol bilirubin} \times \frac{584.73 \text{ g bilirubin}}{\text{mol bilirubin}} = 3.83 \text{ g bilirubin}$$

The mol bilirubin unit cancels. The biochemist needs 3.83 g of bilirubin.

? Exercise 6.3.2

A chemist needs 457.8 g of $KMnO_4$ to make a solution. How many moles of $KMnO_4$ is that?

Answer

$$457.8 \text{ g KMnO}_4 \times \frac{1 \text{ mol KMnO}_4}{158.04 \text{ g KMnO}_4} = 2.897 \text{ mol KMnO}_4$$

To Your Health: Minerals

For our bodies to function properly, we need to ingest certain substances from our diets. Among our dietary needs are minerals, the noncarbon elements our body uses for a variety of functions, such developing bone or ensuring proper nerve transmission. The US Department of Agriculture has established some recommendations for the RDIs of various minerals. The accompanying table lists the RDIs for minerals, both in mass and moles, assuming a 2,000-calorie daily diet.

Table 6.3.1: Essential Minerals and their Composition in Humans

Mineral	Male (age 19–30 y)		Female (age 19–30 y)	
Ca	1,000 mg	0.025 mol	1,000 mg	0.025 mol
Cr	35 µg	6.7×10^{-7} mol	25 µg	4.8×10^{-7} mol
Cu	900 µg	1.4×10^{-5} mol	900 µg	1.4×10^{-5} mol
F	4 mg	2.1×10^{-4} mol	3 mg	1.5×10^{-4} mol
I	150 µg	1.2×10^{-6} mol	150 µg	1.2×10^{-6} mol
Fe	8 mg	1.4×10^{-4} mol	18 mg	3.2×10^{-4} mol
K	3,500 mg	9.0×10^{-2} mol	3,500 mg	9.0×10^{-2} mol
Mg	400 mg	1.6×10^{-2} mol	310 mg	1.3×10^{-2} mol
Mn	2.3 mg	4.2×10^{-5} mol	1.8 mg	3.3×10^{-5} mol
Mo	45 mg	4.7×10^{-7} mol	45 mg	4.7×10^{-7} mol
Na	2,400 mg	1.0×10^{-1} mol	2,400 mg	1.0×10^{-1} mol
P	700 mg	2.3×10^{-2} mol	700 mg	2.3×10^{-2} mol
Se	55 µg	7.0×10^{-7} mol	55 µg	7.0×10^{-7} mol
Zn	11 mg	1.7×10^{-4} mol	8 mg	1.2×10^{-4} mol

Table 6.3.1 illustrates several things. First, the needs of men and women for some minerals are different. The extreme case is for iron; women need over twice as much as men do. In all other cases where there is a different RDI, men need more than women.

Second, the amounts of the various minerals needed on a daily basis vary widely—both on a mass scale and a molar scale. The average person needs 0.1 mol of Na a day, which is about 2.5 g. On the other hand, a person needs only about 25–35 µg of Cr per day, which is under one millionth of a mole. As small as this amount is, a deficiency of chromium in the diet can lead to diabetes-like symptoms or neurological problems, especially in the extremities (hands and feet). For some minerals, the body does not require much to keep itself operating properly.

Although a properly balanced diet will provide all the necessary minerals, some people take dietary supplements. However, too much of a good thing, even minerals, is not good. Exposure to too much chromium, for example, causes a skin irritation, and certain forms of chromium are known to cause cancer (as presented in the movie *Erin Brockovich*).

Key Takeaway

- It is possible to convert between moles of material and mass of material.

6.4: Mole-Mole Relationships in Chemical Reactions

Learning Objectives

- To use a balanced chemical reaction to determine molar relationships between the substances.

Previously, you learned to balance chemical equations by comparing the numbers of each type of atom in the reactants and products. The coefficients in front of the chemical formulas represent the numbers of molecules or formula units (depending on the type of substance). Here, we will extend the meaning of the coefficients in a chemical equation.

Consider the simple chemical equation

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

The convention for writing balanced chemical equations is to use the lowest whole-number ratio for the coefficients. However, the equation is balanced as long as the coefficients are in a 2:1:2 ratio. For example, this equation is also balanced if we write it as

$$4\,\mathrm{H_2} + 2\,\mathrm{O_2} \rightarrow 4\,\mathrm{H_2O}$$

The ratio of the coefficients is 4:2:4, which reduces to 2:1:2. The equation is also balanced if we were to write it as

$$22\,\mathrm{H_2} + 11\,\mathrm{O_2} \rightarrow 22\,\mathrm{H_2O}$$

because 22:11:22 also reduces to 2:1:2.

Suppose we want to use larger numbers. Consider the following coefficients:

$$12.044 \times 10^{23}\ H_2 + 6.022 \times 10^{23}\ O_2 \rightarrow 12.044 \times 10^{23}\ H_2O$$

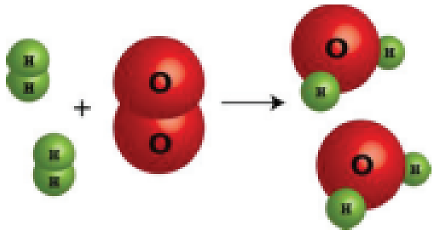
These coefficients also have the ratio 2:1:2 (check it and see), so this equation is balanced. But 6.022×10^{23} is 1 mol, while 12.044×10^{23} is 2 mol (and the number is written that way to make this more obvious), so we can simplify this version of the equation by writing it as

$$2\ \mathrm{mol\ H_2} + 1\ \mathrm{mol\ O_2} \rightarrow 2\ \mathrm{mol\ H_2O}$$

We can leave out the word *mol* and not write the 1 coefficient (as is our habit), so the final form of the equation, still balanced, is

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

Now we interpret the coefficients as referring to molar amounts, not individual molecules. The lesson? *Balanced chemical equations are balanced not only at the molecular level but also in terms of molar amounts of reactants and products.* Thus, we can read this reaction as “two moles of hydrogen react with one mole of oxygen to produce two moles of water.”



2 molecules H_2 1 molecule O_2 2 molecules H_2O

2 moles H_2 1 mole O_2 2 moles H_2O

2 x 2.02 g=4.04 g H_2 32.0 g O_2 2 x 18.02 g=36.04 g H_2O

Figure 6.4.1: This representation of the production of water from oxygen and hydrogen show several ways to interpret the quantitative information of a chemical reaction.

By the same token, the ratios we constructed to describe molecules reaction can also be constructed in terms of moles rather than molecules. For the reaction in which hydrogen and oxygen combine to make water, for example, we can construct the following ratios:

$$\frac{2 \text{ mol } H_2}{1 \text{ mol } O_2} \text{ or } \frac{1 \text{ mol } O_2}{2 \text{ mol } H_2}$$

$$\frac{2 \text{ mol } H_2O}{1 \text{ mol } O_2} \text{ or } \frac{1 \text{ mol } O_2}{2 \text{ mol } H_2O}$$

$$\frac{2 \text{ mol } H_2}{2 \text{ mol } H_2O} \text{ or } \frac{2 \text{ mol } H_2O}{2 \text{ mol } H_2}$$

We can use these ratios to determine what amount of a substance, in moles, will react with or produce a given number of moles of a different substance. The study of the numerical relationships between the reactants and the products in balanced chemical reactions is called ***stoichiometry*.** The ratio of coefficients in a balanced chemical equation, used in computations relating amounts of reactants and products is called the **stoichiometric factor.**

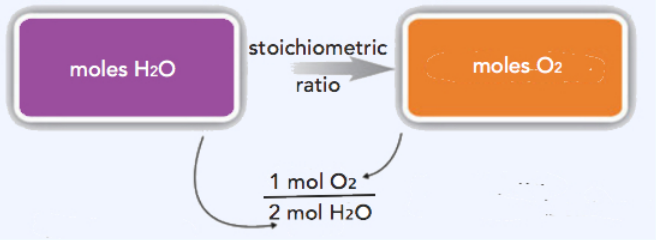
✓ Example 6.4.1

How many moles of oxygen react with hydrogen to produce 27.6 mol of H_2O? The balanced equation is as follows:

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

Solution

Because we are dealing with quantities of H_2O and O_2, we will use the **stoichiometric ratio** that relates those two substances. Because we are given an amount of H_2O and want to determine an amount of O_2, we will use the ratio that has H_2O in the denominator (so it cancels) and O_2 in the numerator (so it is introduced in the answer). Thus,



$$27.6 \text{ mol } H_2O \times \frac{1 \text{ mol } O_2}{2 \text{ mol } H_2O} = 13.8 \text{ mol } O_2$$

To produce 27.6 mol of H_2O, 13.8 mol of O_2 react.

? Exercise 6.4.1

Using $2H_2 + O_2 \rightarrow 2H_2O$, how many moles of hydrogen react with 3.07 mol of oxygen to produce H_2O?

Answer

$$3.07 \text{ mol } O_2 \times \frac{2 \text{ mol } H_2}{1 \text{ mol } O_2} = 6.14 \text{ mol } H_2$$

Key Takeaway

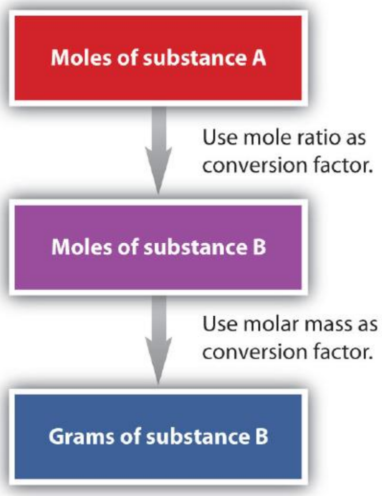
- The balanced chemical reaction can be used to determine molar relationships between substances.

6.5: Mole-Mass and Mass-Mass Problems

Learning Objectives

- To convert from mass or moles of one substance to mass or moles of another substance in a chemical reaction.

We have established that a balanced chemical equation is balanced in terms of moles as well as atoms or molecules. We have used balanced equations to set up ratios, now in terms of moles of materials, that we can use as conversion factors to answer stoichiometric questions, such as how many moles of substance A react with so many moles of reactant B. We can extend this technique even further. Recall that we can relate a molar amount to a mass amount using molar mass. We can use that ability to answer stoichiometry questions in terms of the masses of a particular substance, in addition to moles. We do this using the following sequence:



Collectively, these conversions are called mole-mass calculations.

As an example, consider the balanced chemical equation

$$\mathrm{Fe_2O_3 + 3\,SO_3 \rightarrow Fe_2(SO_4)_3}$$

If we have 3.59 mol of Fe_2O_3, how many grams of SO_3 can react with it? Using the mole-mass calculation sequence, we can determine the required mass of SO_3 in two steps. First, we construct the appropriate molar ratio, determined from the balanced chemical equation, to calculate the number of moles of SO_3 needed. Then using the molar mass of SO_3 as a conversion factor, we determine the mass that this number of moles of SO_3 has.

The first step resembles the exercises we did in Section 6.4. As usual, we start with the quantity we were given:

$$3.59\ \mathrm{mol\ Fe_2O_3} \times \frac{3\ \mathrm{mol\ SO_3}}{1\ \mathrm{mol\ Fe_2O_3}} = 10.77\ \mathrm{mol\ SO_3}$$

The mol Fe_2O_3 units cancel, leaving mol SO_3 unit. Now, we take this answer and convert it to grams of SO_3, using the molar mass of SO_3 as the conversion factor:

$$10.77\ \mathrm{mol\ SO_3} \times \frac{80.07\ \mathrm{g\ SO_3}}{1\ \mathrm{mol\ SO_3}} = 862.4\ \mathrm{g\ SO_3}$$

Our final answer is expressed to three significant figures. Thus, in a two-step process, we find that 862 g of SO_3 will react with 3.59 mol of Fe_2O_3. Many problems of this type can be answered in this manner.

The same two-step problem can also be worked out in a single line, rather than as two separate steps, as follows:

$$3.59\,\cancel{\text{mol Fe}_2\text{O}_3} \times \underbrace{\frac{3\,\cancel{\text{mol SO}_3}}{1\,\cancel{\text{mol Fe}_2\text{O}_3}}}_{\text{converts to moles of SO}_3} \times \underbrace{\frac{80.07\text{ g SO}_3}{1\,\cancel{\text{mol SO}_3}}}_{\text{converts to grams of SO}_3} = 862.4\text{ g SO}_3$$

We get exactly the same answer when combining all the math steps together as we do when we calculate one step at a time.

Example 6.5.1

How many grams of CO_2 are produced if 2.09 mol of HCl are reacted according to this balanced chemical equation?

$$\mathrm{CaCO_3 + 2\,HCl \rightarrow CaCl_2 + CO_2 + H_2O}$$

Solution

Our strategy will be to convert from moles of HCl to moles of CO_2 and then from moles of CO_2 to grams of CO_2. We will need the molar mass of CO_2, which is 44.01 g/mol. Performing these two conversions in a single-line gives 46.0 g of CO_2:

$$2.09\,\cancel{\text{mol HCl}} \times \underbrace{\frac{1\,\cancel{\text{mol CO}_2}}{2\,\cancel{\text{mol HCl}}}}_{\text{from the coefficients of the balanced equation}} \times \frac{44.01\text{ g CO}_2}{1\,\cancel{\text{mol CO}_2}} = 46.0\text{ g CO}_2$$

The molar ratio between CO_2 and HCl comes from the balanced chemical equation.

Exercise

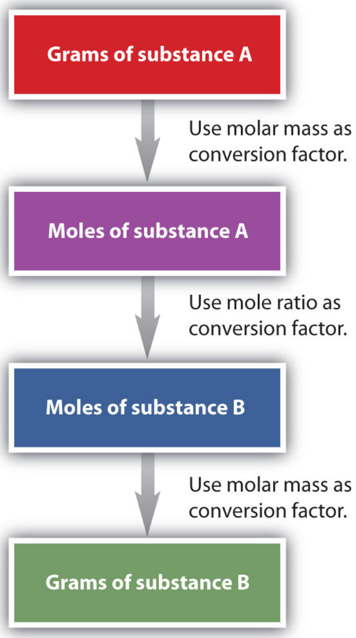
How many grams of glucose ($C_6H_{12}O_6$) are produced if 17.3 mol of H_2O are reacted according to this balanced chemical equation?

$$\mathrm{6\,CO_2 + 6\,H_2O \rightarrow C_6H_{12}O_6 + 6\,O_2}$$

Answer

$$17.3\text{ mol H}_2\text{O} \times \frac{1\text{ mol C}_6\text{H}_{12}\text{O}_6}{6\text{ mol H}_2\text{O}} \times \frac{180.18\text{ g C}_6\text{H}_{12}\text{O}_6}{1\text{ mol C}_6\text{H}_{12}\text{O}_6} = 520\text{ g C}_6\text{H}_{12}\text{O}_6$$

It is a small step from mole-mass calculations to mass-mass calculations. If we start with a known mass of one substance in a chemical reaction (instead of a known number of moles), we can calculate the corresponding masses of other substances in the reaction. The first step in this case is to convert the known mass into moles, using the substance's molar mass as the conversion factor. Then—and only then—we use the balanced chemical equation to construct a conversion factor to convert that quantity to moles of another substance, which in turn can be converted to a corresponding mass. Sequentially, the process is as follows:



This three-part process can be carried out in three discrete steps or combined into a single calculation that contains three conversion factors. The following example illustrates both techniques.

✓ Example 6.5.2: Chlorination of Carbon

Methane can react with elemental chlorine to make carbon tetrachloride (CCl_4). The balanced chemical equation is as follows:

$$CH_4 + 4\,Cl_2 \rightarrow CCl_4 + 4\,HCl$$

How many grams of HCl are produced by the reaction of 100.0 g of CH_4?

Solution

First, let us work the problem in stepwise fashion. We begin by converting the mass of CH_4 to moles of CH_4, using the molar mass of CH_4 (16.05 g/mol) as the conversion factor:

$$100.0\text{ g }CH_4 \times \frac{1\text{ mol }CH_4}{16.05\text{ g }CH_4} = 6.231\text{ mol }CH_4$$

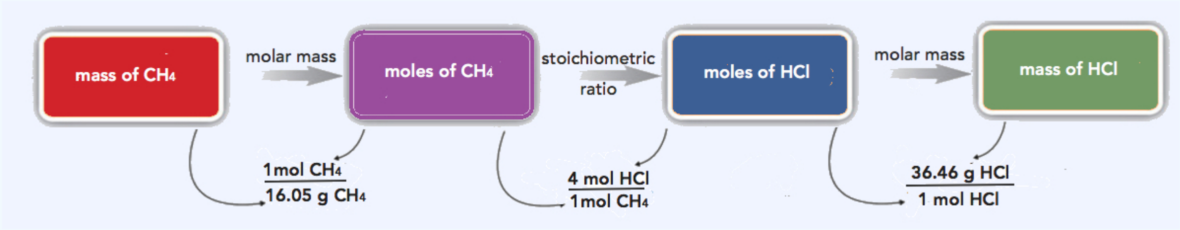
Note that we inverted the molar mass so that the gram units cancel, giving us an answer in moles. Next, we use the balanced chemical equation to determine the ratio of moles CCl_4 and moles HCl and convert our first result into moles of HCl:

$$6.231\text{ mol }CH_4 \times \frac{4\text{ mol HCl}}{1\text{ mol }CH_4} = 24.92\text{ mol HCl}$$

Finally, we use the molar mass of HCl (36.46 g/mol) as a conversion factor to calculate the mass of 24.92 mol of HCl:

$$24.92\text{ mol HCl} \times \frac{36.46\text{ g HCl}}{1\text{ mol HCl}} = 908.5\text{ g HCl}$$

In each step, we have limited the answer to the proper number of significant figures. If desired, we can do all three conversions on a single line:



$$100.0 \text{ g } CH_4 \times \frac{1 \text{ mol } CH_4}{16.05 \text{ g } CH_4} \times \frac{4 \text{ mol HCl}}{1 \text{ mol } CH_4} \times \frac{36.46 \text{ g HCl}}{1 \text{ mol HCl}} = 908.7 \text{ g HCl}$$

This final answer is slightly different from our first answer because only the final answer is restricted to the proper number of significant figures. In the first answer, we limited each intermediate quantity to the proper number of significant figures. As you can see, both answers are essentially the same.

? Exercise 6.5.2: Oxidation of Propanal

The oxidation of propanal (CH_3CH_2CHO) to propionic acid (CH_3CH_2COOH) has the following chemical equation:

$$CH_3CH_2CHO + 2K_2Cr_2O_7 \rightarrow CH_3CH_2COOH + \text{other products}$$

How many grams of propionic acid are produced by the reaction of 135.8 g of $K_2Cr_2O_7$?

Answer

$$135.8 \text{ g } K_2Cr_2O_7 \times \frac{1 \text{ mol } K_2Cr_2O_7}{294.20 \text{ g } K_2Cr_2O_7} \times \frac{1 \text{ mol } CH_3CH_2COOH}{2 \text{ mol } K_2Cr_2O_7} \times \frac{74.09 \text{ g } CH_3CH_2COOH}{1 \text{ mol } CH_3CH_2COOH} = 17.10 \text{ g } CH_3CH_2COOH$$

To Your Health: The Synthesis of Taxol

Taxol is a powerful anticancer drug that was originally extracted from the Pacific yew tree (*Taxus brevifolia*). As you can see from the accompanying figure, taxol is a very complicated molecule, with a molecular formula of $C_{47}H_{51}NO_{14}$. Isolating taxol from its natural source presents certain challenges, mainly that the Pacific yew is a slow-growing tree, and the equivalent of six trees must be harvested to provide enough taxol to treat a single patient. Although related species of yew trees also produce taxol in small amounts, there is significant interest in synthesizing this complex molecule in the laboratory.

After a 20-year effort, two research groups announced the complete laboratory synthesis of taxol in 1994. However, each synthesis required over 30 separate chemical reactions, with an overall efficiency of less than 0.05%. To put this in perspective, to obtain a single 300 mg dose of taxol, you would have to begin with 600 g of starting material. To treat the 26,000 women who are diagnosed with ovarian cancer each year with one dose, almost 16,000 kg (over 17 tons) of starting material must be converted to taxol. Taxol is also used to treat breast cancer, with which 200,000 women in the United States are diagnosed every year. This only increases the amount of starting material needed.

Clearly, there is intense interest in increasing the overall efficiency of the taxol synthesis. An improved synthesis not only will be easier but also will produce less waste materials, which will allow more people to take advantage of this potentially life-saving drug.

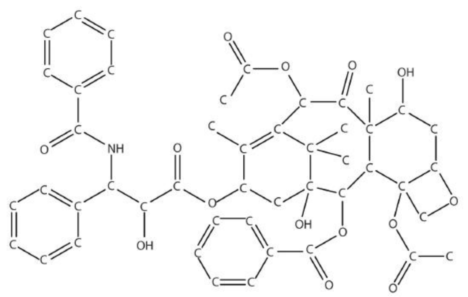


Figure 6.5.1 The Structure of the Cancer Drug Taxol. Because of the complexity of the molecule, hydrogen atoms are not shown, but they are present on every atom to give the atom the correct number of covalent bonds (four bonds for each carbon atom).

Key Takeaway

- A balanced chemical equation can be used to relate masses or moles of different substances in a reaction.

6.E: Quantities in Chemical Reactions (Exercise)

6.1: The Mole

Concept Review Exercise

1. What is a mole?

Answer

1. A mole is 6.022×10^{23} things.

Exercises

1. How many dozens are in 1 mol? Express your answer in proper scientific notation.
2. A gross is a dozen dozen, or 144 things. How many gross are in 1 mol? Express your answer in proper scientific notation.
3. How many moles of each type of atom are in 1.0 mol of $C_6H_{12}O_6$?
4. How many moles of each type of atom are in 1.0 mol of $K_2Cr_2O_7$?
5. How many moles of each type of atom are in 2.58 mol of Na_2SO_4?
6. How many moles of each type of atom are in 0.683 mol of $C_{34}H_{32}FeN_4O_4$? (This is the formula of heme, a component of hemoglobin.)
7. How many molecules are in 16.8 mol of H_2O?
8. How many formula units are in 0.778 mol of iron(III) nitrate?
9. A sample of gold contains 7.02×10^{24} atoms. How many moles of gold is this?
10. A flask of mercury contains 3.77×10^{22} atoms. How many moles of mercury are in the flask?
11. An intravenous solution of normal saline may contain 1.72 mol of sodium chloride (NaCl). How many sodium and chlorine atoms are present in the solution?
12. A lethal dose of arsenic is 1.00×10^{21} atoms. How many moles of arsenic is this?

Answers

1. 5.018×10^{22} dozens

2. $4.18 \text{ x } 10^{21}$ grosses

3. 6.0 mol of C atoms, 12.0 mol of H atoms, and 6.0 mol of O atoms

4. 2.0 mol of K atoms, 2.0 mol of Cr atoms, and 7.0 mol of O atoms

5. 5.16 mol of Na atoms, 2.58 mol of S atoms, and 10.32 mol of O atoms

6. 23.2 mol of C atoms, 21.9 mol of H atoms, 0.683 mol of Fe, 2.73 mol of N and 2.73 mol of O atoms

7. 1.012×10^{25} molecules

8. $4.69 \text{ x } 10^{23}$ formula units

9. 11.7 mol

10. 0.0626 mol

11. 1.04×10^{24} Na atoms and 1.04×10^{24} Cl atoms

12. 0.00166 mol

6.2: Atomic and Molar Masses

Concept Review Exercises

1. How are molar masses of the elements determined?
2. How are molar masses of compounds determined?

Answers

1. Molar masses of the elements are the same numeric value as the masses of a single atom in atomic mass units but in units of grams instead.
2. Molar masses of compounds are calculated by adding the molar masses of their atoms.

Exercises

1. What is the molar mass of Si? What is the molar mass of U?
2. What is the molar mass of Mn? What is the molar mass of Mg?
3. What is the molar mass of $FeCl_2$? What is the molar mass of $FeCl_3$?
4. What is the molar mass of C_6H_6? What is the molar mass of $C_6H_5CH_3$?
5. What is the molar mass of $(NH_4)_2S$? What is the molar mass of $Ca(OH)_2$?
6. What is the molar mass of $(NH_4)_3PO_4$? What is the molar mass of $Sr(HCO_3)_2$?
7. Aspirin ($C_9H_8O_4$) is an analgesic (painkiller) and antipyretic (fever reducer). What is the molar mass of aspirin?
8. Ibuprofen ($C_{13}H_{18}O_2$) is an analgesic (painkiller). What is the molar mass of ibuprofen?
9. Morphine ($C_{17}H_{19}NO_3$) is a narcotic painkiller. What is the mass of 1 mol of morphine?
10. Heroin ($C_{21}H_{23}NO_5$) is a narcotic drug that is a derivative of morphine. What is the mass of 1 mol of heroin?

Answers

1. 28.09 g/mol; 238.0 g/mol

2. 54.94 g/mol; 24.31 g/mol

3. 126.75 g/mol; 162.20 g/mol

4. 78.12 g/mol; 92.15 g/mol

5. 68.16 g/mol; 74.10 g/mol

6. 149.12 g/mol; 209.64 g/mol

7. 180.17 g/mol

8. 206.31 g/mol

9. 285.37 g

10. 369.45 g

6.3: Mole-Mass Conversions

Concept Review Exercises

1. What relationship is needed to perform mole-mass conversions?
2. What information determines which conversion factor is used in a mole-mass conversion?

Answers

1. The atomic or molar mass is needed for a mole-mass conversion.
2. The unit of the initial quantity determines which conversion factor is used.

Exercises

1. What is the mass of 8.603 mol of Fe metal?
2. What is the mass of 0.552 mol of Ag metal?
3. What is the mass of 6.24×10^4 mol of Cl_2 gas?
4. What is the mass of 0.661 mol of O_2 gas?
5. What is the mass of 20.77 mol of $CaCO_3$?
6. What is the mass of 9.02×10^{-3} mol of the hormone epinephrine ($C_9H_{13}NO_3$)?
7. How many moles are present in 977.4 g of $NaHCO_3$?
8. How many moles of erythromycin ($C_{37}H_{67}NO_{13}$), a widely used antibiotic, are in 1.00×10^3 g of the substance?

9. Cortisone ($C_{21}H_{28}O_5$) is a synthetic steroid that is used as an anti-inflammatory drug. How many moles of cortisone are present in one 10.0 mg tablet?
10. Recent research suggests that the daily ingestion of 85 mg of aspirin (also known as acetylsalicylic acid, $C_9H_8O_4$) will reduce a person's risk of heart disease. How many moles of aspirin is that?

Answers

1. 480.5 g

2. 59.6 g

3. 4.42×10^6 g

4. 21.2 g

5. 2,079 g

6. 1.65 g

7. 11.63 mol

8. 1.36 mol

9. 2.77×10^{-5} mol

10. $4.7 \text{ x } 10^{-4}$ mol

6.4: Mole-Mole Relationships in Chemical Reactions

Concept Review Exercise

1. How do we relate molar amounts of substances in chemical reactions?

Answer

1. Amounts of substances in chemical reactions are related by their coefficients in the balanced chemical equation.

Exercises

1. List the molar ratios you can derive from this balanced chemical equation:

$$NH_3 + 2O_2 \rightarrow HNO_3 + H_2O$$

2. List the molar ratios you can derive from this balanced chemical equation

$$2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O$$

3. Given the following balanced chemical equation,

$$6NaOH + 3Cl_2 \rightarrow NaClO_3 + 5NaCl + 3H_2O$$

how many moles of NaCl can be formed if 3.77 mol of NaOH were to react?

4. Given the following balanced chemical equation,

$$C_5H_{12} + 8O_2 \rightarrow 5CO_2 + 6H_2O$$

how many moles of H_2O can be formed if 0.0652 mol of C_5H_{12} were to react?

5. Balance the following unbalanced equation and determine how many moles of H_2O are produced when 1.65 mol of NH_3 react.

$$NH_3 + O_2 \rightarrow N_2 + H_2O$$

6. Trinitrotoluene [$C_6H_2(NO_2)_3CH_3$], also known as TNT, is formed by reacting nitric acid (HNO_3) with toluene ($C_6H_5CH_3$):

$$HNO_3 + C_6H_5CH_3 \rightarrow C_6H_2(NO_2)_3CH_3 + H_2O$$

Balance the equation and determine how many moles of TNT are produced when 4.903 mol of HNO_3 react.

7. Chemical reactions are balanced in terms of molecules and in terms of moles. Are they balanced in terms of dozens? Defend your answer.
8. Explain how a chemical reaction balanced in terms of moles satisfies the law of conservation of matter.

Answers

1. 1 mol NH_3:2 mol O_2:1 mol HNO_3:1 mol H_2O
2. 2 mol C_2H_2:5 mol O_2:4 mol CO_2:2 mol H_2O
3. 3.14 mol
4. 0.3912 mol
5. $4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$; 2.48 mol
6. $3HNO_3 + C_6H_5CH_3 \rightarrow C_6H_2(NO_2)_3CH_3 + 3H_2O$; 1.634 mol
7. Yes, they are still balanced.
8. A chemical reaction, balanced in terms of moles, contains the same number of atoms of each element, before and after the reaction. This means that all the atoms and its masses are conserved.

6.5: Mole-Mass and Mass-Mass Problems

Concept Review Exercises

1. What is the general sequence of conversions for a mole-mass calculation?
2. What is the general sequence of conversions for a mass-mass calculation?

Answers

1. mol first substance → mol second substance → mass second substance
2. mass first substance → mol first substance → mol second substance → mass second substance

Exercises

1. Given the following unbalanced chemical equation,

$$H_3PO_4 + NaOH \rightarrow H_2O + Na_3PO_4$$

what mass of H_2O is produced by the reaction of 2.35 mol of H_3PO_4?

2. Given the following unbalanced chemical equation,

$$C_2H_6 + Br_2 \rightarrow C_2H_4Br_2 + HBr$$

what mass of HBr is produced if 0.884 mol of C_2H_6 is reacted?

3. Certain fats are used to make soap, the first step being to react the fat with water to make glycerol (also known as glycerin) and compounds called fatty acids. One example is as follows:

$$\underset{\text{a fat}}{\mathrm{C_3H_5(OOC(CH_2)_{14}CH_3)_3}} + \mathrm{3H_2O} \rightarrow \underset{\text{glycerol}}{\mathrm{C_3H_5(OH)_3}} + \underset{\text{fatty acid}}{\mathrm{3CH_3(CH_2)_{14}COOH}}$$

How many moles of glycerol can be made from the reaction of 1,000.0 g of $C_3H_5(OOC(CH_2)_{14}CH_3)_3$?

4. Photosynthesis in plants leads to the general overall reaction for producing glucose ($C_6H_{12}O_6$):

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$$

How many moles of glucose can be made from the reaction of 544 g of CO_2?

5. Precipitation reactions, in which a solid (called a precipitate) is a product, are commonly used to remove certain ions from solution. One such reaction is as follows:

$$Ba(NO_3)_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaNO_3(aq)$$

How many grams of Na_2SO_4 are needed to precipitate all the barium ions produced by 43.9 g of $Ba(NO_3)_2$?

6. Nitroglycerin [$C_3H_5(ONO_2)_3$] is made by reacting nitric acid (HNO_3) with glycerol [$C_3H_5(OH)_3$] according to this reaction:

$$C_3H_5(OH)_3 + 3HNO_3 \rightarrow C_3H_5(ONO_2)_3 + 3H_2O$$

If 87.4 g of HNO_3 are reacted with excess glycerol, what mass of nitroglycerin can be made?

7. Antacids are bases that neutralize acids in the digestive tract. Magnesium hydroxide [$Mg(OH)_2$] is one such antacid. It reacts with hydrochloric acid in the stomach according to the following reaction:

   $$Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O$$

   How many grams of HCl can a 200 mg dose of $Mg(OH)_2$ neutralize?
8. Acid rain is caused by the reaction of nonmetal oxides with water in the atmosphere. One such reaction involves nitrogen dioxide (NO_2) and produces nitric acid (HNO_3):

   $$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

   If 1.82×10^{13} g of NO_2 enter the atmosphere every year due to human activities, potentially how many grams of HNO_3 can be produced annually?
9. A simplified version of the processing of iron ore into iron metal is as follows:

   $$2Fe_2O_3 + 3C \rightarrow 4Fe + 3CO_2$$

   How many grams of C are needed to produce 1.00×10^9 g of Fe?
10. The *SS Hindenburg* contained about 5.33×10^5 g of H_2 gas when it burned at Lakehurst, New Jersey, in 1937. The chemical reaction is as follows:

    $$2H_2 + O_2 \rightarrow 2H_2O$$

    How many grams of H_2O were produced?

Answers

1. 127 g

2. 143 g

3. 1.238 mol

4. 2.06 mol

5. 23.9 g

6. 105 g

7. 0.250 g

8. 1.66×10^{13} g

9. 1.61×10^8 g

10. 4.75×10^6 g

Additional Exercises

1. If the average male has a body mass of 70 kg, of which 60% is water, how many moles of water are in an average male?
2. If the average female is 60.0 kg and contains 0.00174% iron, how many moles of iron are in an average female?
3. How many moles of each element are present in 2.67 mol of each compound?
   a. HCl
   b. H_2SO_4
   c. $Al(NO_3)_3$
   d. $Ga_2(SO_4)_3$
4. How many moles of each element are present in 0.00445 mol of each compound?
   a. HCl
   b. H_2SO_4
   c. $Al_2(CO_3)_3$
   d. $Ga_2(SO_4)_3$
5. What is the mass of one hydrogen atom in grams? What is the mass of one oxygen atom in grams? Do these masses have a 1:16 ratio, as expected?

6. What is the mass of one sodium atom in grams?
7. If 6.63 × 10^{-6} mol of a compound has a mass of 2.151 mg, what is the molar mass of the compound?
8. Hemoglobin (molar mass is approximately 64,000 g/mol) is the major component of red blood cells that transports oxygen and carbon dioxide in the body. How many moles are in 0.034 g of hemoglobin?

Answers

1. 2,330 mol

2. 0.0187 mol

3. a. 2.67 mol of H and 2.67 mol of Cl
   b. 5.34 mol of H, 2.67 mol of S, and 10.68 mol of O
   c. 2.67 mol of Al, 8.01 mol of N, and 24.03 mol of O
   d. 5.34 mol of Ga, 8.01 mol of S, and 32.04 mol of O

4.
   a. 0.00445 mol of H and 0.00445 mol of Cl
   b. 0.00890 mol of H, 0.00445 mol of S, and 0.0178 mol of O
   c. 0.00890 mol of Al, 0.0134 mol of C, and 0.0401 mol of O
   d. 0.00890 mol of Ga, 0.0134 mol of S, and 0.0534 mol of O

5. H = 1.68 × 10^{-24} g and O = 2.66 × 10^{-23} g; yes, they are in a 1:16 ratio.

6. 3.819 x 10^{-23} g

7. 324 g/mol

8. 5.3 x 10^{-7} mol

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6.S: Quantities in Chemical Reactions (Summary)

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

Chemical reactions relate quantities of reactants and products. Chemists use the **mole** unit to represent 6.022×10^{23} things, whether the things are atoms of elements or molecules of compounds. This number, called **Avogadro's number**, is important because this number of atoms or molecules has the same mass in grams as one atom or molecule has in atomic mass units. **Molar masses** of substances can be determined by summing the appropriate masses from the periodic table; the final molar mass will have units of grams.

Because one mole of a substance will have a certain mass, we can use that relationship to construct conversion factors that will convert a mole amount into a mass amount, or vice versa. Such **mole-mass conversions** typically take one algebraic step.

Chemical reactions list reactants and products in molar amounts, not just molecular amounts. We can use the coefficients of a balanced chemical equation to relate moles of one substance in the reaction to moles of other substances (stoichiometry). Chemical reactions obey the Law of Conservation of Mass. To balance a chemical reaction, the coefficients in front of each compound can be adjusted until the total number of atoms of each elements is equal on both sides of the reaction arrow.

Collision Theory can be used to described the energetic aspects of chemical reactions. The reactants and products of a chemical reaction store potential energy in the form of chemical bonds and intermolecular forces. The energy difference in the bond energies of the reactants and products is called "Enthalpy". When the products are lower in potential energy than the reactants, then this excess energy is released as heat and the reaction is described as exothermic. When the products are higher in potential energy than the reactants, then energy must be added to the reaction as heat for it to occur and the reaction is described as endothermic.

The rate of a chemical reaction is influenced by its activation energy. The larger the activation energy, the slower the reaction rate. Catalysts can be added to reactions to lower the activation energy and increase the reaction rate.

Not all reactions go to completion. For some reactions, both the forward and reverse reaction can occur simultaneously. When the forward and reverse reaction rates are equal, the reaction is described as being "at equilibrium". Another way to recognize when a system is at equilibrium is when the concentration of reactants and products remain constant. Le Chatlier's principle states that the direction of an equilibrium reaction will shift to reduce the stress.

CHAPTER OVERVIEW

7: Energy and Chemical Processes

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

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7.0: Prelude to Energy and Chemical Processes

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

Table 7.0.1: Average Body Temperatures of Selected Endotherms

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

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

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

7.1: Energy and Its Units

Learning Objectives

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

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

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

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

$$1\ cal = 4.184\ J$$

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

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

✓ Example 7.1.1

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

Solution

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

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

Then we convert calories into joules

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

and then kilojoules

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

The energy content of bread comes mostly from carbohydrates.

rcise

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

Answer

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

The calorie is used in nutrition to express the energy content of foods. However, because a calorie is a rather small quantity, nutritional energies are usually expressed in **kilocalories (kcal)**, also called **Calories (capitalized; Cal)**. For example, a candy bar may provide 120 Cal (nutritional calories) of energy, which is equal to 120,000 cal. Figure 7.1.1 shows an example.

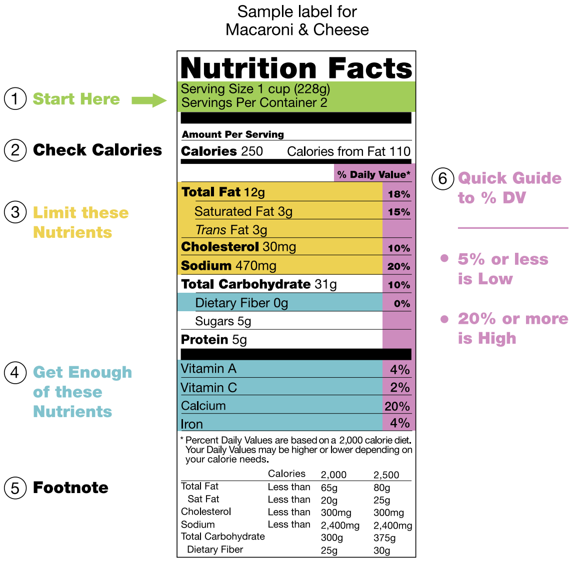


Figure 7.1.1: Figure 7.1.1: Nutritional Energy. A sample nutrition facts label, with instructions from the U.S. Food and Drug Administration. from Wikipedia.

The caloric content of foods is determined by analyzing the food for protein, carbohydrate, fat, water, and "minerals" and then calculating the caloric content using the average values for each component that produces energy (**9 Cal/g for fats, 4 Cal/g for carbohydrates and proteins, and 0 Cal/g for water and minerals**). An example of this approach is shown in Table 7.1.1 for a slice of roast beef.

Table 7.1.1: Approximate Composition and Fuel Value of an 8 oz Slice of Roast Beef

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

The compositions and caloric contents of some common foods are given in 7.1.2.

Table 7.1.2: Approximate Compositions and Fuel Values of Some Common Foods

Food (quantity)	Approximate Composition (%)				Food Value (Cal/g)	Calories
	Water	Carbohydrate	Protein	Fat		
beer (12 oz)	92	3.6	0.3	0	0.4	150
coffee (6 oz)	100	~0	~0	~0	~0	~0
milk (1 cup)	88	4.5	3.3	3.3	0.6	150

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

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

To Your Health: Energy Expenditures

Most health professionals agree that exercise is a valuable component of a healthy lifestyle. Exercise not only strengthens the body and develops muscle tone but also expends energy. After obtaining energy from the foods we eat, we need to expend that energy somehow, or our bodies will store it in unhealthy ways (e.g., fat). Like the energy content in food, the energy expenditures of exercise are also reported in kilocalories, usually kilocalories per hour of exercise. These expenditures vary widely, from about 440 kcal/h for walking at a speed of 4 mph to 1,870 kcal/h for mountain biking at 20 mph. Table $7.1.3$ lists the energy expenditure for a variety of exercises.

Table $7.1.3$: Energy Expenditure of a 180-Pound Person during Selected Exercises

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

Exercise	Energy Expended (kcal/h)
yoga	280

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

Summary

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

7.2: Heat and Temperature

Learning Objectives

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

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

Temperature Scales

Temperature is a measure of the average amount of energy of motion, or *kinetic energy*, a system contains. Temperatures are expressed using scales that use units called degrees. There are three scales used for reporting temperatures. Figure 7.2.1 compares the three temperature scales: Fahrenheit (expressed as °F), Celsius (°C), and Kelvin (K). Thermometers measure temperature by using materials that expand or contract when heated or cooled. Mercury or alcohol thermometers, for example, have a reservoir of liquid that expands when heated and contracts when cooled, so the liquid column lengthens or shortens as the temperature of the liquid changes.

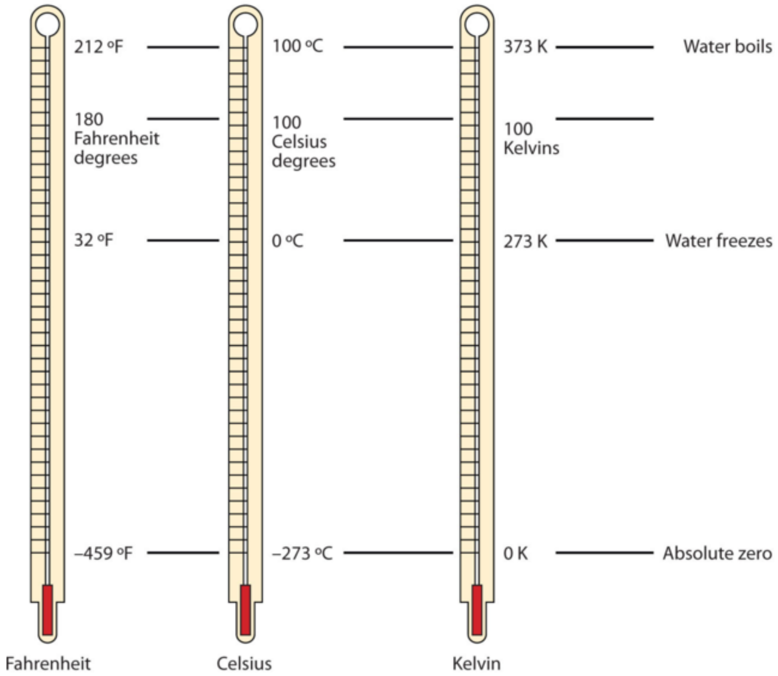


Figure 7.2.1: Fahrenheit, Celsius, and Kelvin Temperatures. A comparison of the three temperature scales. These thermometers have a red-colored liquid which contains alcohol and food coloring. Silver looking thermometers contain mercury, which is a neurotoxin.

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

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

$$^{\circ}C = (^{\circ}F - 32) \times \frac{5}{9} \tag{7.2.1}$$

$$^{\circ}F = \left(^{\circ}C \times \frac{9}{5}\right) + 32 \tag{7.2.2}$$

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

✓ Example 7.2.1: Conversions

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

Solution

a. Using Equation 7.2.1, we have

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

b. Using Equation 7.2.2, we have

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

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

? Exercise 7.2.1

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

Answer a

−17.8°C

Answer b

414°F

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

$$K = ^{\circ}C + 273.15 \tag{7.2.3}$$

For most purposes, it is acceptable to use 273 instead of 273.15 in Equation 7.2.3.

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

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

✓ Example 7.2.2: Room Temperature

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

Solution

First, we use Equation 7.2.1 to determine the temperature in degrees Celsius:

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

Then we use Equation 7.2.3 to determine the temperature in the Kelvin scale:

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

So, room temperature is about 295 K.

Health Application: Body temperature

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

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

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

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

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

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

Heat transfer

Heat is a familiar manifestation of energy. When we touch a hot object, energy flows from the hot object into our fingers, and we perceive that incoming energy as the object being “hot.” Conversely, when we hold an ice cube in our palms, energy flows from our hand into the ice cube, and we perceive that loss of energy as “cold.” In both cases, the temperature of the object is different from the temperature of our hand, so we can conclude that differences in temperatures are the ultimate cause of heat transfer.

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

$$\text{heat} \propto \Delta T \tag{7.2.4}$$

where ∝ means "is proportional to" and **ΔT is the change in temperature of the system**. Any change in a variable is always defined as "the final value minus the initial value" of the variable, so ΔT is $T_{\text{final}} - T_{\text{initial}}$. In addition, the greater the mass of an object, the more heat is needed to change its temperature. We can include a variable representing mass (m) to the proportionality as follows:

$$\text{heat} \propto m\Delta T \tag{7.2.5}$$

To change this proportionality into an equality, we include a proportionality constant. The proportionality constant is called the specific heat and is commonly symbolized by c:

$$\text{heat} = mc\Delta T \tag{7.2.6}$$

Every substance has a characteristic **specific heat**, which is reported in units of cal/g•°C or cal/g•K, depending on the units used to express ΔT. The specific heat of a substance is the amount of energy that must be transferred to or from 1 g of that substance to change its temperature by 1°C. Table 7.2.1 lists the specific heats for various materials.

Table 7.2.1: Specific Heats of Selected Substances

Substance	**c (cal/g•°C)**
aluminum (Al)	0.215
aluminum oxide (Al_2O_3)	0.305
benzene (C_6H_6)	0.251
copper (Cu)	0.092
ethanol (C_2H_6O)	0.578
hexane (C_6H_{14})	0.394
hydrogen (H_2)	3.419
ice [$H_2O(s)$]	0.492
iron (Fe)	0.108
iron(III) oxide (Fe_2O_3)	0.156
mercury (Hg)	0.033
oxygen (O_2)	0.219
sodium chloride (NaCl)	0.207
steam [$H_2O(g)$]	0.488
water [$H_2O(\ell)$]	1.00

> *The proportionality constant c is sometimes referred to as the specific heat capacity or (incorrectly) the heat capacity.*

The *direction* of heat flow is not shown in heat = $mc\Delta T$. If energy goes into an object, the total energy of the object increases, and the values of heat ΔT are positive. If energy is coming out of an object, the total energy of the object decreases, and the values of heat and ΔT are negative.

Example 7.2.3

What quantity of heat is transferred when a 150.0 g block of iron metal is heated from 25.0°C to 73.3°C? What is the direction of heat flow?

Solution

We can use Equation 7.2.6 to determine the amount of heat, but first we need to determine ΔT. Because the final temperature of the iron is 73.3°C and the initial temperature is 25.0°C, ΔT is as follows:

$$\begin{aligned} \Delta T &= T_{final} - T_{initial} \\ &= 73.3^{o}C - 25.0^{o}C \\ &= 48.3^{o}C \end{aligned}$$

The mass is given as 150.0 g, and Table 7.2.1 gives the specific heat of iron as 0.108 cal/g•°C. Substitute the known values into Equation 7.2.6 and solve for amount of heat:

$$\text{heat} = (150.0\ \text{g}) \left(0.108\ \frac{\text{cal}}{\text{g} \cdot {}^{\circ}\text{C}}\right) (48.3^{\circ}\text{C}) = 782\ \text{cal}$$

Note how the gram and °C units cancel algebraically, leaving only the calorie unit, which is a unit of heat. Because the temperature of the iron increases, energy (as heat) must be flowing *into* the metal.

rcise

What quantity of heat is transferred when a 295.5 g block of aluminum metal is cooled from 128.0°C to 22.5°C? What is the direction of heat flow?

Answer

6,700 cal

Example 7.2.4

A 10.3 g sample of a reddish-brown metal gave off 71.7 cal of heat as its temperature decreased from 97.5°C to 22.0°C. What is the specific heat of the metal? Can you identify the metal from the data in Table 7.2.1?

Solution

The question gives us the heat, the final and initial temperatures, and the mass of the sample. The value of ΔT is as follows:

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 22.0°\text{C} - 97.5°\text{C} = -75.5°\text{C}$$

If the sample gives off 71.7 cal, it loses energy (as heat), so the value of heat is written as a negative number, −71.7 cal. Substitute the known values into heat = $mc\Delta T$ and solve for c:

$$-71.7\ \text{cal} = (10.3\ \text{g})(c)(-75.5°\text{C})$$

$$c = \frac{-71.7\ \text{cal}}{(10.3\ \text{g})(-75.5^{\circ}\text{C})}$$

$$c = 0.0923\ \text{cal/g•°C}$$

This value for specific heat is very close to that given for copper in Table 7.2.1.

rcise

A 10.7 g crystal of sodium chloride (NaCl) had an initial temperature of 37.0°C. What is the final temperature of the crystal if 147 cal of heat were supplied to it?

Answer

103.4°C

Notice that water has a very high specific heat compared to most other substances. Water is commonly used as a coolant for machinery because it is able to absorb large quantities of heat (see table above). Coastal climates are much more moderate than inland climates because of the presence of the ocean. Water in lakes or oceans absorbs heat from the air on hot days and releases it back into the air on cool days.

Figure $7.2.2$: This power plant in West Virginia, like many others, is located next to a large lake so that the water from the lake can be used as a coolant. Cool water from the lake is pumped into the plant, while warmer water is pumped out of the plant and back into the lake.

Summary

- Heat transfer is related to temperature change.
- The specific heat of a substance is the amount of energy required to raise the temperature of 1 gram of the substance by $1^{\circ}\mathrm{C}$.

7.3: Phase Changes

Learning Objectives

- Determine the heat associated with a phase change.

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

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

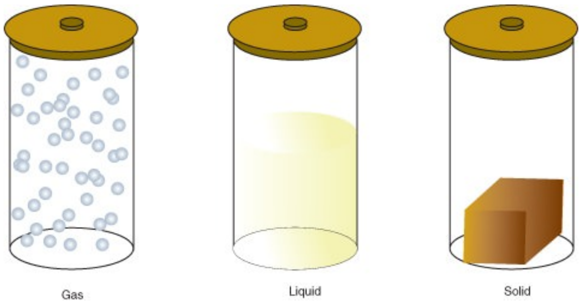


Figure 7.3.1: States of Matter. All three containers contain a substance with the same mass, but the substances are in different states. In the left-hand container, the substance is a gas, which has spread to fill its container. It takes both the shape and volume of the container. In the middle container, the substance is a liquid, which has spread to take the shape of its container but not the volume. In the right-hand container, the substance is a solid, which takes neither the shape nor the volume of its container.

The following are the changes of state:

Changes of State

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

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

Example 7.3.1

Label each of the following processes as endothermic or exothermic.

a. water boiling
b. ice forming on a pond

Solution

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

rcise

Label each of the following processes as endothermic or exothermic.

a. water vapor condensing
b. gold melting

Answer

a. exothermic

b. endothermic

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

Two key points are worth emphasizing. First, at a substance's melting point or boiling point, two phases can exist simultaneously. Take water (H_2O) as an example. On the Celsius scale, H_2O has a melting point of 0°C and a boiling point of 100°C. At 0°C, both the solid and liquid phases of H_2O can coexist. However, if heat is added, some of the solid H_2O will melt and turn into liquid H_2O. If heat is removed, the opposite happens: some of the liquid H_2O turns into solid H_2O. A similar process can occur at 100°C: adding heat increases the amount of gaseous H_2O, while removing heat increases the amount of liquid H_2O (Figure $7.3.1$).

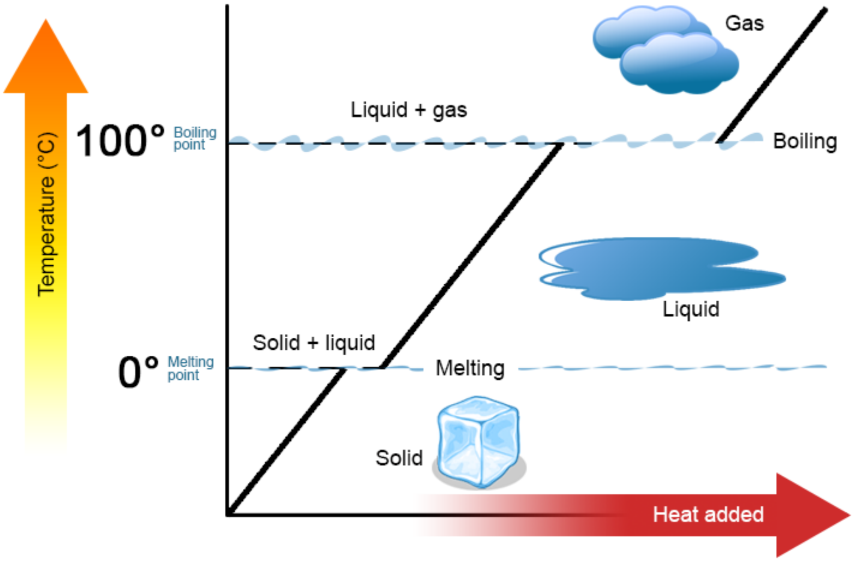


Figure $7.3.2$: Heating curve for water. As heat is added to solid water, the temperature increases until it reaches 0 °C, the melting point. At this point, the phase change, added heat goes into changing the state from a solid to liquid. Only when this phase change is complete, the temperature can increase. (CC BY 3.0 Unported; Community College Consortium for Bioscience Credentials).

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

Second, as shown in Figure 7.3.1, **the temperature of a substance does not change** as the substance goes **from one phase to another**. In other words, phase changes are isothermal (isothermal means "constant temperature"). Again, consider H_2O as an example. Solid water (ice) can exist at 0°C. If heat is added to ice at 0°C, some of the solid changes phase to make liquid, which is also at 0°C. Remember, the solid and liquid phases of H_2O can coexist at 0°C. Only after all of the solid has melted into liquid does the addition of heat change the temperature of the substance.

For each phase change of a substance, there is a characteristic quantity of heat needed to perform the phase change per gram (or per mole) of material. The heat of fusion (ΔH_{fus}) is the amount of heat per gram (or per mole) required for a phase change that occurs at the melting point. The heat of vaporization (ΔH_{vap}) is the amount of heat per gram (or per mole) required for a phase change that occurs at the boiling point. If you know the total number of grams or moles of material, you can use the ΔH_{fus} or the ΔH_{vap} to determine the total heat being transferred for melting or solidification using these expressions:

$$\text{heat} = n \times \Delta H_{fus} \tag{7.3.1}$$

where n is the number of moles and ΔH_{fus} is expressed in energy/mole or

$$\text{heat} = m \times \Delta H_{fus} \tag{7.3.2}$$

where m is the mass in grams and ΔH_{fus} is expressed in energy/gram.

For the boiling or condensation, use these expressions:

$$\text{heat} = n \times \Delta H_{vap} \tag{7.3.3}$$

where n is the number of moles) and ΔH_{vap} is expressed in energy/mole or

$$\text{heat} = m \times \Delta H_{vap} \tag{7.3.4}$$

where m is the mass in grams and ΔH_{vap} is expressed in energy/gram.

Remember that a phase change depends on the direction of the heat transfer. If heat transfers in, solids become liquids, and liquids become solids at the melting and boiling points, respectively. If heat transfers out, liquids solidify, and gases condense into liquids. At these points, there are no changes in temperature as reflected in the above equations.

✓ **Example 7.3.2**

How much heat is necessary to melt 55.8 g of ice (solid H_2O) at 0°C? The heat of fusion of H_2O is 79.9 cal/g.

Solution

We can use the relationship between heat and the heat of fusion (Equation 7.3.1) to determine how many cal of heat are needed to melt this ice:

$$\text{heat} = \mathrm{m} \times \Delta \mathrm{H}_{\mathrm{fus}}$$

$$\text{heat} = (55.8\ \cancel{\mathrm{g}})\left(\frac{79.9\ \mathrm{cal}}{\cancel{\mathrm{g}}}\right) = 4,460\ \mathrm{cal}$$

? **Exercise 7.3.2**

How much heat is necessary to vaporize 685 g of H_2O at 100°C? The heat of vaporization of H_2O is 540 cal/g.

Answer

$$\text{heat} = \mathrm{m} \times \Delta \mathrm{H}_{\mathrm{vap}}$$

$$\text{heat} = (685\ \cancel{\mathrm{g}})\left(\frac{540\ \mathrm{cal}}{\cancel{\mathrm{g}}}\right) = 370,000\ \mathrm{cal}$$

Table 7.3.1 lists the heats of fusion and vaporization for some common substances. Note the units on these quantities; when you use these values in problem solving, make sure that the other variables in your calculation are expressed in units consistent with the units in the specific heats or the heats of fusion and vaporization.

Table 7.3.1: Heats of Fusion and Vaporization for Selected Substances

Substance	ΔH_{fus} (cal/g)	ΔH_{vap} (cal/g)
aluminum (Al)	94.0	2,602
gold (Au)	15.3	409
iron (Fe)	63.2	1,504
water (H_2O)	79.9	540
sodium chloride (NaCl)	123.5	691
ethanol (C_2H_5OH)	45.2	200.3
benzene (C_6H_6)	30.4	94.1

Sublimation

There is also a phase change where a solid goes directly to a gas:

$$\text{solid} \rightarrow \text{gas} \tag{7.3.5}$$

This phase change is called *sublimation*. Each substance has a characteristic heat of sublimation associated with this process. For example, the heat of sublimation (ΔH_{sub}) of H_2O is 620 cal/g.

We encounter sublimation in several ways. You may already be familiar with dry ice, which is simply solid carbon dioxide (CO_2). At −78.5°C (−109°F), solid carbon dioxide sublimes, changing directly from the solid phase to the gas phase:

$$CO_2(s) \xrightarrow{-78.5^\circ C} CO_2(g) \tag{7.3.6}$$

Solid carbon dioxide is called dry ice because it does not pass through the liquid phase. Instead, it does directly to the gas phase. (Carbon dioxide *can* exist as liquid but only under high pressure.) Dry ice has many practical uses, including the long-term preservation of medical samples.

Even at temperatures below 0°C, solid H_2O will slowly sublime. For example, a thin layer of snow or frost on the ground may slowly disappear as the solid H_2O sublimes, even though the outside temperature may be below the freezing point of water. Similarly, ice cubes in a freezer may get smaller over time. Although frozen, the solid water slowly sublimes, redepositing on the colder cooling elements of the freezer, which necessitates periodic defrosting (frost-free freezers minimize this redeposition). Lowering the temperature in a freezer will reduce the need to defrost as often.

Under similar circumstances, water will also sublime from frozen foods (e.g., meats or vegetables), giving them an unattractive, mottled appearance called freezer burn. It is not really a “burn,” and the food has not necessarily gone bad, although it looks unappetizing. Freezer burn can be minimized by lowering a freezer’s temperature and by wrapping foods tightly so water does not have any space to sublime into.

Key Takeaway

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

7.4: Bond Energies and Chemical Reactions

Learning Objectives

The Learning Objectives of this Module are to:

- Define *bond energy*.
- Calculate enthalpy change or heat of reaction.
- Determine if a chemical process is exothermic or endothermic.

What happens when you take a basketball, place it halfway up a playground slide, and then let it go? The basketball rolls down the slide. What happens if you do it again? Does the basketball roll down the slide? It should.

If you were to perform this experiment over and over again, do you think the basketball would ever roll *up* the slide? Probably not. Why not? Well, for starters, in all of our experience, the basketball has always moved to a lower position when given the opportunity. The gravitational attraction of Earth exerts a force on the basketball, and given the chance, the basketball will move down. We say that the basketball is going to a lower *gravitational potential energy*. The basketball can move up the slide, but only if someone exerts some effort (that is, work) on the basketball. A general statement, based on countless observations over centuries of study, is that all objects tend to move spontaneously to a position of minimum energy unless acted on by some other force or object.

Bond Energy

A similar statement can be made about atoms in compounds. Atoms bond together to form compounds because in doing so they attain lower energies than they possess as individual atoms. A quantity of energy, equal to the difference between the energies of the bonded atoms and the energies of the separated atoms, is released, usually as heat. That is, the bonded atoms have a lower energy than the individual atoms do. *When atoms combine to make a compound, energy is always given off, and the compound has a lower overall energy.* In making compounds, atoms act like a basketball on a playground slide; they move in the direction of decreasing energy.

We can reverse the process, just as with the basketball. If we put energy into a molecule, we can cause its bonds to break, separating a molecule into individual atoms. Bonds between certain specific elements usually have a characteristic energy, called the bond energy, that is needed to break the bond. The same amount of energy was liberated when the atoms made the chemical bond in the first place. The term *bond energy* is usually used to describe the strength of interactions between atoms that make covalent bonds. A C–C bond has an approximate bond energy of 80 kcal/mol, while a C=C has a bond energy of about 145 kcal/mol. The C=C bond is stronger than C-C (as discussed in relation to bond length in Section 4.4). For atoms in ionic compounds attracted by opposite charges, the term lattice energy is used. For now, we will deal with covalent bonds in molecules.

Although each molecule has its own characteristic bond energy, some generalizations are possible. For example, although the exact value of a C–H bond energy depends on the particular molecule, all C–H bonds have a bond energy of roughly the same value because they are all C–H bonds. It takes roughly 100 kcal of energy to break 1 mol of C–H bonds, so we speak of the bond energy of a C–H bond as being about 100 kcal/mol. Table 7.4.1 lists the approximate bond energies of various covalent bonds.

Table 7.4.1: Approximate Bond Energies

Bond	Bond Energy (kcal/mol)
C–H	100
C–O	86
C=O	190
C–N	70
C–C	85
C=C	145
C≡C	200

Bond	Bond Energy (kcal/mol)
N–H	93
H–H	105
Br-Br	46
Cl–Cl	58
O–H	110
O=O	119
H–Br	87
H–Cl	103

When a chemical reaction occurs, the atoms in the reactants rearrange their chemical bonds to make products. The new arrangement of bonds does not have the same total energy as the bonds in the reactants. Therefore, when chemical reactions occur, *there will always be an accompanying energy change*. The enthalpy change, for a given reaction can be calculated using the bond energy values from Table 7.4.1.

Enthalpy Change or Heat of Reaction, Δ*H*

Energy changes in chemical reactions are usually measured as changes in enthalpy. In this process, one adds energy to the reaction to break bonds, and extracts energy for the bonds that are formed.

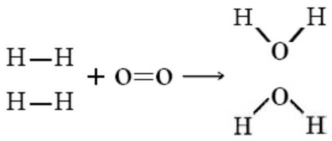
$$\text{enthalpy change} \approx \sum(\text{bonds broken}) - \sum(\text{bonds formed})$$

The ≈ sign is used because we are adding together *average* bond energies (i.e., over many different molecules). Hence, this approach does not give exact values for the enthalpy change, Δ*H*.

Let's consider the reaction of 2 mols of hydrogen gas (H_2) with 1 mol of oxygen gas (O_2) to give 2 mol water:

$$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(g)$$

or shown graphically:



with these average bond energies involved:

- $H-H$ = 105 kcal/mol
- $O=O$ = 119 kcal/mol
- $O-H$ = 110 kcal/mol

In this reaction, 2 H–H bonds and 1 O=O bonds are broken, while 4 O–H bonds (two for each H_2O) are formed. The energy changes can be tabulated and calculated as follows:

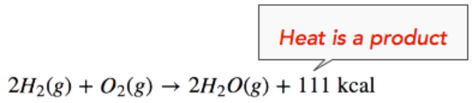
2 H–H bonds and 1 O=O bonds are broken, while 4 O–H bonds (two for each H2O) are formed. The energy changes can be tabulated and calculated as follows:

Bonds Broken (kcal/mol)		Bonds Formed (kcal/mol)	
2 H–H	2 mol x 105 kcal/mol = 210 kcal	4 O–H	4 mols x 110 kcal/mol = 440 kcal
1 O=O	1 mol x 119 kcal/mol = 119 kcal		

Bonds Broken (kcal/mol)		Bonds Formed (kcal/mol)	
	Total = 329 kcal		**Total** = 440 kcal

$$\begin{aligned}\Delta H &\approx \sum(\text{bonds broken}) - \sum(\text{bonds formed}) \\ &\approx 329\text{ kcal} - 440\text{ kcal} \\ &\approx -111\text{ kcal}\end{aligned}$$

The enthalpy change (ΔH) of the reaction is approximately −111 kcal/mol. This means that bonds in the products (440 kcal) are stronger than the bonds in the reactants (329 kcal) by about 111 kcal/mol. Because the bonds in the products are stronger than those in the reactants, the reaction releases more energy than it consumes. This excess energy is **released** as heat, so the reaction is **exothermic**. Hence, we can re-write the reaction with the heat released (111 kcal) on the **product side** of the equation, as follows:



$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) + 111\text{ kcal}$$

We can also re-write the reaction equation with the ΔH information (see below). Note that an **exothermic** reaction has a **negative ΔH** value.

$$2\,\mathrm{H_2(g)}^+\mathrm{O_2(g)} \rightarrow 2\,\mathrm{H_2O(g)} \qquad \Delta H = -111\text{ kcal}$$

✓ Example 7.4.1

What is the enthalpy change for this reaction? Is the reaction exothermic or endothermic?

$$\mathrm{H_2(g) + Br_2(g) \rightarrow 2\,HBr(g)}$$

Solution

Step 1- First look at the equation and identify which bonds exist on in the reactants (bonds broken).

- one H-H bond and
- one Br-Br bond

Step 2- Do the same for the products (bonds formed)

- two H-Br bonds

Step 3- Identify the bond energies of these bonds from Table 7.4.1:

- H-H bonds: 105 kcal/mol
- Br-Br bonds: 46 kcal/mol

Step 4- Set up the table (see below) and apply the formula for enthalpy change.

Solutions to Example 7.4.1

Bonds Broken (kcal/mol)		Bonds Formed (kcal/mol)	
1 H–H	1 mol x 105 kcal/mol = 105 kcal	2 H–*Br*	2 mols x 87 kcal/mol = 174 kcal
1 Br–Br	1 mol x 46 kcal/mol = 46 kcal		
	Total = 151 kcal		**Total** = 174 kcal

$$\begin{aligned}\Delta H &\approx 151\text{ kcal} - 174\text{ kcal} \\ &\approx -23\text{ kcal}\end{aligned}$$

Step 5- Since ΔH is negative (−23 kcal), the reaction is *exothermic*.

rcise

Using the bond energies given in the chart above, find the enthalpy change for the thermal decomposition of water:

$$\mathrm{H_2(g) + Cl_2(g) \rightarrow 2\,HCl(g)}$$

Is the reaction written above exothermic or endothermic? Explain.

Answer

ΔH = −43 kcal

Since ΔH is negative (−43 kcal), the reaction is *exothermic*.

Endothermic and Exothermic Reactions

Endothermic and exothermic reactions can be thought of as having energy as either a reactant of the reaction or a product. **Endothermic** reactions require energy, so energy is a reactant. Heat flows from the surroundings to the system (reaction mixture) and the enthalpy of the system increases (Δ*H* is positive). As discussed in the previous section, in an **exothermic** reaction, heat is released (considered a product) and the enthalpy of the system decreases (Δ*H* is negative).

In the course of an **endothermic** process, the system gains heat from the surroundings and so the **temperature of the surroundings decreases (gets cold).** A chemical reaction is **exothermic** if heat is released by the system into the surroundings. Because the surroundings is gaining heat from the system, **the temperature of the surroundings increases.** See Figure $7.4.1$.

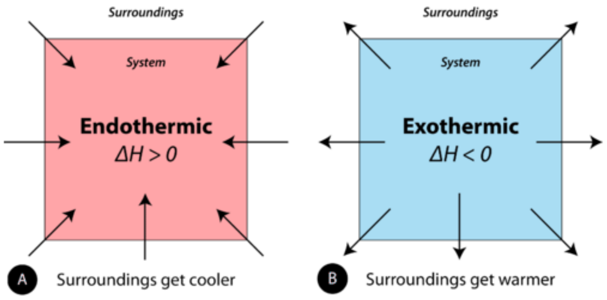
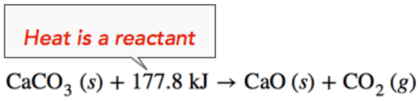


Figure $7.4.1$: (A) Endothermic reaction. (B) Exothermic reaction.

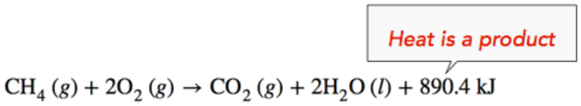
Endothermic reaction: surroundings get cooler and delta H is greater than 0, Exothermic reaction: surroundings get warmer and delta H is less than 0

Endothermic Reaction: When 1 mol of calcium carbonate decomposes into 1 mol of calcium oxide and 1 mol of carbon dioxide, 177.8 kJ of heat is absorbed. Because the heat is absorbed by the system, the 177.8 kJ is written as a **reactant**. The **Δ*H* is positive** for an endothermic reaction.



$$\mathrm{CaCO_3}\,(s) \rightarrow \mathrm{CaO}\,(s) + \mathrm{CO_2}\,(g) \qquad \Delta H = +177.8\text{ kJ}$$

Exothermic Reaction: When methane gas is combusted, heat is released, making the reaction exothermic. Specifically, the combustion of 1 mol of methane releases 890.4 kilojoules of heat energy. This information can be shown as part of the balanced equation in two ways. First, the amount of heat released can be written in the **product** side of the reaction. Another way is to write the **heat of reaction** (Δ*H)* information with a **negative** sign, -890.4 kJ.



$$\mathrm{CH_4}\,(g) + 2\mathrm{O_2}\,(g) \rightarrow \mathrm{CO_2}\,(g) + 2\mathrm{H_2O}\,(l) \qquad \Delta H = -890.4\text{ kJ}$$

Example 7.4.2

Is each chemical reaction exothermic or endothermic?

a. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell) + 213\ kcal$
b. $N_2(g) + O_2(g) + 45\ kcal \rightarrow 2NO(g)$

Solution

a. Because energy (213 kcal) is a product, energy is given off by the reaction. Therefore, this reaction is exothermic.
b. Because energy (45 kcal) is a reactant, energy is absorbed by the reaction. Therefore, this reaction is endothermic.

Exercise 7.4.2

Is each chemical reaction exothermic or endothermic?

a. $H_2(g) + F_2(g) \rightarrow 2HF\ (g) + 130\ kcal$
b. $2C(s) + H_2(g) + 5.3\ kcal \rightarrow C_2H_2(g)$

Answer

a. The energy (130 kcal) is produced, hence the reaction is exothermic

b. The energy (5.3 kcal) is supplied or absorbed to react, hence, the reaction is endothermic

Energy Diagrams

Endothermic and exothermic reactions can be visually represented by *energy-level diagrams* like the ones in **Figure $7.4.2$**. In endothermic reactions, the reactants have higher bond energy (stronger bonds) than the products. **Strong bonds have lower potential energy than weak bonds**. Hence, the **energy of the reactants is lower than that of the products**. This type of reaction is represented by an "uphill" energy-level diagram shown in Figure $7.4.2A$. For an endothermic chemical reaction to proceed, the reactants must absorb energy from their environment to be converted to products.

In an exothermic reaction, the bonds in the product have higher bond energy (stronger bonds) than the reactants. In other words, the **energy of the products is lower than the energy of the reactants,** hence is energetically downhill, shown in Figure $7.4.2B$. Energy is given off as reactants are converted to products. The energy given off is usually in the form of heat (although a few reactions give off energy as light). In the course of an exothermic reaction, heat flows from the system to its surroundings, and thus, gets warm.

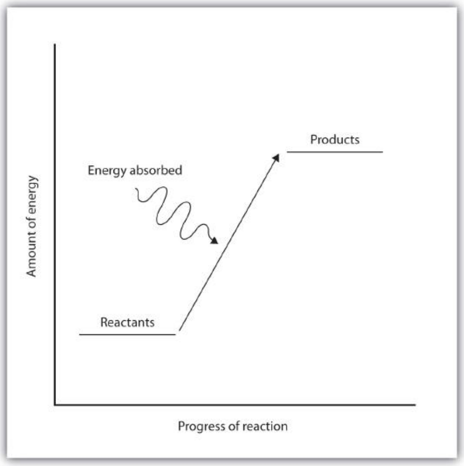


Figure $7.4.2A$: Endothermic Reactions

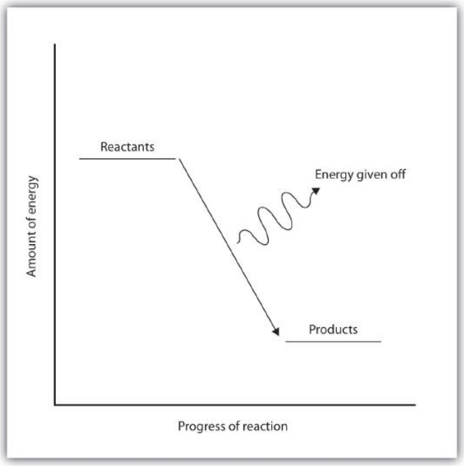


Figure $7.4.2B$: Exothermic Reactions

Table 7.4.2: Endothermic and Exothermic Reactions

Endothermic Reactions	Exothermic Reactions
Heat is absorbed by reactants to form products.	Heat is released.
Heat is absorbed from the surroundings; as a result, the surroundings get cold.	Heat is released by the reaction to surroundings; surroundings feel hot.
ΔH_{rxn} is positive	ΔH_{rxn} is negative
The bonds broken in the reactants are stronger than the bonds formed in the products	The bonds formed in the products are stronger than the bonds broken in the reactants
The reactants are lower in energy than the products	The products are lower in energy than the reactants
Represented by an "uphill" energy diagram	Represented by an "downhill" energy diagram

Key Takeaways

- Atoms are held together by a certain amount of energy called bond energy.
- Energy is required to break bonds. Energy is released when chemical bonds are formed because atoms become more stable.
- Chemical processes are labeled as exothermic or endothermic based on whether they give off or absorb energy, respectively.

7.5: The Energy of Biochemical Reactions

Learning Objectives

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

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

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

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

$$C_6H_{12}O_6(s) + 6\,O_2(g) \rightarrow 6\,CO_2(g) + 6\,H_2O(\ell) + 670\text{ kcal} \tag{7.5.1}$$

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

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

Another important reaction is the conversion of adenosine triphosphate (ATP) to adenosine diphosphate (ADP), which is shown in Figure $7.5.1$. Under physiological conditions, the breaking of an O–P bond and the formation of an O–P and two O–H bonds gives off about 7.5 kcal/mol of ATP. This may not seem like much energy, especially compared to the amount of energy given off when glucose reacts. It is enough energy, however, to fuel other biochemically important chemical reactions in our cells.

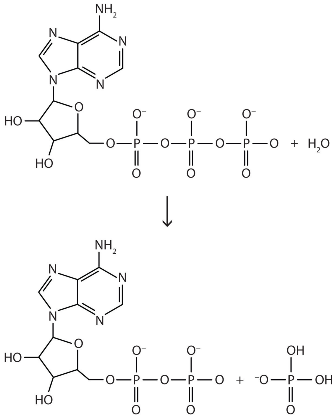


Figure $7.5.1$: ATP to ADP. The conversion of ATP (top) to ADP (bottom) provides energy for the cells of the body.

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

Career Focus: Dietitian

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

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

Key Takeaway

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

7.E: Energy and Chemical Processes (Exercises)

7.1: Energy and Its Units

Concept Review Exercises

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

Answers

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

Exercises

1. Define *energy*.
2. What is heat?
3. What is the relationship between a calorie and a joule? Which unit is larger?
4. What is the relationship between a calorie and a kilocalorie? Which unit is larger?
5. Express 1,265 cal in kilocalories and in joules.
6. Express 9,043.3 J in calories and in kilocalories.
7. One kilocalorie equals how many kilojoules?
8. One kilojoule equals how many kilocalories?
9. Many nutrition experts say that an average person needs 2,000 Cal per day from his or her diet. How many joules is this?
10. Baby formula typically has 20.0 Cal per ounce. How many ounces of formula should a baby drink per day if the RDI is 850 Cal?

Answers

1. Energy is the ability to do work.

2. Heat is a form of enery (thermal) that can be transferred from one object to another.

3. 1 cal = 4.184 J; the calorie is larger.

4. 1 kilocalorie(1 Cal) = 1000 cal; the kcal is larger.

5. 1.265 kcal; 5,293 J

6. 2161.4 cal; 2.1614 kcal

7. 1 kcal = 4.184 kJ

8. 1 kJ = 0.239 kcal

9. 8.4×10^6 J

10. 42.5 oz

7.2: Heat and Temperature

Concept Review Exercise

1. Describe the relationship between heat transfer and the temperature change of an object.

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

Answer

1. Heat is equal to the product of the mass, the change in temperature, and a proportionality constant called the specific heat.

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

Exercises

1. The melting point of mercury is −38.84^{o}C. Convert this value to degrees Fahrenheit and Kelvin.

2. A pot of water is set on a hot burner of a stove. What is the direction of heat flow?

3. Some uncooked macaroni is added to a pot of boiling water. What is the direction of heat flow?

4. How much energy in calories is required to heat 150 g of H_2O from 0°C to 100°C?

5. How much energy in calories is required to heat 125 g of Fe from 25°C to 150°C?

6. If 250 cal of heat were added to 43.8 g of Al at 22.5°C, what is the final temperature of the aluminum?

7. If 195 cal of heat were added to 33.2 g of Hg at 56.2°C, what is the final temperature of the mercury?

8. A sample of copper absorbs 145 cal of energy, and its temperature rises from 37.8°C to 41.7°C. What is the mass of the copper?

9. A large, single crystal of sodium chloride absorbs 98.0 cal of heat. If its temperature rises from 22.0°C to 29.7°C, what is the mass of the NaCl crystal?

10. If 1.00 g of each substance in Table 7.2.1 were to absorb 100 cal of heat, which substance would experience the largest temperature change?

11. If 1.00 g of each substance in Table 7.2.1 were to absorb 100 cal of heat, which substance would experience the smallest temperature change?

12. Determine the heat capacity of a substance if 23.6 g of the substance gives off 199 cal of heat when its temperature changes from 37.9°C to 20.9°C.

13. What is the heat capacity of gold if a 250 g sample needs 133 cal of energy to increase its temperature from 23.0°C to 40.1°C?

Answers

1. -37.91^{0}F and 234.31 K

2. Heat flows into the pot of water.

3. Heat flows to the macaroni.

4. 15,000 cal

5. 1,690 cal

6. 49.0°C

7. 234°C

8. 404 g

9. 61 g

10. Mercury would experience the largest temperature change.

11. hydrogen (H_2)

12. 0.496 cal/g•°C

13. 0.031 cal/g•°C

7.3: Phase Changes

Concept Review Exercises

1. Explain what happens when heat flows into or out of a substance at its melting point or boiling point.
2. How does the amount of heat required for a phase change relate to the mass of the substance?
3. What is the direction of heat transfer in boiling water?
4. What is the direction of heat transfer in freezing water?
5. What is the direction of heat transfer in sweating?

Answers

1. The energy goes into changing the phase, not the temperature.

2. The amount of heat is a constant per gram of substance.

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

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

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

Exercises

1. How much energy is needed to melt 43.8 g of Au at its melting point of 1,064°C?
2. How much energy is given off when 563.8 g of NaCl solidifies at its freezing point of 801°C?
3. What mass of ice can be melted by 558 cal of energy?
4. How much ethanol (C_2H_5OH) in grams can freeze at its freezing point if 1,225 cal of heat are removed?
5. What is the heat of vaporization of a substance if 10,776 cal are required to vaporize 5.05 g? Express your final answer in joules per gram.
6. If 1,650 cal of heat are required to vaporize a sample that has a heat of vaporization of 137 cal/g, what is the mass of the sample?
7. What is the heat of fusion of water in calories per mole?
8. What is the heat of vaporization of benzene (C_6H_6) in calories per mole?
9. What is the heat of vaporization of gold in calories per mole?
10. What is the heat of fusion of iron in calories per mole?

Answers

1. 670 cal

2. 69,630 cal

3. 6.98 g

4. 27.10 g

5. 8,930 J/g

6. 12.0 g

7. 1,440 cal/mol

8. 7,350 cal/mol

9. 80,600 cal/mol

10. 3,530 cal/mol

7.4: Bond Energies and Chemical Reactions

Concept Review Exercises

1. What is the connection between energy and chemical bonds?
2. Why does energy change during the course of a chemical reaction?
3. Two different reactions are performed in two identical test tubes. In reaction A, the test tube becomes very warm as the reaction occurs. In reaction B, the test tube becomes cold. Which reaction is endothermic and which is exothermic? Explain.
4. Classify "burning paper" as endothermic or exothermic processes.

Answers

1. Chemical bonds have a certain energy that is dependent on the elements in the bond and the number of bonds between the atoms.
2. Energy changes because bonds rearrange to make new bonds with different energies.
3. Reaction A is exothermic because heat is leaving the system making the test tube feel hot. Reaction B is endothermic because heat is being absorbed by the system making the test tube feel cold.
4. "Burning paper" is exothermic because burning (also known as combustion) releases heat

Exercises

1. Using the data in Table 7.4.1, calculate the energy of one C–H bond (as opposed to 1 mol of C–H bonds). Recall that 1 mol = 6.022 x 10^{23} C–H bonds

2. Using the data in Table 7.4.1, calculate the energy of one C=C bond (as opposed to 1 mol of C=C bonds). Recall that 1 mol = 6.022 x 10^{23} C=C bonds

3. Is a bond-breaking process exothermic or endothermic?

4. Is a bond-making process exothermic or endothermic?

5. Is each chemical reaction exothermic or endothermic?
   a. $2SnCl_2(s) + 33\text{ kcal} \rightarrow Sn(s) + SnCl_4(s)$
   b. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell) + 213\text{ kcal}$

6. Is each chemical reaction exothermic or endothermic?
   a. $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g) + 137\text{ kJ}$
   b. C(s, graphite) + 1.9 kJ → C(s, diamond)

Answers

1. 1.661×10^{-19} cal

2. 2.408 x 10^{-19} cal

3. endothermic

4. exothermic

5.

   a. endothermic

   b. exothermic

6.

   a. exothermic

   b. endothermic

7.5: The Energy of Biochemical Reactions

Concept Review Exercise

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

Answer

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

Exercises

1. An 8 oz serving of whole milk has 8.0 g of fat, 8.0 g of protein, and 13 g of carbohydrates. Approximately how many kilocalories does it contain?
2. A serving of potato chips has 160 kcal. If the chips have 15 g of carbohydrates and 2.0 g of protein, about how many grams of fat are in a serving of potato chips?
3. The average body temperature of a person is 37°C, while the average surrounding temperature is 22°C. Is overall human metabolism exothermic or endothermic?
4. Cold-blooded animals absorb heat from the environment for part of the energy they need to survive. Is this an exothermic or an endothermic process?
5. If the reaction ATP → ADP gives off 7.5 kcal/mol, then the reverse process, ADP → ATP requires 7.5 kcal/mol to proceed. How many moles of ADP can be converted to ATP using the energy from 1 serving of potato chips (see Exercise 2)?
6. If the oxidation of glucose yields 670 kcal of energy per mole of glucose oxidized, how many servings of potato chips (see Exercise 2) are needed to provide the same amount of energy?

Answers

1. 156 kcal

2. 10.2 g
3. exothermic
4. endothermic

5. 21.3 mol

6. 4.2 servings

Additional Exercises

1. Sulfur dioxide (SO_2) is a pollutant gas that is one cause of acid rain. It is oxidized in the atmosphere to sulfur trioxide (SO_3), which then combines with water to make sulfuric acid (H_2SO_4).
    a. Write the balanced reaction for the oxidation of SO_2 to make SO_3. (The other reactant is diatomic oxygen.)
    b. When 1 mol of SO_2 reacts to make SO_3, 23.6 kcal of energy are given off. If 100 lb (1 lb = 454 g) of SO_2 were converted to SO_3, what would be the total energy change?
2. Ammonia (NH_3) is made by the direct combination of H_2 and N_2 gases according to this reaction:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) + 22.0\ \text{kcal}$$

    a. Is this reaction endothermic or exothermic?
    b. What is the overall energy change if 1,500 g of N_2 are reacted to make ammonia?
3. A 5.69 g sample of iron metal was heated in boiling water to 99.8°C. Then it was dropped into a beaker containing 100.0 g of H_2O at 22.6°C. Assuming that the water gained all the heat lost by the iron, what is the final temperature of the H_2O and Fe?
4. A 5.69 g sample of copper metal was heated in boiling water to 99.8°C. Then it was dropped into a beaker containing 100.0 g of H_2O at 22.6°C. Assuming that the water gained all the heat lost by the copper, what is the final temperature of the H_2O and Cu?
5. When 1 g of steam condenses, 540 cal of energy is released. How many grams of ice can be melted with 540 cal?

6. When 1 g of water freezes, 79.9 cal of energy is released. How many grams of water can be boiled with 79.9 cal?
7. The change in energy is +65.3 kJ for each mole of calcium hydroxide [$Ca(OH)_2$] according to the following reaction:

$$Ca(OH)_2(s) \rightarrow CaO(s) + H_2O(g)$$

   How many grams of $Ca(OH)_2$ could be reacted if 575 kJ of energy were available?
8. The thermite reaction gives off so much energy that the elemental iron formed as a product is typically produced in the liquid state:

$$2Al(s) + Fe_2O_3(s) \rightarrow Al_2O_3(s) + 2Fe(\ell) + 204\text{ kcal}$$

   How much heat will be given off if 250 g of Fe are to be produced?
9. A normal adult male requires 2,500 kcal per day to maintain his metabolism.
    a. Nutritionists recommend that no more than 30% of the calories in a person’s diet come from fat. At 9 kcal/g, what is the maximum mass of fat an adult male should consume daily?
    b. At 4 kcal/g each, how many grams of protein and carbohydrates should an adult male consume daily?
10. A normal adult male requires 2,500 kcal per day to maintain his metabolism.
    a. At 9 kcal/g, what mass of fat would provide that many kilocalories if the diet was composed of nothing but fats?
    b. At 4 kcal/g each, what mass of protein and/or carbohydrates is needed to provide that many kilocalories?
11. The volume of the world’s oceans is approximately 1.34×10^{24} cm^3.
    a. How much energy would be needed to increase the temperature of the world’s oceans by 1°C? Assume that the heat capacity of the oceans is the same as pure water.
    b. If Earth receives 6.0×10^{22} J of energy per day from the sun, how many days would it take to warm the oceans by 1°C, assuming all the energy went into warming the water?
12. Does a substance that has a small specific heat require a small or large amount of energy to change temperature? Explain.
13. Some biology textbooks represent the conversion of adenosine triphosphate (ATP) to adenosine diphosphate (ADP) and phosphate ions as follows:

$$\text{ATP} \rightarrow \text{ADP} + \text{phosphate} + \text{energy}$$

   What is wrong with this reaction?
14. Assuming that energy changes are additive, how much energy is required to change 15.0 g of ice at −15°C to 15.0 g of steam at 115°C? (Hint: you will have five processes to consider.)

Answers

1.
    a. $2SO_2 + O_2 \rightarrow 2SO_3$
    b. 16,700 kcal
2.
    a. exothermic
    b. 1177 kcal
3. about 23.1°C
4. about 23.0°C
5. 6.76 g
6. 0.148 g

7. 652 g

8. 457 kcal

9.
   a. 83.3 g
   b. 438 g

10.
   a. 278 g
   b. 625 g

11.
   a. 1.34 × 10^{24} cal
   b. 93 days

12. A substance with **smaller specific heat** requires **less energy** per unit of mass to raise its temperature,

13. A reactant is missing: H_2O is missing.

14. Total energy = 11,019 cal

7.S: Energy and Chemical Processes (Summary)

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

Energy is the ability to do work. The transfer of energy from one place to another is **heat**. Heat and energy are measured in units of **joules**, **calories**, or kilocalories (equal to 1,000 calories). The amount of heat gained or lost when the temperature of an object changes can be related to its mass and a constant called the **specific heat** of the substance.

The transfer of energy can also cause a substance to change from one phase to another. During the transition, called a **phase change**, heat is either added or lost. Despite the fact that heat is going into or coming out of a substance during a phase change, the temperature of the substance does not change until the phase change is complete; that is, phase changes are **isothermal**. Analogous to specific heat, a constant called the **heat of fusion** of a substance describes how much heat must be transferred for a substance to melt or solidify (that is, to change between solid and liquid phases), while the **heat of vaporization** describes the amount of heat transferred in a boiling or condensation process (that is, to change between liquid and gas phases).

Every chemical change is accompanied by an energy change. This is because the interaction between atoms bonding to each other has a certain **bond energy**, the energy required to break the bond (called **lattice energy** for ionic compounds), and the bond energies of the reactants will not be the same as the bond energies of the products. Reactions that give off energy are called **exothermic**, while reactions that absorb energy are called **endothermic**. Energy-level diagrams can be used to illustrate the energy changes that accompany chemical reactions.

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

CHAPTER OVERVIEW

8: Solids, Liquids, and Gases

Most of us are familiar with the three phases of matter: solid, liquid, and gas. Indeed, we addressed the energy changes involved in phase changes. The substance we are probably most familiar with has those three phases: water. In everyday life, we commonly come in contact with water as a solid (ice), as a liquid, and as a gas (steam). All we have to do is change the conditions of the substance—typically temperature—and we can change the phase from solid to liquid to gas and back again. Under the proper conditions of temperature and pressure, many substances—not only water—can experience the three different phases. An understanding of the phases of matter is important for our understanding of all matter. In this chapter, we will explore the three phases of matter.

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8.0: Prelude to Solids, Liquids, and Gases

We normally experience carbon dioxide (CO_2) as a gas, but if it were cooled down to about −78°C, it would become a solid. The everyday term for solid carbon dioxide is dry ice.

Why “dry” ice? Solid carbon dioxide is called dry ice because it converts from a solid to a gas directly, without going through the liquid phase, in a process called sublimation. Thus, there is no messy liquid phase to worry about. Although it is a novelty, dry ice has some potential dangers. Because it is so cold, it can freeze living tissues very quickly, so people handling dry ice should wear special protective gloves. The cold carbon dioxide gas is also heavier than air (because it is cold and more dense), so people in the presence of dry ice should be in a well-ventilated area.

Figure 8.0.1: Dry ice. (CC BY SA 3.0 unported; ProjectManhattan).

Dry ice has several common uses. Because it is so cold, it is used as a refrigerant to keep other things cold or frozen (e.g., meats or ice cream). In the medical field, dry ice is used to preserve medical specimens, blood products, and drugs. It also has dermatological applications (e.g., freezing off warts). Organs for transplant are kept cool with dry ice until the recipient of the new organ is ready for surgery. In this respect, carbon dioxide is much like water—more than one phase of the same substance has significant uses in the real world.

8.1: Intermolecular Interactions

Learning Objectives

- Define *phase*.
- Identify the types of interactions between molecules.

A phase is a certain form of matter that includes a specific set of physical properties. That is, the atoms, the molecules, or the ions that make up the phase do so in a consistent manner throughout the phase. Science recognizes three stable phases: the ***solid** phase*, in which individual particles can be thought of as in contact and held in place; the ***liquid** phase*, in which individual particles are in contact but moving with respect to each other; and the ***gas** phase*, in which individual particles are separated from each other by relatively large distances (see Figure 8.1.1). Not all substances will readily exhibit all phases. For example, carbon dioxide does not exhibit a liquid phase unless the pressure is greater than about six times normal atmospheric pressure. Other substances, especially complex organic molecules, may decompose at higher temperatures, rather than becoming a liquid or a gas.

> *For many substances, there are different arrangements the particles can take in the solid phase, depending on temperature and pressure.*

Which phase a substance adopts depends on the pressure and the temperature it experiences. Of these two conditions, temperature variations are more obviously related to the phase of a substance. When it is very cold, H_2O exists in the solid form as ice. When it is warmer, the liquid phase of H_2O is present. At even higher temperatures, H_2O boils and becomes steam.

Pressure changes can also affect the presence of a particular phase (as we indicated for carbon dioxide), but its effects are less obvious most of the time. We will mostly focus on the temperature effects on phases, mentioning pressure effects only when they are important. Most chemical substances follow the same pattern of phases when going from a low temperature to a high temperature: the solid phase, then the liquid phase, and then the gas phase. However, the temperatures at which these phases are present differ for all substances and can be rather extreme. Table 8.1.1 shows the temperature ranges for solid, liquid, and gas phases for three substances. As you can see, there is extreme variability in the temperature ranges.

Table 8.1.1: Temperature Ranges for the Three Phases of Various Substances

Substance	Solid Phase Below	Liquid Phase Above	Gas Phase Above
hydrogen (H_2)	−259°C	−259°C	−253°C
water (H_2O)	0°C	0°C	100°C
sodium chloride (NaCl)	801°C	801°C	1413°C

The *melting point* of a substance is the temperature that separates a solid and a liquid. The *boiling point* of a substance is the temperature that separates a liquid and a gas.

What accounts for this variability? Why do some substances become liquids at very low temperatures, while others require very high temperatures before they become liquids? It all depends on the strength of the **intermolecular forces (IMF)** between the **particles** of substances and the **kinetic energies** (KE) of its molecules. (Although ionic compounds are not composed of discrete molecules, we will still use the term *intermolecular* to include interactions between the ions in such compounds.) Substances that experience **strong intermolecular interactions** require **higher temperatures to become liquids and, finally, gases.** Substances that experience **weak intermolecular interactions** do not need much energy (as measured by temperature) to become liquids and gases and will exhibit these phases at **lower temperatures.**

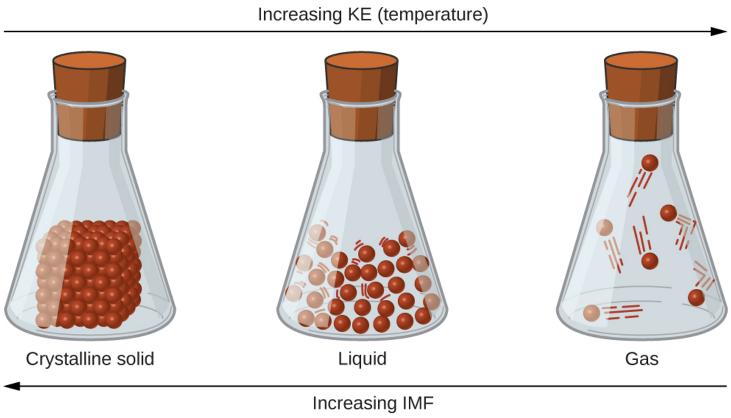


Figure 8.1.1: Transitions between solid, liquid, and gaseous states of a substance occur when conditions of temperature or pressure favor the associated changes in intermolecular forces. (Note: The space between particles in the gas phase is much greater than shown.)

Three sealed flasks are labeled, “Crystalline solid,” “Liquid,” and “Gas,” from left to right. The first flask holds a cube composed of small spheres sitting on the bottom while the second flask shows a lot of small spheres in the bottom that are spaced a small distance apart from one another and have lines around them to indicate motion. The third flask shows a few spheres spread far from one another with larger lines to indicate motion. There is a right-facing arrow that spans the top of all three flasks. The arrow is labeled, “Increasing K E (temperature).” There is a left-facing arrow that spans the bottom of all three flasks. The arrow is labeled, “Increasing I M F.”

Covalent Network Materials

Substances with the highest melting and boiling points have **covalent network** bonding. This type of intermolecular interaction is actually a covalent bond. In these substances, all the atoms in a sample are covalently bonded to one another; in effect, the entire sample is essentially **one giant molecule**. Many of these substances are solid over a large temperature range because it takes a lot of energy to disrupt all the covalent bonds at once. One example of a substance that shows covalent network bonding is diamond (Figure 8.1.2). Diamond is composed entirely of carbon atoms, each bonded to four other carbon atoms in a tetrahedral geometry. Melting a covalent network solid is not accomplished by overcoming the relatively weak intermolecular forces. Rather, all of the covalent bonds must be broken, a process that requires extremely high temperatures. Diamond, in fact, does not melt at all. Instead, it vaporizes to a gas at temperatures above 3,500°C. Diamond is extremely hard and is one of the few materials that can cut glass.

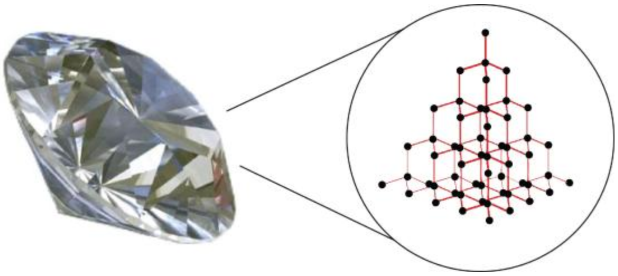


Figure 8.1.2: Diamond. Diamond, a form of pure carbon, has covalent network bonding. It takes a very high temperature—over 3,500°C—for diamond to leave the solid state. Source: Photo © Thinkstock

Ionic Compounds

The strongest force between any two particles is the ionic bond, in which two ions of opposing charge are attracted to each other. Thus, ionic interactions between particles are another type of intermolecular interaction. Substances that contain ionic interactions are relatively strongly held together, so these substances typically have high melting and boiling points. Sodium chloride (Figure 8.1.3) is an example of a substance whose particles experience ionic interactions (Table 8.1.1). These attractive forces are sometimes referred to as ion-ion interactions.

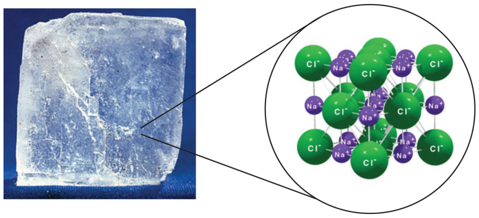


Figure 8.1.3: Sodium Chloride. Solid NaCl is held together by ionic interactions. Source: Photo © Thinkstock

Covalent Molecular Compounds

There are two different covalent structures: molecular and network. Covalent network compounds like SiO_2 (quartz) have structures of atoms in a network like diamond described earlier. In this section, we are dealing with the molecular type that contains individual molecules. The bonding between atoms in the individual molecule is covalent but the attractive forces between the molecules are called ***intermolecular forces (IMF)***.

In contrast to *intramolecular* forces (see Figure 8.1.4), such as the covalent bonds that hold atoms together in molecules and polyatomic ions, intermolecular forces hold molecules together in a **liquid or solid**. Intermolecular forces are generally much weaker than covalent bonds. For example, it requires 927 kJ to overcome the intramolecular forces and break both O–H bonds in 1 mol of water, but it takes only about 41 kJ to overcome the intermolecular attractions and convert 1 mol of liquid water to water vapor at 100°C. (Despite this seemingly low value, the intermolecular forces in liquid water are among the strongest such forces known!) Given the large difference in the strengths of intra- and intermolecular forces, changes between the solid, liquid, and gaseous states almost invariably occur for molecular substances ***without breaking covalent bonds.***

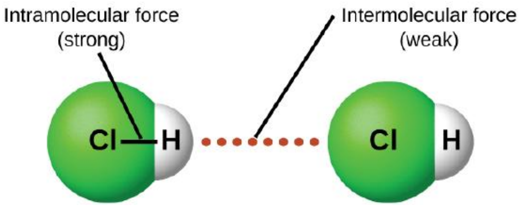


Figure 8.1.4: **Intramolecular** forces keep a molecule intact. **Intermolecular** forces hold multiple molecules together and determine many of a substance’s properties.

In this section, we will discuss the three types of IMF in molecular compounds: dipole-dipole, hydrogen bonding and London dispersion forces.

Dipole-dipole Intermolecular Forces

As discussed in Section 4.4, covalent bond that has an unequal sharing of electrons is called a **polar covalent** bond. (A covalent bond that has an equal sharing of electrons, as in a covalent bond with the same atom on each side, is called a **nonpolar covalent** bond.) A molecule with a net unequal distribution of electrons in its covalent bonds is a polar molecule. HF is an example of a polar molecule (see Figure 8.1.5).

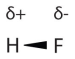


Figure 8.1.5: Polar Covalent Bonds. The electrons in the HF molecule are not equally shared by the two atoms in the bond. Because the fluorine atom has nine protons in its nucleus, it attracts the negatively charged electrons in the bond more than the hydrogen atom does with its one proton in its nucleus. Thus, electrons are more strongly attracted to the fluorine atom, leading to an imbalance in the electron distribution between the atoms. The fluorine side of the bond picks up a partial overall negative charge (represented by the δ− in the diagram), while the hydrogen side of the bond has an overall partial positive charge (represented by the δ+ in the diagram). Such a bond is called a *polar covalent bond*.

The charge separation in a **polar covalent bond** is not as extreme as is found in ionic compounds, but there is a related result: oppositely charged ends of different molecules will attract each other. This type of intermolecular interaction is called a **dipole-dipole interaction**. Many molecules with polar covalent bonds experience dipole-dipole interactions.

The covalent bonds in some molecules are oriented in space in such a way that the bonds in the molecules cancel each other out. The individual bonds are polar, but due to molecular symmetry, the overall molecule is not polar; rather, the molecule is ***nonpolar.*** Such molecules experience little or no dipole-dipole interactions. Carbon dioxide (CO_2) and carbon tetrachloride (CCl_4) are examples of such molecules (Figure 8.1.6).

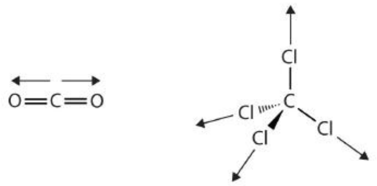


Figure 8.1.6: Nonpolar Molecules. Although the individual bonds in both CO_2 and CCl_4 are polar, their effects cancel out because of the spatial orientation of the bonds in each molecule. As a result, such molecules experience little or no dipole-dipole interaction.

Recall from the Sections 4.4 and 4.5, on chemical bonding and molecular geometry that *polar* molecules have a partial positive charge on one side and a partial negative charge on the other side of the molecule—a separation of charge called a ***dipole.*** Consider a polar molecule such as hydrogen chloride, HCl. In the HCl molecule, the more electronegative Cl atom bears the partial negative charge, whereas the less electronegative H atom bears the partial positive charge. An attractive force between HCl molecules results from the attraction between the positive end of one HCl molecule and the negative end of another. This attractive force is called a dipole-dipole attraction—the electrostatic force between the partially positive end of one polar molecule and the partially negative end of another, as illustrated in Figure 8.1.7.

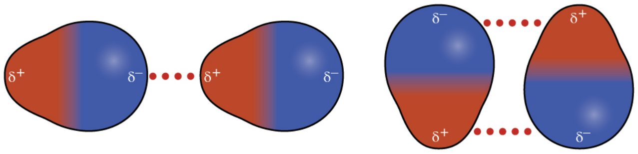


Figure 8.1.7: This image shows two arrangements of polar molecules, such as HCl, that allow an attraction between the partial negative end of one molecule and the partial positive end of another.

Two pairs of molecules are shown where each molecule has one larger blue side labeled “delta sign, negative sign” and a smaller red side labeled “delta sign, positive sign. In the first pair, the red sides of the two molecules both face to the left and the blue side to the right. A horizontal dotted line lies in between the two. In the second pair, the molecules face up and down, with the red and blue ends aligning. A horizontal dotted line lies between the red and blue ends facing upward and another lies between the red and blue ends facing downward.

The effect of a dipole-dipole attraction is apparent when we compare the properties of HCl molecules to nonpolar F_2 molecules. Both HCl and F_2 consist of the same number of atoms and have approximately the same molecular mass. At a temperature of 150 K, molecules of both substances would have the same average kinetic energy. However, the dipole-dipole attractions between HCl molecules are sufficient to cause them to “stick together” to form a liquid, whereas the relatively weaker dispersion forces between nonpolar F_2 molecules are not, and so this substance is gaseous at this temperature. The higher normal boiling point of HCl (188 K) compared to F_2 (85 K) is a reflection of the greater strength of dipole-dipole attractions between HCl molecules, compared to the attractions between nonpolar F_2 molecules. We will often use values such as boiling or freezing points as indicators of the relative strengths of IMFs of attraction present within different substances.

✓ Example 8.1.1

Predict which will have the higher boiling point: N_2 or CO. Explain your reasoning.

Solution

CO and N_2 are both diatomic molecules with masses of about 28 amu, so they experience similar London dispersion forces. Because CO is a polar molecule, it experiences dipole-dipole attractions. Because N_2 is nonpolar, its molecules cannot exhibit dipole-dipole attractions. The dipole-dipole attractions between CO molecules are comparably stronger than the dispersion forces between nonpolar N_2 molecules, so CO is expected to have the higher boiling point.

− rcise

Predict which will have the higher boiling point: ICl or Br_2. Explain your reasoning.

Answer

ICl. ICl and Br_2 have similar masses (~160 amu) and therefore experience similar London dispersion forces. ICl is polar and thus also exhibits dipole-dipole attractions; Br_2 is nonpolar and does not. The relatively stronger dipole-dipole attractions require more energy to overcome, so ICl will have the higher boiling point.

Hydrogen Bonding Intermolecular Forces

Molecules with **hydrogen atoms** bonded to electronegative atoms such as **O, N, and F** tend to exhibit unusually strong intermolecular interactions due to a particularly strong type of dipole-dipole attraction called **hydrogen bonding**. The very large difference in electronegativity between the H atom (2.1) and the atom to which it is bonded (4.0 for an F atom, 3.5 for an O atom, or 3.0 for a N atom), combined with the very small size of a H atom and the relatively small sizes of F, O, or N atoms, leads to ***highly concentrated partial charges*** with these atoms. Because the hydrogen atom does not have any electrons other than the ones in the covalent bond, its positively charged nucleus is almost completely exposed, allowing strong attractions to other nearby lone pairs of electrons.

Examples of hydrogen bonds include $HF\cdots HF$, $H_2O\cdots HOH$, and $H_3N\cdots HNH_2$, in which the **hydrogen bonds** are denoted by **dots**. Figure $8.1.8$ illustrates hydrogen bonding between water molecules. The physical properties of water, which has two O–H bonds, are strongly affected by the presence of hydrogen bonding between water molecules. Most molecular compounds that have a mass similar to water are gases at room temperature. However, because of the strong hydrogen bonds, water molecules are able to stay condensed in the liquid state.

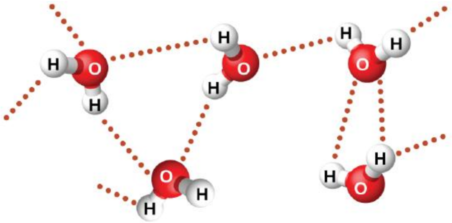


Figure $8.1.8$: Water molecules participate in multiple hydrogen-bonding interactions with nearby water molecules.

Five water molecules are shown near one another, but not touching. A dotted line lies between many of the hydrogen atoms on one molecule and the oxygen atom on another molecule.

A **hydrogen bond** is an intermolecular attractive force in which *a* **hydrogen atom**, that is covalently bonded to a small, highly electronegative atom, is attracted to a **lone pair of electrons** on an atom in a neighboring molecule. Figure $8.1.9$ shows how methanol (CH_3OH) molecules experience hydrogen bonding. Methanol contains both a hydrogen atom attached to O; methanol can thus form hydrogen bonds by acting as either a hydrogen bond donor or a hydrogen bond acceptor (lone pair). The hydrogen-bonded structure of methanol is as follows:

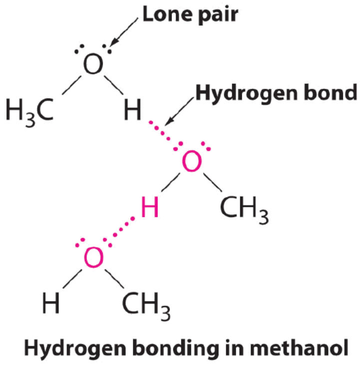


Figure $8.1.9$: Methanol molecules participate in multiple hydrogen-bonding interactions with nearby water molecules.

Despite use of the word "bond," keep in mind that hydrogen bonds are *intermolecular* attractive forces, not *intramolecular* attractive forces (covalent bonds). Hydrogen bonds are much weaker than covalent bonds, but are generally much stronger than other dipole-dipole attractions and dispersion forces.

✓ Effect of Hydrogen Bonding on Boiling Points

Consider the compounds dimethylether (CH_3OCH_3), ethanol (CH_3CH_2OH), and propane ($CH_3CH_2CH_3$). Their boiling points, not necessarily in order, are −42.1 °C, −24.8 °C, and 78.4 °C. Match each compound with its boiling point. Explain your reasoning.

Solution

The shapes of CH_3OCH_3, CH_3CH_2OH, and $CH_3CH_2CH_3$ are similar, as are their molar masses (46 g/mol, 46 g/mol, and 44 g/mol, respectively), so they will exhibit similar dispersion forces. Since $CH_3CH_2CH_3$ is nonpolar, it may exhibit *only* dispersion forces. Because CH_3OCH_3 is polar, it will also experience dipole-dipole attractions. Finally, CH_3CH_2OH has an −OH group, and so it will experience the uniquely strong dipole-dipole attraction known as hydrogen bonding. So the ordering in terms of strength of IMFs, and thus boiling points, is $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CH_2OH$. The boiling point of propane is −42.1 °C, the boiling point of dimethylether is −24.8 °C, and the boiling point of ethanol is 78.5 °C.

? Exercise 8.1.2

Ethane (CH_3CH_3) has a melting point of −183 °C and a boiling point of −89 °C. Predict the melting and boiling points for methylamine (CH_3NH_2). Explain your reasoning.

Answer

> The melting point and boiling point for methylamine are predicted to be significantly greater than those of ethane. CH_3CH_3 and CH_3NH_2 are similar in size and mass, but methylamine possesses an −NH group and therefore may exhibit hydrogen bonding. This greatly increases its IMFs, and therefore its melting and boiling points. It is difficult to predict values, but the known values are a melting point of −93 °C and a boiling point of −6 °C.

Hydrogen Bonding and DNA

Deoxyribonucleic acid (DNA) is found in every living organism and contains the genetic information that determines the organism’s characteristics, provides the blueprint for making the proteins necessary for life, and serves as a template to pass this information on to the organism’s offspring. A DNA molecule consists of two (anti-)parallel chains of repeating nucleotides, which form its well-known double helical structure, as shown in Figure 8.1.10.

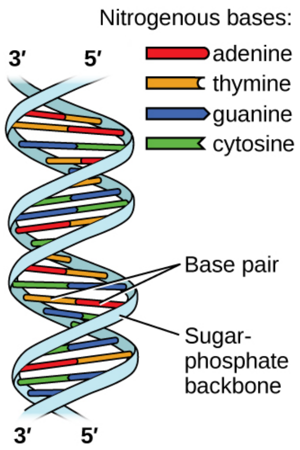


Figure 8.1.10: Two separate DNA molecules form a double-stranded helix in which the molecules are held together via hydrogen bonding. (credit: modification of work by Jerome Walker, Dennis Myts)

Two images are shown. The first lies on the left side of the page and shows a helical structure like a twisted ladder where the rungs of the ladder, labeled “Base pair” are red, yellow, green and blue paired bars. The red and yellow bars, which are always paired together, are labeled in the legend, which is titled “Nitrogenous bases” as “adenine” and “thymine,” respectively. The blue and green bars, which are always paired together, are labeled in the legend as “guanine” and “cytosine,” respectively. At the top of the helical structure, the left-hand side rail, or “Sugar, dash, phosphate backbone,” is labeled as “3, prime” while the right is labeled as “5, prime.” These labels are reversed at the bottom of the helix. To the right of the page is a large Lewis structure. The top left corner of this structure, labeled “5, prime,” shows a phosphorus atom single bonded to three oxygen atoms, one of which has a superscripted negative charge, and double bonded to a fourth oxygen atom. One of the single bonded oxygen atoms is single bonded to the left corner of a five-membered ring with an oxygen atom at its top point and which is single bonded to an oxygen atom on the bottom left. This oxygen atom is single bonded to a phosphorus atom that is single bonded to two other hydrogen atoms and double bonded to a fourth oxygen atom. The lower left of these oxygen atoms is single bonded to another oxygen atom that is single bonded to a five-membered ring with an oxygen in the upper bonding site. The bottom left of this ring has a hydroxyl group attached to it while the upper right carbon is single bonded to a nitrogen atom that is part of a five-membered ring bonded to a six-membered ring. Both of these rings have points of unsaturation and nitrogen atoms bonded into their structures. On the right side of the six-membered ring are two single bonded amine groups and a double bonded oxygen. Three separate dotted lines extend from these sites to corresponding sites on a second six-membered ring. This ring has points of unsaturation and a nitrogen atom in the bottom right bonding position that is single bonded to a five-membered ring on the right side of the image. This ring is single bonded to a carbon that is single bonded to an oxygen that is single bonded to a phosphorus. The phosphorus is single bonded to two other oxygen atoms and double bonded to a fourth oxygen atom. This group is labeled “5, prime.” The five-membered ring is also bonded on the top side to an oxygen that is bonded to a phosphorus single bonded to two other oxygen atoms and double bonded to a fourth oxygen atom. The upper left oxygen of this group is single bonded to a carbon that is single bonded to a five-membered ring with an oxygen in the bottom bonding position. This ring has a hydroxyl group on its upper right side that is labeled “3, prime” and is bonded on the left side to a nitrogen that is a member of a five-membered ring. This ring is bonded to a six-membered ring and both have points of unsaturation. This ring has a nitrogen on the left side, as well as an amine group, that have two dotted lines leading from them to an oxygen and amine group on a six membered ring. These dotted lines are labeled “Hydrogen bonds.” The six membered ring also has a double bonded oxygen on its lower side and a nitrogen atom on its left side that is single bonded to a five-membered ring. This ring connects to the two phosphate groups mentioned at the start of this to form a large circle. The name “guanine” is written below the lower left side of this image while the name “cytosine” is written on the lower right. The name “thymine” is written above the right side of the image and “adenine” is written on the top right. Three sections are indicated below the images where the left is labeled “Sugar, dash, phosphate backbone,” the middle is labeled “Bases” and the right is labeled “Sugar, dash, phosphate backbone.”

Each nucleotide contains a (deoxyribose) sugar bound to a phosphate group on one side, and one of four nitrogenous bases on the other. Two of the bases, cytosine (C) and thymine (T), are single-ringed structures known as pyrimidines. The other two, adenine (A) and guanine (G), are double-ringed structures called purines. These bases form complementary base pairs consisting of one purine and one pyrimidine, with adenine pairing with thymine, and cytosine with guanine. Each base pair is held together by hydrogen bonding. A and T share two hydrogen bonds, C and G share three, and both pairings have a similar shape and structure Figure 8.1.11

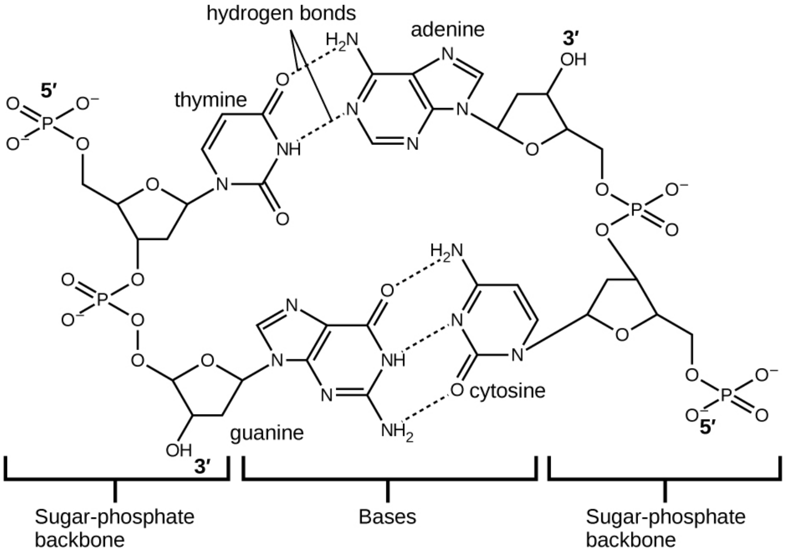


Figure 8.1.11: The geometries of the base molecules result in maximum hydrogen bonding between adenine and thymine (AT) and between guanine and cytosine (GC), so-called "complementary base pairs."

A large Lewis structure is shown. The top left corner of this structure, labeled "5, prime," shows a phosphorus atom single bonded to three oxygen atoms, one of which has a superscripted negative charge, and double bonded to a fourth oxygen atom. One of the single bonded oxygen atoms is single bonded to the left corner of a five-membered ring with an oxygen atom at its top point and which is single bonded to an oxygen atom on the bottom left. This oxygen atom is single bonded to a phosphorus atom that is single bonded to two other hydrogen atoms and double bonded to a fourth oxygen atom. The lower left of these oxygen atoms is single bonded to another oxygen atom that is single bonded to a five-membered ring with an oxygen in the upper bonding site. The bottom left of this ring has a hydroxyl group attached to it while the upper right carbon is single bonded to a nitrogen atom that is part of a five-membered ring bonded to a six-membered ring. Both of these rings have points of unsaturation and nitrogen atoms bonded into their structures. On the right side of the six-membered ring are two single bonded amine groups and a double bonded oxygen. Three separate dotted lines extend from these sites to corresponding sites on a second six-membered ring. This ring has points of unsaturation and a nitrogen atom in the bottom right bonding position that is single bonded to a five-membered ring on the right side of the image. This ring is single bonded to a carbon that is single bonded to an oxygen that is single bonded to a phosphorus. The phosphorus is single bonded to two other oxygen atoms and double bonded to a fourth oxygen atom. This group is labeled "5, prime." The five-membered ring is also bonded on the top side to an oxygen that is bonded to a phosphorus single bonded to two other oxygen atoms and double bonded to a fourth oxygen atom. The upper left oxygen of this group is single bonded to a carbon that is single bonded to a five-membered ring with an oxygen in the bottom bonding position. This ring has a hydroxyl group on its upper right side that is labeled "3, prime" and is bonded on the left side to a nitrogen that is a member of a five-membered ring. This ring is bonded to a six-membered ring and both have points of unsaturation. This ring has a nitrogen on the left side, as well as an amine group, that have two dotted lines leading from them to an oxygen and amine group on a six membered ring. These dotted lines are labeled "Hydrogen bonds." The six membered ring also has a double bonded oxygen on its lower side and a nitrogen atom on its left side that is single bonded to a five-membered ring. This ring connects to the two phosphate groups mentioned at the start of this to form a large circle. The name "guanine" is written below the lower left side of this image while the name "cytosine" is written on the lower right. The name "thymine" is written above the right side of the image and "adenine" is written on the top right. Three sections are indicated below the images where the left is labeled "Sugar, dash, phosphate backbone," the middle is labeled "Bases" and the right is labeled "Sugar, dash, phosphate backbone."

The cumulative effect of millions of hydrogen bonds effectively holds the two strands of DNA together. Importantly, the two strands of DNA can relatively easily "unzip" down the middle since hydrogen bonds are relatively weak compared to the covalent bonds that hold the atoms of the individual DNA molecules together. This allows both strands to function as a template for replication.

London Dispersion Forces

Finally, there are forces between all molecules that are caused by electrons being in different places in a molecule at any one time, which sets up a temporary separation of charge that disappears almost as soon as it appears. These are very weak intermolecular interactions and are called **dispersion forces (or London forces)**. (An alternate name is London dispersion forces.) Molecules that experience no other type of intermolecular interaction will at least experience dispersion forces. Substances that experience only dispersion forces are typically soft in the solid phase and have relatively low melting points. Examples include *waxes*, which are long hydrocarbon chains that are solids at room temperature because the molecules have so many electrons. The resulting dispersion forces between these molecules make them assume the solid phase at normal temperatures.

Dispersion forces that develop between atoms in different molecules can attract the two molecules to each other. The forces are relatively weak, however, and become significant only when the molecules are very close. **Larger and heavier atoms and molecules** exhibit **stronger dispersion forces** than do smaller and lighter atoms and molecules. F_2 and Cl_2 are gases at room temperature (reflecting weaker attractive forces); Br_2 is a liquid, and I_2 is a solid (reflecting stronger attractive forces). Trends in observed melting and boiling points for the halogens clearly demonstrate this effect, as seen in Table 8.1.2.

Table 8.1.2: **Melting and Boiling Points of the Halogens**

Halogen	Molar Mass	Atomic Radius	Melting Point	Boiling Point
fluorine, F_2	38 g/mol	72 pm	53 K	85 K
chlorine, Cl_2	71 g/mol	99 pm	172 K	238 K
bromine, Br_2	160 g/mol	114 pm	266 K	332 K
iodine, I_2	254 g/mol	133 pm	387 K	457 K
astatine, At_2	420 g/mol	150 pm	575 K	610 K

The increase in melting and boiling points with increasing atomic/molecular size may be rationalized by considering how the strength of dispersion forces is affected by the electronic structure of the atoms or molecules in the substance. In a larger atom, the valence electrons are, on average, farther from the nuclei than in a smaller atom. Thus, they are less tightly held and can more easily form the temporary dipoles that produce the attraction. The measure of how easy or difficult it is for another electrostatic charge (for example, a nearby ion or polar molecule) to distort a molecule’s charge distribution (its electron cloud) is known as **polarizability**. A molecule that has a charge cloud that is easily distorted is said to be very polarizable and will have large dispersion forces; one with a charge cloud that is difficult to distort is not very polarizable and will have small dispersion forces.

✓ Example 8.1.3

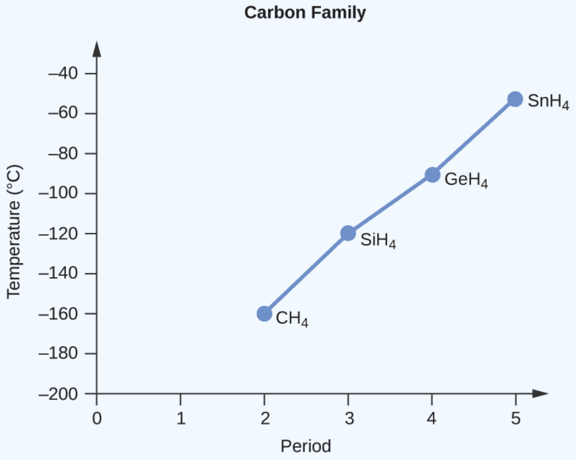
Order the following compounds of a group 14 element and hydrogen from lowest to highest boiling point: CH_4, SiH_4, GeH_4, and SnH_4. Explain your reasoning.

Solution

Applying the skills acquired in the chapter on chemical bonding and molecular geometry, all of these compounds are predicted to be nonpolar, so they may experience only dispersion forces: the smaller the molecule, the less polarizable and the weaker the dispersion forces; the larger the molecule, the larger the dispersion forces. The molar masses of CH_4, SiH_4, GeH_4, and SnH_4 are approximately 16 g/mol, 32 g/mol, 77 g/mol, and 123 g/mol, respectively. Therefore, CH_4 is expected to have the lowest boiling point and SnH_4 the highest boiling point. The ordering from lowest to highest boiling point is expected to be

$CH_4 < SiH_4 < GeH_4 < SnH_4$

A graph of the actual boiling points of these compounds versus the period of the group 14 elementsshows this prediction to be correct:



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.”

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Order the following hydrocarbons from lowest to highest boiling point: C_2H_6, C_3H_8, and C_4H_{10}.

Answer

All of these compounds are nonpolar and only have London dispersion forces: the larger the molecule, the larger the dispersion forces and the higher the boiling point. The ordering from lowest to highest boiling point is therefore

$$C_2H_6 < C_3H_8 < C_4H_{10}.$$

Applications: Geckos and Intermolecular Forces

Geckos have an amazing ability to adhere to most surfaces. They can quickly run up smooth walls and across ceilings that have no toe-holds, and they do this without having suction cups or a sticky substance on their toes. And while a gecko can lift its feet easily as it walks along a surface, if you attempt to pick it up, it sticks to the surface. How are geckos (as well as spiders and some other insects) able to do this? Although this phenomenon has been investigated for hundreds of years, scientists only recently uncovered the details of the process that allows geckos’ feet to behave this way.

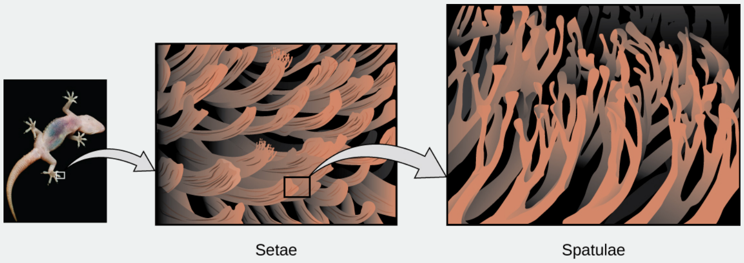


Figure 8.1.12*: Geckos’ toes contain large numbers of tiny hairs (setae), which branch into many triangular tips (spatulae). Geckos adhere to surfaces because of van der Waals attractions between the surface and a gecko’s millions of spatulae. By changing how the spatulae contact the surface, geckos can turn their stickiness “on” and “off.” (credit photo: modification of work by “JC*+A!”/Flickr)*

Three figures are shown. The first is a photo of the bottom of a gecko’s foot. The second is bigger version which shows the setae. The third is a bigger version of the setae and shows the spatulae.

Geckos’ toes are covered with hundreds of thousands of tiny hairs known as *setae*, with each seta, in turn, branching into hundreds of tiny, flat, triangular tips called *spatulae*. The huge numbers of spatulae on its setae provide a gecko, shown in Figure 8.1.12, with a large total surface area for sticking to a surface. In 2000, Kellar Autumn, who leads a multi-institutional gecko research team, found that geckos adhered equally well to both polar silicon dioxide and nonpolar gallium arsenide. This proved that geckos stick to surfaces because of dispersion forces—weak intermolecular attractions arising from temporary, synchronized charge distributions between adjacent molecules. Although dispersion forces are very weak, the total attraction over millions of spatulae is large enough to support many times the gecko's weight.

In 2014, two scientists developed a model to explain how geckos can rapidly transition from "sticky" to "non-sticky." Alex Greaney and Congcong Hu at Oregon State University described how geckos can achieve this by changing the angle between their spatulae and the surface. Geckos' feet, which are normally nonsticky, become sticky when a small shear force is applied. By curling and uncurling their toes, geckos can alternate between sticking and unsticking from a surface, and thus easily move across it. Further investigations may eventually lead to the development of better adhesives and other applications.

Boiling Points and Bonding Types

In order for a substance to enter the gas phase, its particles must completely overcome the intermolecular forces holding them together. Therefore, a comparison of boiling points is essentially equivalent to comparing the strengths of the attractive intermolecular forces exhibited by the individual molecules. For small molecular compounds, London dispersion forces are the weakest intermolecular forces. Dipole-dipole forces are somewhat stronger, and hydrogen bonding is a particularly strong form of dipole-dipole interaction. However, when the mass of a nonpolar molecule is sufficiently large, its dispersion forces can be stronger than the dipole-dipole forces in a lighter polar molecule. Thus, nonpolar Cl_2 has a higher boiling point than polar HCl.

Table 8.1.3: Intermolecular Forces and Boiling Points

Substance	**Strongest Intermolecular Force**	**Boiling Point** (°C)
H_2	dispersion	-253
Ne	dispersion	-246
O_2	dispersion	-183
Cl_2	dispersion	-34
HCl	dipole-dipole	-85
HBr	dipole-dipole	-66
H_2S	dipole-dipole	-61
NH_3	hydrogen bonding	-33
HF	hydrogen bonding	20
H_2O	hydrogen bonding	100

✓ Example 8.1.4: Intermolecular Forces

What intermolecular forces besides dispersion forces, if any, exist in each substance? Are any of these substances solids at room temperature?

a. potassium chloride (KCl)
b. ethanol (C_2H_5OH)
c. bromine (Br_2)

Solution

a. Potassium chloride is composed of ions, so the intermolecular interaction in potassium chloride is ionic forces. Because ionic interactions are strong, it might be expected that potassium chloride is a solid at room temperature.
b. Ethanol has a hydrogen atom attached to an oxygen atom, so it would experience hydrogen bonding. If the hydrogen bonding is strong enough, ethanol might be a solid at room temperature, but it is difficult to know for certain. (Ethanol is actually a liquid at room temperature.)

c. Elemental bromine has two bromine atoms covalently bonded to each other. Because the atoms on either side of the covalent bond are the same, the electrons in the covalent bond are shared equally, and the bond is a nonpolar covalent bond. Thus, diatomic bromine does not have any intermolecular forces other than dispersion forces. It is unlikely to be a solid at room temperature unless the dispersion forces are strong enough. Bromine is a liquid at room temperature.

? Exercise 8.1.4

What intermolecular forces besides dispersion forces, if any, exist in each substance? Are any of these substances solids at room temperature?

a. methylamine (CH_3NH_2)
b. calcium sulfate ($CaSO_4$)
c. carbon monoxide (CO)

Answer

a. dipole-dipole, hydrogen bonding

b. ionic forces (solid at room temperature)

c. dipole-dipole

Key Takeaways

- A phase is a form of matter that has the same physical properties throughout.
- Molecules interact with each other through various forces: dipole-dipole interactions, hydrogen bonding, and dispersion forces.
- Dipole-dipole attractions result from the electrostatic attraction of the partial negative end of one dipolar molecule for the partial positive end of another.
- Hydrogen bonds are a special type of dipole-dipole attraction that results when hydrogen is bonded to one of the three most electronegative elements: F, O, or N.
- The temporary dipole that results from the motion of the electrons in an atom can induce a dipole in an adjacent atom and give rise to the London dispersion force. London forces increase with increasing molecular size.

8.2: Solids and Liquids

Learning Objectives

- To describe the solid and liquid phases.

Solids and liquids are collectively called *condensed phases* because their particles are in virtual contact. The two states share little else, however.

Solids

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

Figure $8.2.1$: Crystalline Arrangement of Quartz crystal cluster. Some large crystals look the way they do because of the regular arrangement of atoms (ions) in their crystal structure. from Wikipedia.

Solids usually have their constituent particles arranged in a regular, three-dimensional array of alternating positive and negative ions called a crystal. The effect of this regular arrangement of particles is sometimes visible macroscopically, as shown in Figure $8.2.1$. Some solids, especially those composed of large molecules, cannot easily organize their particles in such regular crystals and exist as amorphous (literally, “without form”) solids. Glass is one example of an amorphous solid.

Liquids

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

Figure $8.2.2$: The formation of a spherical droplet of liquid water minimizes the surface area, which is the natural result of surface tension in liquids. from Wikipedia.

Gases

If the particles of a substance have enough energy to completely overcome intermolecular interactions, then the particles can separate from each other and move about randomly in space. Like liquids, gases have no definite shape, but unlike solids and liquids, gases have no definite volume either.

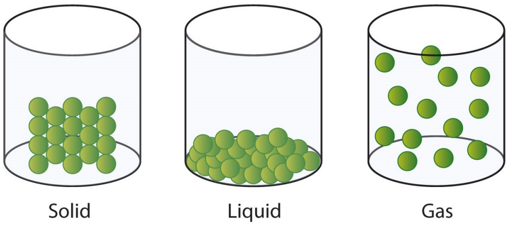


Figure 8.2.3: A Representation of the Solid, Liquid, and Gas States. A solid has definite volume and shape, a liquid has a definite volume but no definite shape, and a gas has neither a definite volume nor shape.

The change from solid to liquid usually does not significantly change the volume of a substance. However, the change from a liquid to a gas significantly increases the volume of a substance, by a factor of 1,000 or more. Figure 8.2.3 shows the differences among solids, liquids, and gases at the molecular level, while Table 8.2.1 lists the different characteristics of these states.

Table 8.2.1: Characteristics of the Three States of Matter

Characteristic	Solid	Liquid	Gas
shape	definite	indefinite	indefinite
volume	definite	definite	indefinite
relative intermolecular interaction strength	strong	moderate	weak
relative particle positions	in contact and fixed in place	in contact but not fixed	not in contact, random positions

✓ Example 8.2.1

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

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

Solution

a. This statement describes either the liquid state or the solid state.
b. This statement describes either the liquid state or the gas state.
c. This statement describes the liquid state.

? Exercise 8.2.1

What state or states of matter does each statement describe?

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

Answer

a. solid
b. gas
c. solid

Looking Closer: Water, the Most Important Liquid

Earth is the only known body in our solar system that has liquid water existing freely on its surface. That is a good thing because life on Earth would not be possible without the presence of liquid water.

Water has several properties that make it a unique substance among substances. It is an excellent solvent; it dissolves many other substances and allows those substances to react when in solution. In fact, water is sometimes called the *universal solvent* because of this ability. Water has unusually high melting and boiling points (0°C and 100°C, respectively) for such a small molecule. The boiling points for similar-sized molecules, such as methane (BP = −162°C) and ammonia (BP = −33°C), are more than 100° lower. Though a liquid at normal temperatures, water molecules experience a relatively strong intermolecular interaction that allows them to maintain the liquid phase at higher temperatures than expected.

Unlike most substances, the solid form of water is less dense than its liquid form, which allows ice to float on water. The most energetically favorable configuration of H_2O molecules is one in which each molecule is hydrogen-bonded to four neighboring molecules. Owing to the thermal motions, this ideal is never achieved in the liquid, but when water freezes to ice, the molecules settle into exactly this kind of an arrangement in the ice crystal. This arrangement requires that the molecules be somewhat farther apart than would otherwise be the case; as a consequence, ice, in which hydrogen bonding is at its maximum, has a more open structure, and thus a lower density than water.

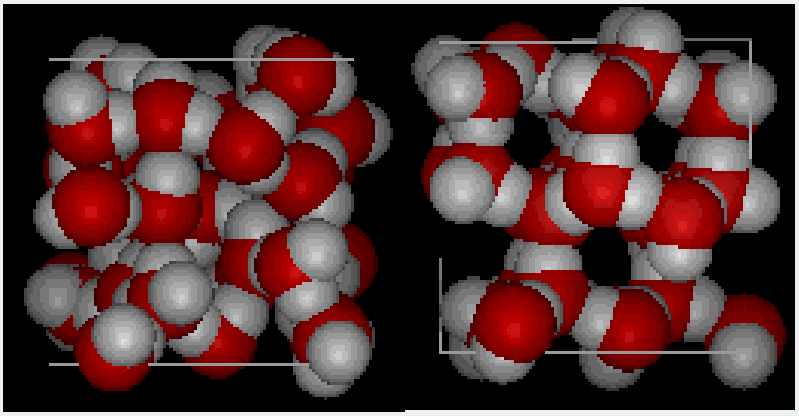


Figure 8.2.4: Three-dimensional views of a typical local structure of liquid water (left) and ice (right).

Here are three-dimensional views of a typical local structure of water (left) and ice (right.) Notice the greater openness of the ice structure which is necessary to ensure the strongest degree of hydrogen bonding in a uniform, extended crystal lattice. The structure of liquid water is very similar, but in the liquid, the hydrogen bonds are continually broken and formed because of rapid molecular motion. Because ice is less dense than liquid water, rivers, lakes, and oceans freeze from the top down. In fact, the ice forms a protective surface layer that insulates the rest of the water, allowing fish and other organisms to survive in the lower levels of a frozen lake or sea. If ice were denser than the liquid, the ice formed at the surface in cold weather would sink as fast as it formed. Bodies of water would freeze from the bottom up, which would be lethal for most aquatic creatures. The expansion of water when freezing also explains why automobile or boat engines must be protected by “antifreeze” and why unprotected pipes in houses break if they are allowed to freeze.

Water also requires an unusually large amount of energy to change temperature. While 100 J of energy will change the temperature of 1 g of Fe by 230°C, this same amount of energy will change the temperature of 1 g of H_2O by only 100°C. Thus, water changes its temperature slowly as heat is added or removed. This has a major impact on weather, as storm systems like hurricanes can be impacted by the amount of heat that ocean water can store.

Water’s influence on the world around us is affected by these properties. Isn’t it fascinating that such a small molecule can have such a big impact?

Key Takeaway

- Solids and liquids are phases that have their own unique properties.

8.3: Gases and Pressure

Learning Objectives

- To describe the gas phase.

The gas phase is unique among the three states of matter in that there are some simple models we can use to predict the physical behavior of all gases—independent of their identities. We cannot do this for the solid and liquid states. In fact, the development of this understanding of the behavior of gases represents the historical dividing point between alchemy and modern chemistry. Initial advances in the understanding of gas behavior were made in the mid 1600s by Robert Boyle, an English scientist who founded the Royal Society (one of the world's oldest scientific organizations).

How is it that we can model all gases independent of their chemical identity? The answer is in a group of statements called the kinetic theory of gases:

- Gases are composed of tiny particles that are separated by large distances.
- Gas particles are constantly moving, experiencing collisions with other gas particles and the walls of their container.
- The velocity of gas particles is related to the temperature of a gas.
- Gas particles do not experience any force of attraction or repulsion with each other.

Did you notice that none of these statements relates to the identity of the gas? This means that all gases should behave similarly. A gas that follows these statements perfectly is called an *ideal gas*. Most gases show slight deviations from these statements and are called *real gases*. However, the existence of real gases does not diminish the importance of the kinetic theory of gases.

One of the statements of the kinetic theory mentions collisions. As gas particles are constantly moving, they are also constantly colliding with each other and with the walls of their container. There are forces involved as gas particles bounce off the container walls (Figure 8.3.1). The force generated by gas particles divided by the area of the container walls yields pressure. Pressure is a property we can measure for a gas, but we typically do not consider pressure for solids or liquids.

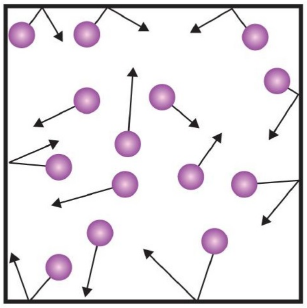


Figure 8.3.1: Gas Pressure. Pressure is what results when gas particles rebound off the walls of their container.

The basic unit of pressure is the newton per square meter (N/m^2). This combined unit is redefined as a pascal (Pa). One pascal is not a very large amount of pressure. A more useful unit of pressure is the bar, which is 100,000 Pa (1 bar = 100,000 Pa). Other common units of pressure are the atmosphere (atm), which was originally defined as the average pressure of Earth's atmosphere at sea level; and mmHg (millimeters of mercury), which is the pressure generated by a column of mercury 1 mm high. The unit millimeters of mercury is also called a torr, named after the Italian scientist Evangelista Torricelli, who invented the barometer in the mid-1600s. A more precise definition of atmosphere, in terms of torr, is that there are exactly 760 torr in 1 atm. A bar equals 1.01325 atm. Given all the relationships between these pressure units, the ability to convert from one pressure unit to another is a useful skill.

✓ Example 8.3.1: Converting Pressures

Write a conversion factor to determine how many atmospheres are in 1,547 mmHg.

Solution

Because 1 mmHg equals 1 torr, the given pressure is also equal to 1,547 torr. Because there are 760 torr in 1 atm, we can use this conversion factor to do the mathematical conversion:

$$1,547 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 2.04 \text{ atm}$$

Note how the torr units cancel algebraically.

Exercise 8.3.1: Converting Pressures

Write a conversion factor to determine how many millimeters of mercury are in 9.65 atm.

Answer

$$9.65 \text{ atm} \times \frac{760 \text{ mmHg}}{1 \text{ atm}} = 7,334 \text{ mmHg}$$

The kinetic theory also states that there is no interaction between individual gas particles. Although we know that there are, in fact, intermolecular interactions in real gases, the kinetic theory assumes that gas particles are so far apart that the individual particles don't "feel" each other. Thus, we can treat gas particles as tiny bits of matter whose identity isn't important to certain physical properties.

Key Takeaway

- The gas phase has certain general properties characteristic of that phase.

8.4: Gas Laws

Learning Objectives

- To predict the properties of gases using the gas laws.

Experience has shown that several properties of a gas can be related to each other under certain conditions. The properties are pressure (*P*), volume (*V*), temperature (*T*, in kelvins), and amount of material expressed in moles (*n*). What we find is that a sample of gas cannot have any random values for these properties. Instead, only certain values, dictated by some simple mathematical relationships, will occur.

Boyle's Law

The first simple relationship, referred to as a gas law, is between the pressure of a gas and its volume. If the amount of gas in a sample and its temperature are kept constant, then as the pressure of a gas is increased, the volume of the gas decreases proportionately. Mathematically, this is written as

$$\mathrm{P} \propto \frac{1}{\mathrm{V}}$$

where the "∝" symbol means "is proportional to." This is one form of Boyle's law, which relates the pressure of a gas to its volume.

A more useful form of Boyle's law involves a change in conditions of a gas. For a given amount of gas at a constant temperature, if we know the initial pressure and volume of a gas sample and the pressure or volume changes, we can calculate what the new volume or pressure will be. That form of Boyle's law is written

$$P_iV_i = P_fV_f \tag{8.4.1}$$

where the subscript i refers to initial conditions and the subscript f refers to final conditions.

To use 8.4.1, you need to know any three of the variables so that you can algebraically calculate the fourth variable. Also, the pressure quantities must have the same units, as must the two volume quantities. If the two similar variables don't have the same variables, one value must be converted to the other value's unit.

✓ Example 8.4.1: Increasing Pressure in a Gas

What happens to the volume of a gas if its pressure is increased? Assume all other conditions remain the same.

Solution

If the pressure of a gas is increased, the volume decreases in response.

? Exercise 8.4.1: Increasing Volume in a Gas

What happens to the pressure of a gas if its volume is increased? Assume all other conditions remain the same.

Answer

If the volume of a gas is increased, the pressure decreases.

✓ Example 8.4.2: Gas Compression

If a sample of gas has an initial pressure of 1.56 atm and an initial volume of 7.02 L, what is the final volume if the pressure is reduced to 0.987 atm? Assume that the amount and the temperature of the gas remain constant.

Solution

The key in problems like this is to be able to identify which quantities represent which variables from the relevant equation. The way the question is worded, you should be able to tell that 1.56 atm is P_i, 7.02 L is V_i, and 0.987 atm is P_f. What we are looking for is the final volume—V_f. Therefore, substituting these values into $P_iV_i = P_fV_f$:

$$(1.56 \text{ atm})(7.02 \text{ L}) = (0.987 \text{ atm}) \times V_f$$

The expression has atmospheres on both sides of the equation, so they cancel algebraically:

$$(1.56)(7.02 \text{ L}) = (0.987) \times V_f$$

Now we divide both sides of the expression by 0.987 to isolate V_f, the quantity we are seeking:

$$\frac{(1.56)(7.02 \text{ L})}{0.987} = \mathrm{V_f}$$

Performing the multiplication and division, we get the value of V_f, which is 11.1 L. The volume increases. This should make sense because the pressure decreases, so pressure and volume are inversely related.

Exercise 8.4.2

If a sample of gas has an initial pressure of 3.66 atm and an initial volume of 11.8 L, what is the final pressure if the volume is reduced to 5.09 L? Assume that the amount and the temperature of the gas remain constant.

Answer

8.48 atm

If the units of similar quantities are not the same, one of them must be converted to the other quantity's units for the calculation to work out properly. It does not matter which quantity is converted to a different unit; the only thing that matters is that the conversion and subsequent algebra are performed properly. The following example illustrates this process.

Example 8.4.3

If a sample of gas has an initial pressure of 1.56 atm and an initial volume of 7.02 L, what is the final volume if the pressure is changed to 1,775 torr? Does the answer make sense? Assume that the amount and the temperature of the gas remain constant.

Solution

This example is similar to Example 8.4.2, except now the final pressure is expressed in torr. For the math to work out properly, one of the pressure values must be converted to the other unit. Let us change the initial pressure to torr:

$$1.56 \text{ atm} \times \frac{760 \text{ torr}}{1 \text{ atm}} = 1,190 \text{ torr}$$

Now we can use Boyle's law:

$$(1{,}190 \text{ torr})(7.02 \text{ L}) = (1{,}775 \text{ torr}) \times V_f$$

Torr cancels algebraically from both sides of the equation, leaving

$$(1{,}190)(7.02 \text{ L}) = (1{,}775) \times V_f$$

Now we divide both sides of the equation by 1,775 to isolate V_f on one side. Solving for the final volume,

$$\mathrm{V_f} = \frac{(1,190)(7.02 \text{ L})}{1,775} = 4.71 \text{ L}$$

Because the pressure increases, it makes sense that the volume decreases.

The answer for the final volume is essentially the same if we converted the 1,775 torr to atmospheres: $1,775 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 2.336 \text{ atm}$. Using Boyle's law: (1.56 atm)(7.02 L) = (2.335 atm) × V_f; $\mathrm{V_f} = \frac{(1.56 \text{ atm})(7.02 \text{ L})}{2.336 \text{ atm}} = 4.69 \text{ L}$.

Exercise 8.4.3

If a sample of gas has an initial pressure of 375 torr and an initial volume of 7.02 L, what is the final pressure if the volume is changed to 4,577 mL? Does the answer make sense? Assume that amount and the temperature of the gas remain constant.

Answer

575 torr

To Your Health: Breathing

Breathing certainly is a major contribution to your health! Without breathing, we could not survive. Curiously, the act of breathing itself is little more than an application of Boyle's law.

The lungs are a series of ever-narrowing tubes that end in a myriad of tiny sacs called alveoli. It is in the alveoli that oxygen from the air transfers to the bloodstream and carbon dioxide from the bloodstream transfers to the lungs for exhalation. For air to move in and out of the lungs, the pressure inside the lungs must change, forcing the lungs to change volume—just as predicted by Boyle's law.

The pressure change is caused by the diaphragm, a muscle that covers the bottom of the lungs. When the diaphragm moves down, it expands the size of our lungs. When this happens, the air pressure inside our lungs decreases slightly. This causes new air to rush in, and we inhale. The pressure decrease is slight—only 3 torr, or about 0.4% of an atmosphere. We inhale only 0.5–1.0 L of air per normal breath.

Exhaling air requires that we relax the diaphragm, which pushes against the lungs and slightly decreases the volume of the lungs. This slightly increases the pressure of the air in the lungs, and air is forced out; we exhale. Only 1–2 torr of extra pressure is needed to exhale. So with every breath, our own bodies are performing an experimental test of Boyle's law.

Charles's Law

Another simple gas law relates the volume of a gas to its temperature. Experiments indicate that as the temperature of a gas sample is increased, its volume increases as long as the pressure and the amount of gas remain constant. The way to write this mathematically is

$$\mathrm{V} \propto T$$

At this point, the concept of temperature must be clarified. Although the Kelvin scale is the preferred temperature scale, the Celsius scale is also a common temperature scale used in science. The Celsius scale is based on the melting and boiling points of water and is actually the common temperature scale used by most countries around the world (except for the United States, which still uses the Fahrenheit scale). The value of a Celsius temperature is directly related to its Kelvin value by a simple expression:

$$\text{Kelvin temperature} = \text{Celsius temperature} + 273$$

Thus, it is easy to convert from one temperature scale to another.

The Kelvin scale is sometimes referred to as the absolute scale because the zero point on the Kelvin scale is at absolute zero, the coldest possible temperature. On the other temperature scales, absolute zero is −260°C or −459°F.

The expression relating a gas volume to its temperature begs the following question: to which temperature scale is the volume of a gas related? The answer is that gas volumes are directly related to the *Kelvin temperature*. Therefore, the temperature of a gas sample should always be expressed in (or converted to) a Kelvin temperature.

Example 8.4.4: Increasing Temperature

What happens to the volume of a gas if its temperature is decreased? Assume that all other conditions remain constant.

Solution

If the temperature of a gas sample is decreased, the volume decreases as well.

Exercise 8.4.4

What happens to the temperature of a gas if its volume is increased? Assume that all other conditions remain constant.

Answer

The temperature increases.

As with Boyle's law, the relationship between volume and temperature can be expressed in terms of initial and final values of volume and temperature, as follows:

$$\frac{\mathrm{V_i}}{\mathrm{T_i}} = \frac{\mathrm{V_f}}{\mathrm{T_f}}$$

where V_i and T_i are the initial volume and temperature, and V_f and T_f are the final volume and temperature. This is Charles's law. The restriction on its use is that the pressure of the gas and the amount of gas must remain constant. (Charles's law is sometimes referred to as Gay-Lussac's law, after the scientist who promoted Charles's work.)

Example 8.4.5

A gas sample at 20°C has an initial volume of 20.0 L. What is its volume if the temperature is changed to 60°C? Does the answer make sense? Assume that the pressure and the amount of the gas remain constant.

Solution

Although the temperatures are given in degrees Celsius, we must convert them to the kelvins before we can use Charles's law. Thus,

$$20°\mathrm{C} + 273 = 293\ \mathrm{K} = T_\mathrm{i}\ 60°\mathrm{C} + 273 = 333\ \mathrm{K} = T_\mathrm{f}$$

Now we can substitute these values into Charles's law, along with the initial volume of 20.0 L:

$$\frac{20.0\ \mathrm{L}}{293\ \mathrm{K}} = \frac{\mathrm{V_f}}{333\ \mathrm{K}}$$

Multiplying the 333 K to the other side of the equation, we see that our temperature units will cancel:

$$\frac{(333\ \mathrm{K})(20.0\ \mathrm{L})}{293\ \mathrm{K}} = \mathrm{V_f}$$

Solving for the final volume, V_f = 22.7 L. So, as the temperature is increased, the volume increases. This makes sense because volume is directly proportional to the absolute temperature (as long as the pressure and the amount of the remain constant).

Exercise 8.4.5

A gas sample at 35°C has an initial volume of 5.06 L. What is its volume if the temperature is changed to −35°C? Does the answer make sense? Assume that the pressure and the amount of the gas remain constant.

Answer

3.91 L

Combined Gas Law

Other gas laws can be constructed, but we will focus on only two more. The combined gas law brings Boyle's and Charles's laws together to relate pressure, volume, and temperature changes of a gas sample:

$$\frac{\mathrm{P_i V_i}}{\mathrm{T_i}} = \frac{\mathrm{P_f V_f}}{\mathrm{T_f}}$$

To apply this gas law, the amount of gas should remain constant. As with the other gas laws, the temperature must be expressed in kelvins, and the units on the similar quantities should be the same. Because of the dependence on three quantities at the same time, it is difficult to tell in advance what will happen to one property of a gas sample as two other properties change. The best way to know is to work it out mathematically.

Example 8.4.6

A sample of gas has P_i = 1.50 atm, V_i = 10.5 L, and T_i = 300 K. What is the final volume if P_f = 0.750 atm and T_f = 350 K?

Solution

Using the combined gas law, substitute for five of the quantities:

$$\frac{(1.50\text{ atm})(10.5\text{ L})}{300\text{ K}}=\frac{(0.750\text{ atm})(\mathrm{V_f})}{350\text{ K}}$$

We algebraically rearrange this expression to isolate V_f on one side of the equation:

$$\mathrm{V_f}=\frac{(1.50\text{ atm})(10.5\text{ L})(350\text{ K})}{(300\text{ K})(0.750\text{ atm})}=24.5\text{ L}$$

Note how all the units cancel except the unit for volume.

rcise

A sample of gas has P_i = 0.768 atm, V_i = 10.5 L, and T_i = 300 K. What is the final pressure if V_f = 7.85 L and T_f = 250 K?

Answer

0.856 atm

Example 8.4.7

A balloon containing a sample of gas has a temperature of 22°C and a pressure of 1.09 atm in an airport in Cleveland. The balloon has a volume of 1,070 mL. The balloon is transported by plane to Denver, where the temperature is 11°C and the pressure is 655 torr. What is the new volume of the balloon?

Solution

The first task is to convert all quantities to the proper and consistent units. The temperatures must be expressed in kelvins, and the pressure units are different so one of the quantities must be converted. Let us convert the atmospheres to torr:

$$22°\text{C} + 273 = 295\text{ K} = T_i$$

$$11°\text{C} + 273 = 284\text{ K} = T_f$$

$$1.09\text{ atm}\times\frac{760\text{ torr}}{1\text{ atm}}=828\text{ torr}=\mathrm{P_i}$$

Now we can substitute the quantities into the combined has law:

$$\frac{(828\text{ torr})(1,070\text{ mL})}{295\text{ K}}=\frac{(655\text{ torr})\times\mathrm{V_f}}{284\text{ K}}$$

To solve for V_f, we multiply the 284 K in the denominator of the right side into the numerator on the left, and we divide 655 torr in the numerator of the right side into the denominator on the left:

$$\frac{(828\text{ torr})(1,070\text{ mL})(284\text{ K})}{(295\text{ K})(655\text{ torr})}=\mathrm{V_f}$$

Notice that torr and kelvins cancel, as they are found in both the numerator and denominator. The only unit that remains is milliliters, which is a unit of volume. So V_f = 1,300 mL. The overall change is that the volume of the balloon has increased by 230 mL.

rcise

A balloon used to lift weather instruments into the atmosphere contains gas having a volume of 1,150 L on the ground, where the pressure is 0.977 atm and the temperature is 18°C. Aloft, this gas has a pressure of 6.88 torr and a temperature of −15°C. What is the new volume of the gas?

Answer

110,038 L

The Ideal Gas Law

So far, the gas laws we have used have focused on changing one or more properties of the gas, such as its volume, pressure, or temperature. There is one gas law that relates all the independent properties of a gas under any particular condition, rather than a change in conditions. This gas law is called the ideal gas law. The formula of this law is as follows:

$$PV = nRT$$

In this equation, *P* is pressure, *V* is volume, *n* is amount of moles, and *T* is temperature. *R* is called the ideal gas law constant and is a proportionality constant that relates the values of pressure, volume, amount, and temperature of a gas sample. The variables in this equation do not have the subscripts *i* and *f* to indicate an initial condition and a final condition. The ideal gas law relates the four independent properties of a gas under *any* conditions.

The value of *R* depends on what units are used to express the other quantities. If volume is expressed in liters and pressure in atmospheres, then the proper value of *R* is as follows:

$$\mathrm{R = 0.08205\ \frac{L \cdot atm}{mol \cdot K}}$$

This may seem like a strange unit, but that is what is required for the units to work out algebraically.

✓ Example 8.4.8

What is the volume in liters of 1.45 mol of N_2 gas at 298 K and 3.995 atm?

Solution

Using the ideal gas law where *P* = 3.995 atm, *n* = 1.45, and *T* = 298,

$$\mathrm{(3.995\ atm) \times V = (1.45\ mol) \left(0.08205\ \frac{L \cdot atm}{mol \cdot K}\right) (298\ K)}$$

On the right side, the moles and kelvins cancel. Also, because atmospheres appear in the numerator on both sides of the equation, they also cancel. The only remaining unit is liters, a unit of volume. So

$$3.995 \times V = (1.45)(0.08205)(298)\ \mathrm{L}$$

Dividing both sides of the equation by 3.995 and evaluating, we get *V* = 8.87 L. Note that the conditions of the gas are not changing. Rather, the ideal gas law allows us to determine what the fourth property of a gas (here, volume) *must* be if three other properties (here, amount, pressure, and temperature) are known.

rcise

What is the pressure of a sample of CO_2 gas if 0.557 mol is held in a 20.0 L container at 451 K?

Answer

1.03 atm

For convenience, scientists have selected 273 K (0°C) and 1.00 atm pressure as a set of standard conditions for gases. This combination of conditions is called standard temperature and pressure (STP). Under these conditions, 1 mol of any gas has about the same volume. We can use the ideal gas law to determine the volume of 1 mol of gas at STP:

$$(1.00\ \mathrm{atm}) \times \mathrm{V} = (1.00\ \mathrm{mol}) \left(0.08205\ \frac{\mathrm{L} \cdot \mathrm{atm}}{\mathrm{mol} \cdot \mathrm{K}}\right) (273\ \mathrm{K})$$

This volume is 22.4 L. Because this volume is independent of the identity of a gas, the idea that 1 mol of gas has a volume of 22.4 L at STP makes a convenient conversion factor:

1 mol gas = 22.4 L (at STP)

Example 8.4.9

Cyclopropane (C_3H_6) is a gas that formerly was used as an anesthetic. How many moles of gas are there in a 100.0 L sample if the gas is at STP?

Solution

We can set up a simple, one-step conversion that relates moles and liters:

$$100.0\ \mathrm{L}\ \mathrm{C_3H_6} \times \frac{1\ \mathrm{mol}}{22.4\ \mathrm{L}} = 4.46\ \mathrm{mol}\ \mathrm{C_3H_6}$$

There are almost 4.5 mol of gas in 100.0 L.

Note: Because of its flammability, cyclopropane is no longer used as an anesthetic gas.

rcise

Freon is a trade name for a series of fluorine- and chlorine-containing gases that formerly were used in refrigeration systems. What volume does 8.75 mol of Freon have at STP?

Note: Many gases known as Freon are no longer used because their presence in the atmosphere destroys the ozone layer, which protects us from ultraviolet light from the sun.

Answer

196 L

Airbags

Airbags (Figure 8.4.3) are a safety feature provided in most automobiles since the 1990s. The effective operation of an airbag requires that it be rapidly inflated with an appropriate amount (volume) of gas when the vehicle is involved in a collision. This requirement is satisfied in many automotive airbag systems through use of explosive chemical reactions, one common choice being the decomposition of sodium azide, NaN_3. When sensors in the vehicle detect a collision, an electrical current is passed through a carefully measured amount of NaN_3 to initiate its decomposition:

$$2\ \mathrm{NaN_3}(s) \rightarrow 3\ \mathrm{N_2}(g) + 2\ \mathrm{Na}(s)$$

This reaction is very rapid, generating gaseous nitrogen that can deploy and fully inflate a typical airbag in a fraction of a second (~0.03–0.1 s). Among many engineering considerations, the amount of sodium azide used must be appropriate for generating enough nitrogen gas to fully inflate the air bag and ensure its proper function. For example, a small mass (~100 g) of NaN_3 will generate approximately 50 L of N_2.

Figure 8.4.3: Airbags deploy upon impact to minimize serious injuries to passengers. (credit: Jon Seidman)

Dalton's Law of Partial Pressures

The ideal gas equation of state applies to mixtures just as to pure gases. It was in fact with a gas mixture, ordinary air, that Boyle, Gay-Lussac and Charles did their early experiments. The only new concept we need in order to deal with gas mixtures is the *partial pressure*, a concept invented by the famous English chemist John Dalton (1766-1844). Dalton reasoned that the low density and high compressibility of gases indicates that they consist mostly of empty space; from this it follows that when two or more different gases occupy the same volume, they behave entirely independently. The contribution that each component of a gaseous mixture makes to the total pressure of the gas is known as the *partial pressure* of that gas.

The definition of Dalton's Law of Partial Pressures that address this is:

The total pressure of a gas is the sum of the partial pressures of its components

which is expressed algebraically as

$$P_{total} = P_1 + P_2 + P_3 \ldots = \sum_i P_i$$

or, equivalently

$$P_{total} = \frac{RT}{V} \sum_i n_i$$

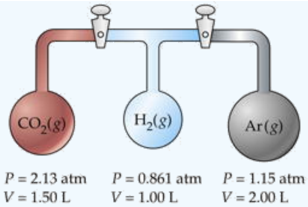
There is also a similar relationship based on *volume fractions*, known as *Amagat's law of partial volumes*. It is exactly analogous to Dalton's law, in that it states that the total volume of a mixture is just the sum of the partial volumes of its components. But there are two important differences: Amagat's law holds only for ideal gases which must all be at the same temperature and pressure. Dalton's law has neither of these restrictions. Although Amagat's law seems intuitively obvious, it sometimes proves useful in chemical engineering applications. We will make no use of it in this course.

✓ Example 8.4.10

Three flasks having different volumes and containing different gases at various pressures are connected by stopcocks as shown. When the stopcocks are opened,

a. What will be the pressure in the system?
b. Which gas will be most abundant in the mixture?

Assume that the temperature is uniform and that the volume of the connecting tubes is negligible.



Solution

The trick here is to note that the total number of moles n_T and the temperature remain unchanged, so we can make use of Boyle's law PV = constant. We will work out the details for CO_2 only, denoted by subscripts *a*.

For CO_2,

$$P_aV_a = (2.13\ atm)(1.50\ L) = 3.20\ L \cdot atm$$

Adding the PV products for each separate container, we obtain

\[A\sum_i P_i V_i = 6.36\; L \cdot atm = n_T RT \nonumber \]

We will call this sum P_1V_1. After the stopcocks have been opened and the gases mix, the new conditions are denoted by P_2V_2.

From Boyle's law (8.4.1,

$$P_1V_1 = P_2V_2 = 6.36\ L \cdot atm$$

$$V_2 = \sum_i V_i = 4.50\ L$$

Solving for the final pressure P_2 we obtain (6.36 L-atm)/(4.50 L) = **1.41 atm**.

For part *(b)*, note that the number of moles of each gas is $n = PV/RT$. The mole fraction of any one gas is $X_i = n_i / n_T$. For CO_2, this works out to (3.19/*RT*) / (6.36/*RT*) = 0.501. Because this exceeds 0.5, we know that this is the most abundant gas in the final mixture.

Dalton's law states that in a gas mixture (P_{total}) each gas will exert a pressure independent of the other gases (P_n) and each gas will behave as if it alone occupies the total volume. By extension, the partial pressure of each gas can be calculated by multiplying the total pressure (P_{total}) by the gas percentage (%).

$$P_{Total} = P_1 + P_2 + P_3 + P_4 + \ldots + P_n$$

or

$$P_n = \frac{\%\text{ of individual gas}_n}{P_{Total}}$$

Table 8.4.1: Partial Pressures for the gases in air on a typical day

Gas	Partial Pressure (mm Hg)	Percentage (%)
Nitrogen, (N_2\)	P_{N_2} = 594	78
Oxygen, O_2	P_{O_2} = 160	21
Carbon Dioxide, CO_2	P_{CO_2} = 0.25	0.033
Water Vapor, H_2O	P_{H_2O} = 5.7	0.75
Other trace gases	P_{Other} = 0.05	0.22
Total air	P_{Total} = 760	1

Application of Dalton's Law: Collecting Gases over Water

A common laboratory method of collecting the gaseous product of a chemical reaction is to conduct it into an inverted tube or bottle filled with water, the opening of which is immersed in a larger container of water. This arrangement is called a *pneumatic trough*, and was widely used in the early days of chemistry. As the gas enters the bottle it displaces the water and becomes trapped in the upper part.

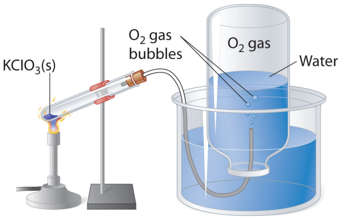


Figure 8.4.1:An Apparatus for Collecting Gases by the Displacement of Water

The volume of the gas can be observed by means of a calibrated scale on the bottle, but what about its pressure? The total pressure confining the gas is just that of the atmosphere transmitting its force through the water. (An exact calculation would also have to take into account the height of the water column in the inverted tube.) But liquid water itself is always in equilibrium with its vapor, so the space in the top of the tube is a mixture of two gases: the gas being collected, and gaseous H_2O. The partial pressure of H_2O is known as the vapor pressure of water and it depends on the temperature. In order to determine the quantity of gas we have collected, we must use Dalton's Law to find the partial pressure of that gas.

Example 8.4.11

Oxygen gas was collected over water as shown above. The atmospheric pressure was 754 torr, the temperature was 22°C, and the volume of the gas was 155 mL. The vapor pressure of water at 22°C is 19.8 torr. Use this information to estimate the number of moles of O_2 produced.

Solution

From Dalton's law,

$$P_{O_2} = P_{total} - P_{H_2O} = 754 - 19.8 = 734\ torr = 0.966\ atm$$

Now use the Ideal Gas Law to convert to moles

$$n = \frac{PV}{RT} = \frac{(0.966\ atm)(0.155\ L)}{(0.082\ Latmmol^{-1}K^{-1})(295\ K)} = 0.00619\ mol$$

Henry’s Law

Henry's law is one of the gas laws formulated by William Henry in 1803. It states: "At a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid." An equivalent way of stating the law is that the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the liquid.

To explain this law, Henry derived the equation:

$$C = kP_{gas}$$

where

Henry’s Law tells us that the greater the pressure of gas above the surface of a liquid, the higher the concentration of the gas in the liquid. Also, Henry’s law tells us that gases diffuse from areas of high gas concentration to areas of low gas concentration.

Applicability of Henry's Law

- Henry's law only works if the molecules are at equilibrium.
- Henry's law does not work for gases at high pressures (e.g., $N_{2\ (g)}$ at high pressure becomes very soluble and harmful when in the blood supply).

- Henry's law does not work if there is a chemical reaction between the solute and solvent (e.g., $HCl_{(g)}$ reacts with water by a dissociation reaction to generate H_3O^+ and Cl^- ions).

Application of Henry's Law: Scuba diving

Our respiratory systems are designed to maintain the proper oxygen concentration in the blood when the partial pressure of O_2 is 0.21 atm, its normal sea-level value. Below the water surface, the pressure increases by 1 atm for each 10.3 m increase in depth; thus a scuba diver at 10.3 m experiences a total of 2 atm pressure pressing on the body. In order to prevent the lungs from collapsing, the air the diver breathes should also be at about the same pressure.

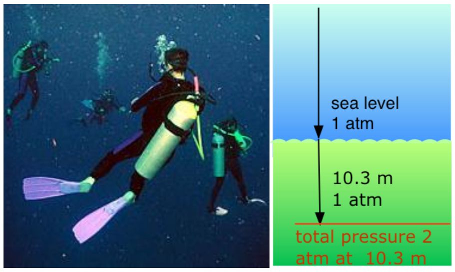


Figure 8.4.2: Scuba Diving actively takes into account both Henry's and Dalton's Laws

But at a total pressure of 2 atm, the partial pressure of O_2 in ordinary air would be 0.42 atm; at a depth of 100 ft (about 30 m), the O_2 pressure of 0.8 atm would be far too high for health. For this reason, the air mixture in the pressurized tanks that scuba divers wear must contain a smaller fraction of O_2. This can be achieved most simply by raising the nitrogen content, but high partial pressures of N_2 can also be dangerous, resulting in a condition known as nitrogen narcosis. The preferred diluting agent for sustained deep diving is helium, which has very little tendency to dissolve in the blood even at high pressures.

Career Focus: Respiratory Therapist

Certain diseases—such as emphysema, lung cancer, and severe asthma—primarily affect the lungs. Respiratory therapists help patients with breathing-related problems. They can evaluate, help diagnose, and treat breathing disorders and even help provide emergency assistance in acute illness where breathing is compromised.

Most respiratory therapists must complete at least two years of college and earn an associate’s degree, although therapists can assume more responsibility if they have a college degree. Therapists must also pass state or national certification exams. Once certified, respiratory therapists can work in hospitals, doctor’s offices, nursing homes, or patient’s homes. Therapists work with equipment such as oxygen tanks and respirators, may sometimes dispense medication to aid in breathing, perform tests, and educate patients in breathing exercises and other therapy.

Because respiratory therapists work directly with patients, the ability to work well with others is a must for this career. It is an important job because it deals with one of the most crucial functions of the body.

Key Takeaway

- The physical properties of gases are predictable using mathematical formulas known as gas laws.
- C is the solubility of a gas at a fixed temperature in a particular solvent (in units of M or mL gas/L)
- k is Henry's law constant (often in units of M/atm)
- P_{gas} is the partial pressure of the gas (often in units of Atm)

8.E: Solids, Liquids, and Gases (Exercises)

8.1: Intermolecular Interactions

Concept Review Exercise

1. What types of intermolecular interactions can exist in compounds?

2. What is the difference between covalent network and covalent molecular compounds?

Answer

1. ionic bonding, network covalent, dispersion forces, dipole-dipole interactions, and hydrogen bonding.

2. Covalent network compounds contain atoms that are covalently bonded to other individual atoms in a giant 3-dimensional network. Covalent molecular compounds contain individual molecules that are attracted to one another through dispersion, dipole-dipole or hydrogen bonding.

Exercises

1. List the three common phases in the order you are likely to find them—from lowest temperature to highest temperature.
2. List the three common phases in the order they exist from lowest energy to highest energy.
3. List these intermolecular interactions from weakest to strongest: London forces, hydrogen bonding, and ionic interactions.
4. List these intermolecular interactions from weakest to strongest: covalent network bonding, dipole-dipole interactions, and dispersion forces.
5. What type of intermolecular interaction is predominate in each substance?
    a. water (H_2O)
    b. sodium sulfate (Na_2SO_4)
    c. decane ($C_{10}H_{22}$)
6. What type of intermolecular interaction is predominate in each substance?
    a. diamond (C, crystal)
    b. helium (He)
    c. ammonia (NH_3)
7. Explain how a molecule like carbon dioxide (CO_2) can have polar covalent bonds but be nonpolar overall.
8. Sulfur dioxide (SO_2) has a formula similar to that of carbon dioxide (see Exercise 7) but is a polar molecule overall. What can you conclude about the shape of the SO_2 molecule?
9. What are some of the physical properties of substances that experience covalent network bonding?
10. What are some of the physical properties of substances that experience only dispersion forces?

Answers

1. solid, liquid, and gas

2. solid, liquid, and gas

3. London forces, hydrogen bonding, and ionic interactions

4. dispersion, dipole-dipole, network covalent

5. a. hydrogen bonding
    b. ionic interactions
    c. dispersion forces

6. a. network covalent
b. dispersion
c. hydrogen bonding

7. The two covalent bonds are oriented in such a way that their dipoles cancel out.

8. SO_2 is not a linear molecule. It has a bent or V-shape.

9. very hard, high melting point

10. very soft, very low melting point

8.2: Solids and Liquids

Concept Review Exercise

1. How do the strengths of intermolecular interactions in solids and liquids differ?

Answer

1. Solids have stronger intermolecular interactions than liquids do.

Exercises

1. What are the general properties of solids?
2. What are the general properties of liquids
3. What are the general properties of gases?
4. What phase or phases have a definite volume? What phase or phases do not have a definite volume?
5. Name a common substance that forms a crystal in its solid state.
6. Name a common substance that forms an amorphous solid in its solid state.
7. Are substances with strong intermolecular interactions likely to be solids at higher or lower temperatures? Explain.
8. Are substances with weak intermolecular interactions likely to be liquids at higher or lower temperatures? Explain.
9. State two similarities between the solid and liquid states.
10. State two differences between the solid and liquid states.
11. If individual particles are moving around with respect to each other, a substance may be in either the _______ or ________ state but probably not in the _______ state.
12. If individual particles are in contact with each other, a substance may be in either the ______ or _______ state but probably not in the ______ state.

Answers

1. hard, specific volume and shape, high density, cannot be compressed

2. fixed volume, no definite shape, high density, individual molecules touch each other but in a random way

3. variable volume and shape, low density, compressible

4. solid and liquid have definite volume; gas has no definite volume

5. sodium chloride (answers will vary)

6. glass

7. At higher temperatures, their intermolecular interactions are strong enough to hold the particles in place.

8. Substances with weak intermolecular interactions are likely to be liquids at lower temperatures. Their attractive forces are more easily broken hence they melt more readily.

9. high density; definite volume

10. Solids have definite shape while liquids don't. In solids, molecules occupy fixed positions in a pattern, while in liquids, the molecules are moving in a random arrangement.

11. liquid; gas; solid

12. solid; liquid; gas

8.3: Gases and Pressure

Concept Review Exercise

1. What is pressure, and what units do we use to express it?

Answer

1. Pressure is the force per unit area; its units can be pascals, torr, millimeters of mercury, or atmospheres.

Exercises

1. What is the kinetic theory of gases?
2. According to the kinetic theory of gases, the individual gas particles are (always, frequently, never) moving.
3. Why does a gas exert pressure?
4. Why does the kinetic theory of gases allow us to presume that all gases will show similar behavior?
5. Arrange the following pressure quantities in order from smallest to largest: 1 mmHg, 1 Pa, and 1 atm.
6. Which unit of pressure is larger—the torr or the atmosphere?
7. How many torr are there in 1.56 atm?
8. Convert 760 torr into pascals.
9. Blood pressures are expressed in millimeters of mercury. What would be the blood pressure in atmospheres if a patient's systolic blood pressure is 120 mmHg and the diastolic blood pressure is 82 mmHg? (In medicine, such a blood pressure would be reported as "120/82," spoken as "one hundred twenty over eighty-two.")
10. In weather forecasting, barometric pressure is expressed in inches of mercury (in. Hg), where there are exactly 25.4 mmHg in every 1 in. Hg. What is the barometric pressure in millimeters of mercury if the barometric pressure is reported as 30.21 in. Hg?

Answers

1. Gases are composed of tiny particles that are separated by large distances. Gas particles are constantly moving, experiencing collisions with other gas particles and the walls of their container. The velocity of gas particles is related to the temperature of a gas. Gas particles do not experience any force of attraction or repulsion with each other.
2. always
3. A gas exerts pressure as its particles rebound off the walls of its container.
4. Because the molecules are far apart and don't have attractive forces between them
5. 1 Pa, 1 mmHg, and 1 atm
6. atm
7. 1,190 torr
8. 98,700 Pa
9. 0.158 atm; 0.108 atm
10. 767.3 mm Hg

8.4: Gas Laws

Concept Review Exercises

1. What properties do the gas laws help us predict?
2. What makes the ideal gas law different from the other gas laws?

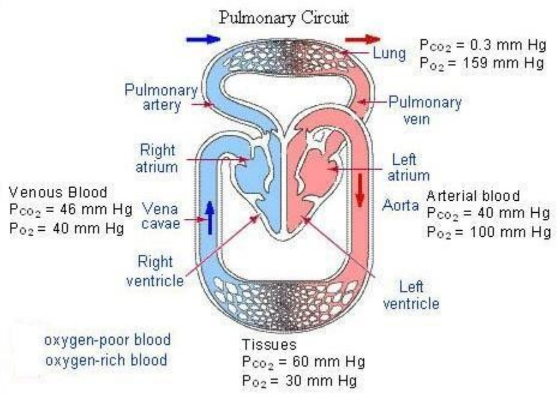
Answers

1. Gas laws relate four properties: pressure, volume, temperature, and number of moles.
2. The ideal gas law does not require that the properties of a gas change.

Exercises

1. What conditions of a gas sample should remain constant for Boyle's law to be used?
2. What conditions of a gas sample should remain constant for Charles's law to be used?
3. Does the identity of a gas matter when using Boyle's law? Why or why not?
4. Does the identity of a gas matter when using Charles's law? Why or why not?
5. A sample of nitrogen gas is confined to a balloon that has a volume of 1.88 L and a pressure of 1.334 atm. What will be the volume of the balloon if the pressure is changed to 0.662 atm? Assume that the temperature and the amount of the gas remain constant.
6. A sample of helium gas in a piston has a volume of 86.4 mL under a pressure of 447 torr. What will be the volume of the helium if the pressure on the piston is increased to 1,240 torr? Assume that the temperature and the amount of the gas remain constant.
7. If a gas has an initial pressure of 24,650 Pa and an initial volume of 376 mL, what is the final volume if the pressure of the gas is changed to 775 torr? Assume that the amount and the temperature of the gas remain constant.
8. A gas sample has an initial volume of 0.9550 L and an initial pressure of 564.5 torr. What would the final pressure of the gas be if the volume is changed to 587.0 mL? Assume that the amount and the temperature of the gas remain constant.
9. A person draws a normal breath of about 1.00 L. If the initial temperature of the air is 18°C and the air warms to 37°C, what is the new volume of the air? Assume that the pressure and amount of the gas remain constant.
10. A person draws a normal breath of about 1.00 L. If the initial temperature of the air is −10°C and the air warms to 37°C, what is the new volume of the air? Assume that the pressure and the amount of the gas remain constant.
11. An air/gas vapor mix in an automobile cylinder has an initial temperature of 450 K and a volume of 12.7 cm^3. The gas mix is heated to 565°C. If pressure and amount are held constant, what is the final volume of the gas in cubic centimeters?
12. Given the following conditions for a gas: $V_i = 0.665$ L, $T_i = 23.6$°C, $V_f = 1.034$ L. What is T_f in degrees Celsius and kelvins?
13. Assuming the amount remains the same, what must be the final volume of a gas that has an initial volume of 387 mL, an initial pressure of 456 torr, an initial temperature of 65.0°C, a final pressure of 1.00 atm, and a final temperature of 300 K?
14. When the nozzle of a spray can is depressed, 0.15 mL of gas expands to 0.44 mL, and its pressure drops from 788 torr to 1.00 atm. If the initial temperature of the gas is 22.0°C, what is the final temperature of the gas?
15. Use the ideal gas law to show that 1 mol of a gas at STP has a volume of about 22.4 L.
16. Use a standard conversion factor to determine a value of the ideal gas law constant R that has units of L•torr/mol•K.
17. How many moles of gas are there in a 27.6 L sample at 298 K and a pressure of 1.44 atm?
18. How many moles of gas are there in a 0.066 L sample at 298 K and a pressure of 0.154 atm?
19. A 0.334 mol sample of carbon dioxide gas is confined to a volume of 20.0 L and has a pressure of 0.555 atm. What is the temperature of the carbon dioxide in kelvins and degrees Celsius?
20. What must V be for a gas sample if $n = 4.55$ mol, $P = 7.32$ atm, and $T = 285$ K?
21. What is the pressure of 0.0456 mol of Ne gas contained in a 7.50 L volume at 29°C?
22. What is the pressure of 1.00 mol of Ar gas that has a volume of 843.0 mL and a temperature of −86.0°C?
23. A mixture of the gases N_2, O_2, and Ar has a total pressure of 760 mm Hg. If the partial pressure of N_2 is 220 mm Hg and of O_2 is 470 mm Hg, What is the partial pressure of Ar?
24. What percent of the gas above is Ar?
25. Apply Henry's Law to the diagram below to explain:

why oxygen diffuses from the alveoli of the lungs into the blood and from the blood into the tissues of the body. why carbon dioxide diffuses from the tissues into the blood and from the blood into the alveoli and then finally out into the atmosphere.



Answers

1. temperature and amount of the gas

2. pressure and amount of the gas
3. The identity does not matter because the variables of Boyle's law do not identify the gas.
4. The identity does not matter because the variables of Charles law do not identify the gas.
5. 3.79 L

6. 31.1 mL

7. 92.1 mL

8. 918.4 torr

9. 1.07 L

10. 1.18 L

11. 23.7 cm^3

12. 461 K; 188^0C

13. 206 mL

14. 835 K; 562^0C

15. The ideal gas law confirms that 22.4 L equals 1 mol.

16. $\frac{760\ torr}{1\ atm}$

17. 1.63 mol

18. 4.2 x 10^{-4} mol

19. 405 K; 132°C

20. 14.5 L

21. 0.151 atm

22. 18.2 atm

23. 70 mm Hg

24. 9.2%

25. Gases diffuse from high concentration to low concentration (Henry's Law). The partial pressure of **oxygen** is high in the **alveoli** and low in the **blood** of the pulmonary capillaries. As a result, **oxygen diffuses** across the respiratory membrane from the **alveoli** into the **blood**. It's also higher partial pressure in the blood than in the tissues, hence it transfers to the tissues. On the other hand,

carbon dioxide **diffuses** from the tissues (highest CO_2 partial pressure) and across the respiratory membrane from the **blood** into the **alveoli** and out **to the atmosphere.**

Additional Exercises

1. How many grams of oxygen gas are needed to fill a 25.0 L container at 0.966 atm and 22°C?
2. A breath of air is about 1.00 L in volume. If the pressure is 1.00 atm and the temperature is 37°C, what mass of air is contained in each breath? Use an average molar mass of 28.8 g/mol for air.
3. The balanced chemical equation for the combustion of propane is as follows:

   $$C_3H_{8(g)} + 5O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(\ell)} \tag{8.E.1}$$

   a. If 100.0 g of propane are combusted, how many moles of oxygen gas are necessary for the reaction to occur?
   b. At STP, how many liters of oxygen gas would that be?
4. The equation for the formation of ammonia gas (NH_3) is as follows:

   $$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)} \tag{8.E.2}$$

   At 500°C and 1.00 atm, 10.0 L of N_2 gas are reacted to make ammonia.

   a. If the pressures and temperatures of H_2 and NH_3 were the same as those of N_2, what volume of H_2 would be needed to react with N_2, and what volume of NH_3 gas would be produced?
   b. Compare your answers to the balanced chemical equation. Can you devise a “shortcut” method to answer Exercise 4a?
5. At 20°C, 1 g of liquid H_2O has a volume of 1.002 mL. What volume will 1 g of water vapor occupy at 20°C if its pressure is 17.54 mmHg? By what factor has the water expanded in going from the liquid phase to the gas phase?
6. At 100°C, 1 g of liquid H_2O has a volume of 1.043 mL. What volume will 1 g of steam occupy at 100°C if its pressure is 760.0 mmHg? By what factor has the water expanded in going from the liquid phase to the gas phase?
7. Predict whether NaCl or NaI will have the higher melting point. Explain. (Hint: consider the relative strengths of the intermolecular interactions of the two compounds.)
8. Predict whether CH_4 or CH_3OH will have the lower boiling point. Explain. (Hint: consider the relative strengths of the intermolecular interactions of the two compounds.)
9. A standard automobile tire has a volume of about 3.2 ft^3 (where 1 ft^3 equals 28.32 L). Tires are typically inflated to an absolute pressure of 45.0 pounds per square inch (psi), where 1 atm equals 14.7 psi. Using this information with the ideal gas law, determine the number of moles of air needed to fill a tire if the air temperature is 18.0°C.
10. Another gas law, Amontons’s law, relates pressure and temperature under conditions of constant amount and volume:

    $$\frac{\mathrm{P_i}}{\mathrm{T_i}} = \frac{\mathrm{P_f}}{\mathrm{T_f}}$$

    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.

$$10.0\ \mathrm{L\ N_2} \times \frac{3\ \mathrm{L\ H_2}}{1\ \mathrm{L\ N_2}} = 30.0\ \mathrm{L\ H_2}$$

$$10.0\ \mathrm{L\ N_2} \times \frac{2\ \mathrm{L\ NH_3}}{1\ \mathrm{L\ N_2}} = 20.0\ \mathrm{L\ NH_3}$$

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

8.S: Solids, Liquids, and Gases (Summary)

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

A **phase** is a certain form of matter that has the same physical properties throughout. Three phases are common: the solid, the liquid, and the gas phase. What determines the phase of a substance? Generally, the strength of the **intermolecular interactions** determines whether a substance is a solid, liquid, or gas under any particular conditions. **Covalent network bonding** is a very strong form of intermolecular interaction. Diamond is one example of a substance that has this intermolecular interaction. **Ionic interactions**, the forces of attraction due to oppositely charged ions, are also relatively strong. Covalent bonds are another type of interaction within molecules, but if the bonds are **polar covalent bonds**, then the unequal sharing of electrons can cause charge imbalances within molecules that cause interactions between molecules. These molecules are described as **polar**, and these interactions are called **dipole-dipole interactions**. A certain rather strong type of dipole-dipole interaction, involving a hydrogen atom, is called **hydrogen bonding**. On the other hand, equal sharing of electrons forms **nonpolar covalent bonds**, and the interactions between different molecules is less because the molecules are nonpolar. All substances have very weak **dispersion forces** (also called **London forces**) caused by the movement of electrons within the bonds themselves.

In the solid phase, intermolecular interactions are so strong that they hold the individual atoms or molecules in place. In many solids, the regular three-dimensional arrangement of particles makes a **crystal**. In other solids, the irregular arrangement of particles makes an **amorphous** solid. In liquids, the intermolecular interactions are strong enough to keep the particles of substance together but not in place. Thus, the particles are free to move over each other but still remain in contact.

In gases, the intermolecular interactions are weak enough that the individual particles are separated from each other in space. The **kinetic theory of gases** is a collection of statements that describe the fundamental behavior of all gases. Among other properties, gases exert a **pressure** on their container. Pressure is measured using units like **pascal**, **bar**, **atmosphere**, or **mmHg** (also called a **torr**).

There are several simple relationships between the variables used to describe a quantity of gas. These relationships are called **gas laws**. **Boyle's law** relates the pressure and volume of a gas, while **Charles's law** relates the volume and absolute temperature of a gas. The **combined gas law** relates the volume, pressure, and absolute temperature of a gas sample. All of these gas laws allow us to understand the changing conditions of a gas. The **ideal gas law** relates the pressure, volume, amount, and absolute temperature of a gas under any conditions. These four variables are related to the **ideal gas law constant**, which is the proportionality constant used to calculate the conditions of a gas. Because the conditions of a gas can change, a set of benchmark conditions called **standard temperature and pressure (STP)** is defined. Standard temperature is 0ºC, and standard pressure is 1.00 atm.

CHAPTER OVERVIEW

9: Solutions

Solutions are all around us. Air, for example, is a solution. If you live near a lake, a river, or an ocean, that body of water is not pure H_2O but most probably a solution. Much of what we drink—for example, soda, coffee, tea, and milk—is at least in part a solution. Solutions are a large part of everyday life. A lot of the chemistry occurring around us happens in solution. In fact, much of the chemistry that occurs in our own bodies takes place in solution, and many solutions—such as the Ringer's lactate IV solution—are important for our health. In our understanding of chemistry, we need to understand a little bit about solutions. In this chapter, you will learn about the special characteristics of solutions, how solutions are characterized, and some of their properties.

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9.0: Prelude to Solutions

If you watch any of the medical dramas on television, you may have heard a doctor (actually an actor) call for an intravenous solution of “Ringer’s lactate” (or “lactated Ringer’s” or "Ri-Lac"). So what is Ringer’s lactate?

Intravenous (IV) solutions are administered for two main reasons:

1. to introduce necessary substances into the bloodstream, such as ions for proper body function, sugar and other food substances for energy, or drugs to treat a medical condition, and
2. to increase the volume of the bloodstream.

Many people with acute or long-term medical conditions have received some type of an IV solution.

One basic IV solution, called a *normal saline solution*, is simply a dilute solution of NaCl dissolved in water. Normal saline is 9.0 g of NaCl dissolved in each liter of solution. *Ringer’s lactate* is a normal saline solution that also has small amounts of potassium and calcium ions mixed in. In addition, it contains about 2.5 g of lactate ions ($C_3H_5O_3^-$) per liter of solution. The liver metabolizes lactate ions into bicarbonate (HCO_3^-) ions, which help maintain the acid-base balance of blood. Many medical problems, such as heart attacks and shock, affect the acid-base balance of blood, and the presence of lactate in the IV solution eases problems caused by this imbalance.

Physicians can select from a range of premade IV solutions, in accordance with a patient’s particular needs. Ringer’s lactate is commonly used when a patient’s blood volume must be increased quickly. Another frequently used IV solution, called D5W, is a 5% solution of dextrose (a form of sugar) in water.

9.1: Solutions

Learning Objectives

- To understand what causes solutions to form.

A solution is another name for a homogeneous mixture. A *mixture* as a material composed of two or more substances. In a solution, the combination is so intimate that the different substances cannot be differentiated by sight, even with a microscope. Compare, for example, a mixture of salt and pepper and another mixture consisting of salt and water. In the first mixture, we can readily see individual grains of salt and the flecks of pepper. A mixture of salt and pepper is not a solution. However, in the second mixture, no matter how carefully we look, we cannot see two different substances. Salt dissolved in water is a solution.

The major component of a solution, called the **solvent**, is typically the same phase as the solution itself. Each minor component of a solution (and there may be more than one) is called the **solute**. In most of the solutions we will describe in this textbook, there will be no ambiguity about whether a component is the solvent or the solute. For example, in a solution of salt in water, the solute is salt, and solvent is water.

Solutions come in all phases, and the solvent and the solute do not have to be in the same phase to form a solution (such as salt and water). For example, air is a gaseous solution of about 80% nitrogen and about 20% oxygen, with some other gases present in much smaller amounts. An alloy is a solid solution consisting of a metal (like iron) with some other metals or nonmetals dissolved in it. Steel, an alloy of iron and carbon and small amounts of other metals, is an example of a solid solution. Table $9.1.1$ lists some common types of solutions, with examples of each.

Table $9.1.1$: Types of Solutions

Solvent Phase	Solute Phase	Example
gas	gas	air
liquid	gas	carbonated beverages
liquid	liquid	ethanol (C_2H_5OH) in H_2O (alcoholic beverages)
liquid	solid	saltwater
solid	gas	H_2 gas absorbed by Pd metal
solid	liquid	Hg(ℓ) in dental fillings
solid	solid	steel alloys

What causes a solution to form? The simple answer is that the solvent and the solute must have similar intermolecular interactions. When this is the case, the individual particles of solvent and solute can easily mix so intimately that each particle of solute is surrounded by particles of solvent, forming a solution. However, if two substances have very different intermolecular interactions, large amounts of energy are required to force their individual particles to mix intimately, so a solution does not form. Thus two alkanes like *n*-heptane, C_7H_{16}, and *n*-hexane, C_6H_{14}, are completely miscible in all proportions. The C_7H_{16} and C_6H_{14} molecules are so similar (recall Section 4.6) that there are only negligible differences in intermolecular forces.

For a similar reason, methanol, CH_3OH, is completely miscible with water. In this case both molecules are polar and can form hydrogen bonds among themselves, and so there are strong intermolecular attractions within each liquid. However, CH_3OH dipoles can align with H_2O dipoles, and CH_3OH molecules can hydrogen bond to H_2O molecules, and so the attractions among unlike molecules in the solution are similar to those among like molecules in each pure liquid.

This process leads to a simple rule of thumb: *like dissolves like*. Solvents that are very polar will dissolve solutes that are very polar or even ionic. Solvents that are nonpolar will dissolve nonpolar solutes. Thus water, being polar, is a good solvent for ionic compounds and polar solutes like ethanol (C_2H_5OH). However, water does not dissolve nonpolar solutes, such as many oils and greases (Figure $9.1.1$).

Figure 9.1.1: A beaker holds water with blue food dye (upper liquid layer) and a much more dense perfluoroheptane (a fluorocarbon) lower liquid layer. The two fluids cannot mix and the dye cannot dissolve in fluorocarbon. A goldfish and a crab have been introduced into the water. The goldfish cannot penetrate the dense fluorocarbon. The crab floats at the liquid boundary with only parts of his legs penetrating the fluorocarbon fluid, unable to sink to the bottom of the beaker. Quarter coins rest on the bottom of the beaker. Animals were rescued from their predicament after the photo was taken. Figure used with permission from Wikipedia (Sbharris (Steven B. Harris)).

We use the word soluble to describe a solute that dissolves in a particular solvent, and the word insoluble for a solute that does not dissolve in a solvent. Thus, we say that sodium chloride is soluble in water but insoluble in hexane (C_6H_{14}). If the solute and the solvent are both liquids and soluble in any proportion, we use the word miscible, and the word immiscible if they are not.

✓ Example 9.1.1

Water is considered a polar solvent. Which substances should dissolve in water?

1. methanol (CH_3OH)
2. sodium sulfate (Na_2SO_4)
3. octane (C_8H_{18})

Solution

Because water is polar, substances that are polar or ionic will dissolve in it.

1. Because of the OH group in methanol, we expect its molecules to be polar. Thus, we expect it to be soluble in water. As both water and methanol are liquids, the word *miscible* can be used in place of *soluble*.
2. Sodium sulfate is an ionic compound, so we expect it to be soluble in water.
3. Like other hydrocarbons, octane is nonpolar, so we expect that it would not be soluble in water.

? Exercise 9.1.1

Toluene ($C_6H_5CH_3$) is widely used in industry as a nonpolar solvent. Which substances should dissolve in toluene?

a. water (H_2O)
b. sodium sulfate (Na_2SO_4)
c. octane (C_8H_{18})

Answer

Octane only.

✓ Example 9.1.2

Predict which of the following compounds will be most soluble in water:

a. $\underset{\text{Ethanol}}{CH_3CH_2OH}$
b. $\underset{\text{Hexanol}}{CH_3CH_2CH_2CH_2CH_2CH_2OH}$

Solution

Since ethanol contains an **OH** group, it can hydrogen bond to water. Although the same is true of hexanol, the OH group is found only at one end of a fairly large molecule. The rest of the molecule can be expected to behave much as though it were a nonpolar alkane. This substance should thus be much less soluble than the first. Experimentally we find that ethanol is completely miscible with water, while only 0.6 g hexanol dissolves in 100 g water.

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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.

9.2: Concentration

Learning Objectives

- Calculate percentage concentration (m/m, v/v, m/v), ppm and ppb.
- Calculate the molarity of a solution.
- Use concentration units to calculate the amount of solute in a solution.
- Use molarity to determine quantities in chemical reactions.
- Determine the resulting concentration of a diluted solution.

To define a solution precisely, we need to state its concentration: how much solute is dissolved in a certain amount of solvent. Words such as *dilute* or *concentrated* are used to describe solutions that have a little or a lot of dissolved solute, respectively, but these are relative terms whose meanings depend on various factors.

Solubility

There is usually a limit to how much solute will dissolve in a given amount of solvent. This limit is called the **solubility** of the solute. Some solutes have a very small solubility, while other solutes are soluble in all proportions. Table 9.2.1 lists the solubilities of various solutes in water. Solubilities vary with temperature, so Table 9.2.1 includes the temperature at which the solubility was determined.

Table 9.2.1: Solubilities of Various Solutes in Water at 25°C (Except as Noted)

Substance	Solubility (g in 100 mL of H2O)
AgCl(s)	0.019
$C_6H_6(\ell)$ (benzene)	0.178
$CH_4(g)$	0.0023
$CO_2(g)$	0.150
$CaCO_3(s)$	0.058
$CaF_2(s)$	0.0016
$Ca(NO_3)_2(s)$	143.9
$C_6H_{12}O_6$ (glucose)	120.3 (at 30°C)
KBr(s)	67.8
$MgCO_3(s)$	2.20
NaCl(s)	36.0
$NaHCO_3(s)$	8.41
$C_{12}H_{22}O_{11}$ (sucrose)	204.0 (at 20°C)

If a solution contains so much solute that its solubility limit is reached, the solution is said to be **saturated**, and its concentration is known from information contained in Table 9.2.1. If a solution contains less solute than the solubility limit, it is **unsaturated**. Under special circumstances, more solute can be dissolved even after the normal solubility limit is reached; such solutions are called ***supersaturated*** and are not stable. If the solute is solid, excess solute can easily recrystallize. If the solute is a gas, it can bubble out of solution uncontrollably, like what happens when you shake a soda can and then immediately open it.

Precipitation from Supersaturated Solutions

Recrystallization of excess solute from a supersaturated solution usually gives off energy as heat. Commercial heat packs containing supersaturated sodium acetate ($NaC_2H_3O_2$) take advantage of this phenomenon. You can probably find them at your local drugstore.

Video* 9.2.1*: Watered-down sodium acetate trihydrate. Needle crystal is truly wonderful structures

Most solutions we encounter are unsaturated, so knowing the solubility of the solute does not accurately express the amount of solute in these solutions. There are several common ways of specifying the concentration of a solution.

Percent Composition

There are several ways of expressing the concentration of a solution by using a percentage. The **mass/mass percent** (% m/m) is defined as the mass of a solute divided by the mass of a solution times 100:

$$\%\ \mathrm{m/m} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

If you can measure the masses of the solute and the solution, determining the mass/mass percent is easy. Each mass must be expressed in the same units to determine the proper concentration.

✓ Example 9.2.1

A saline solution with a mass of 355 g has 36.5 g of NaCl dissolved in it. What is the mass/mass percent concentration of the solution?

Solution

We can substitute the quantities given in the equation for mass/mass percent:

$$\%\ \mathrm{m/m} = \frac{36.5\ \mathrm{g}}{355\ \mathrm{g}} \times 100\% = 10.3\%$$

? Exercise 9.2.1

A dextrose (also called D-glucose, $C_6H_{12}O_6$) solution with a mass of 2.00×10^2 g has 15.8 g of dextrose dissolved in it. What is the mass/mass percent concentration of the solution?

Answer

7.90%

For gases and liquids, volumes are relatively easy to measure, so the concentration of a liquid or a gas solution can be expressed as a **volume/volume percent** (% v/v): the volume of a solute divided by the volume of a solution times 100:

$$\%\ \mathrm{v/v} = \frac{\text{volume of solute}}{\text{volume of solution}} \times 100\%$$

Again, the units of the solute and the solution must be the same. A hybrid concentration unit, **mass/volume percent** (% m/v), is commonly used for intravenous (IV) fluids (Figure 9.2.1). It is defined as the mass in grams of a solute, divided by volume in milliliters of solution times 100:

$$\% \mathrm{~m/v}=\frac{\text{mass of solute (g)}}{\text{volume of solution (mL)}} \times 100\%$$

Figure 9.2.1: Mass/Volume Percent.The 0.9% NaCl concentration on this IV bag is mass/volume percent (left). Such solution is used for other purposes and available in bottles (right). Figures used with permission from Wikipedia

Using Percent Composition in Calculations

The **percent concentration** can be used to produce a **conversion factor** between the **amount of solute** and the **amount of solution**. As such, concentrations can be useful in a variety of stoichiometry problems as discussed in Chapter 6. In many cases, it is best to use the original definition of the concentration unit; it is that definition that provides the conversion factor.

As an example, if the given concentration is **5% v/v solution of alcohol**, this means that there are 5 mL of alcohol dissolved in every 100 mL solution.

5 mL alcohol = 100 mL solution

The two possible conversion factors are written as follows:

$$\frac{\mathbf{5\ mL\ alcohol}}{\mathbf{100\ mL\ solution}} \text{ or } \frac{\mathbf{100\ mL\ solution}}{\mathbf{5\ mL\ alcohol}}$$

Use the first conversion factor to convert from a given amount of solution to amount of solute. The second conversion factor is used to convert from a given amount of solute to amount of solution. Given any two quantities in any percent composition, the third quantity can be calculated, as the following example illustrates.

✓ Example 9.2.2

A sample of 45.0% v/v solution of ethanol (C_2H_5OH) in water has a volume of 115 mL. What volume of ethanol solute does the sample contain?

Solution

A percentage concentration is simply the number of parts of solute per 100 parts of solution. Thus, the percent concentration of 45.0% v/v implies the following:

$$45.0\% \mathrm{~v/v} \rightarrow \frac{45 \mathrm{~mL~} C_2H_5OH}{100 \mathrm{~mL~solution}}$$

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:

$$115 \mathrm{~mL~solution} \times \frac{45 \mathrm{~mL~} C_2H_5OH}{100 \mathrm{~mL~solution}} = 51.8 \mathrm{~mL~} C_2H_5OH$$

? Exercise 9.2.2

What volume of a 12.75% m/v solution of glucose ($C_6H_{12}O_6$) in water is needed to obtain 50.0 g of $C_6H_{12}O_6$?

Answer

$$50.0 \text{ g } C_6H_12O_6 \times \frac{100 \text{ mL solution}}{12.75 \text{ g } C_6H_12O_6} = 392 \text{ mL solution}$$

✓ Example 9.2.3

A normal saline IV solution contains 9.0 g of NaCl in every liter of solution. What is the mass/volume percent of normal saline?

Solution

We can use the definition of mass/volume percent, but first we have to express the volume in milliliter units:

1 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 9.2.3

The chlorine bleach that you might find in your laundry room is typically composed of 27.0 g of sodium hypochlorite (NaOCl), dissolved to make 500.0 mL of solution. What is the mass/volume percent of the bleach?

Answer

$$\% \text{ m/v} = \frac{27.0 \text{ g NaOCl}}{500.0 \text{ mL solution}} \times 100\% = 5.40\% \text{ m/v}$$

In addition to percentage units, the units for expressing the concentration of extremely dilute solutions are parts per million (ppm) and parts per billion (ppb). Both of these units are mass based and are defined as follows:

$$\text{ppm} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 1,000,000$$

$$\text{ppb} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 1,000,000,000$$

> *Similar to parts per million and parts per billion, related units include parts per thousand (ppth) and parts per trillion (ppt).*

Concentrations of *trace elements* in the body—elements that are present in extremely low concentrations but are nonetheless necessary for life—are commonly expressed in parts per million or parts per billion. Concentrations of poisons and pollutants are also described in these units. For example, cobalt is present in the body at a concentration of 21 ppb, while the State of Oregon's Department of Agriculture limits the concentration of arsenic in fertilizers to 9 ppm.

> *In aqueous solutions, 1 ppm is essentially equal to 1 mg/L, and 1 ppb is equivalent to 1 µg/L.*

✓ Example 9.2.4

If the concentration of cobalt in a human body is 21 ppb, what mass in grams of Co is present in a body having a mass of 70.0 kg?

Solution

A concentration of 21 ppb means “21 g of solute per 1,000,000,000 g of solution.” Written as a **conversion factor,** this concentration of Co is as follows:

$$21 \text{ ppb Co} \rightarrow \frac{21 \text{ g Co}}{1,000,000,000 \text{ g solution}}$$

We can use this as a conversion factor, but first we must convert 70.0 kg to gram units:

$$70.0 \text{ kg} \times \frac{1,000 \text{ g}}{1 \text{ kg}} = 7.00 \times 10^4 \text{ g}$$

Now we determine the amount of Co:

$$7.00 \times 10^4 \text{ g solution} \times \frac{21 \text{ g Co}}{1,000,000,000 \text{ g solution}} = 0.0015 \text{ g Co}$$

This is only 1.5 mg.

? Exercise 9.2.4

An 85 kg body contains 0.012 g of Ni. What is the concentration of Ni in parts per million?

Answer

0.14 ppm

Molarity

Another way of expressing concentration is to give the number of moles of solute per unit volume of solution. Such concentration units are useful for discussing chemical reactions in which a solute is a product or a reactant. Molar mass can then be used as a conversion factor to convert amounts in moles to amounts in grams.

Molarity is defined as the number of moles of a solute dissolved per liter of solution:

$$\text{molarity} = \frac{\text{number of moles of solute}}{\text{number of liters of solution}}$$

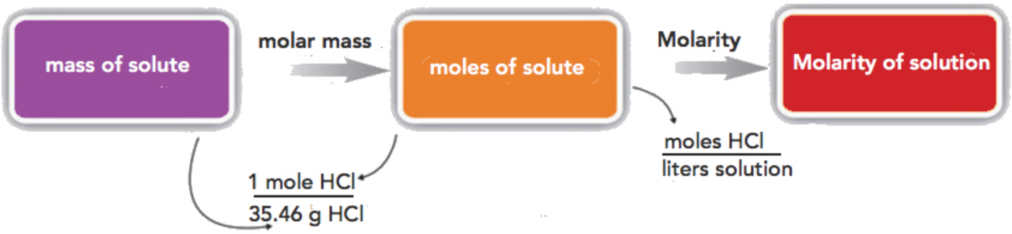
Molarity is abbreviated M (often referred to as “molar”), and the units are often abbreviated as mol/L. It is important to remember that “mol” in this expression refers to moles of solute and that “L” refers to liters of solution. For example, if you have 1.5 mol of NaCl dissolved in 0.500 L of solution, its molarity is therefore

$$\frac{1.5 \text{ mol NaCl}}{0.500 \text{ L solution}} = 3.0 \text{ M NaCl}$$

which is read as “three point oh **molar** sodium chloride.” Sometimes (aq) is added when the solvent is water, as in “3.0 M NaCl(aq).”

Before a molarity concentration can be calculated, the amount of the **solute must be expressed in moles**, and the **volume of the solution** must be expressed in **liters**.

If the quantity of the solute is given in mass units, you must convert mass units to mole units before using the definition of molarity to calculate concentration. For example, what is the molar concentration of a solution of 22.4 g of HCl dissolved in 1.56 L?



Step 1: convert the **mass of solute** to **moles** using the **molar mass of HCl (36.46 g/mol):**

$$22.4\ g\cancel{HCl} \times \frac{1\ mol\ HCl}{36.46\ g\cancel{HCl}} = 0.614\ mol\ HCl$$

Step 2: use the **definition of molarity** to determine the concentration:

$$M\ = \frac{0.614\ mol\ HCl}{1.56L\ solution} = 0.394\ MHCl$$

Example 9.2.5

What is the molarity of an aqueous solution of 25.0 g of NaOH in 750 mL?

Solution

Before we substitute these quantities into the definition of molarity, we must convert them to the proper units. The mass of NaOH must be converted to moles of NaOH. The molar mass of NaOH is 40.00 g/mol:

$$25.0\text{ g NaOH} \times \frac{1\text{ mol NaOH}}{40.00\text{ g NaOH}} = 0.625\text{ mol NaOH}$$

Next, we convert the volume units from milliliters to liters:

$$750\text{ mL} \times \frac{1\text{ L}}{1,000\text{ mL}} = 0.750\text{ L}$$

Now that the quantities are expressed in the proper units, we can substitute them into the definition of molarity:

$$\text{M} = \frac{0.625\text{ mol NaOH}}{0.750\text{ L}} = 0.833\text{ M NaOH}$$

Exercise 9.2.5

If a 350 mL cup of coffee contains 0.150 g of caffeine ($C_8H_{10}N_4O_2$), what is the molarity of this caffeine solution?

Answer

0.00221 M

Using Molarity in Calculations

The definition of molarity can also be used to calculate a needed volume of solution, given its concentration and the number of moles desired, or the number of moles of solute (and subsequently, the mass of the solute), given its concentration and volume. As in the percent concentration, molarity can also be expressed as a **conversion factor**.

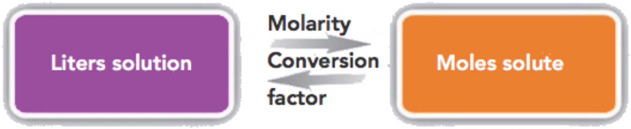
Molarity is defined as moles solute per liter solution. There is an understood 1 in the denominator of the conversion factor. For example, a **3.0 M solution of sucrose** means that there are three moles of sucrose dissolved in every **liter of solution**. Mathematically, this is stated as follows:

3.0 moles sucrose = 1 L solution

Dividing both sides of this expression by either side, we generate two possible conversion factors:

$$\frac{\mathbf{3.0\ mol\ sucrose}}{\mathbf{1\ L\ solution}} \text{ or } \frac{\mathbf{1\ L\ solution}}{\mathbf{3.0\ mol\ sucrose}}$$

The first conversion factor can be used to convert from *volume (L) of solution to moles solute*, and the *second converts from moles of solute to volume (L) of solution*.



For example, suppose we are asked how many moles of sucrose are present in 0.108 L of a 3.0 M sucrose solution. The given volume (0.108 L) is multiplied by the first conversion factor to cancel the L units, and find that 0.32 moles of sucrose are present.

$$0.108\ L\ \cancel{solution} \times \frac{3.0\, mol\ sucrose}{1 L\ \cancel{solution}} = 0.32\, mol\ sucrose$$

How many liters of 3.0 M sucrose solution are needed to obtain 4.88 mol of sucrose? In such a conversion, we multiply the given (4.88 moles sucrose) with the second conversion factor. This cancels the moles units and converts it to liters of solution.

$$4.88\ mol\ \cancel{sucrose} \times \frac{1\ L\ solution}{3.0\ mol\ \cancel{sucrose}} = 1.63\ L\ solution$$

✓ Example 9.2.6

1. What volume of a 0.0753 M solution of dimethylamine [$(CH_3)_2NH$] is needed to obtain 0.450 mol of the compound?
2. Ethylene glycol ($C_2H_6O_2$) is mixed with water to make auto engine coolants. How many grams of $C_2H_6O_2$ are in 5.00 L of a 6.00 M aqueous solution?

Solution

1. To solve for the volume, multiply the "given" (0.450 mol of dimethylamine) with the molarity conversion factor (0.0753 M). Use the proper conversion factor to cancel the unit "mol" and get the unit volume (L) of solution:

$$0.450 \text{ mol dimethylamine} \times \frac{1 \text{ L solution}}{0.0753 \text{ mol dimethylamine}} = 5.98 \text{ L solution}$$

2. The strategy in solving this problem is to convert the given volume (5.00 L) using the 6.00 M (conversion factor) to solve for moles of ethylene glycol, which can then be converted to grams.

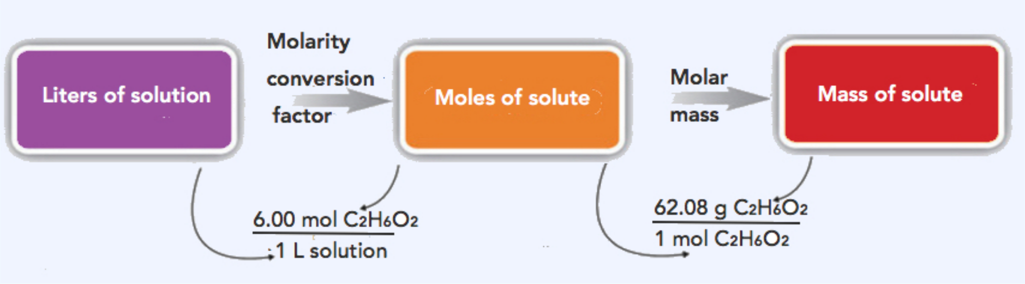
Step 1: Convert the given volume (5.00 L) to moles ethylene glycol.

$$5.00 \text{ L solution} \times \frac{6.00 \text{ mol } C_2H_6O_2}{1 \text{ L solution}} = 30.0 \text{ mol } C_2H_6O_2$$

Step 2: Convert 30.0 mols $C_2H_6O_2$ to grams $C_2H_6O_2$. Molar mass of $C_2H_6O_2$= 62.08 g/mol

$$30.0 \text{ mol } C_2H_6O_2 \times \frac{62.08 \text{ g } C_2H_6O_2}{1 \text{ mol } C_2H_6O_2} = 1,860 \text{ g } C_2H_6O_2$$

The same two-step problem can also be worked out in a single line, rather than as two separate steps, as follows:



$$5.00 \text{ L solution} \times \frac{6.00 \text{ mol } C_2H_6O_2}{1 \text{ L solution}} \times \frac{62.08 \text{ g } C_2H_6O_2}{1 \text{ mol } C_2H_6O_2} = 1,860 \text{ g } C_2H_6O_2$$

The final answer is rounded off to 3 significant figures. Thus, there are 1,860 g of $C_2H_6O_2$ in the specified amount of engine coolant.

Note: Dimethylamine has a “fishy” odor. In fact, organic compounds called amines cause the odor of decaying fish.

✓ Example 9.2.6A

1. What volume of a 0.0753 M solution of dimethylamine [$(CH_3)_2NH$] is needed to obtain 0.450 mol of the compound?
2. Ethylene glycol ($C_2H_6O_2$) is mixed with water to make auto engine coolants. How many grams of $C_2H_6O_2$ are in 5.00 L of a 6.00 M aqueous solution?

Solution

This is an alternative method in case you don't want to use the conversion factor for molarity. In both parts, we will use the definition of molarity to solve for the desired quantity.

1. $0.0753\ \text{M} = \dfrac{0.450\ \text{mol}\ (\text{CH}_3)_2\text{NH}}{\text{volume of solution}}$

   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:

   $$\text{volume of solution} = \frac{0.450\ \text{mol}\ (\text{CH}_3)_2\text{NH}}{0.0753\ \text{M}} = 5.98\ \text{L}$$

   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:

   moles of solute = (6.00 M)(5.00 L) = 30.0 mol

   Note that because the definition of molarity is mol/L, the product M × L gives mol, a unit of amount. Now, using the molar mass of $C_3H_8O_3$, we convert mol to g:

   $$30.0\ \text{mol} \times \frac{62.08\ \text{g}}{\text{mol}} = 1,860\ \text{g}$$

   Thus, there are 1,860 g of $C_2H_6O_2$ in the specified amount of engine coolant.

? Exercise 9.2.6

a. What volume of a 0.0902 M solution of formic acid (HCOOH) is needed to obtain 0.888 mol of HCOOH?
b. Acetic acid ($HC_2H_3O_2$) is the acid in vinegar. How many grams of $HC_2H_3O_2$ are in 0.565 L of a 0.955 M solution?

Answer

a. 9.84 L

b. 32.4 g

Using Molarity in Stoichiometry Problems

Of all the ways of expressing concentration, molarity is the one most commonly used in stoichiometry problems because it is directly related to the mole unit. Consider the following chemical equation:

$$\text{HCl(aq)} + \text{NaOH(s)} \rightarrow \text{H}_2\text{O}(\ell) + \text{NaCl(aq)}$$

Suppose we want to know how many liters of aqueous HCl solution will react with a given mass of NaOH. A typical approach to answering this question is as follows:

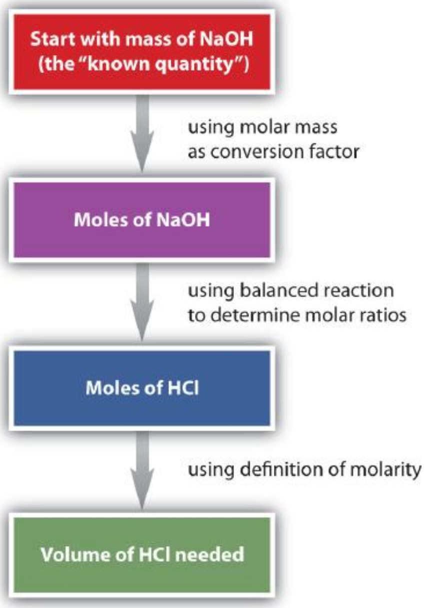


Figure 9.2.2: *Typical approach to solving Molarity problems*

In itself, each step is a straightforward conversion. It is the combination of the steps that is a powerful quantitative tool for problem solving.

✓ Example 9.2.7

How many milliliters of a 2.75 M HCl solution are needed to react with 185 g of NaOH? The balanced chemical equation for this reaction is as follows:

$$HCl(aq) + NaOH(s) \rightarrow H_2O(\ell) + NaCl(aq)$$

Solution

We will follow the flowchart to answer this question. First, we convert the mass of NaOH to moles of NaOH using its molar mass, 40.00 g/mol:

$$185\text{ g NaOH} \times \frac{1\text{ mol NaOH}}{40.00\text{ g NaOH}} = 4.63\text{ mol NaOH}$$

Using the balanced chemical equation, we see that there is a one-to-one ratio of moles of HCl to moles of NaOH. We use this to determine the number of moles of HCl needed to react with the given amount of NaOH:

$$4.63\text{ mol NaOH} \times \frac{1\text{ mol HCl}}{1\text{ mol NaOH}} = 4.63\text{ mol HCl}$$

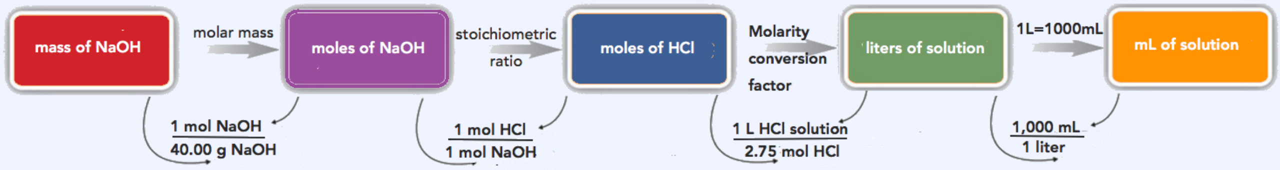
Finally, we use the definition of molarity to determine the volume of 2.75 M HCl needed:

$$2.75\text{ M HCl} = \frac{4.63\text{ mol HCl}}{\text{volume of HCl solution}}$$

$$\text{volume of HCl} = \frac{4.63\text{ mol HCl}}{2.75\text{ M HCl}} = 1.68\text{ L} \times \frac{1,000\text{ mL}}{1\text{ L}} = 1,680\text{ mL}$$

We need 1,680 mL of 2.75 M HCl to react with the NaOH.

The same multi-step problem can also be worked out in a single line, rather than as separate steps, as follows:



$$185\text{ g NaOH}\times\frac{1\text{ mol NaOH}}{40.00\text{ g NaOH}}\times\frac{1\text{ mol HCl}}{1\text{ mol NaOH}}\times\frac{1\text{ L HCl solution}}{2.75\text{ mol HCl}}\times\frac{1000\text{ mL HCl solution}}{1\text{ L HCl solution}}=1,680\text{ mL HCl solution}$$

Our final answer (rounded off to three significant figures) is 1,680 mL HCl solution.

? Exercise 9.2.7

How many milliliters of a 1.04 M H_2SO_4 solution are needed to react with 98.5 g of $Ca(OH)_2$? The balanced chemical equation for the reaction is as follows:

$$H_2SO_{4(aq)}+Ca(OH)_{2(s)}\rightarrow 2H_2O_{(\ell)}+CaSO_{4(aq)}$$

Answer

1,280 mL

The general steps for performing stoichiometry problems such as this are shown in Figure 9.2.3. You may want to consult this figure when working with solutions in chemical reactions. The double arrows in Figure 9.2.3 indicate that you can start at either end of the chart and, after a series of simple conversions, determine the quantity at the other end.

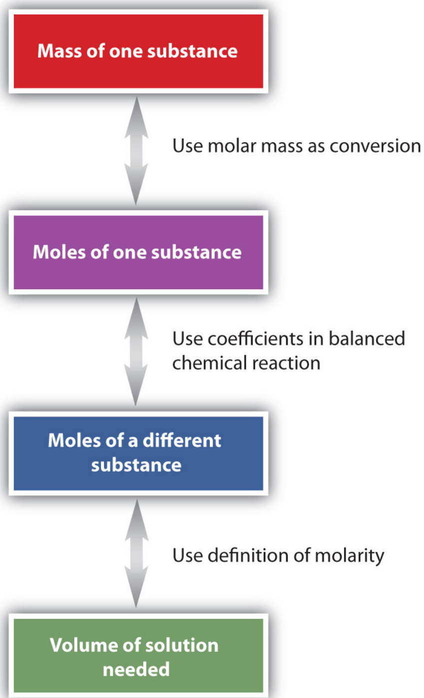


Figure 9.2.3: Diagram of Steps for Using Molarity in Stoichiometry Calculations. When using molarity in stoichiometry calculations, a specific sequence of steps usually leads you to the correct answer.

Many of the fluids found in our bodies are solutions. The solutes range from simple ionic compounds to complex proteins. Table 9.2.2 lists the typical concentrations of some of these solutes.

Table 9.2.2: Approximate Concentrations of Various Solutes in Some Solutions in the Body*

Solution	Solute	Concentration (M)
blood plasma	Na^+	0.138
	K^+	0.005
	Ca^{2+}	0.004
	Mg^{2+}	0.003
	$Cl^−$	0.110
	$HCO_3^−$	0.030
stomach acid	HCl	0.10
urine	NaCl	0.15
	$PO_4^{3−}$	0.05
	NH_2CONH_2 (urea)	0.30
*Note: Concentrations are approximate and can vary widely.		

Looking Closer: The Dose Makes the Poison

Why is it that we can drink 1 qt of water when we are thirsty and not be harmed, but if we ingest 0.5 g of arsenic, we might die? There is an old saying: *the dose makes the poison*. This means that what may be dangerous in some amounts may not be dangerous in other amounts.

Take arsenic, for example. Some studies show that arsenic deprivation limits the growth of animals such as chickens, goats, and pigs, suggesting that arsenic is actually an essential trace element in the diet. Humans are constantly exposed to tiny amounts of arsenic from the environment, so studies of completely arsenic-free humans are not available; if arsenic is an essential trace mineral in human diets, it is probably required on the order of 50 ppb or less. A toxic dose of arsenic corresponds to about 7,000 ppb and higher, which is over 140 times the trace amount that may be required by the body. Thus, arsenic is not poisonous in and of itself. Rather, it is the amount that is dangerous: the dose makes the poison.

Similarly, as much as water is needed to keep us alive, too much of it is also risky to our health. Drinking too much water too fast can lead to a condition called water intoxication, which may be fatal. The danger in water intoxication is not that water itself becomes toxic. It is that the ingestion of too much water too fast dilutes sodium ions, potassium ions, and other salts in the bloodstream to concentrations that are not high enough to support brain, muscle, and heart functions. Military personnel, endurance athletes, and even desert hikers are susceptible to water intoxication if they drink water but do not replenish the salts lost in sweat. As this example shows, even the right substances in the wrong amounts can be dangerous!

Equivalents

Concentrations of ionic solutes are occasionally expressed in units called equivalents (Eq). One equivalent equals 1 mol of positive or negative charge. Thus, 1 mol/L of Na^+(aq) is also 1 Eq/L because sodium has a 1+ charge. A 1 mol/L solution of Ca^{2+}(aq) ions has a concentration of 2 Eq/L because calcium has a 2+ charge. Dilute solutions may be expressed in milliequivalents (mEq)—for example, human blood plasma has a total concentration of about 150 mEq/L. (For more information about the ions present in blood plasma, see Chapter 3, Section 3.3.)

Dilutions

When additional water is added to an aqueous solution, the concentration of that solution decreases. This is because the number of **moles of the solute does not change**, while the **volume of the solution increases**. We can set up an equality between the moles of the solute before the dilution (1) and the moles of the solute after the dilution (2).

$$\text{mol}_1 = \text{mol}_2$$

Since the moles of solute in a solution is equal to the molarity multiplied by the liters, we can set those equal.

$$M_1 \times L_1 = M_2 \times L_2$$

Finally, because the two sides of the equation are set equal to one another, the volume can be in any units we choose, as long as that unit is the same on both sides. Our equation for calculating the molarity of a diluted solution becomes:

$$M_1 \times V_1 = M_2 \times V_2$$

Suppose that you have $100.\ \text{mL}$ of a $2.0\ \text{M}$ solution of HCl. You dilute the solution by adding enough water to make the solution volume $500.\ \text{mL}$. The new molarity can easily be calculated by using the above equation and solving for M_2.

$$M_2 = \frac{M_1 \times V_1}{V_2} = \frac{2.0\ \text{M} \times 100.\ \text{mL}}{500.\ \text{mL}} = 0.40\ \text{M HCl}$$

The solution has been diluted by one-fifth since the new volume is five times as great as the original volume. Consequently, the molarity is one-fifth of its original value.

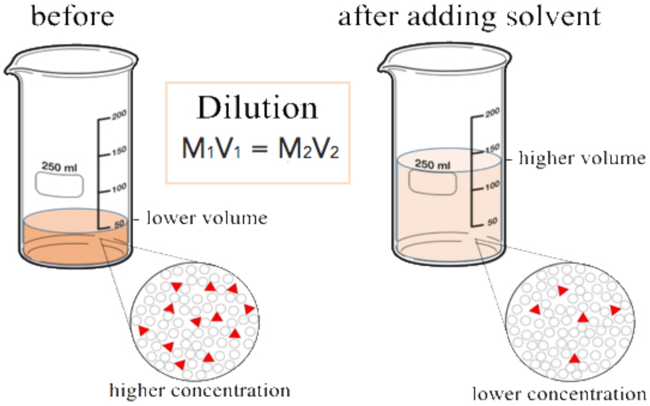


Figure 9.2.1: Figure 9.2.4: Diluting a solution by adding more solvent. Through the dilution process, the volume increases and the concentrations of the solutes decrease. As a consequence, there is more solution in the beaker after dilution, and the color of the solution becomes fainter. The inset shows that at the particular level (picometer to nanometer scale), there are less solute particles (red triangles) per volume. The content in the central box shows the dilution law, i.e. that the product of concentration and volume stays constant upon dilution. CC BY-SA 4.0.

Dilution Equations

Any units of concentration and volume can be used, as long as both concentrations and both volumes have the same unit. For example, if we are using M (molarity), then we can express the equation as follows:

$$\text{Molarity}_{\text{initial}} \times \text{volume}_{\text{initial}} = \text{Molarity}_{\text{final}} \times \text{volume}_{\text{final}} \text{ or}$$

$$\boldsymbol{M_1V_1 = M_2V_2}$$

If we are using percent, the dilution equation is as follows:

$$\%_{\text{initial}} \times \text{volume}_{\text{initial}} = \%_{\text{final}} \times \text{volume}_{\text{final}} \text{ or}$$

$$\boldsymbol{\%_1V_1 = \%_2V_2}$$

✓ Example 9.2.8

A 125 mL sample of 0.900 M NaCl is diluted to 1,125 mL. What is the final concentration of the diluted solution?

Solution

Because the volume units are the same, and we are looking for the molarity of the final solution, we can use (concentration × volume)$_{\text{initial}}$ = (concentration × volume)$_{\text{final}}$:

$$(0.900\ \text{M} \times 125\ \text{mL}) = (\text{concentration} \times 1{,}125\ \text{mL})$$

We solve by isolating the unknown concentration by itself on one side of the equation. Dividing by 1,125 mL gives

$$\text{concentration} = \frac{0.900\ \text{M} \times 125\ \text{mL}}{1,125\ \text{mL}} = 0.100\ \text{M}$$

as the final concentration.

Exercise 9.2.8

a. A nurse uses a syringe to inject 5.00 mL of 0.550 M heparin solution (heparin is an anticoagulant drug) into a 250 mL IV bag, for a final volume of 255 mL. What is the concentration of the resulting heparin solution?

b. A 0.885 M solution of KBr whose initial volume is 76.5 mL has more water added until its concentration is 0.500 M. What is the new volume of the solution?

Answer

a. 0.0108 M

b. 135.4 mL

Preparing IV Solutions

In a hospital emergency room, a physician orders an intravenous (IV) delivery of 100 mL of 0.5% KCl for a patient suffering from hypokalemia (low potassium levels). Does an aide run to a supply cabinet and take out an IV bag containing this concentration of KCl?

Not likely. It is more probable that the aide must make the proper solution from an IV bag of sterile solution and a more concentrated, sterile solution, called a *stock solution*, of KCl. The aide is expected to use a syringe to draw up some stock solution and inject it into the waiting IV bag and dilute it to the proper concentration. Thus the aide must perform a dilution calculation.

Figure 9.2.5 *Preparing IV Solution © Thinkstock. Medical personnel commonly must perform dilutions for IV solutions.*

If the stock solution is 10.0% KCl and the final volume and concentration need to be 100 mL and 0.50%, respectively, then it is an easy calculation to determine how much stock solution to use:

$$(10\%)V_1 = (0.50\%)(100\text{ mL})$$

$$V_1 = 5\text{ mL}$$

Of course, the addition of the stock solution affects the total volume of the diluted solution, but the final concentration is likely close enough even for medical purposes.

Medical and pharmaceutical personnel are constantly dealing with dosages that require concentration measurements and dilutions. It is an important responsibility: calculating the *wrong* dose can be useless, harmful, or even fatal!

Key Takeaways

- Various concentration units are used to express the amounts of solute in a solution.
- Concentration units can be used as conversion factors in stoichiometry problems.
- New concentrations can be easily calculated if a solution is diluted.

9.3: The Dissolution Process

Learning Objectives

- To describe the dissolution process at the molecular level

The Dissolution Process

What occurs at the molecular level to cause a solute to dissolve in a solvent? The answer depends in part on the solute, but there are some similarities common to all solutes.

Recall the rule that *like dissolves like*. This means that substances must have similar intermolecular forces to form solutions. When a soluble solute is introduced into a solvent, the particles of solute can interact with the particles of solvent. In the case of a solid or liquid solute, the interactions between the solute particles and the solvent particles are so strong that the individual solute particles separate from each other and, surrounded by solvent molecules, enter the solution. (Gaseous solutes already have their constituent particles separated, but the concept of being surrounded by solvent particles still applies.) This process is called **solvation** and is illustrated in Figure $9.3.1$. When the solvent is water, the word **hydration**, rather than solvation, is used.

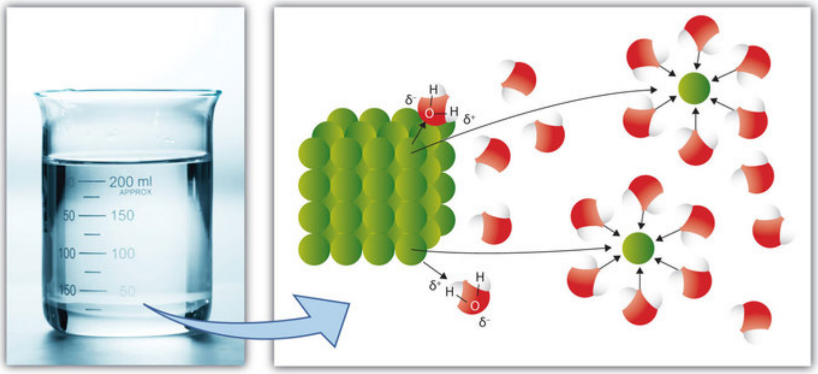


Figure $9.3.1$: Solvation. When a solute dissolves, the individual particles of solute become surrounded by solvent particles. Eventually the particle detaches from the remaining solute, surrounded by solvent molecules in solution. Source: Photo © Thinkstock

Ionic Compounds and Covalent Compounds as Solutes

In the case of molecular solutes like glucose, the solute particles are individual molecules. However, if the solute is ionic, the individual ions separate from each other and become surrounded by solvent particles. That is, the cations and anions of an ionic solute separate when the solute dissolves. This process is referred to as **dissociation** (Figure $9.3.1$).

The dissociation of soluble ionic compounds gives solutions of these compounds an interesting property: they conduct electricity. Because of this property, soluble ionic compounds are referred to as electrolytes. Many ionic compounds dissociate completely and are therefore called **strong electrolytes**. Sodium chloride is an example of a strong electrolyte. Some compounds dissolve but dissociate only partially, and solutions of such solutes may conduct electricity only weakly. These solutes are called **weak electrolytes**. Acetic acid (CH_3COOH), the compound in vinegar, is a weak electrolyte. Solutes that dissolve into individual neutral molecules without dissociation do not impart additional electrical conductivity to their solutions and are called nonelectrolytes. Table sugar ($C_{12}H_{22}O_{11}$) is an example of a nonelectrolyte.

> *The term electrolyte is used in medicine to mean any of the important ions that are dissolved in aqueous solution in the body. Important physiological electrolytes include* Na^+, K^+, Ca^{2+}, Mg^{2+}, *and* Cl^-.

Example $9.3.1$

The following substances all dissolve to some extent in water. Classify each as an electrolyte or a nonelectrolyte.

1. potassium chloride (KCl)

2. fructose ($C_6H_{12}O_6$)
3. isopropyl alcohol [$CH_3CH(OH)CH_3$]
4. magnesium hydroxide [$Mg(OH)_2$]

Solution

Each substance can be classified as an ionic solute or a nonionic solute. Ionic solutes are electrolytes, and nonionic solutes are nonelectrolytes.

1. Potassium chloride is an ionic compound; therefore, when it dissolves, its ions separate, making it an electrolyte.
2. Fructose is a sugar similar to glucose. (In fact, it has the same molecular formula as glucose.) Because it is a molecular compound, we expect it to be a nonelectrolyte.
3. Isopropyl alcohol is an organic molecule containing the alcohol functional group. The bonding in the compound is all covalent, so when isopropyl alcohol dissolves, it separates into individual molecules but not ions. Thus, it is a nonelectrolyte
4. Magnesium hydroxide is an ionic compound, so when it dissolves it dissociates. Thus, magnesium hydroxide is an electrolyte.

? Exercise 9.3.1

The following substances all dissolve to some extent in water. Classify each as an electrolyte or a nonelectrolyte.

a. acetone (CH_3COCH_3)
b. iron(III) nitrate [$Fe(NO_3)_3$]
c. elemental bromine (Br_2)
d. sodium hydroxide (NaOH)

Answer

a. nonelectrolyte

b. electrolyte

c. nonelectrolyte

d. electrolyte

Electrolytes in Body Fluids

Our body fluids are solutions of electrolytes and many other things. The combination of blood and the circulatory system is the *river of life*, because it coordinates all the life functions. When the heart stops pumping in a heart attack, the life ends quickly. Getting the heart restarted as soon as one can is crucial in order to maintain life.

The primary electrolytes required in the body fluid are cations (of calcium, potassium, sodium, and magnesium) and anions (of chloride, carbonates, aminoacetates, phosphates, and iodide). These are nutritionally called **macrominerals**.

Electrolyte balance is crucial to many body functions. Here's some extreme examples of what can happen with an imbalance of electrolytes: elevated potassium levels may result in cardiac arrhythmias; decreased extracellular potassium produces paralysis; excessive extracellular sodium causes fluid retention; and decreased plasma calcium and magnesium can produce muscle spasms of the extremities.

When a patient is dehydrated, a carefully prepared (commercially available) electrolyte solution is required to maintain health and well being. In terms of child health, oral electrolyte is given when a child is dehydrated due to diarrhea. The use of oral electrolyte maintenance solutions, which is responsible for saving millions of lives worldwide over the last 25 years, is one of the most important medical advances in protecting the health of children in the century, explains Juilus G.K. Goepp, MD, assistant director of the Pediatric Emergency Department of the Children's Center at Johns Hopkins Hospital. If a parent provides an oral electrolyte maintenance solution at the very start of the illness, dehydration can be prevented. The functionality of electrolyte solutions is related to their properties, and interest in electrolyte solutions goes far beyond chemistry.

Sports drinks are designed to rehydrate the body after excessive fluid depletion. Electrolytes in particular promote normal rehydration to prevent fatigue during physical exertion. Are they a good choice for achieving the recommended fluid intake? Are they performance and endurance enhancers like they claim? Who should drink them?

Typically, eight ounces of a sports drink provides between fifty and eighty calories and 14 to 17 grams of carbohydrate, mostly in the form of simple sugars. Sodium and potassium are the most commonly included electrolytes in sports drinks, with the levels of these in sports drinks being highly variable. The American College of Sports Medicine says a sports drink should contain 125 milligrams of sodium per 8 ounces as it is helpful in replenishing some of the sodium lost in sweat and promotes fluid uptake in the small intestine, improving hydration.

Gatorade

In the summer of 1965, the assistant football coach of the University of Florida Gators requested scientists affiliated with the university study why the withering heat of Florida caused so many heat-related illnesses in football players and provide a solution to increase athletic performance and recovery post-training or game. The discovery was that inadequate replenishment of fluids, carbohydrates, and electrolytes was the reason for the “wilting” of their football players. Based on their research, the scientists concocted a drink for the football players containing water, carbohydrates, and electrolytes and called it “Gatorade.” In the next football season the Gators were nine and two and won the Orange Bowl. The Gators’ success launched the sports-drink industry, which is now a multibillion-dollar industry that is still dominated by Gatorade.

University of Florida football player Chip Hinton testing Gatorade in 1965, pictured next to the leader of its team of inventors, Robert Cade.

Key Takeaway

- When a solute dissolves, its individual particles are surrounded by solvent molecules and are separated from each other.

9.4: Properties of Solutions

Learning Objectives

- To describe how the properties of solutions differ from those of pure solvents.

Solutions are likely to have properties similar to those of their major component—usually the solvent. However, some solution properties differ significantly from those of the solvent. Here, we will focus on liquid solutions that have a solid solute, but many of the effects we will discuss in this section are applicable to all solutions.

Colligative Properties

Solutes affect some properties of solutions that depend only on the concentration of the dissolved particles. These properties are called **colligative properties**. Four important colligative properties that we will examine here are vapor pressure depression, boiling point elevation, freezing point depression, and osmotic pressure.

Molecular compounds separate into individual molecules when they are dissolved, so for every 1 mol of molecules dissolved, we get 1 mol of particles. In contrast, **ionic** compounds separate into their constituent ions when they dissolve, so 1 mol of an ionic compound will produce more than 1 mol of dissolved particles. For example, **every mole of NaCl** that dissolves yields **1 mol of Na^+ ions** and **1 mol of $Cl^−$ ions**, for a **total of 2 mol** of particles in solution. Thus, the effect on a solution's properties by dissolving NaCl may be twice as large as the effect of dissolving the same amount of moles of glucose ($C_6H_{12}O_6$).

Vapor Pressure Depression

All liquids evaporate. In fact, given enough volume, a liquid will turn completely into a vapor. If enough volume is not present, a liquid will evaporate only to the point where the rate of evaporation equals the rate of vapor condensing back into a liquid. The pressure of the vapor at this point is called the **vapor pressure** of the liquid.

The presence of a dissolved solid lowers the characteristic vapor pressure of a liquid so that it evaporates more slowly. (The exceptions to this statement are if the solute itself is a liquid or a gas, in which case the solute will also contribute something to the evaporation process. We will not discuss such solutions here.) This property is called vapor pressure depression and is depicted in Figure $9.4.1$.

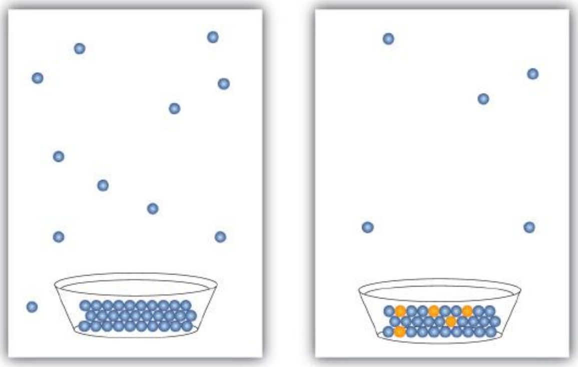


Figure 9.4.1: Vapor Pressure Depression. The presence of solute particles blocks some of the ability for liquid particles to evaporate. Thus, solutions of solid solutes typically have a lower vapor pressure than the pure solvent.

Boiling Point and Freezing Point Effects

A related property of solutions is that their boiling points are higher than the boiling point of the pure solvent. Because the presence of solute particles decreases the vapor pressure of the liquid solvent, a higher temperature is needed to reach the boiling point. This phenomenon is called boiling point elevation. **For every mole of particles dissolved in a liter of water, the boiling point of water increases by about 0.5°C.** The addition of one mole of sucrose (molecular compound) in one liter of water will raise the boiling point from 100^0C to 100.5^0C but the addition of one mole of NaCl in one liter of water will raise the boiling point by 2 x 0.5^0C = 1^0C. Furthermore, the addition of one mole of $CaCl_2$ in one liter of water will raise the boiling point by 3 x 0.5^0C = 1.5^0C.

> Some people argue that putting a pinch or two of salt in water used to cook spaghetti or other pasta makes a solution that has a higher boiling point, so the pasta cooks faster. In actuality, the amount of solute is so small that the boiling point of the water is practically unchanged.

The presence of solute particles has the opposite effect on the freezing point of a solution. When a solution freezes, only the solvent particles come together to form a solid phase, and the presence of solute particles interferes with that process. Therefore, for the liquid solvent to freeze, more energy must be removed from the solution, which lowers the temperature. Thus, solutions have lower freezing points than pure solvents do. This phenomenon is called freezing point depression. **For every mole of particles in a liter of water, the freezing point decreases by about 1.9°C.**

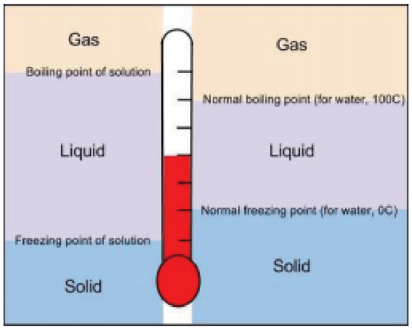


Figure 9.4.2: Comparison of boiling and freezing points of a pure liquid (right side) with a solution (left side).

Both boiling point elevation and freezing point depression have practical uses. For example, solutions of water and ethylene glycol ($C_2H_6O_2$) are used as coolants in automobile engines because the boiling point of such a solution is greater than 100°C, the normal boiling point of water. In winter, salts like NaCl and $\mathrm{CaCl_2}$ are sprinkled on the ground to melt ice or keep ice from forming on roads and sidewalks (Figure 9.4.2). This is because the solution made by dissolving sodium chloride or calcium chloride in water has a lower freezing point than pure water, so the formation of ice is inhibited.

Figure 9.4.2: Effect of Freezing Point Depression. The salt sprinkled on this sidewalk makes the water on the sidewalk have a lower freezing point than pure water, so it does not freeze as easily. This makes walking on the sidewalk less hazardous in winter. © Thinkstock

✓ Example 9.4.1

Which solution's freezing point deviates more from that of pure water—a 1 M solution of NaCl or a 1 M solution of $\mathrm{CaCl_2}$?

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 $\mathrm{CaCl_2}$ dissolves, it separates into three ions—one Ca^{2+} ion and two Cl^- ions. Thus, mole for mole, $\mathrm{CaCl_2}$ will have 50% more impact on freezing point depression than NaCl.

? Exercise 9.4.1

Which solution's boiling point deviates more from that of pure water—a 1 M solution of $\mathrm{CaCl_2}$ or a 1 M solution of $MgSO_4$?

Answer

$\mathrm{CaCl_2}$

Example 9.4.2

Estimate the boiling point of 0.2 M $\mathrm{CaCl_2}$ solution.

Solution

The boiling point increases 0.5^{0}C for every mole of solute per liter of water. For this estimation, let's assume that 1 liter of solution is roughly the same volume as 1 liter of water. A 0.2 M $\mathrm{CaCl_2}$ solution contains 0.2 moles of $\mathrm{CaCl_2}$ solution formula units per liter of solution. Each $\mathrm{CaCl_2}$ unit separates into three ions.

$$0.2 \text{ mol } \mathrm{CaCl_2} \times \frac{3 \text{ mol ions}}{1 \text{ mol } \mathrm{CaCl_2}} \times \frac{0.5 \text{ deg C}}{1 \text{ mol ion}} = 0.3 \text{ deg C}$$

The normal boiling point of water is 100^{0}C, so the boiling point of the solution is raised to 100.3^{0}C.

rcise

Estimate the freezing point of 0.3 M $\mathrm{CaCl_2}$ solution.

Answer

minus 1.7^{0}C

Osmotic Pressure

The last colligative property of solutions we will consider is a very important one for biological systems. It involves **osmosis**, the process by which solvent molecules can pass through certain membranes but solute particles cannot. When two solutions of different concentration are present on either side of these membranes (called *semipermeable membranes*), there is a tendency for solvent molecules to move from the more dilute solution to the more concentrated solution until the concentrations of the two solutions are equal. This tendency is called **osmotic pressure**. External pressure can be exerted on a solution to counter the flow of solvent; the pressure required to halt the osmosis of a solvent is equal to the osmotic pressure of the solution.

Osmolarity (osmol) is a way of reporting the total number of particles in a solution to determine osmotic pressure. It is defined as the molarity of a solute times the number of particles a formula unit of the solute makes when it dissolves (represented by i):

$$osmol = M \times i \tag{9.4.1}$$

If more than one solute is present in a solution, the individual osmolarities are additive to get the total osmolarity of the solution. Solutions that have the same osmolarity have the same osmotic pressure. If solutions of differing osmolarities are present on opposite sides of a semipermeable membrane, solvent will transfer from the lower-osmolarity solution to the higher-osmolarity solution. Counterpressure exerted on the high-osmolarity solution will reduce or halt the solvent transfer. An even higher pressure can be exerted to force solvent from the high-osmolarity solution to the low-osmolarity solution, a process called *reverse osmosis*. Reverse osmosis is used to make potable water from saltwater where sources of fresh water are scarce.

Example 9.4.3

A 0.50 M NaCl aqueous solution and a 0.30 M $\mathrm{Ca(NO_3)_2}$ 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—$\mathrm{Na^+}$ and $\mathrm{Cl^-}$—when it dissolves, so its osmolarity is as follows:

$$\text{osmol (NaCl)} = 0.50 \text{ M} \times 2 = 1.0 \text{ osmol}$$

The $\mathrm{Ca(NO_3)_2}$ solute separates into three ions—one $\mathrm{Ca^{2+}}$ and two $\mathrm{NO_3^-}$—when it dissolves, so its osmolarity is as follows:

$$\text{osmol } [\mathrm{Ca(NO_3)_2}] = 0.30 \text{ M} \times 3 = 0.90 \text{ osmol}$$

The osmolarity of the $Ca(NO_3)_2$ solution is lower than that of the NaCl solution, so water will transfer through the membrane from the $Ca(NO_3)_2$ solution to the NaCl solution.

Exercise 9.4.3

A 1.5 M $C_6H_{12}O_6$ aqueous solution and a 0.40 M $Al(NO_3)_3$ aqueous solution are placed on opposite sides of a semipermeable membrane. Determine the osmolarity of each solution and predict the direction of solvent flow.

Answer

osmol $C_6H_{12}O_6$ = 1.5; osmol $Al(NO_3)_3$ = 1.6

The solvent flows from $C_6H_{12}O_6$ solution (lower osmolarity) to $Al(NO_3)_3$ solution (higher osmolarity).

To Your Health: Dialysis

The main function of the kidneys is to filter the blood to remove wastes and extra water, which are then expelled from the body as urine. Some diseases rob the kidneys of their ability to perform this function, causing a buildup of waste materials in the bloodstream. If a kidney transplant is not available or desirable, a procedure called dialysis can be used to remove waste materials and excess water from the blood.

In one form of dialysis, called *hemodialysis*, a patient's blood is passed though a length of tubing that travels through an *artificial kidney machine* (also called a *dialysis machine*). A section of tubing composed of a semipermeable membrane is immersed in a solution of sterile water, glucose, amino acids, and certain electrolytes. The osmotic pressure of the blood forces waste molecules and excess water through the membrane into the sterile solution. Red and white blood cells are too large to pass through the membrane, so they remain in the blood. After being cleansed in this way, the blood is returned to the body.

Figure 9.4.3: A patient undergoing hemodialysis depends on osmosis to cleanse the blood of waste products that the kidneys are incapable of removing due to disease. from Wikipedia.

Dialysis is a continuous process, as the osmosis of waste materials and excess water takes time. Typically, 5–10 lb of waste-containing fluid is removed in each dialysis session, which can last 2–8 hours and must be performed several times a week. Although some patients have been on dialysis for 30 or more years, dialysis is always a temporary solution because waste materials are constantly building up in the bloodstream. A more permanent solution is a kidney transplant.

Cell walls are semipermeable membranes, so the osmotic pressures of the body's fluids have important biological consequences. If solutions of different osmolarity exist on either side of the cells, solvent (water) may pass into or out of the cells, sometimes with disastrous results. Consider what happens if red blood cells are placed in a *hypotonic* solution, meaning a solution of lower osmolarity than the liquid inside the cells. The cells swell up as water enters them, disrupting cellular activity and eventually causing the cells to burst. This process is called *hemolysis*. If red blood cells are placed in a *hypertonic* solution, meaning one having a higher osmolarity than exists inside the cells, water leaves the cells to dilute the external solution, and the red blood cells shrivel and die. This process is called *crenation*. Only if red blood cells are placed in *isotonic* solutions that have the same osmolarity as exists inside the cells are they unaffected by negative effects of osmotic pressure. **Glucose solutions of about 0.31 M, or sodium chloride solutions of about 0.16 M, are isotonic with blood plasma.**

The concentration of an isotonic sodium chloride (NaCl) solution is only half that of an isotonic glucose ($C_6H_{12}O_6$) solution because NaCl produces two ions when a formula unit dissolves, while molecular $C_6H_{12}O_6$ produces only one particle when a formula unit dissolves. The osmolarities are therefore the same even though the concentrations of the two solutions are different.

Osmotic pressure explains why you should not drink seawater if you are abandoned in a life raft in the middle of the ocean. Its osmolarity is about three times higher than most bodily fluids. You would actually become thirstier as water from your cells was drawn out to dilute the salty ocean water you ingested. Our bodies do a better job coping with hypotonic solutions than with hypertonic ones. The excess water is collected by our kidneys and excreted.

Osmotic pressure effects are used in the food industry to make pickles from cucumbers and other vegetables and in brining meat to make corned beef. It is also a factor in the mechanism of getting water from the roots to the tops of trees!

Career Focus: Perfusionist

A perfusionist is a medical technician trained to assist during any medical procedure in which a patient's circulatory or breathing functions require support. The use of perfusionists has grown rapidly since the advent of open-heart surgery in 1953.

Most perfusionists work in operating rooms, where their main responsibility is to operate heart-lung machines. During many heart surgeries, the heart itself must be stopped. In these situations, a heart-lung machine keeps the patient alive by aerating the blood with oxygen and removing carbon dioxide. The perfusionist monitors both the machine and the status of the blood, notifying the surgeon and the anesthetist of any concerns and taking corrective action if the status of the blood becomes abnormal.

Despite the narrow parameters of their specialty, perfusionists must be highly trained. Certified perfusion education programs require a student to learn anatomy, physiology, pathology, chemistry, pharmacology, math, and physics. A college degree is usually required. Some perfusionists work with other external artificial organs, such as hemodialysis machines and artificial livers.

9.5: Chemical Equilibrium

Learning Outcomes

- Explain chemical equilibrium.
- Write expression for calculating K.
- Calculate and compare Q and K values.
- Predict relative amounts of reactants and products based on equilibrium constant K.

Hydrogen and iodine gases react to form hydrogen iodide according to the following reaction:

$$\mathrm{H_2}\,(g) + \mathrm{I_2}\,(g) \rightleftharpoons 2\mathrm{HI}\,(g)$$

$$\text{Forward reaction: } \mathrm{H_2}\,(g) + \mathrm{I_2}\,(g) \rightarrow 2\mathrm{HI}\,(g) \tag{9.5.1}$$

$$\text{Reverse reaction: } 2\mathrm{HI}\,(g) \rightarrow \mathrm{H_2}\,(g) + \mathrm{I_2}\,(g) \tag{9.5.2}$$

Initially, only the forward reaction occurs because no HI is present. As soon as some HI has formed, it begins to decompose back into $\mathrm{H_2}$ and $\mathrm{I_2}$. Gradually, the rate of the forward reaction decreases while the rate of the reverse reaction increases. Eventually the rate of combination of $\mathrm{H_2}$ and $\mathrm{I_2}$ to produce HI becomes equal to the rate of decomposition of HI into $\mathrm{H_2}$ and $\mathrm{I_2}$. When the rates of the forward and reverse reactions have become equal to one another, the reaction has achieved a state of balance. **Chemical equilibrium** is the state of a system in which the rate of the forward reaction is equal to the rate of the reverse reaction.

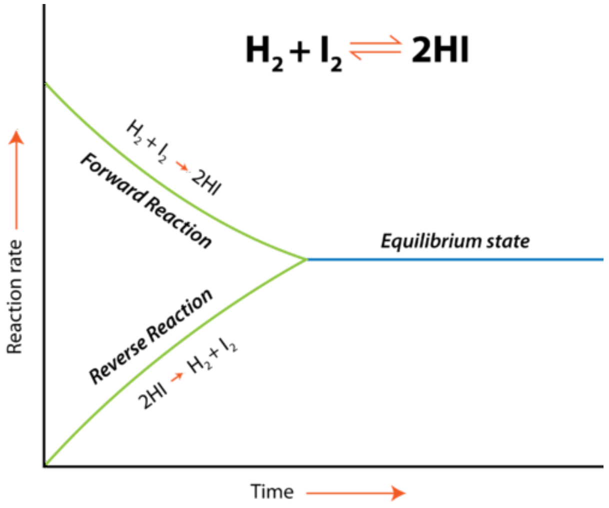


Figure 9.5.1: Equilibrium in reaction: $\mathrm{H_2}\,(g) + \mathrm{I_2}\,(g) \rightleftharpoons 2\mathrm{HI}\,(g)$.

Chemical equilibrium can be attained whether the reaction begins with all reactants and no products, all products and no reactants, or some of both. The figure below shows changes in concentration of $\mathrm{H_2}$, $\mathrm{I_2}$, and HI for two different reactions. In the reaction depicted by the graph on the left (A), the reaction begins with only $\mathrm{H_2}$ and $\mathrm{I_2}$ present. There is no HI initially. As the reaction proceeds towards equilibrium, the concentrations of the $\mathrm{H_2}$ and $\mathrm{I_2}$ gradually decrease, while the concentration of the HI gradually increases. When the curve levels out and the concentrations all become constant, equilibrium has been reached. At equilibrium, concentrations of all substances are constant.

In reaction B, the process begins with only HI and no $\mathrm{H_2}$ or $\mathrm{I_2}$. In this case, the concentration of HI gradually decreases while the concentrations of $\mathrm{H_2}$ and $\mathrm{I_2}$ gradually increase until equilibrium is again reached. Notice that in both cases, the relative position of equilibrium is the same, as shown by the relative concentrations of reactants and products. The concentration of HI at equilibrium is significantly higher than the concentrations of $\mathrm{H_2}$ and $\mathrm{I_2}$. This is true whether the reaction began with all reactants or all products. The position of equilibrium is a property of the particular reversible reaction and does not depend upon how equilibrium was achieved.

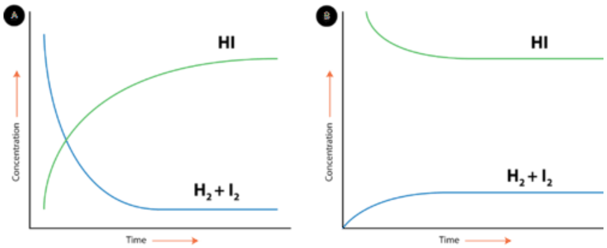


Figure 9.5.2: Equilibrium between reactants and products is achieved regardless of whether the reaction starts with the reactants or products.

Conditions for Equilibrium and Types of Equilibrium

It may be tempting to think that once equilibrium has been reached, the reaction stops. Chemical equilibrium is a dynamic process. The forward and reverse reactions continue to occur even after equilibrium has been reached. However, because the rates of the reactions are the same, there is no change in the relative concentrations of reactants and products for a reaction that is at equilibrium. The conditions and properties of a system at equilibrium are summarized below.

1. The system must be closed, meaning no substances can enter or leave the system.
2. Equilibrium is a dynamic process. Even though we don't necessarily see the reactions, both forward and reverse are taking place.
3. The rates of the forward and reverse reactions must be equal.
4. The amount of reactants and products do not have to be equal. However, after equilibrium is attained, the amounts of reactants and products will be constant.

The description of equilibrium in this concept refers primarily to equilibrium between reactants and products in a chemical reaction. Other types of equilibrium include phase equilibrium and solution equilibrium. A phase equilibrium occurs when a substance is in equilibrium between two states. For example, a stoppered flask of water attains equilibrium when the rate of evaporation is equal to the rate of condensation. A solution equilibrium occurs when a solid substance is in a saturated solution. At this point, the rate of dissolution is equal to the rate of recrystallization. Although these are all different types of transformations, most of the rules regarding equilibrium apply to any situation in which a process occurs reversibly.

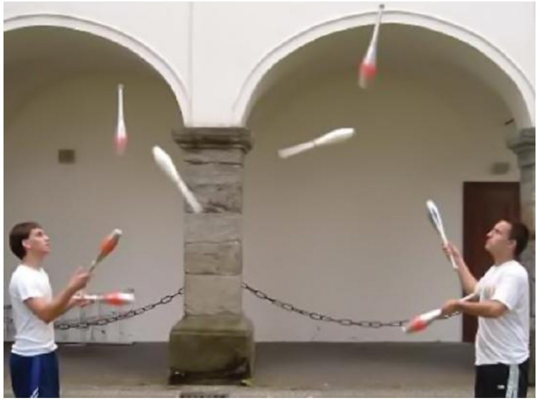


Figure 9.5.3: These jugglers provide an illustration of dynamic equilibrium. Each throws clubs to the other at the same rate at which he receives clubs from that person. Because clubs are thrown continuously in both directions, the number of clubs moving in each direction is constant, and the number of clubs each juggler has at a given time remains (roughly) constant.

Red blood cells transport oxygen to the tissues so they can function. In the absence of oxygen, cells cannot carry out their biochemical responsibilities. Oxygen moves to the cells attached to hemoglobin, a protein found in the red cells. In cases of carbon monoxide poisoning, CO binds much more strongly to the hemoglobin, blocking oxygen attachment and lowering the amount of oxygen reaching the cells. Treatment involves the patient breathing pure oxygen to displace the carbon monoxide. The equilibrium reaction shown below illustrates the shift toward the right when excess oxygen is added to the system:

$$\mathrm{Hb(CO)_4}\,(aq) + 4\mathrm{O_2}\,(g) \rightleftharpoons \mathrm{Hb(O_2)_4}\,(aq) + 4\mathrm{CO}\,(g)$$

Equilibrium Constant

Consider the hypothetical reversible reaction in which reactants A and B react to form products C and D. This equilibrium can be shown below, where the lowercase letters represent the coefficients of each substance.

$$a\mathrm{A}+b\mathrm{B}\rightleftharpoons c\mathrm{C}+d\mathrm{D}$$

As we have established, the rates of the forward and reverse reactions are the same at equilibrium, and so the concentrations of all of the substances are constant. Since that is the case, it stands to reason that a ratio of the concentration for any given reaction at equilibrium maintains a constant value. The **equilibrium constant** $(\boldsymbol{K}_{\text{eq}})$ is the ratio of the mathematical product of the products of a reaction to the mathematical product of the concentrations of the reactants of the reaction. Each concentration is raised to the power of its coefficient in the balanced chemical equation. For the general reaction above, the equilibrium constant expression is written as follows:

$$K_{\text{eq}}=\frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b}$$

The concentrations of each substance, indicated by the square brackets around the formula, are measured in molarity units $(\mathrm{mol/L})$.

The value of the equilibrium constant for any reaction is only determined by experiment. As detailed in the above section, the position of equilibrium for a given reaction does not depend on the starting concentrations and so the value of the equilibrium constant is truly constant. It does, however, depend on the temperature of the reaction. This is because equilibrium is defined as a condition resulting from the rates of forward and reverse reactions being equal. If the temperature changes, the corresponding change in those reaction rates will alter the equilibrium constant. For any reaction in which a K_{eq} is given, the temperature should be specified.

The equilibrium constant can vary over a wide range of values. Because products are in the numerator of the equilibrium constant expression and reactants are in the denominator, values of K greater than 10^3 indicate a strong tendency for reactants to form products. In this case, chemists say that equilibrium lies to the right as written, favoring the formation of products. An example is the reaction between H_2 and Cl_2 to produce HCl, which has an equilibrium constant of 1.6×10^{33} at 300 K. Because H_2 is a good reducing agent and Cl_2 is a good oxidizing agent, the reaction proceeds essentially to completion.

$$H_{2(g)}+Cl_{2(g)}\rightleftharpoons 2HCl_{(g)}\quad K{=}1.6\times10^{33}\text{ at 300K}$$

In contrast, values of K less than 10^{-3} indicate that the ratio of products to reactants at equilibrium is very small. That is, reactants do not tend to form products readily, and the equilibrium lies to the left as written, favoring the formation of reactants. An example is the decomposition of water. No wonder you won't find water a very good source of oxygen gas and hydrogen gas at ordinary temperatures!

$$H_2O_{(g)}\rightleftharpoons H_{2(g)}+½O_{2(g)}\quad K{=}8\times10^{-41}\text{ at 25°C}$$

Figure $9.5.4$ summarizes the relationship between the magnitude of K and the relative concentrations of reactants and products at equilibrium for a general reaction, written as reactants $\rightleftharpoons$ products.

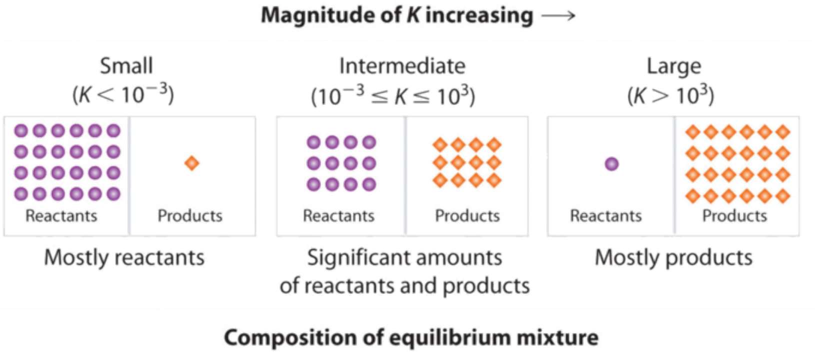


Figure $9.5.4$: The Relationship between the Composition of the Mixture at Equilibrium and the Magnitude of the Equilibrium Constant. The larger the K, the farther the reaction proceeds to the right before equilibrium is reached, and the greater the ratio of products to reactants at equilibrium.

> *A large value of the equilibrium constant K means that products predominate at equilibrium; a small value means that reactants predominate at equilibrium.*

- When K is a very **large** number, the reaction is essentially irreversible, products predominate at equilibrium.
- When K is between 1 and 1000, more products than reactants are present at equilibrium
- When K is between 1 and 0.001, more reactants than products are present at equilibrium.
- When K is a very **small** number, the reaction produces almost no products; only reactants are present at equilibrium.

✓ Example 9.5.1

Write the expression for the equilibrium constant K for the following reaction:

N_2 *(g)* + 3 H_2 *(g)* ⇄ 2 NH_3 *(g)*

Solution

The equilibrium constant equation is the ratio of the concentration of the products (NH_3) to the concentration of the reactants (N_2 and H_2), each raised to the power of its coefficient in the balanced chemical equation.

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

rcise

Write the expression of the equilibrium constant K for the following reaction:.

2 NOCl *(g)* ⇄ 2 NO *(g)* + Cl_2 *(g)*

Answer

$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2}$$

✓ Example 9.5.2

Predict which systems at equilibrium will (a) contain essentially only products, (b) contain essentially only reactants, and (c) contain appreciable amounts of both products and reactants.

1. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \qquad K_{(700K)} = 54$
2. $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)} \qquad K_{(1200K)} = 3.1 \times 10^{-18}$
3. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \qquad K_{(613K)} = 97$
4. $2O_{3(g)} \rightleftharpoons 3O_{2(g)} \qquad K_{(298K)} = 5.9 \times 10^{55}$

Solution

Use the value of the equilibrium constant to determine whether the equilibrium mixture will contain essentially only products, essentially only reactants, or significant amounts of both.

a. Only system 4 has $K \gg 10^3$, so at equilibrium it will consist of essentially only products.
b. System 2 has $K \ll 10^{-3}$, so the reactants have little tendency to form products under the conditions specified; thus, at equilibrium the system will contain essentially only reactants.
c. Both systems 1 and 3 have equilibrium constants in the range $10^3 \geq K \geq 10^{-3}$, indicating that the equilibrium mixtures will contain appreciable amounts of both products and reactants.

rcise

Hydrogen and nitrogen react to form ammonia according to the following balanced chemical equation:

$$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

Values of the equilibrium constant at various temperatures were reported as

- $K_{25^\circ C} = 3.3 \times 10^8$,
- $K_{177^\circ C} = 2.6 \times 10^3$, and
- $K_{327^\circ C} = 4.1$.

a. At which temperature would you expect to find the highest proportion of H_2 and N_2 in the equilibrium mixture?
b. At which temperature would you expect to find the highest proportion of ammonia in the equilibrium mixture?

Answer

a. 327°C, where K is smallest

b. 25°C

Reaction Quotient

The reaction quotient, Q, is used when questioning if we are at equilibrium. The calculation for Q is **exactly** the same as for K but we can only use K when we know we are at equilibrium. Comparing Q and K allows the direction of the reaction to be predicted.

- $Q = K$ equilibrium
- $Q < K$ reaction proceeds to the right to form more products and decrease amount of reactants so value of Q will increase
- $Q > K$ reaction proceeds to the left to form more reactants and decrease amount of products so value of Q will decrease

Key Takeaway

- As a chemical change proceeds, the quantities of the reactants/products will decrease, and those of the products/reactants will increase. Eventually the reaction slows down and the composition of the system stops changing. At this point the reaction is in its *equilibrium state*, and no further change in composition will occur as long as the system is left undisturbed.

Contributors and Attributions

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9.6: Le Chatelier's Principle

Learning Outcomes

- Define Le Chatelier's principle.
- Predict how the change in amounts of substances, temperature, or pressure will affect amounts of reactants and products present at equilibrium.

Le Chatelier's Principle

Chemical equilibrium was studied by the French chemist Henri Le Chatelier (1850 - 1936) and his description of how a system responds to a stress to equilibrium has become known as **Le Chatelier's principle**: When a chemical system that is at equilibrium is disturbed by a stress, the system will respond in order to relieve the stress. Stresses to a chemical system involve changes in the concentrations of reactants or products, changes in the temperature of the system, or changes in the pressure of the system. We will discuss each of these stresses separately. The change to the equilibrium position in every case is either a favoring of the forward reaction or a favoring of the reverse reaction. When the forward reaction is favored, the concentrations of products increase, while the concentrations of reactants decrease. When the reverse reaction is favored, the concentrations of the products decrease, while the concentrations of reactants increase.

Original Equilibrium	**Favored Reaction**	**Result**
$A \rightleftharpoons B$	Forward: $A \rightarrow B$	$[A]$ decreases; $[B]$ increases
$A \rightleftharpoons B$	Reverse: $A \leftarrow B$	$[A]$ increases; $[B]$ decreases

Figure 9.6.1: *Henri Le Chatelier.*

Effect of Concentration

A change in concentration of one of the substances in an equilibrium system typically involves either the addition or the removal of one of the reactants or products. Consider the Haber-Bosch process for the industrial production of ammonia from nitrogen and hydrogen gases.

$$N_2\left(g\right)+3H_2\left(g\right)\rightleftharpoons 2NH_3\left(g\right)$$

If the concentration of one substance in a system is increased, the system will respond by favoring the reaction that removes that substance. When more N_2 is added, the forward reaction will be favored because the forward reaction uses up N_2 and converts it to NH_3. The forward reaction speeds up temporarily as a result of the addition of a reactant. The position of equilibrium shifts as more NH_3 is produced. The concentration of NH_3 increases, while the concentrations of N_2 and H_2 decrease. After some time passes, equilibrium is reestablished with new concentrations of all three substance. As can be seen in the figure below, if more N_2 is added, a new equilibrium is achieved by the system. The new concentration of NH_3 is higher because of the favoring of the forward reaction. The new concentration of the H_2 is lower .The concentration of N_2 is higher than in the original equilibrium, but went down slightly following the addition of the N_2 that disturbed the original equilibrium. By responding in this way, the value of the equilibrium constant for the reaction, K_eq, does not change as a result of the stress to the system.

In other words, the amount of each substance is different but the ratio of the amount of each remains the same.

If more NH_3 were added, the reverse reaction would be favored. This "favoring" of a reaction means temporarily speeding up the reaction in that direction until equilibrium is reestablished. Recall that once equilibrium is reestablished, the rates of the forward and reverse reactions are again equal. The addition of NH_3 would result in increased formation of the reactants, N_2 and H_2.

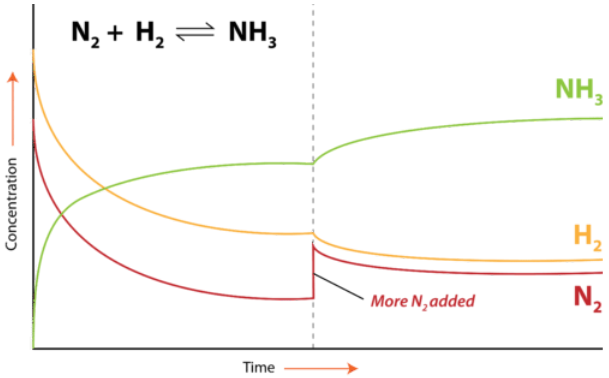

Figure 9.6.2: *The Haber-Bosch process is an equilibrium between reactants* N_2 *and* H_2 *and product* NH_3.

An equilibrium can also be disrupted by the removal of one of the substances. If the concentration of a substance is decreased, the system will respond by favoring the reaction that replaces that substance. In the industrial Haber-Bosch process, NH_3 is removed from the equilibrium system as the reaction proceeds. As a result, the forward reaction is favored so that more NH_3 is produced. The concentrations of N_2 and H_2 decrease. Continued removal of NH_3 will eventually force the reaction to go to completion until all of the reactants are used up. If either N_2 or H_2 were removed from the equilibrium system, the reverse reaction would be favored and the concentration of NH_3 would decrease.

The effect of changes in concentration on an equilibrium system according to Le Chatelier's principle is summarized in the table below.

Table 9.6.1

Stress	Response
addition of reactant	forward reaction favored
addition of product	reverse reaction favored
removal of reactant	reverse reaction favored
removal of product	forward reaction favored

✓ Example 9.6.1

Given this reaction at equilibrium:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

How will it affect the reaction if the equilibrium is stressed by each change?

1. H_2 is added.
2. NH_3 is added.
3. NH_3 is removed.

Solution

1. If H_2 is added, there is now more reactant, so the reaction will shift to the right (toward products) to reduce the added H_2.
2. If NH_3 is added, there is now more product, so the reaction will shift to the left (toward reactants) to reduce the added NH_3.
3. If NH_3 is removed, there is now less product, so the reaction will shift to the right (toward products) to replace the product removed.

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Given this reaction at equilibrium:

$$CO(g) + Br_2(g) \rightleftharpoons COBr_2(g)$$

How will it affect the reaction if the equilibrium is stressed by each change?

1. Br_2 is removed.
2. $COBr_2$ is added.

Answer

1. shift to the left (toward reactants)
2. shift to the left (toward reactants)

Effect of Temperature

Increasing or decreasing the temperature of a system at equilibrium is also a stress to the system. The equation for the Haber-Bosch process is written again below, as a thermochemical equation (i.e. it contains information about the energy gained or lost when the reaction occurs).

$$\mathrm{N_2}\ (g) + 3\mathrm{H_2}\ (g) \rightleftharpoons 2\mathrm{NH_3}\ (g) + 91\ \mathrm{kJ}$$

The forward reaction is the exothermic direction: the formation of $\mathrm{NH_3}$ releases heat which is why that is shown as a product. The reverse reaction is the endothermic direction: as $\mathrm{NH_3}$ decomposes to $\mathrm{N_2}$ and $\mathrm{H_2}$, heat is absorbed. An increase in the temperature for this is like adding a product because heat is being released by the reaction. If we add a product then the reaction proceeds towards the formation of more reactants. Reducing the temperature for this system would be similar to removing a product which would favor the formation of more products. The amount of $\mathrm{NH_3}$ will increase and the amount of $\mathrm{N_2}$ and $\mathrm{H_2}$ will decrease.

For changes in concentration, the system responds in such a way that the value of the equilibrium constant, K_{eq} is unchanged. However, a change in temperature shifts the equilibrium and the K_{eq} value either increases or decreases. As discussed in the previous section, values of K_{eq} are dependent on the temperature. When the temperature of the system for the Haber-Bosch process is increased, the resultant shift in equilibrium towards the reactants means that the K_{eq} value decreases. When the temperature is decreased, the shift in equilibrium towards the products means that the K_{eq} value increases.

Le Chatelier's principle as related to temperature changes can be illustrated easily be the reaction in which dinitrogen tetroxide is in equilibrium with nitrogen dioxide.

$$\mathrm{N_2O_4}\ (g) + \mathrm{heat} \rightleftharpoons 2\mathrm{NO_2}\ (g)$$

Dinitrogen tetroxide $\left(\mathrm{N_2O_4}\right)$ is colorless, while nitrogen dioxide $\left(\mathrm{NO_2}\right)$ is dark brown in color. When $\mathrm{N_2O_4}$ breaks down into $\mathrm{NO_2}$, heat is absorbed (endothermic) according to the forward reaction above. Therefore, an increase in temperature (adding heat) of the system will favor the forward reaction. Conversely, a decrease in temperature (removing heat) will favor the reverse reaction.

✓ Example 9.6.2

Predict the effect of increasing the temperature on this equilibrium.

$$PCl_3 + Cl_2 \rightleftharpoons PCl_5 + 60kJ$$

Solution

Because energy is listed as a product, it is being produced, so the reaction is exothermic. If the temperature is increasing, a product is being added to the equilibrium, so the equilibrium shifts to minimize the addition of extra product: it shifts to the left (back toward reactants).

rcise

Predict the effect of decreasing the temperature on this equilibrium.

$$N_2O_4 + 57kJ \rightleftharpoons 2NO_2$$

Answer

Equilibrium shifts to the left (toward reactants).

Effect of Pressure

Changing the pressure of an equilibrium system in which gases are involved is also a stress to the system. A change in the pressure on a liquid or a solid has a negligible effect. We will return again the equilibrium for the Haber-Bosch process. Imagine the gases are contained in a closed system in which the volume of the system is controlled by an adjustable piston as shown in the figure below.

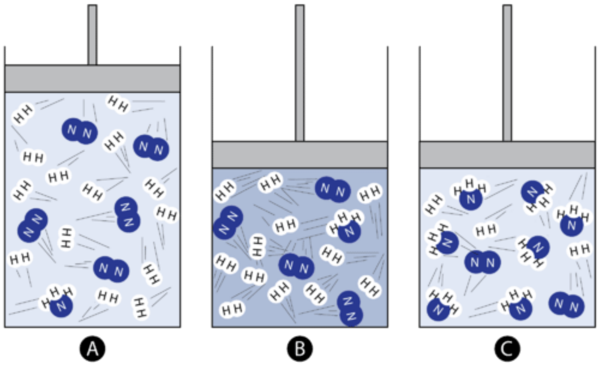

Figure 9.6.3: *Effect of pressure on equilibrium. (A) is at equilibrium, (B) increase of pressure through decreased volume, and (C) equilibrium is reestablished.*

On the far left, the reaction system contains primarily N_2 and H_2, with only one molecule of NH_3 present. As the piston is pushed inwards, the pressure of the system increases according to Boyle's law. This is a stress to the equilibrium. In the middle image, the same number of molecules is now confined in a smaller space and so the pressure has increased. According to Le Chatelier's principle, the system responds in order to relieve the stress. In the image on the right, the forward reaction has been favored and more NH_3 is produced. The overall result is a decrease in the number of gas molecules in the entire system. This in turn decreases the pressure and provides a relief to the original stress of a pressure increase. An increase in pressure on an equilibrium system favors the reaction which products fewer total moles of gas. In this case, it is the forward reaction that is favored.

A decrease in pressure on the above system could be achieved by pulling the piston outward, increasing the container volume. The equilibrium would respond by favoring the reverse reaction in which NH_3 decomposes to N_2 and H_2. This is because the overall number of gas molecules would increase and so would the pressure. A decrease in pressure on an equilibrium system favors the reaction which produces more total moles of gas. This is summarized in the table below.

Table 9.6.2

Stress	Response
pressure increase	reaction produces fewer gas molecules
pressure decrease	reaction produces more gas molecules

Like changes in concentration, the K_{eq} value for a given reaction is unchanged by a change in pressure. The amounts of each substance will change but the ratio will not. It is important to remember when analyzing the effect of a pressure change on equilibrium that only gases are affected. If a certain reaction involves liquids or solids, they should be ignored. For example, calcium carbonate decomposes according to the equilibrium reaction:

$$\text{CaCO}_3\,(s) \rightleftharpoons \text{CaO}\,(s) + \text{O}_2\,(g)$$

Oxygen is the only gas in the system. An increase in the pressure of the system slows the rate of decomposition of CaCO_3 because the reverse reaction is favored. When a system contains equal moles of gas on both sides of the equation, pressure has no effect on the equilibrium position, as in the formation of HCl from H_2 and Cl_2.

$$\text{H}_2\,(g) + \text{Cl}_2\,(g) \rightleftharpoons 2\text{HCl}\,(g)$$

✓ Example 9.6.3

What is the effect on this equilibrium if pressure is increased?

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Solution

According to Le Chatelier's principle, if pressure is increased, then the equilibrium shifts to the side with the fewer number of moles of gas. This particular reaction shows a total of 4 mol of gas as reactants and 2 mol of gas as products, so the reaction shifts to the right (toward the products side).

rcise

What is the effect on this equilibrium if pressure is decreased?

$$3O_2(g) \rightleftharpoons 2O_3(g)$$

Answer

Reaction shifts to the left (toward reactants).

Application of Le Chatelier's Principle

Oxygen transport by the blood

In aerobic respiration, oxygen is transported to the cells where it is combined with glucose and metabolized to carbon dioxide, which then moves back to the lungs from which it is expelled.

hemoglobin + O_2 $\rightleftharpoons$ oxyhemoglobin

The partial pressure of O_2 in the air is 0.2 atm, sufficient to allow these molecules to be taken up by hemoglobin (the red pigment of blood) in which it becomes loosely bound in a complex known as oxyhemoglobin. At the ends of the capillaries which deliver the blood to the tissues, the O_2 concentration is reduced by about 50% owing to its consumption by the cells. This shifts the equilibrium to the left, releasing the oxygen so it can diffuse into the cells.

Key Takeaways

- In a reaction at equilibrium, the introduction of more products will shift the mass balance towards more reactants, and the introduction of more reactants will lead to the formation of more products, but the *ratio* of *Products/Reactants* (*equilibrium constant*), *K* is unchanged.
- If temperature is changed, the numeric value *K* will change. If a reaction is *exothermic* (releases heat), an increase in the **temperature** will force the equilibrium to the left, causing the system to absorb heat and thus partially offsetting the rise in temperature. The opposite effect occurs for *endothermic* reactions, which are shifted to the right by rising temperature.
- The effect of **pressure** on an equilibrium is significant only for reactions which involve different numbers of moles of gases on the two sides of the equation. An increase in the total pressure will shift to the side with fewer moles of gas. A decrease in pressure will shift to the side with more moles of gas.

Contributors and Attributions

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9.7: Osmosis and Diffusion

Learning Outcomes

- Define osmosis and diffusion.
- Distinguish among hypotonic, hypertonic, and isotonic solutions.
- Describe a semipermeable membrane.
- Predict behavior of blood cells in different solution types.
- Describe flow of solvent molecules across a membrane.
- Identify the polar and nonpolar regions of a cell membrane.
- Explain the components present in a phospholipid.

Fish cells, like all cells, have semipermeable membranes. Eventually, the concentration of "stuff" on either side of them will even out. A fish that lives in salt water will have somewhat salty water inside itself. Put it in freshwater, and the freshwater will, through osmosis, enter the fish, causing its cells to swell, and the fish will die. What will happen to a freshwater fish in the ocean?

Osmosis

Imagine you have a cup that has 100 mL water, and you add 15 g of table sugar to the water. The sugar dissolves and the mixture that is now in the cup is made up of a **solute** (the sugar) that is dissolved in the **solvent** (the water). The mixture of a solute in a solvent is called a **solution**.

Imagine now that you have a second cup with 100 mL of water, and you add 45 g of table sugar to the water. Just like the first cup, the sugar is the solute, and the water is the solvent. But now you have two mixtures of different solute concentrations. In comparing two solutions of unequal solute concentration, the solution with the higher solute concentration is **hypertonic**, and the solution with the lower solute concentration is **hypotonic**. Solutions of equal solute concentration are **isotonic**. The first sugar solution is hypotonic to the second solution. The second sugar solution is hypertonic to the first.

You now add the two solutions to a beaker that has been divided by a semipermeable membrane, with pores that are too small for the sugar molecules to pass through, but are big enough for the water molecules to pass through. The hypertonic solution is one side of the membrane and the hypotonic solution on the other. The hypertonic solution has a lower water concentration than the hypotonic solution, so a concentration gradient of water now exists across the membrane. Water molecules will move from the side of higher water concentration to the side of lower concentration until both solutions are isotonic. At this point, **equilibrium** is reached.

Red blood cells behave the same way (see figure below). When red blood cells are in a hypertonic (higher concentration) solution, water flows out of the cell faster than it comes in. This results in *crenation* (shriveling) of the blood cell. On the other extreme, a red blood cell that is hypotonic (lower concentration outside the cell) will result in more water flowing into the cell than out. This results in swelling of the cell and potential *hemolysis* (bursting) of the cell. In an isotonic solution, the flow of water in and out of the cell is happening at the same rate.

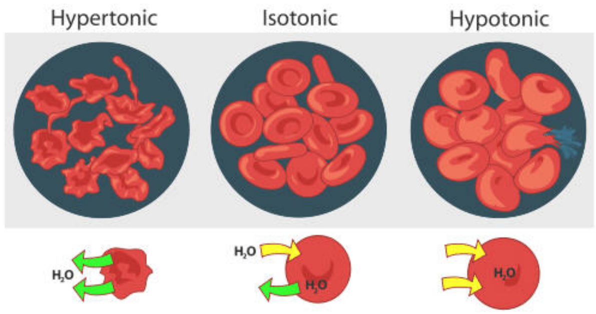

Figure 9.7.1: Red blood cells in hypertonic, isotonic, and hypotonic solutions.

Osmosis is the diffusion of water molecules across a semipermeable membrane from an area of lower concentration solution (i.e., higher concentration of water) to an area of higher concentration solution (i.e., lower concentration of water). Water moves into and out of cells by osmosis.

- If a cell is in a hypertonic solution, the solution has a lower water concentration than the cell cytosol, and water moves out of the cell until both solutions are isotonic.
- Cells placed in a hypotonic solution will take in water across their membranes until both the external solution and the cytosol are isotonic.

A red blood cell will swell and undergo hemolysis (burst) when placed in a hypotonic solution. When placed in a hypertonic solution, a red blood cell will lose water and undergo *crenation* (shrivel). Animal cells tend to do best in an isotonic environment, where the flow of water in and out of the cell is occurring at equal rates.

Diffusion

Passive transport is a way that small molecules or ions move across the cell membrane without input of energy by the cell. The three main kinds of passive transport are diffusion (or simple diffusion), osmosis, and facilitated diffusion. Simple diffusion and osmosis do not involve transport proteins. Facilitated diffusion requires the assistance of proteins.

Diffusion is the movement of molecules from an area of high concentration of the molecules to an area with a lower concentration. For cell transport, diffusion is the movement of small molecules across the cell membrane. The difference in the concentrations of the molecules in the two areas is called the **concentration gradient**. The kinetic energy of the molecules results in random motion, causing diffusion. In simple diffusion, this process proceeds without the aid of a transport protein. It is the random motion of the molecules that causes them to move from an area of high concentration to an area with a lower concentration.

Diffusion will continue until the concentration gradient has been eliminated. Since diffusion moves materials from an area of higher concentration to the lower, it is described as moving solutes "down the concentration gradient". The end result is an equal concentration, or **equilibrium**, of molecules on both sides of the membrane. At equilibrium, movement of molecules does not stop. At equilibrium, there is equal movement of materials in both directions.

Not everything can make it into your cells. Your cells have a plasma membrane that helps to guard your cells from unwanted intruders.

The Plasma Membrane and Cytosol

If the outside environment of a cell is water-based, and the inside of the cell is also mostly water, something has to make sure the cell stays intact in this environment. What would happen if a cell dissolved in water, like sugar does? Obviously, the cell could not survive in such an environment. So something must protect the cell and allow it to survive in its water-based environment. All cells have a barrier around them that separates them from the environment and from other cells. This barrier is called the **plasma membrane**, or cell membrane.

The Plasma Membrane

The plasma membrane (see figure below) is made of a double layer of special lipids, known as **phospholipids**. The phospholipid is a lipid molecule with a hydrophilic ("water-loving") head and two hydrophobic ("water-hating") tails. Because of the hydrophilic and hydrophobic nature of the phospholipid, the molecule must be arranged in a specific pattern as only certain parts of the molecule can physically be in contact with water. Remember that there is water outside the cell, and the **cytoplasm** inside the cell is mostly water as well. So the phospholipids are arranged in a double layer (a bilayer) to keep the cell separate from its environment. Lipids do not mix with water (recall that oil is a lipid), so the phospholipid bilayer of the cell membrane acts as a barrier, keeping water out of the cell, and keeping the cytoplasm inside the cell. The cell membrane allows the cell to stay structurally intact in its water-based environment.

The function of the plasma membrane is to control what goes in and out of the cell. Some molecules can go through the cell membrane to enter and leave the cell, but some cannot. The cell is therefore not completely permeable. "Permeable" means that anything can cross a barrier. An open door is completely permeable to anything that wants to enter or exit through the door. The plasma membrane is **semipermeable**, meaning that some things can enter the cell, and some things cannot.

Molecules that cannot easily pass through the bilayer include ions and small hydrophilic molecules, such as glucose, and macromolecules, including proteins and RNA. Examples of molecules that can easily diffuse across the plasma membrane include carbon dioxide and oxygen gas. These molecules diffuse freely in and out of the cell, along their concentration gradient. Though water is a polar molecule, it can also diffuse through the plasma membrane.

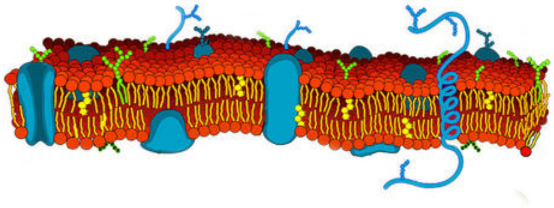

Figure 9.7.2: Plasma membranes are primarily made up of phospholipids (orange). The hydrophilic ("water-loving") head and two hydrophobic ("water-hating") tails are shown. The phospholipids form a bilayer (two layers). The middle of the bilayer is an area without water. There can be water on either side of the bilayer. There are many proteins throughout the membrane.

Cytosol

The inside of all cells also contain a jelly-like substance called **cytosol**. Cytosol is composed of water and other molecules, including **enzymes**, which are proteins that speed up the cell's chemical reactions. Everything in the cell sits in the cytosol, like fruit in a Jell-o mold. The term cytoplasm refers to the cytosol and all of the organelles, the specialized compartments of the cell. The cytoplasm does not include the nucleus. As a prokaryotic cell does not have a nucleus, the DNA is in the cytoplasm.

Supplemental Resources

- The Plasma Membrane: www.youtube.com/watch?v=moPJkCbKjBs

Key Takeaways

- Water moves into and out of cells by osmosis.
- Water (solvent) moves from an area of <u>lower</u> concentration solution (i.e., higher concentration of water) to an area of <u>higher</u> concentration solution (i.e., lower concentration of water).

9.E: Solutions (Exercises)

9.1: Solutions

Concept Review Exercises

1. What causes a solution to form?
2. How does the phrase *like dissolves like* relate to solutions?

Answers

1. Solutions form because a solute and a solvent have similar intermolecular interactions.
2. It means that substances with similar intermolecular interactions will dissolve in each other.

Exercises

1. Define *solution*.
2. Give several examples of solutions.
3. What is the difference between a solvent and a solute?
4. Can a solution have more than one solute in it? Can you give an example?
5. Does a solution have to be a liquid? Give several examples to support your answer.
6. Give at least two examples of solutions found in the human body.
7. Which substances will probably be soluble in water, a very polar solvent?
   a. sodium nitrate ($NaNO_3$)
   b. hexane (C_6H_{14})
   c. isopropyl alcohol [$(CH_3)_2CHOH$]
   d. benzene (C_6H_6)
8. Which substances will probably be soluble in toluene ($C_6H_5CH_3$), a nonpolar solvent?
   a. sodium nitrate ($NaNO_3$)
   b. hexane (C_6H_{14})
   c. isopropyl alcohol [$(CH_3)_2CHOH$]
   d. benzene (C_6H_6)
9. The solubility of alcohols in water varies with the length of carbon chain. For example, ethanol (CH_3CH_2OH) is soluble in water in any ratio, while only 0.0008 mL of heptanol ($CH_3CH_2CH_2CH_2CH_2CH_2CH_2OH$) will dissolve in 100 mL of water. Propose an explanation for this behavior.
10. Dimethyl sulfoxide [$(CH_3)_2SO$] is a polar liquid. Based on the information in Exercise 9, which do you think will be more soluble in it—ethanol or heptanol?

Answers

1. a homogeneous mixture

2. vinegar, dextrose IV, saline IV, coffee, tea, wine

3. A solvent is the majority component of a solution; a solute is the minority component of a solution.

4. yes. Coke or Pepsi has sugar, caffeine and carbon dioxide as solutes.

5. A solution does not have to be liquid; air is a gaseous solution, while some alloys are solid solutions (answers will vary).

6. Urine, plasma

7. a. probably soluble
   b. probably not soluble
   c. probably soluble
   d. probably not soluble

8.

- a. probably not soluble
- b. probably soluble
- c. probably not soluble
- d. probably soluble

9. Small alcohol molecules have strong polar intermolecular interactions, so they dissolve in water. In large alcohol molecules, the nonpolar end overwhelms the polar end, so they do not dissolve very well in water.

10. Ethanol is a smaller molecule. It will be more soluble in water than heptanol.

9.2: Concentration

Concept Review Exercises

1. What are some of the units used to express concentration?
2. Distinguish between the terms *solubility* and *concentration*.

Answers

1. % m/m, % m/v, ppm, ppb, molarity, and Eq/L (answers will vary)
2. Solubility is typically a limit to how much solute can dissolve in a given amount of solvent. Concentration is the quantitative amount of solute dissolved at any concentration in a solvent.

Exercises

1. Define *solubility*. Do all solutes have the same solubility?
2. Explain why the terms *dilute* or *concentrated* are of limited usefulness in describing the concentration of solutions.
3. If the solubility of sodium chloride (NaCl) is 30.6 g/100 mL of H_2O at a given temperature, how many grams of NaCl can be dissolved in 250.0 mL of H_2O?
4. If the solubility of glucose ($C_6H_{12}O_6$) is 120.3 g/100 mL of H_2O at a given temperature, how many grams of $C_6H_{12}O_6$ can be dissolved in 75.0 mL of H_2O?
5. How many grams of sodium bicarbonate ($NaHCO_3$) can a 25.0°C saturated solution have if 150.0 mL of H_2O is used as the solvent?
6. If 75.0 g of potassium bromide (KBr) are dissolved in 125 mL of H_2O, is the solution saturated, unsaturated, or supersaturated?
7. Calculate the mass/mass percent of a saturated solution of NaCl. Use the data from Table $9.E.1$ "Solubilities of Various Solutes in Water at 25°C (Except as Noted)", assume that masses of the solute and the solvent are additive, and use the density of H_2O (1.00 g/mL) as a conversion factor.
8. Calculate the mass/mass percent of a saturated solution of $MgCO_3$ Use the data from Table $9.E.1$ "Solubilities of Various Solutes in Water at 25°C (Except as Noted)", assume that masses of the solute and the solvent are additive, and use the density of H_2O (1.00 g/mL) as a conversion factor.
9. Only 0.203 mL of C_6H_6 will dissolve in 100.000 mL of H_2O. Assuming that the volumes are additive, find the volume/volume percent of a saturated solution of benzene in water.
10. Only 35 mL of aniline ($C_6H_5NH_2$) will dissolve in 1,000 mL of H_2O. Assuming that the volumes are additive, find the volume/volume percent of a saturated solution of aniline in water.
11. A solution of ethyl alcohol (C_2H_5OH) in water has a concentration of 20.56% v/v. What volume of C_2H_5OH is present in 255 mL of solution?
12. What mass of KCl is present in 475 mL of a 1.09% m/v aqueous solution?
13. The average human body contains 5,830 g of blood. What mass of arsenic is present in the body if the amount in blood is 0.55 ppm?

14. The Occupational Safety and Health Administration has set a limit of 200 ppm as the maximum safe exposure level for carbon monoxide (CO). If an average breath has a mass of 1.286 g, what is the maximum mass of CO that can be inhaled at that maximum safe exposure level?
15. Which concentration is greater—15 ppm or 1,500 ppb?
16. Express the concentration 7,580 ppm in parts per billion.
17. What is the molarity of 0.500 L of a potassium chromate solution containing 0.0650 mol of K_2CrO_4?
18. What is the molarity of 4.50 L of a solution containing 0.206 mol of urea $[(NH_2)_2CO]$?
19. What is the molarity of a 2.66 L aqueous solution containing 56.9 g of NaBr?
20. If 3.08 g of $Ca(OH)_2$ is dissolved in enough water to make 0.875 L of solution, what is the molarity of the $Ca(OH)_2$?
21. What mass of HCl is present in 825 mL of a 1.25 M solution?
22. What mass of isopropyl alcohol (C_3H_8O) is dissolved in 2.050 L of a 4.45 M aqueous C_3H_8O solution?
23. What volume of 0.345 M NaCl solution is needed to obtain 10.0 g of NaCl?
24. How many milliliters of a 0.0015 M cocaine hydrochloride ($C_{17}H_{22}ClNO_4$) solution is needed to obtain 0.010 g of the solute?
25. Aqueous calcium chloride reacts with aqueous silver nitrate according to the following balanced chemical equation:

$$CaCl_2(aq) + 2AgNO_3(aq) \rightarrow 2AgCl(s) + Ca(NO_3)_2(aq)$$

    How many moles of AgCl(s) are made if 0.557 L of 0.235 M $CaCl_2$ react with excess $AgNO_3$? How many grams of AgCl are made?
26. Sodium bicarbonate ($NaHCO_3$) is used to react with acid spills. The reaction with sulfuric acid (H_2SO_4) is as follows:

$$2NaHCO_3(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(\ell) + 2CO_2(g)$$

    If 27.6 mL of a 6.25 M H_2SO_4 solution were spilled, how many moles of $NaHCO_3$ would be needed to react with the acid? How many grams of $NaHCO_3$ is this?
27. The fermentation of glucose to make ethanol and carbon dioxide has the following overall chemical equation:

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

    If 1.00 L of a 0.567 M solution of $C_6H_{12}O_6$ were completely fermented, what would be the resulting concentration of the C_2H_5OH solution? How many moles of CO_2 would be formed? How many grams is this? If each mole of CO_2 had a volume of 24.5 L, what volume of CO_2 is produced?
28. Aqueous sodium bisulfite gives off sulfur dioxide gas when heated:

$$2NaHSO_3(aq) \rightarrow Na_2SO_3(aq) + H_2O(\ell) + SO_2(g)$$

    If 567 mL of a 1.005 M $NaHSO_3$ solution were heated until all the $NaHSO_3$ had reacted, what would be the resulting concentration of the Na_2SO_3 solution? How many moles of SO_2 would be formed? How many grams of SO_2 would be formed? If each mole of SO_2 had a volume of 25.78 L, what volume of SO_2 would be produced?
29. What is the concentration of a 1.0 M solution of $K^+(aq)$ ions in equivalents/liter?
30. What is the concentration of a 1.0 M solution of $SO_4^{2-}(aq)$ ions in equivalents/liter?
31. A solution having initial concentration of 0.445 M and initial volume of 45.0 mL is diluted to 100.0 mL. What is its final concentration?
32. A 50.0 mL sample of saltwater that is 3.0% m/v is diluted to 950 mL. What is its final mass/volume percent?

Answers

1. Solubility is the amount of a solute that can dissolve in a given amount of solute, typically 100 mL. The solubility of solutes varies widely.

2. The term *dilute* means relatively less solute and the term *concentrated* implies relatively more solute. Both are of limited usefulness because these are not accurate.

3. 76.5 g
4. 90.2 g

5. 12.6 g

6. unsaturated

7. 26.5%

8. 2.15%

9. 0.203%

10. 3.4%

11. 52.4 mL

12. 5.18 g

13. 0.00321 g

14. 2.57 x 10^{-4} g

15. 15 ppm

16. 7,580,000 ppb

17. 0.130 M
18. 0.0458 M

19. 0.208 M

20. 0.0475 M

21. 37.6 g

22. 548 g

23. 0.496 L

24. 20 mL

25. 0.262 mol; 37.5 g

26. 0.345 mol; 29.0 g

27. 1.13 M C_2H_5OH; 1.13 mol of CO_2; 49.7 g of CO_2; 27.7 L of CO_2
28. 0.503 M Na_2SO_3; 0.285 mol SO_2; 18.3 g SO_2; 471 L SO_2
29. 1.0 Eq/L
30. 2.0 Eq/L
31. 0.200 M

32. 0.16 % m/v

9.3: The Dissolution Process

Concept Review Exercise

1. Explain how the solvation process describes the dissolution of a solute in a solvent.

Answer

1. Each particle of the solute is surrounded by particles of the solvent, carrying the solute from its original phase.

Exercises

1. Describe what happens when an ionic solute like Na_2SO_4 dissolves in a polar solvent.

2. Describe what happens when a molecular solute like sucrose ($C_{12}H_{22}O_{11}$) dissolves in a polar solvent.

3. Classify each substance as an electrolyte or a nonelectrolyte. Each substance dissolves in H_2O to some extent.
    a. NH_4NO_3

   b. CO_2
   c. NH_2CONH_2
   d. HCl

4. Classify each substance as an electrolyte or a nonelectrolyte. Each substance dissolves in H_2O to some extent.
   a. $CH_3CH_2CH_2OH$
   b. $Ca(CH_3CO_2)_2$
   c. I_2
   d. KOH
5. Will solutions of each solute conduct electricity when dissolved?
   a. $AgNO_3$
   b. $CHCl_3$
   c. $BaCl_2$
   d. Li_2O
6. Will solutions of each solute conduct electricity when dissolved?
   a. CH_3COCH_3
   b. $N(CH_3)_3$
   c. $CH_3CO_2C_2H_5$
   d. $FeCl_2$

Answers

1. Each ion of the ionic solute is surrounded by particles of solvent, carrying the ion from its associated crystal.
2. Each sucrose molecule is surrounded by solvent molecules (attracted to each other via intermolecular forces of attraction).
3. a. electrolyte
   b. nonelectrolyte
   c. nonelectrolyte
   d. electrolyte
4.
   a. nonelectrolyte
   b. electrolyte
   c. nonelectrolyte
   d. electrolyte
5.
   a. yes
   b. no
   c. yes
   d. yes
6.
   a. no
   b. no
   c. no
   d. yes

9.4: Properties of Solutions

Concept Review Exercises

1. What are the colligative properties of solutions?

2. Explain how the following properties of solutions differ from those of the pure solvent: vapor pressure, boiling point, freezing point, and osmotic pressure.

Answers

1. Colligative properties are characteristics that a solution has that depend on the number, not the identity, of solute particles.
2. In solutions, the vapor pressure is lower, the boiling point is higher, the freezing point is lower, and the osmotic pressure is higher.

Exercises

1. In each pair of aqueous systems, which will have the lower vapor pressure?
   a. pure water or 1.0 M NaCl
   b. 1.0 M NaCl or 1.0 M $C_6H_{12}O_6$
   c. 1.0 M $\mathrm{CaCl_2}$ 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 $\mathrm{CaCl_2}$ 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 ($\mathrm{CaCl_2}$) 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. $\mathrm{CaCl_2}$ splits up into 3 ions while NaCl splits up into 2 ions only. $\mathrm{CaCl_2}$ will be more effective.

9.
   a. 0.500 osmol
   b. 1.000 osmol
   c. 1.500 osmol

10.
   a. 0.300 osmol
   b. 0.450 osmol
   c. 2.50 osmol

11. It must separate into three ions when it dissolves.

12. Both NaCl and $Al(NO_3)_3$ have 3.0 osmol. There will be no net difference in the solvent flow.

9.5: Chemical Equilibrium

Concept Review Exercises

1. What is chemical equilibrium?

2. What does the equilibrium constant tell us?

Answers

1. The rate of the forward reaction equals the rate of the reverse reaction.

2. The ratio of products and reactants when the system is at equilibrium.

EXERCISES

1. If the reaction $H_2 + I_2 \rightleftharpoons 2HI$ is at equilibrium, do the concentrations of HI, H_2, and I_2 have to be equal?

2. Do the concentrations at equilibrium depend upon how the equilibrium was reached?

3. What does it mean if the K_{eq} is > 1?

4. What does it mean if the K_{eq} is < 1?

5. Does the equilibrium state depend on the starting concentrations?

6. Write an expression for the equilibrium constant K equation.

   a. $PCl_5\ (g) \rightleftarrows PCl_3\ (g) + Cl_2\ (g)$

   b. $2\,O_3\ (g) \rightleftharpoons 3\,O_2\ (g)$

7. Benzene is one of the compounds used as octane enhancers in unleaded gasoline. It is manufactured by the catalytic conversion of acetylene to benzene: $3C_2H_2(g) \longrightarrow C_6H_6(g)$. Which value of K would make this reaction most useful commercially? Explain your answer.

   a. $K \approx 0.01$

   b. $K \approx 1$

   c. $K \approx 10$.

8. Tell whether the reactants or the products are favored at equilibrium:

   a. $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $K = 172$

   b. $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ $K = 0.230$

   c. $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$ $K = 4.6 \times 10^4$

   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. $K = \dfrac{[PCl_3][Cl_2]}{[PCl_5]}$

   b. $K = \dfrac{[O_2]^3}{[O_3]^2}$

7. The answer is c. $K \approx 10$.

Since $K = \dfrac{[C_6H_6]^2}{[C_2H_2]^3}$ ($K \approx 10$), 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?

$PCl_5(g) + \text{heat} \rightleftharpoons PCl_3(g) + Cl_2(g)$

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?

$HNO_2(aq) \rightleftharpoons H^+(aq) + NO_2^-(aq)$

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?

$CO_2(g) + C(s) \rightleftharpoons 2CO(g)$ $\Delta H = 172.5 kJ$

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?

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ $\Delta H = -9.48 kJ$

a. Addition of H_2
b. Removal of H_2
c. Increasing temperature

d. Decreasing temperature
e. Increasing volume
f. Decreasing volume

AnswerS

1.

a. shift right
b. shift left
c. shift right
d. shift right
e. shift left
f. shift left

2.

a. shift left
b. shift left
c. no effect
d. no effect
e. shift right
f. shift right

3.

a. shift right
b. shift left
c. shift right
d. shift left
e. shift right
f. shift left

4.

a. shift right
b. shift left
c. shift left
d. shift right
e. no effect
f. no effect

9.7: Osmosis and Diffusion

Concept Review Exercises

1. What are some of the features of a semipermeable membrane?

2. What do the prefixes hyper, hypo, and iso mean?

Answers

1. A semipermeable membrane allows some substances to pass through but not others.

2. hyper – higher; hypo – lower; iso - same

EXERCISES

1. Two solutions are separated by a semipermeable membrane. Solution A contains 25.0 g of NaCl in 100.0 mL of water and solution B contains 35.0 g of NaCl in 100.0 mL of water.

   a. Which one has a higher concentration?
   b. Which way will water molecules flow?
   c. Which volume will increase?
   d. Which volume will decrease?
   e. What will happen to the concentration of solution A?
   f. What will happen to the concentration of solution B?

2. Two solutions with different concentrations and compositions are separated by a semipermeable membrane. The left-hand solution is a .50 M solution of $MgSO_4$, while the right-hand solution contains $CaCl_2$ at a concentration of .40 M. Determine the direction of the flow of solvent, left or right.

3. Given the following situations, wherein two tanks of different solutions are separated by a semipermeable membrane, determine the direction of the flow of solvent (water).

   a. Solution A contains a 0.40 M concentration of $CaCl_2$, while Solution B contains a 0.45 M concentration of KI

   b. Solution A contains a 1.00 M concentration of NH_4Cl, while Solution B contains a 1.00 M concentration of CH_2O

4. Cells are placed in a solution and the cells then undergo hemolysis. What can be said about the relative concentrations of solute in the cell and the solution?

5. Describe the relative concentrations inside and outside a red blood cell when crenation occurs.

6. A saltwater fish is placed in a freshwater tank. What will happen to the fish? Describe the flow of water molecules to explain the outcome.

7. What makes up the "head" region of a phospholipid? Is it hydrophobic or hydrophilic?

8. What makes up the "tail" region of a phospholipid? Is it hydrophobic or hydrophilic?

Answers

1. Two solutions are separated by a semipermeable membrane. Solution A contains 25.0 g of NaCl in 100.0 mL of water and solution B contains 35.0 g of NaCl in 100.0 mL of water.

   a. Solution B
   b. A → → B
   c. B
   d. A
   e. increase
   f. decrease

2. Water (solvent) flows from left to right.

3.

   a. Water flows from Solution B to Solution A.

   b. Water flows from Solution B to Solution A.

4. Cells contain fluid with higher concentration than solution outside the cell.

5. Cells contain fluid with a lower concentration than the solution outside the cell.

6. Water molecules will flow from the tank water into the fish because the fish has a higher concentration of salt. If the fish absorbs too much water, it will die.

7. The "head" region is a phosphate group and it is hydrophilic.

8. The "tail" is a hydrocarbon tail and it is hydrophobic.

Contributors

-
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Additional Exercises

1. Calcium nitrate reacts with sodium carbonate to precipitate solid calcium carbonate:

$$Ca(NO_3)_{2(aq)} + Na_2CO_{3(aq)} \rightarrow CaCO_{3(s)} + NaNO_{3(aq)} \tag{9.E.1}$$

   a. Balance the chemical equation.
   b. How many grams of Na_2CO_3 are needed to react with 50.0 mL of 0.450 M $Ca(NO_3)_2$?
   c. Assuming that the Na_2CO_3 has a negligible effect on the volume of the solution, find the osmolarity of the $NaNO_3$ solution remaining after the $CaCO_3$ precipitates from solution.

2. The compound HCl reacts with sodium carbonate to generate carbon dioxide gas:

$$HCl_{(aq)} + Na_2CO_{3(aq)} \rightarrow H_2O_{(\ell)} + CO_{2(g)} + NaCl_{(aq)} \tag{9.E.2}$$

   a. Balance the chemical equation.
   b. How many grams of Na_2CO_3 are needed to react with 250.0 mL of 0.755 M HCl?
   c. Assuming that the Na_2CO_3 has a negligible effect on the volume of the solution, find the osmolarity of the NaCl solution remaining after the reaction is complete.

3. Estimate the freezing point of concentrated aqueous HCl, which is usually sold as a 12 M solution. Assume complete ionization into H^+ and Cl^- ions.

4. Estimate the boiling point of concentrated aqueous H_2SO_4, which is usually sold as an 18 M solution. Assume complete ionization into H^+ and HSO_4^- ions.

5. Seawater can be approximated by a 3.0% m/m solution of NaCl in water. Determine the molarity and osmolarity of seawater. Assume a density of 1.0 g/mL.

6. Human blood can be approximated by a 0.90% m/m solution of NaCl in water. Determine the molarity and osmolarity of blood. Assume a density of 1.0 g/mL.

7. How much water must be added to 25.0 mL of a 1.00 M NaCl solution to make a resulting solution that has a concentration of 0.250 M?

8. Sports drinks like Gatorade are advertised as capable of resupplying the body with electrolytes lost by vigorous exercise. Find a label from a sports drink container and identify the electrolytes it contains. You should be able to identify several simple ionic compounds in the ingredients list.

9. Occasionally we hear a sensational news story about people stranded in a lifeboat on the ocean who had to drink their own urine to survive. While distasteful, this act was probably necessary for survival. Why not simply drink the ocean water? (Hint: See Exercise 5 and Exercise 6 above. What would happen if the two solutions in these exercises were on opposite sides of a semipermeable membrane, as we would find in our cell walls?)

Answers

1.
   a. $Ca(NO_3)_2(aq) + Na_2CO_3(aq) \rightarrow CaCO_3(s) + 2NaNO_3(aq)$
   b. 2.39 g
   c. 1.80 osmol

2.
   a. $2HCl\ (aq) + Na_2CO_3(aq) \rightarrow H_2O(\ell) + CO_2(g) + 2NaCl\ (aq)$

   b. 10.0 g

   c. 1.51 M

3. −45.6°C
4. 118°C
5. 0.513 M; 1.026 osmol
6. molarity = 0.15 M; osmolarity = 0.31 M
7. 75.0 mL
8. magnesium chloride, calcium chloride (answers may vary)
9. The osmotic pressure of seawater is too high. Drinking seawater would cause water to go from inside our cells into the more concentrated seawater, ultimately killing the cells.

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9.S: Solutions (Summary)

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

A **solution** is a homogeneous mixture. The major component is the **solvent**, while the minor component is the **solute**. Solutions can have any phase; for example, an **alloy** is a solid solution. Solutes are **soluble** or **insoluble**, meaning they dissolve or do not dissolve in a particular solvent. The terms **miscible** and **immiscible**, instead of soluble and insoluble, are used for liquid solutes and solvents. The statement *like dissolves like* is a useful guide to predicting whether a solute will dissolve in a given solvent.

The amount of solute in a solution is represented by the **concentration** of the solution. The maximum amount of solute that will dissolve in a given amount of solvent is called the **solubility** of the solute. Such solutions are **saturated**. Solutions that have less than the maximum amount are **unsaturated**. Most solutions are unsaturated, and there are various ways of stating their concentrations. **Mass/mass percent**, **volume/volume percent**, and **mass/volume percent** indicate the percentage of the overall solution that is solute. **Parts per million (ppm)** and **parts per billion (ppb)** are used to describe very small concentrations of a solute. **Molarity**, defined as the number of moles of solute per liter of solution, is a common concentration unit in the chemistry laboratory. **Equivalents** express concentrations in terms of moles of charge on ions. When a solution is diluted, we use the fact that the amount of solute remains constant to be able to determine the volume or concentration of the final diluted solution.

Dissolving occurs by **solvation**, the process in which particles of a solvent surround the individual particles of a solute, separating them to make a solution. For water solutions, the word **hydration** is used. If the solute is molecular, it dissolves into individual molecules. If the solute is ionic, the individual ions separate from each other, forming a solution that conducts electricity. Such solutions are called **electrolytes**. If the dissociation of ions is complete, the solution is a **strong electrolyte**. If the dissociation is only partial, the solution is a **weak electrolyte**. Solutions of molecules do not conduct electricity and are called **nonelectrolytes**.

Solutions have properties that differ from those of the pure solvent. Some of these are **colligative** properties, which are due to the number of solute particles dissolved, not the chemical identity of the solute. Colligative properties include **vapor pressure depression**, **boiling point elevation**, **freezing point depression**, and **osmotic pressure**. Osmotic pressure is particularly important in biological systems. It is caused by **osmosis**, the passage of solvents through certain membranes like cell walls. The **osmolarity** of a solution is the product of a solution's molarity and the number of particles a solute separates into when it dissolves. Osmosis can be reversed by the application of pressure; this reverse osmosis is used to make fresh water from saltwater in some parts of the world. Because of osmosis, red blood cells placed in hypotonic or hypertonic solutions lose function through either hemolysis or crenation. If they are placed in isotonic solutions, however, the cells are unaffected because osmotic pressure is equal on either side of the cell membrane.

CHAPTER OVERVIEW

10: Acids and Bases

Many of us are familiar with the group of chemicals called acids. But do you know what it takes for a compound to be an acid? Actually, there are several different definitions of acid that chemistry uses, and each definition is appropriate under different circumstances. Less familiar—but just as important to chemistry and ultimately to us—is the group of chemicals known as bases. Both acids and bases are important enough that we devote an entire chapter to them—their properties and their reactions.

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10.0: Prelude to Acids and Bases

One of the most concentrated acids in the body is stomach acid, which can be approximated as a 0.05 M hydrochloric acid solution. Special cells in the stomach wall secrete this acid, along with special enzymes, as part of the digestion process. In a laboratory, a 0.05 M solution of hydrochloric acid would dissolve some metals. How does the stomach survive the presence of such a reactive acid?

Actually, the stomach has several mechanisms for withstanding this chemical onslaught. First, the lining of the stomach is coated with a thin layer of mucus that contains some bicarbonate ions (HCO_3^-). These react with the hydrochloric acid to produce water, carbon dioxide, and harmless chloride ions. If any acid penetrates through the mucus, it can attack the surface layer of stomach cells, called the *gastric epithelium*. Cells in the gastric epithelium are being constantly shed, so damaged cells are quickly removed and replaced with healthy cells.

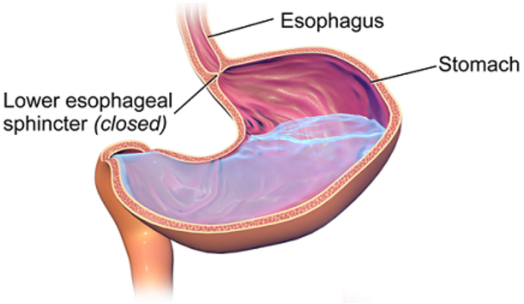


Figure 10.0.1: Stomach with acidic digestive juices. (CC BY-SA 4.0; BruceBlaus).

However, if the gastric epithelium is destroyed faster than it can be replaced, the acid may reach the wall of the stomach, resulting in ulcers. If an ulcer grows large enough, it can expose blood vessels in the stomach wall, causing bleeding. In extreme situations, the loss of blood through a severe ulcer can threaten a person's health.

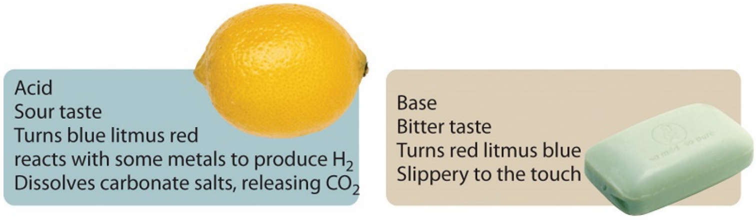
Ulcers can also result from the presence of a certain bacterium—*Helicobacter pylori*—in the stomach. The mechanism for this ulcer formation is not the same as that for ulcers caused by stomach acid and is not completely understood. However, there are two main treatments for ulcers: (1) *antacids* to react chemically with excess hydrochloric acid in the stomach and (2) *antibiotics* to destroy the *H. pylori* bacteria in the stomach.

10.1: Arrhenius Definition of Acids and Bases

Learning Objectives

- To recognize a compound as an Arrhenius acid or an Arrhenius base.
- To describe characteristics of acids and bases.
- To write equations of neutralization reactions.

One way to define a class of compounds is by describing the various characteristics its members have in common. In the case of the compounds known as acids, the common characteristics include a sour taste, the ability to change the color of the vegetable dye *litmus* to red, and the ability to dissolve certain metals and simultaneously produce hydrogen gas. For the compounds called bases, the common characteristics are a slippery texture, a bitter taste, and the ability to change the color of litmus to blue. Acids and bases also react with each other to form compounds generally known as salts.



Although we include their tastes among the common characteristics of acids and bases, we never advocate tasting an unknown chemical!

Chemists prefer, however, to have definitions for acids and bases in chemical terms. The Swedish chemist Svante Arrhenius developed the first chemical definitions of acids and bases in the late 1800s. Arrhenius defined an acid as a compound that increases the concentration of hydrogen ion (H^+) in aqueous solution. Many acids are simple compounds that release a hydrogen cation into solution when they dissolve. Similarly, Arrhenius defined a base as a compound that increases the concentration of hydroxide ion (OH^-) in aqueous solution. Many bases are ionic compounds that have the hydroxide ion as their anion, which is released when the base dissolves in water.

Table 10.1.1: Formulas and Names for Some Acids and Bases

Acids		**Bases**	
Formula	Name	Formula	Name
$HCl(aq)$	hydrochloric acid	$NaOH(aq)$	sodium hydroxide
$HBr(aq)$	hydrobromic acid	$KOH(aq)$	potassium hydroxide
$HI(aq)$	hydriodic acid	$Mg(OH)_2(aq)$	magnesium hydroxide
$H_2S(aq)$	hydrosulfuric acid	$Ca(OH)_2(aq)$	calcium hydroxide
$HC_2H_3O_2(aq)$	acetic acid	$NH_3(aq)$	ammonia
$HNO_3(aq)$	nitric acid	$NaHCO_3$ (aq)	sodium bicarbonate
$HNO_2(aq)$	nitrous acid	$CaCO_3$ (aq)	calcium carbonate
$H_2SO_4(aq)$	sulfuric acid		
$H_2SO_3(aq)$	sulfurous acid		
$HClO_3(aq)$	chloric acid		
$HClO_4(aq)$	perchloric acid		
$HClO_2(aq)$	chlorous acid		
$H_3PO_4(aq)$	phosphoric acid		

Acids		Bases	
$H_3PO_3(aq)$	phosphorous acid		
$H_2CO_3(aq)$	carbonic acid		

Many bases and their aqueous solutions are named using the normal rules of ionic compounds that were presented previously; that is, they are named as hydroxide compounds. For example, the base sodium hydroxide (NaOH) is both an ionic compound and an aqueous solution. However, aqueous solutions of acids have their own naming rules. The names of *binary acids* (compounds with hydrogen and one other element in their formula) are based on the root of the name of the other element preceded by the prefix *hydro*- and followed by the suffix -*ic acid*. Thus, an aqueous solution of HCl [designated "HCl(aq)"] is called hydrochloric acid, $H_2S(aq)$ is called hydrosulfuric acid, and so forth. Acids composed of more than two elements (typically hydrogen and oxygen and some other element) have names based on the name of the other element, followed by the suffix -*ic acid* or -*ous acid*, depending on the number of oxygen atoms in the acid's formula. Other prefixes, like *per*- and *hypo*-, also appear in the names for some acids. Unfortunately, there is no strict rule for the number of oxygen atoms that are associated with the -*ic acid* suffix; the names of these acids are best memorized. Table 10.1.1 lists some acids and bases and their names. Note that acids have hydrogen written first, as if it were the cation, while most bases have the negative hydroxide ion, if it appears in the formula, written last.

> *The name oxygen comes from the Latin meaning "acid producer" because its discoverer, Antoine Lavoisier, thought it was the essential element in acids. Lavoisier was wrong, but it is too late to change the name now.*

✓ Example 10.1.1

Name each substance.

a. HF(aq)
b. $Sr(OH)_2(aq)$

Solution

a. This acid has only two elements in its formula, so its name includes the *hydro*- prefix. The stem of the other element's name, fluorine, is *fluor*, and we must also include the -*ic acid* ending. Its name is hydrofluoric acid.
b. This base is named as an ionic compound between the strontium ion and the hydroxide ion: strontium hydroxide.

? Exercise 10.1.1

Name each substance.

a. $H_2Se(aq)$
b. $Ba(OH)_2(aq)$

Answer

a. hydroselenic acid

b. barium hydroxide

Notice that one base listed in Table 10.1.1—ammonia—does not have hydroxide as part of its formula. How does this compound increase the amount of hydroxide ion in aqueous solution? Instead of dissociating into hydroxide ions, ammonia molecules react with water molecules by taking a hydrogen ion from the water molecule to produce an ammonium ion and a hydroxide ion:

$$NH_{3(aq)} + H_2O_{(\ell)} \rightarrow NH^+_{4(aq)} + OH^-_{(aq)} \tag{10.1.1}$$

Because this reaction of ammonia with water causes an increase in the concentration of hydroxide ions in solution, ammonia satisfies the Arrhenius definition of a base. Many other nitrogen-containing compounds are bases because they too react with water to produce hydroxide ions in aqueous solution.

Neutralization

As we noted previously, acids and bases react chemically with each other to form *salts*. A salt is a general chemical term for any ionic compound formed from an acid and a base. In reactions where the acid is a hydrogen ion containing compound and the base is a hydroxide ion containing compound, water is also a product. The general reaction is as follows:

acid + base → water + salt

The reaction of acid and base to make water and a salt is called **neutralization**. Like any chemical equation, a neutralization chemical equation must be properly balanced. For example, the neutralization reaction between sodium hydroxide and hydrochloric acid is as follows:

$$NaOH(aq) + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(\ell)} \tag{10.1.2}$$

with coefficients all understood to be one. The neutralization reaction between sodium hydroxide and sulfuric acid is as follows:

$$2NaOH_{(aq)} + H_2SO_{4(aq)} \rightarrow Na_2SO_{4(aq)} + 2H_2O_{(\ell)} \tag{10.1.3}$$

Once a neutralization reaction is properly balanced, we can use it to perform stoichiometry calculations, such as the ones we practiced earlier.

There are a number of examples of acid-base chemistry in everyday life. One example is the use of baking soda, or sodium bicarbonate in baking. $NaHCO_3$ is a base. When it reacts with an acid such as lemon juice, buttermilk, or sour cream in a batter, bubbles of carbon dioxide gas are formed from decomposition of the resulting carbonic acid, and the batter “rises.” Baking powder is a combination of sodium bicarbonate, and one or more acid salts that react when the two chemicals come in contact with water in the batter.

$$HCO_3^-(aq) + H^+(aq) \rightarrow H_2CO_3(aq) \tag{10.1.4}$$

$$H_2CO_3(aq) \rightarrow CO_2(g) + H_2O(l)$$

✓ Example 10.1.2

Nitric acid [HNO_3(aq)] can be neutralized by calcium hydroxide [$Ca(OH)_2$(aq)].

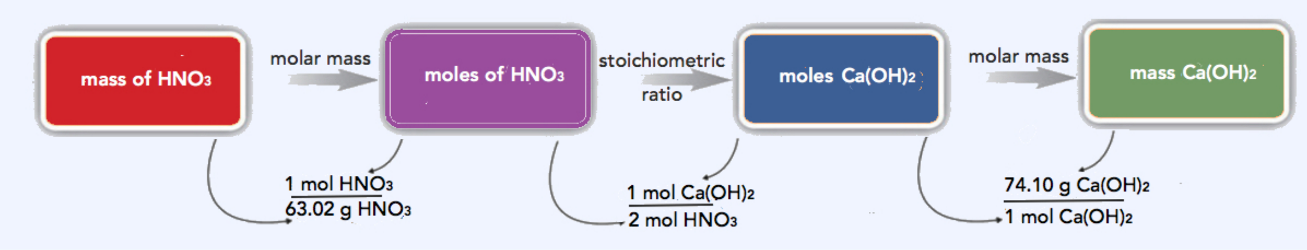
a. Write a balanced chemical equation for the reaction between these two compounds and identify the salt it produces.
b. For one reaction, 16.8 g of HNO_3 is present initially. How many grams of $Ca(OH)_2$ are needed to neutralize that much HNO_3?
c. In a second reaction, 805 mL of 0.672 M $Ca(OH)_2$ is present initially. What volume of 0.432 M HNO_3 solution is necessary to neutralize the $Ca(OH)_2$ solution?

Solution

a. Because there are two OH^- ions in the formula for $Ca(OH)_2$, we need two moles of HNO_3 to provide H^+ ions. The balanced chemical equation is as follows: $Ca(OH)_2(aq) + 2HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + 2H_2O(\ell)$

   The salt formed is calcium nitrate.

b. This calculation is much like the calculations we did in Chapter 6. First we convert the mass of HNO_3 to moles using its molar mass of 1.01 + 14.01 + 3(16.00) = 63.02 g/mol; then we use the balanced chemical equation to determine the related number of moles of $Ca(OH)_2$ needed to neutralize it; and then we convert that number of moles of $Ca(OH)_2$ to the mass of $Ca(OH)_2$ using its molar mass of 40.08 + 2(1.01) + 2(16.00) = 74.10 g/mol.



$$16.8 \text{ g HNO}_3 \times \frac{1 \text{ mol HNO}_3}{63.02 \text{ g HNO}_3} \times \frac{1 \text{ mol Ca(OH)}_2}{2 \text{ mol HNO}_3} \times \frac{74.10 \text{ g Ca(OH)}_2}{1 \text{ mol Ca(OH)}_2} = 9.88 \text{ g Ca(OH)}_2 \text{ needed}$$

c. Having concentration information allows us to employ the skills we developed in Chapter 9. We have two alternative solutions: the multi-step process and the combined one-line process (found at the bottom).

First, we use the concentration and volume data to determine the number of moles of $Ca(OH)_2$ present. Recognizing that 805 mL = 0.805 L,

$$0.672 \text{ M Ca(OH)}_2 = \frac{\text{mol Ca(OH)}_2}{0.805 \text{ L soln}}$$

$$0.672 \text{ M CaOH)}_2 \times (0.805 \text{ L soln}) = \text{mol Ca(OH)}_2 = 0.541 \text{ mol Ca(OH)}_2$$

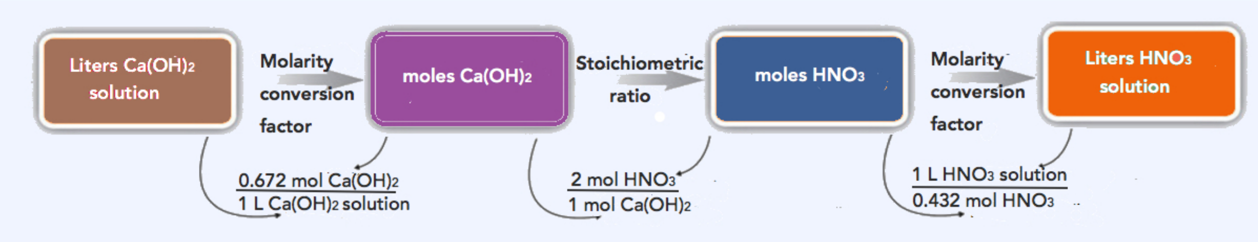
We combine this information with the proper ratio from the balanced chemical equation to determine the number of moles of HNO_3 needed:

$$0.541 \text{ mol Ca(OH)}_2 \times \frac{2 \text{ mol HNO}_3}{1 \text{ mol Ca(OH)}_2} = 1.08 \text{ mol HNO}_3$$

Now, using the definition of molarity one more time, we determine the volume of acid solution needed:

$$0.432 \text{ M HNO}_3 = \frac{1.08 \text{ mol HNO}_3}{\text{volume of HNO}_3}$$

$$\text{volume of HNO}_3 = \frac{1.08 \text{ mol HNO}_3}{0.432 \text{ M HNO}_3} = 2.50 \text{ L} = 2.50 \times 10^3 \text{ mL HNO}_3$$



$$0.805 \text{ L Ca(OH)}_2 \text{ soln} \times \frac{0.672 \text{ mol Ca(OH)}_2}{1 \text{ L Ca(OH)}_2 \text{ soln}} \times \frac{2 \text{ mol HNO}_3}{1 \text{ mol Ca(OH)}_2} \times \frac{1 \text{ L HNO}_3 \text{ soln}}{0.432 \text{ mol HNO}_3} = 2.50 \text{ L HNO}_3 \text{ soln needed}$$

? Exercise 10.1.2

Hydrocyanic acid [HCN(aq)] can be neutralized by potassium hydroxide [KOH(aq)].

a. Write a balanced chemical equation for the reaction between these two compounds and identify the salt it produces.
b. For one reaction, 37.5 g of HCN is present initially. How many grams of KOH are needed to neutralize that much HCN?
c. In a second reaction, 43.0 mL of 0.0663 M KOH is present initially. What volume of 0.107 M HCN solution is necessary to neutralize the KOH solution?

Answer

a. $KOH(aq) + HCN(aq) \rightarrow KCN(aq) + H_2O(\ell)$ KCN is the salt.

b. 77.8 g

c. 0.0266 L or 26.6 mL

Hydrocyanic acid (HCN) is one exception to the acid-naming rules that specify using the prefix *hydro-* for binary acids (acids composed of hydrogen and only one other element).

Stomach Antacids

Our stomachs contain a solution of roughly 0.03 *M* HCl, which helps us digest the food we eat. The burning sensation associated with heartburn is a result of the acid of the stomach leaking through the muscular valve at the top of the stomach into the lower reaches of the esophagus. The lining of the esophagus is not protected from the corrosive effects of stomach acid the way the lining of the stomach is, and the results can be very painful. When we have heartburn, it feels better if we reduce the excess acid in the esophagus by taking an antacid. As you may have guessed, antacids are bases. One of the most common antacids is calcium carbonate, $CaCO_3$. The reaction,

$$CaCO_3(s) + 2HCl(aq) \rightleftharpoons CaCl_2(aq) + H_2O(l) + CO_2(g)$$

not only neutralizes stomach acid, it also produces $CO_2(g)$, which may result in a satisfying belch.

Milk of Magnesia is a suspension of the sparingly soluble base magnesium hydroxide, $Mg(OH)_2$. It works according to the reaction:

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$$

The hydroxide ions generated in this equilibrium then go on to react with the hydronium ions from the stomach acid, so that :

$$H_3O^+ + OH^- \rightleftharpoons 2H_2O(l)$$

This reaction does not produce carbon dioxide, but magnesium-containing antacids can have a laxative effect. Several antacids have aluminum hydroxide, $Al(OH)_3$, as an active ingredient. The aluminum hydroxide tends to cause constipation, and some antacids use aluminum hydroxide in concert with magnesium hydroxide to balance the side effects of the two substances.

✓ Example 10.1.3

Assume that the stomach of someone suffering from acid indigestion contains 75 mL of 0.20 M HCl. How many Tums tablets are required to neutralize 90% of the stomach acid, if each tablet contains 500 mg of $CaCO_3$? (Neutralizing all of the stomach acid is not desirable because that would completely shut down digestion.)

Solution

A. Write the balanced chemical equation for the reaction and then decide whether the reaction will go to completion.
B. Calculate the number of moles of acid present. Multiply the number of moles by the percentage to obtain the quantity of acid that must be neutralized. Using mole ratios, calculate the number of moles of base required to neutralize the acid.
C. Calculate the number of moles of base contained in one tablet by dividing the mass of base by the corresponding molar mass. Calculate the number of tablets required by dividing the moles of base by the moles contained in one tablet.

A. We first write the balanced chemical equation for the reaction:

$$2HCl(aq) + CaCO_3(s) \rightarrow CaCl_2(aq) + H_2CO_3(aq)$$

Each carbonate ion can react with 2 mol of H^+ to produce H_2CO_3, which rapidly decomposes to H_2O and CO_2. Because HCl is a strong acid and CO_3^{2-} is a weak base, the reaction will go to completion.

B. Next we need to determine the number of moles of HCl present:

$$75\ m\cancel{L} \left(\frac{1\ \cancel{L}}{1000\ m\cancel{L}}\right)\left(\frac{0.20\ mol\ HCl}{\cancel{L}}\right) = 0.015\ mol\ HCl$$

Because we want to neutralize only 90% of the acid present, we multiply the number of moles of HCl by 0.90:

$$(0.015\ mol\ HCl)(0.90) = 0.014\ mol\ HCl$$

We know from the stoichiometry of the reaction that each mole of $CaCO_3$ reacts with 2 mol of HCl, so we need

$$moles\ CaCO_3 = 0.014\ \ mol\ \cancel{HCl} \left(\frac{1\ mol\ CaCO_3}{2\ \ mol\ \cancel{HCl}}\right) = 0.0070\ mol\ CaCO_3$$

C. Each Tums tablet contains

$$\left(\frac{500\ \ mg\, \cancel{CaCO_3}}{1\, Tums\, tablet}\right)\left(\frac{1\ \ \cancel{g}}{1000\ \ mg\, \cancel{CaCO_3}}\right)\left(\frac{1\, mol\, CaCO_3}{100.1\ \ \cancel{g}}\right) = 0.00500\, mol\, CaCO_3$$

Thus we need $\frac{0.0070\ \ mol\, \cancel{CaCO_3}}{0.00500\ \ mol\, \cancel{CaCO_3}} = 1.4$ Tums tablets.

cise

Assume that as a result of overeating, a person’s stomach contains 300 mL of 0.25 M HCl. How many Rolaids tablets must be consumed to neutralize 95% of the acid, if each tablet contains 400 mg of $NaAl(OH)_2CO_3$? The neutralization reaction can be written as follows:

$$NaAl(OH)_2CO_3(s) + 4HCl(aq) \rightarrow AlCl_3(aq) + NaCl(aq) + CO_2(g) + 3H_2O(l)$$

Answer

6.4 tablets

Key Takeaway

- An Arrhenius acid increases the H^+ ion concentration in water, while an Arrhenius base increases the OH^- ion concentration in water.

10.2: Brønsted-Lowry Definition of Acids and Bases

Learning Objectives

1. Recognize a compound as a Brønsted-Lowry acid or a Brønsted-Lowry base.
2. Illustrate the proton transfer process that defines a Brønsted-Lowry acid-base reaction.

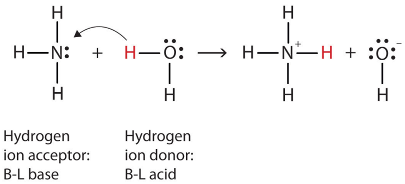
Ammonia (NH_3) increases the hydroxide ion concentration in aqueous solution by reacting with water rather than releasing hydroxide ions directly. In fact, the Arrhenius definitions of an acid and a base focus on hydrogen ions and hydroxide ions. Are there more fundamental definitions for acids and bases?

In 1923, the Danish scientist Johannes Brønsted and the English scientist Thomas Lowry independently proposed new definitions for acids and bases. Rather than considering both hydrogen and hydroxide ions, they focused on the hydrogen ion only. A Brønsted-Lowry acid is a compound that supplies a hydrogen ion in a reaction. A Brønsted-Lowry base, conversely, is a compound that accepts a hydrogen ion in a reaction. Thus, the Brønsted-Lowry definitions of an acid and a base focus on the movement of hydrogen ions in a reaction, rather than on the production of hydrogen ions and hydroxide ions in an aqueous solution.

Let us use the reaction of ammonia in water to demonstrate the Brønsted-Lowry definitions of an acid and a base. Ammonia and water molecules are reactants, while the ammonium ion and the hydroxide ion are products:

$$NH_3(aq) + H_2O(\ell) \rightarrow NH_4^+(aq) + OH^-(aq) \tag{10.2.1}$$

What has happened in this reaction is that the original water molecule has donated a hydrogen ion to the original ammonia molecule, which in turn has accepted the hydrogen ion. We can illustrate this as follows:



Because the water molecule donates a hydrogen ion to the ammonia, it is the Brønsted-Lowry acid, while the ammonia molecule—which accepts the hydrogen ion—is the Brønsted-Lowry base. Thus, ammonia acts as a base in both the Arrhenius sense and the Brønsted-Lowry sense.

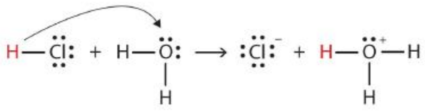
Is an Arrhenius acid like hydrochloric acid still an acid in the Brønsted-Lowry sense? Yes, but it requires us to understand what really happens when HCl is dissolved in water. Recall that the hydrogen *atom* is a single proton surrounded by a single electron. To make the hydrogen *ion*, we remove the electron, leaving a bare proton. Do we *really* have bare protons floating around in aqueous solution? No, we do not. What really happens is that the H^+ ion attaches itself to H_2O to make H_3O^+, which is called the *hydronium ion*. For most purposes, H^+ and H_3O^+ represent the same species, but writing H_3O^+ instead of H^+ shows that we understand that there are no bare protons floating around in solution. Rather, these protons are actually attached to solvent molecules.

> A proton in aqueous solution may be surrounded by more than one water molecule, leading to formulas like $H_5O_2^+$ or $H_9O_4^+$ rather than H_3O^+. It is simpler, however, to use H_3O^+.

With this in mind, how do we define HCl as an acid in the Brønsted-Lowry sense? Consider what happens when HCl is dissolved in H_2O:

$$HCl(g) + H_2O(\ell) \rightarrow H_3O^+(aq) + Cl^-(aq) \tag{10.2.2}$$

We can depict this process using Lewis electron dot diagrams:



Now we see that a hydrogen ion is transferred from the HCl molecule to the H_2O molecule to make chloride ions and hydronium ions. As the hydrogen ion donor, **HCl acts as a Brønsted-Lowry acid**; as a hydrogen ion acceptor, **H_2O is a Brønsted-Lowry base**. So HCl is an acid not just in the Arrhenius sense but also in the Brønsted-Lowry sense. Moreover, by the Brønsted-Lowry definitions, H_2O is a base in the formation of aqueous HCl. So the Brønsted-Lowry definitions of an acid and a base classify the dissolving of HCl in water as a reaction between an acid and a base—although the Arrhenius definition would not have labeled H_2O a base in this circumstance.

> All Arrhenius acids and bases are Brønsted-Lowry acids and bases as well. However, not all Brønsted-Lowry acids and bases are Arrhenius acids and bases.

✓ Example 10.2.1

Aniline ($C_6H_5NH_2$) is slightly soluble in water. It has a nitrogen atom that can accept a hydrogen ion from a water molecule just like the nitrogen atom in ammonia does. Write the chemical equation for this reaction and identify the Brønsted-Lowry acid and base.

Solution

$C_6H_5NH_2$ and H_2O are the reactants. When $C_6H_5NH_2$ accepts a proton from H_2O, it gains an extra H and a positive charge and leaves an $OH^−$ ion behind. The reaction is as follows:

$$C_6H_5NH_2(aq) + H_2O(\ell) \rightarrow C_6H_5NH_3^+(aq) + OH^-(aq)$$

Because $C_6H_5NH_2$ accepts a proton, it is the Brønsted-Lowry base. The H_2O molecule, because it donates a proton, is the Brønsted-Lowry acid.

? Exercise 10.2.1

Caffeine ($C_8H_{10}N_4O_2$) is a stimulant found in coffees and teas. When dissolved in water, it can accept a proton from a water molecule. Write the chemical equation for this process and identify the Brønsted-Lowry acid and base.

Answer

$C_8H_{10}N_4O_2(aq) + H_2O(\ell) \rightarrow C_8H_{11}N_4O_2^+(aq) + OH^-(aq)$

B-L base B-L acid

The Brønsted-Lowry definitions of an acid and a base can be applied to chemical reactions that occur in solvents other than water. The following example illustrates.

✓ Example 10.2.2

Sodium amide ($NaNH_2$) dissolves in methanol (CH_3OH) and separates into sodium ions and amide ions (NH_2^-). The amide ions react with methanol to make ammonia and the methoxide ion (CH_3O^-). Write a balanced chemical equation for this process and identify the Brønsted-Lowry acid and base.

Solution

The equation for the reaction is between NH_2^- and CH_3OH to make NH_3 and CH_3O^- is as follows:

$$NH_2^-(solv) + CH_3OH(\ell) \rightarrow NH_3(solv) + CH_3O^-(solv)$$

The label *(solv)* indicates that the species are dissolved in some solvent, in contrast to *(aq)*, which specifies an aqueous (H_2O) solution. In this reaction, we see that the NH_2^- ion accepts a proton from a CH_3OH molecule to make an NH_3 molecule. Thus, as the proton acceptor, NH_2^- is the Brønsted-Lowry base. As the proton donor, CH_3OH is the Brønsted-Lowry acid.

Exercise 10.2.2

Pyridinium chloride (C_5H_5NHCl) dissolves in ethanol (C_2H_5OH) and separates into pyridinium ions ($C_5H_5NH^+$) and chloride ions. The pyridinium ion can transfer a hydrogen ion to a solvent molecule. Write a balanced chemical equation for this process and identify the Brønsted-Lowry acid and base.

Answer

$C_5H_5NH^+(solv) + C_2H_5OH(\ell) \rightarrow C_5H_5N(solv) + C_2H_5OH_2{}^+(solv)$

B-L acid B-L base

Application in Everyday Life

Many people like to put lemon juice or vinegar, both of which are acids, on cooked fish (Figure 10.2.1). It turns out that fish have volatile amines (bases) in their systems, which are neutralized by the acids to yield involatile ammonium salts. This reduces the odor of the fish, and also adds a “sour” taste that we seem to enjoy.

$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Putrescine}}{NH_2CH_2CH_2CH_2CH_2NH_2} \longrightarrow \underset{\text{Acetate ion}}{CH_3COO^-} + \underset{\text{Putrescinium ion}}{NH_3{}^+CH_2CH_2CH_2CH_2NH_2}$$

Figure 10.2.1: A neutralization reaction takes place between citric acid or acetic acid (proton donors) in lemons or vinegar and putrescine (proton acceptor) in the flesh of fish. (CC BY 4.0; OpenStax)

Pickling is a method used to preserve vegetables using a naturally produced acidic environment. The vegetable, such as a cucumber, is placed in a sealed jar submerged in a brine solution. The brine solution favors the growth of beneficial bacteria and suppresses the growth of harmful bacteria. The beneficial bacteria feed on starches in the cucumber and produce lactic acid as a waste product in a process called fermentation. The lactic acid eventually increases the acidity of the brine to a level that kills any harmful bacteria, which require a basic environment. Without the harmful bacteria consuming the cucumbers they are able to last much longer than if they were unprotected. A byproduct of the pickling process changes the flavor of the vegetables with the acid making them taste sour.

To Your Health: Brønsted-Lowry Acid-Base Reactions in Pharmaceuticals

There are many interesting applications of Brønsted-Lowry acid-base reactions in the pharmaceutical industry. For example, drugs often need to be water soluble for maximum effectiveness. However, many complex organic compounds are not soluble or are only slightly soluble in water. Fortunately, those drugs that contain proton-accepting nitrogen atoms (and there are a lot of them) can be reacted with dilute hydrochloric acid [HCl(aq)]. The nitrogen atoms—acting as Brønsted-Lowry bases—accept the hydrogen ions from the acid to make an ion, which is usually much more soluble in water. The modified drug molecules can then be isolated as chloride salts:

$$\mathrm{RN(sl\: aq) + H^+(aq) \rightarrow RNH^+(aq) \xrightarrow{Cl^-(aq)} RNHCl(s)} \label{Eq3}$$

where RN represents some organic compound containing nitrogen. The label *(sl aq)* means “slightly aqueous,” indicating that the compound RN is only slightly soluble. Drugs that are modified in this way are called *hydrochloride salts*. Examples include the powerful painkiller codeine, which is commonly administered as codeine hydrochloride. Acids other than hydrochloric acid are also used. Hydrobromic acid, for example, gives *hydrobromide salts*. Dextromethorphan, an ingredient in many cough medicines, is dispensed as dextromethorphan hydrobromide. The accompanying figure shows another medication (lidocaine) as a hydrochloride salt.

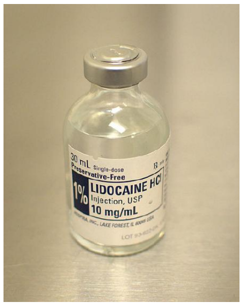


Figure used with permission from Wikipedia.

Conjugate Acid-Base Pairs

According to the Bronsted-Lowry theory of acids and bases, an acid is a proton donor and a base is a proton acceptor. Once an acid has given up a proton, the part that remains is called the acid's **conjugate base**. This species is a base because it can accept a proton (to re-form the acid). The conjugate base of HF (first example below) is fluoride ion, F⁻.

$$\text{Acid} = \text{H}^+ + \text{Conjugate base of Acid}^-$$

$$\text{HF} \rightleftharpoons \text{H}^+ + \text{F}^-$$

$$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$$

$$\text{NH}_4^+ \rightleftharpoons \text{H}^+ + \text{NH}_3$$

Similarly, the part of the base that remains after a base accepts a proton is called the base's **conjugate acid**. This species is an acid because it can give up a proton (and thus re-form the base). The conjugate acid of fluoride ion, F^- (first example below) is HF.

$$\text{H}^+ + \text{Base} = \text{Conjugate acid of Base}^+$$

$$\text{H}^+ + \text{F}^- \rightleftharpoons \text{HF}$$

$$\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O}$$

$$\text{H}^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+$$

$$\text{H}^+ + \text{NH}_3 \rightleftharpoons \text{NH}_4^+$$

To summarize, the conjugate base of HF is fluoride ion, F^-, and the conjugate acid of fluoride ion, F^-, is HF. The HF/F- pair is referred to as a conjugate acid-base pair. The difference in the formulas of a conjugate acid-base pair (example: HF and F^-) is H^+. The table below lists conjugate acid-base pairs for your reference so that you can figure out the strategy of identifying them. For any given acid or base, you should be able to give its conjugate base or conjugate acid. The formula of an acid's conjugate base is generated by **removing a proton** (H^+) from the acid formula. The formula of the base's conjugate acid is formed by **adding a proton** (H^+) to the formula of the base.

Table 10.2.1. Conjugate acid-base pairs.

Conjugate Acid	Conjugate Base
H_3O^+	H_2O
H_2O	OH^-
H_2SO_4	HSO_4^-
HSO_4^-	SO_4^{2-}
NH_4^+	NH_3

Conjugate Acid	Conjugate Base
NH_3	NH_2^-
CH_3COOH	CH_3COO^-
$CH_3NH_3^+$	CH_3NH_2

✓ Example 10.2.3 : Conjugate Pairs

Write the formula of the conjugate base of (a) HCl and (b) HCO_3^- .

Write the formula of the conjugate acid of (c) CH_3NH_2 and (d) OH^-.

Solution:

A conjugate base is formed by removing a proton (H^+). A conjugate acid is formed by accepting a proton (H^+).

a. After HCl donates a proton, a Cl^- ion is produced, and so Cl^- is the conjugate base.
b. After hydrogen carbonate ion, HCO_3^-, donates a proton, its conjugate base, CO_3^{2-} is produced.
c. After accepting a proton (H^+), CH_3NH_2 is converted to $CH_3NH_3^+$, its conjugate acid.
d. After accepting a proton (H^+), OH^- is converted to H_2O, its conjugate acid.

Exercise : Conjugate Pairs

Write the formula of the conjugate base of (a) HNO_2 and (b) H_2CO_3.

Write the formula of the conjugate acid of (c) C_6H5NH_2 and (d) HCO_3^-.

Answer

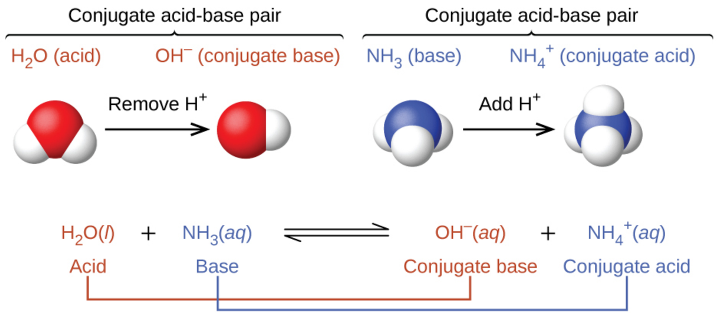
a. NO_2^- is the conjugate base of HNO_2.

b. HCO_3^- is the conjugate base of H_2CO_3

c. $C_6H5NH_3^+$ is the conjugate acid of C_6H5NH_2.

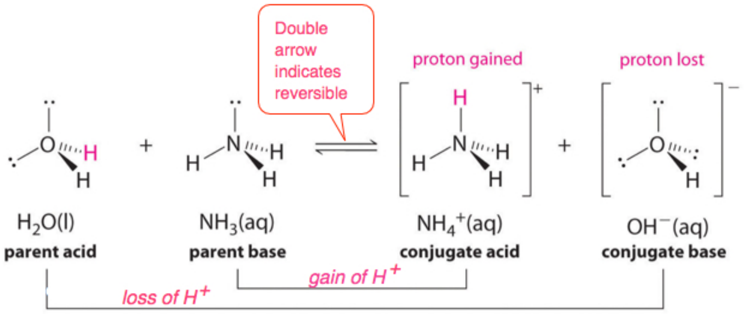
d. H_2CO_3 is the conjugate acid of HCO_3^-

In the reaction of ammonia with water to give ammonium ions and hydroxide ions, ammonia acts as a base by accepting a proton from a water molecule, which in this case means that water is acting as an acid. In the reverse reaction, an ammonium ion acts as an acid by donating a proton to a hydroxide ion, and the hydroxide ion acts as a base. The **conjugate acid–base pairs** for this reaction are NH_4^+/NH_3 and H_2O/OH^-. This means that the conjugate acid of the base NH_3 is NH_4^+ while the conjugate base of the acid NH_4^+ is NH_3. Similarly, the conjugate base of the acid H_2O is OH^-, and the conjugate acid of the base OH^- is H_2O.



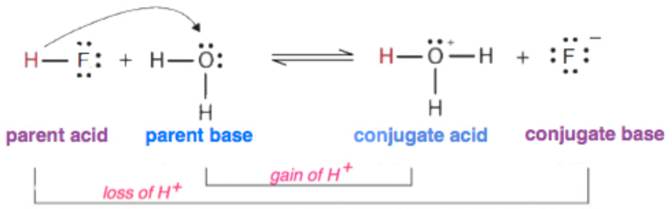
This figure has three parts in two rows. In the first row, two diagrams of acid-base pairs are shown. On the left, a space filling model of H subscript 2 O is shown with a red O atom at the center and two smaller white H atoms attached in a bent shape. Above this model is the label “H subscript 2 O (acid)” in purple. An arrow points right, which is labeled “Remove H superscript plus.” To the right is another space filling model with a single red O atom to which a single smaller white H atom is attached. The label in purple above this model reads, “O H superscript negative (conjugate base).” Above both of these red and white models is an upward pointing bracket that is labeled “Conjugate acid-base pair.” To the right is a space filling model with a central blue N atom to which three smaller white H atoms are attached in a triangular pyramid arrangement. A label in green above reads “N H subscript 3 (base).” An arrow labeled “Add H superscript plus” points right. To the right of the arrow is another space filling model with a blue central N atom and four smaller white H atoms in a tetrahedral arrangement. The green label above reads “N H subscript 3 superscript plus (conjugate acid).” Above both of these blue and white models is an upward pointing bracket that is labeled “Conjugate acid-base pair.” The second row of the figure shows the chemical reaction, H subscript 2 O (l) is shown in purple, and is labeled below in purple as “acid,” plus N H subscript 3 (a q) in green, labeled below in green as “base,” followed by a double sided arrow arrow and O H superscript negative (a q) in purple, labeled in purple as “conjugate base,” plus N H subscript 4 superscript plus (a q)” in green, which is labeled in green as “conjugate acid.” The acid on the left side of the equation is connected to the conjugate base on the right with a purple line. Similarly, the base on the left is connected to the conjugate acid on the right side.

In the **forward** reaction, the parent acid is H_2O and and the parent base is NH_3 (shown in the illustration below). The acid H_2O loses a proton (H^+) to form its conjugate base OH^-. The base NH_3 gains a proton, to produce its conjugate acid NH_4^+. In the **reverse** reaction, the acid NH_4^+ loses a proton (H^+) to form its conjugate base NH_3. The base OH^- gains a proton, to produce its conjugate acid H_2O.



When hydrogen fluoride (HF) dissolves in water and ionizes, protons are transferred from hydrogen fluoride (parent acid) molecules to water (parent base) molecules, yielding hydronium ions (conjugate acid of water) and fluoride ions (conjugate base of HF):

$$\mathrm{HF} + H_2O \rightleftharpoons H_3O^+ + \mathrm{F}^-$$



Example 10.2.3

Identify the conjugate acid-base pairs in this equilibrium.

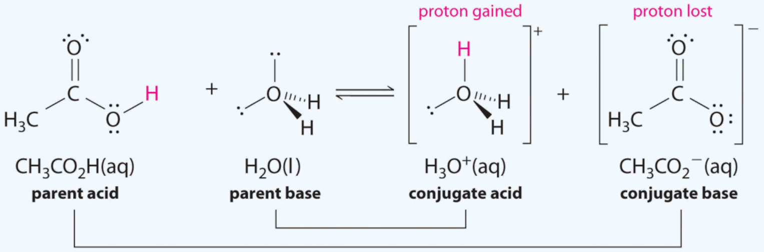
$$CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-$$

Solution

Similarly, in the reaction of acetic acid with water, acetic acid **donates** a proton to water, which acts as the base. In the reverse reaction, H_3O^+ is the acid that donates a proton to the acetate ion, which acts as the base.

Once again, we have two conjugate acid–base pairs:

- the parent acid and its conjugate base ($CH_3CO_2H/CH_3CO_2^-$) and
- the parent base and its conjugate acid (H_3O^+/H_2O).



Example 10.2.4

Identify the conjugate acid-base pairs in this equilibrium.

$$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$$

Solution

One pair is H_2O and OH^-, where H_2O has one more H^+ and is the conjugate acid, while OH^- has one less H^+ and is the conjugate base.

The other pair consists of $(CH_3)_3N$ and $(CH_3)_3NH^+$, where $(CH_3)_3NH^+$ is the conjugate acid (it has an additional proton) and $(CH_3)_3N$ is the conjugate base.

Exercise 10.2.4

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)

The use of conjugate acid-base pairs allows us to make a very simple statement about relative strengths of acids and bases. *The stronger an acid, the weaker its conjugate base*, and, conversely, *the stronger a base, the weaker its conjugate acid.*

Key Takeaways

- A Brønsted-Lowry acid is a proton donor, and a Brønsted-Lowry base is a proton acceptor.
- Brønsted-Lowry acid-base reactions are essentially proton transfer reactions.

10.3: Water - Both an Acid and a Base

Learning Objectives

- To write chemical equations for water acting as an acid and as a base.

Water (H_2O) is an interesting compound in many respects. Here, we will consider its ability to behave as an acid or a base.

In some circumstances, a water molecule will accept a proton and thus act as a **Brønsted-Lowry base**. We saw an example in the dissolving of HCl in H_2O:

$$\mathrm{HCl} + \mathrm{H_2O}(\ell) \rightarrow \mathrm{H_3O^+}(\mathrm{aq}) + \mathrm{Cl^-}(\mathrm{aq}) \tag{10.3.1}$$

In other circumstances, a water molecule can donate a proton and thus act as a **Brønsted-Lowry acid**. For example, in the presence of the amide ion (see Example 4 in Section 10.2), a water molecule donates a proton, making ammonia as a product:

$$H_2O(\ell) + NH_2^-(aq) \rightarrow OH^-(aq) + NH_3(aq) \tag{10.3.2}$$

In this case, NH_2^- is a Brønsted-Lowry base (the proton acceptor).

So, depending on the circumstances, H_2O can act as either a Brønsted-Lowry acid or a Brønsted-Lowry base. Water is not the only substance that can react as an acid in some cases or a base in others, but it is certainly the most common example—and the most important one. A substance that can either donate or accept a proton, depending on the circumstances, is called an **amphiprotic** compound.

A water molecule can act as an acid or a base even in a sample of pure water. About 6 in every 100 million (6 in 10^8) water molecules undergo the following reaction:

$$H_2O(\ell) + H_2O(\ell) \rightarrow H_3O^+(aq) + OH^-(aq) \tag{10.3.3}$$

This process is called the **autoionization of water** (Figure 10.3.1) and occurs in every sample of water, whether it is pure or part of a solution. Autoionization occurs to some extent in any amphiprotic liquid. (For comparison, liquid ammonia undergoes autoionization as well, but only about 1 molecule in a million billion (1 in 10^{15}) reacts with another ammonia molecule.)

Note

It is rare to truly have pure water. Water exposed to air will usually be slightly acidic because dissolved carbon dioxide gas, or carbonic acid, decreases the pH slightly below 7. Alternatively, dissolved minerals, like calcium carbonate (limestone), can make water slightly basic.

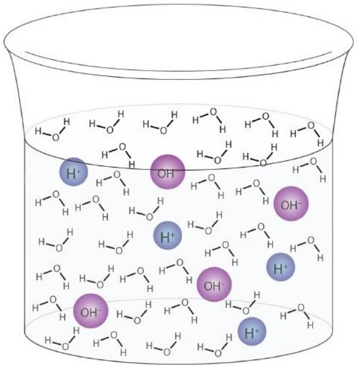


Figure 10.3.1 Autoionization. A small fraction of water molecules—approximately 6 in 100 million—ionize spontaneously into hydronium ions and hydroxide ions. This picture necessarily overrepresents the amount of autoionization that really occurs in pure water.

✓ Example 10.3.1

Identify water as either a Brønsted-Lowry acid or a Brønsted-Lowry base.

1. $H_2O(\ell) + NO_2^-(aq) \rightarrow HNO_2(aq) + OH^-(aq)$
2. $HC_2H_3O_2(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + C_2H_3O_2^-(aq)$

Solution

1. In this reaction, the water molecule donates a proton to the NO_2^- ion, making $OH^-(aq)$. As the proton donor, H_2O acts as a Brønsted-Lowry acid.
2. In this reaction, the water molecule accepts a proton from $HC_2H_3O_2$, becoming $H_3O^+(aq)$. As the proton acceptor, H_2O is a Brønsted-Lowry base.

? Exercise 10.3.2

Identify water as either a Brønsted-Lowry acid or a Brønsted-Lowry base.

1. $HCOOH(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + HCOO^-(aq)$
2. $H_2O(\ell) + PO_4^{3-}(aq) \rightarrow OH^-(aq) + HPO_4^{2-}(aq)$

Answer

1. H_2O acts as the proton acceptor (Brønsted-Lowry base)
2. H_2O acts as the proton donor (Brønsted-Lowry acid)

Key Takeaway

- Water molecules can act as both an acid and a base, depending on the conditions.

10.4: The Strengths of Acids and Bases

Learning Objectives

- Describe the difference between strong and weak acids and bases.
- Describe how a chemical reaction reaches chemical equilibrium.
- Define the pH scale and use it to describe acids and bases.

Acids and bases do not all demonstrate the same degree of chemical activity in solution. Different acids and bases have different strengths.

Strong and Weak Acids

Let us consider the strengths of acids first. A small number of acids ionize completely in aqueous solution. For example, when HCl dissolves in water, every molecule of HCl separates into a hydronium ion and a chloride ion:

$$\mathrm{HCl(g)+H_2O(l)\xrightarrow{\sim 100\%}H_3O^+(aq)+Cl^-(aq)} \tag{10.4.1}$$

HCl(aq) is one example of a **strong acid**, which is a compound that is essentially **100% ionized** in aqueous solution. There are very few strong acids. The important ones are listed in Table 10.4.1.

Table 10.4.1: Strong Acids and Bases (All in Aqueous Solution)

Acids	Bases
HCl	LiOH
HBr	NaOH
HI	KOH
HNO_3	$Mg(OH)_2$
H_2SO_4	$Ca(OH)_2$
$HClO_4$	

By analogy, a strong base is a compound that is essentially 100% ionized in aqueous solution. As with acids, there are only a few strong bases, which are also listed in Table 10.4.1.

If an acid is **not listed** in Table 10.4.1, it is likely a **weak acid**, which is a compound that is not 100% ionized in aqueous solution. Similarly, a weak base is a compound that is not 100% ionized in aqueous solution. For example, acetic acid ($HC_2H_3O_2$) is a weak acid. The ionization reaction for acetic acid is as follows:

$$\mathrm{HC_2H_3O_2(aq)+H_2O(\ell)\rightarrow H_3O^+(aq)+C_2H_3O_2^-(aq)} \tag{10.4.2}$$

Depending on the concentration of $HC_2H_3O_2$, the ionization reaction may occur only for 1%–5% of the acetic acid molecules.

Looking Closer: Household Acids and Bases

Many household products are acids or bases. For example, the owner of a swimming pool may use muriatic acid to clean the pool. Muriatic acid is another name for hydrochloric acid [$HCl(aq)$]. Vinegar has already been mentioned as a dilute solution of acetic acid [$HC_2H_3O_2(aq)$]. In a medicine chest, one may find a bottle of vitamin C tablets; the chemical name of vitamin C is ascorbic acid ($HC_6H_7O_6$).

One of the more familiar household bases is ammonia (NH_3), which is found in numerous cleaning products. As we mentioned previously, ammonia is a base because it increases the hydroxide ion concentration by reacting with water:

$$\mathrm{NH_3(aq)+H_2O(\ell)\rightarrow NH_4^+(aq)+OH^-(aq)} \tag{10.4.3}$$

Many soaps are also slightly basic because they contain compounds that act as Brønsted-Lowry bases, accepting protons from water and forming excess hydroxide ions. This is one reason that soap solutions are slippery.

Figure 10.4.1: (left) Bottles of alkaline drain cleaners containing sodium hydroxide can dissolve greases and hair. (right) Chemical burns caused by sodium hydroxide solution photographed 44 hours after exposure. Figures used with permission from Wikipedia.

Perhaps the most dangerous household chemical is the lye-based drain cleaner. Lye is a common name for sodium hydroxide, although it is also used as a synonym for potassium hydroxide. Lye is an extremely caustic chemical that can react with grease, hair, food particles, and other substances that may build up and form a clog in a pipe. Unfortunately, lye can also attack tissues and other substances in our bodies. Thus, when we use lye-based drain cleaners, we must be very careful not to touch any of the solid drain cleaner or spill the water it was poured into. Safer, nonlye drain cleaners use peroxide compounds to react on the materials in the clog and clear the drain.

Chemical Equilibrium in Weak Acids and Bases

The behavior of **weak acids and bases** illustrates a key concept in chemistry. Does the chemical reaction describing the ionization of a weak acid or base just stop when the acid or base is done ionizing? Actually, no. Rather, the reverse process—the reformation of the molecular form of the acid or base—occurs, ultimately at the same rate as the ionization process. For example, the ionization of the weak acid $\mathrm{HC_2H_3O_2(aq)}$ is as follows:

$$\mathrm{HC_2H_3O_2(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + C_2H_3O_2^-(aq)} \tag{10.4.4}$$

The reverse process also begins to occur:

$$\mathrm{H_3O^+(aq) + C_2H_3O_2^-(aq) \rightarrow HC_2H_3O_2(aq) + H_2O(\ell)} \tag{10.4.5}$$

Eventually, there is a balance between the two opposing processes, and no additional change occurs. The chemical reaction is better represented at this point with a double arrow:

$$\mathrm{HC_2H_3O_2(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + C_2H_3O_2^-(aq)} \tag{10.4.6}$$

The $\rightleftharpoons$ implies that **both the forward and reverse reactions** are occurring, and their effects cancel each other out. A process at this point is considered to be at **chemical equilibrium** (or equilibrium). It is important to note that the processes do not stop. They balance out each other so that there is no further net change; that is, chemical equilibrium is a *dynamic equilibrium*.

✓ Example 10.4.1: Partial Ionization

Write the equilibrium chemical equation for the partial ionization of each weak acid or base.

a. $\mathrm{HNO_2(aq)}$
b. $\mathrm{C_5H_5N(aq)}$

Solution

a. $\mathrm{HNO_2(aq) + H_2O(\ell) \leftrightarrows NO_2^-(aq) + H_3O^+(aq)}$
b. $\mathrm{C_5H_5N(aq) + H_2O(\ell) \leftrightarrows C_5H_5NH^+(aq) + OH^-(aq)}$

Exercise 10.4.1

Write the equilibrium chemical equation for the partial ionization of each weak acid or base.

a. $HF_{(aq)}$
b. $AgOH_{(aq)}$
c. $CH_3NH_2(aq)$

Answer

a. $HF(aq) + H_2O(\ell) \leftrightarrows F^-(aq) + H_3O^+(aq)$

b. $AgOH(aq) \leftrightarrows Ag^+(aq) + OH^-(aq)$

c. $CH_3NH_2(aq) + H_2O(\ell) \leftrightarrows CH_3NH_3^+(aq) + OH^-(aq)$

Acid Ionization Constant, $\boldsymbol{K}_\text{a}$

The ionization for a general weak acid, HA, can be written as follows:

$$\text{HA}\,(aq) \rightleftharpoons \text{H}^+\,(aq) + \text{A}^-\,(aq)$$

Because the acid is weak, an equilibrium expression can be written. An **acid ionization constant** $(\boldsymbol{K}_\text{a})$ is the equilibrium constant for the ionization of an acid.

$$K_\text{a} = \frac{[\text{H}^+]\,[\text{A}^-]}{[\text{HA}]}$$

The acid ionization represents the fraction of the original acid that has been ionized in solution. Therefore, the numerical value of K_a is a reflection of the strength of the acid. Weak acids with relatively higher K_a values are stronger than acids with relatively lower K_a values. Because strong acids are essentially 100% ionized, the concentration of the acid in the denominator is nearly zero and the K_a value approaches infinity. For this reason, K_a values are generally reported for weak acids only.

The table below is a listing of acid ionization constants for several acids. Note that polyprotic acids have a distinct ionization constant for each ionization step, with each successive ionization constant being smaller than the previous one.

Table 10.4.2: Acid Ionization Constants at 25^oC

Name of Acid	Ionization Equation	K_a
Sulfuric acid	$\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}^+ + \text{HSO}_4^-$ $\text{HSO}_4 \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$	very large 1.3×10^{-2}
Hydrofluoric acid	$\text{HF} \rightleftharpoons \text{H}^+ + \text{F}^-$	7.1×10^{-4}
Nitrous acid	$\text{HNO}_2 \rightleftharpoons \text{H}^+ + \text{NO}_2^-$	4.5×10^{-4}
Benzoic acid	$\text{C}_6\text{H}_5\text{COOH} \rightleftharpoons \text{H}^+ + \text{C}_6\text{H}_5\text{COO}^-$	6.5×10^{-5}
Acetic acid	$\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^-$	1.8×10^{-5}
Carbonic acid	$\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$ $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$	4.2×10^{-7} 4.8×10^{-11}

Hydrofluoric acid $HF_{(aq)}$ reacts directly with glass (very few chemicals react with glass). Hydrofluoric acid is used in glass etching.

Strong and Weak Bases and Base Ionization Constant, K_b

As with acids, bases can either be strong or weak, depending on their extent of ionization. A **strong base** is a base, which ionizes completely in an aqueous solution. The most common strong bases are soluble metal hydroxide compounds such as potassium hydroxide. Some metal hydroxides are not as strong simply because they are not as soluble. Calcium hydroxide is only slightly soluble in water, but the portion that does dissolve also dissociates into ions.

A **weak base** is a base that ionizes only slightly in an aqueous solution. Recall that a base can be defined as a substance, which accepts a hydrogen ion from another substance. When a weak base such as ammonia is dissolved in water, it accepts an H^+ ion from water, forming the hydroxide ion and the conjugate acid of the base, the ammonium ion.

$$NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)$$

The equilibrium greatly favors the reactants and the extent of ionization of the ammonia molecule is very small.

An equilibrium expression can be written for the reactions of weak bases with water. Because the concentration of water is extremely large and virtually constant, the water is not included in the expression. A **base ionization constant** $(\boldsymbol{K_b})$ is the equilibrium constant for the ionization of a base. For ammonia the expression is:

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

The numerical value of K_b is a reflection of the strength of the base. Weak bases with relatively higher K_b values are stronger than bases with relatively lower K_b values. Table $10.4.3$is a listing of base ionization constants for several weak bases.

Table 10.4.3: Base Ionization Constants at $25^\circ C$

Name of Base	Ionization Equation	K_b
Methylamine	$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$	5.6×10^{-4}
Ammonia	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.8×10^{-5}
Pyridine	$C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^+ + OH^-$	1.7×10^{-9}
Acetate ion	$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$	5.6×10^{-10}
Fluoride ion	$F^- + H_2O \rightleftharpoons HF + OH^-$	1.4×10^{-11}
Urea	$H_2NCONH_2 + H_2O \rightleftharpoons H_2NCONH_3^+ + OH^-$	1.5×10^{-14}

The Ion-Product of Water

As we have already seen, H_2O can act as an acid or a base. Within any given sample of water, some H_2O molecules are acting as acids, and other H_2O molecules are acting as bases. The chemical equation is as follows:

$$\underbrace{H_2O}_{\text{acid}} + \underbrace{H_2O}_{\text{base}} \rightleftharpoons H_3O^+ + OH^- \tag{10.4.7}$$

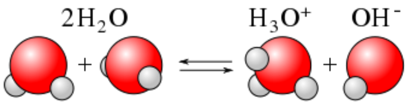


Figure 10.4.2: Autoionization of water, giving hydroxide and hydronium ions.

Similar to a weak acid, the autoionization of water is an equilibrium process, and is more properly written as follows:

$$H_2O(\ell) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \tag{10.4.8}$$

We often use the simplified form of the reaction:

$$H_2O(l) \rightleftharpoons H^+(aq) + OH-(aq)$$

The equilibrium constant for the autoionization of water is referred to as the ion-product for water and is given the symbol Kw.

$$K_w = [H^+][OH^-]$$

The **ion-product of water (*Kw*)** is the mathematical product of the concentration of hydrogen ions and hydroxide ions. Note that H_2O is not included in the ion-product expression because it is a pure liquid. The value of Kw is very small, in accordance with a reaction that favors the reactants. At 25°C, the experimentally determined value of K_w in pure water is 1.0×10^{-14}.

$$K_w = [\mathrm{H}^+][\mathrm{OH}^-] = 1.0 \times 10^{-14}$$

In a sample of pure water, the concentrations of hydrogen and hydroxide ions are equal to one another. Pure water or any other aqueous solution in which this ratio holds is said to be **neutral.** To find the molarity of each ion, the square root of Kw is taken.

$$[\mathrm{H}^+] = [\mathrm{OH}^-] = 1.0\times10^{-7}$$

The product of these two concentrations is 1.0×10^{-14}

$$[\mathrm{H}^+] \times [\mathrm{OH}^-] = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

- For acids, the concentration of H^+ or $[H^+]$) is greater than 1.0×10^{-7} M
- For bases, the concentration of OH^- or $[OH^-]$ is greater than 1.0×10^{-7} M.

Aqueous HCl is an example of acidic solution. Hydrogen chloride (HCl) ionizes to produce H^+ and Cl^- ions upon dissolving in water. This **increases the concentration of H^+ ions** in the solution. According to **Le Chatelier's principle**, the equilibrium represented by

$$\mathrm{H_2O(l)} \rightleftharpoons \mathrm{H^+(aq)} + \mathrm{OH^-(aq)}$$

$$\mathrm{HCl(g)} \longrightarrow \mathrm{H^+(aq)} + \mathrm{Cl^-(aq)}$$

is **forced to the left**, towards the reactant. As a result, the **concentration of the hydroxide ion decreases**.

Now, consider KOH (aq), a **basic solution**. Solid potassium hydroxide (KOH) dissociates in water to yield potassium ions and hydroxide ions.

$$\mathrm{KOH(s)} \rightarrow \mathrm{K^+(aq)} + \mathrm{OH^-(aq)}$$

The **increase in concentration of the OH^- ions** will cause a decrease in the concentration of the H^+ ions.

No matter whether the aqueous solution is an acid, a base, or neutral:and the ion-product of $[H^+][OH^-]$ remains constant.

- For acidic solutions, $[H^+]$) is greater than $[OH^-]$.
- For basic solutions, $[OH−]$ is greater than $[H^+]$.
- For neutral solutions, $[H_3O^+] = [OH−] = 1.0\times10^{-7}$M

This means that if you know $[\mathrm{H}^+]$ for a solution, you can calculate what $[\mathrm{OH}^-]$) has to be for the product to equal 1.0×10^{-14}, or if you know $[\mathrm{OH}^-]$), you can calculate $[\mathrm{H}^+]$. This also implies that as one concentration goes up, the other must go down to compensate so that their product always equals the value of K_w.

$$K_w = [\mathrm{H_3O^+}][\mathrm{OH^-}] = 1.0 \times 10^{-14} \tag{10.4.9}$$

✓ Example 10.4.2

Hydrochloric acid (HCl) is a strong acid, meaning it is 100% ionized in solution. What is the $[H^+]$ and the $[OH^-]$ in a solution of 2.0×10^{-3} M HCl?

Solution

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

Known

- $[HCl] = 2.0\times10^{-3}$ M
- $Kw = 1.0\times10^{-14}$

Unknown

- $[H^+]$=?M
- $[OH^-]$=?M

Because HCl is 100% ionized, the concentration of H+ ions in solution will be equal to the original concentration of HCl. Each HCl molecule that was originally present ionizes into one H+ ion and one Cl− ion. The concentration of OH− can then be determined from the [H+] and Kw.

Step 2: Solve.

$$[H^+]=2.0\times10^{-3}\text{ M}$$

$$Kw = [H^+][OH^-] = 1.0\times10^{-14}$$

$$[OH^-] = Kw/[H^+] = 1.0\times10^{-14}/2.0\times10^{-3} = 5.0\times10^{-12}\text{ M}$$

Step 3: Think about your result.

The $[H^+]$ is much higher than the $[OH^-]$ because the solution is acidic. As with other equilibrium constants, the unit for Kw is customarily omitted.

cise

Sodium hydroxide (NaOH) is a strong base. What is the $[H^+]$ and the $[OH^-]$ in a 0.001 M NaOH solution at 25 °C?

Answer

$[OH^-]$ = 0.001M or 1 x 10^{-3}M; $[H^+]=1\times10^{-11}$M.

The pH Scale

One qualitative measure of the strength of an acid or a base solution is the pH scale, which is based on the concentration of the hydronium (or hydrogen) ion in aqueous solution.

$$pH = -\log[H^+]$$

or

$$pH = -\log[H_3O^+]$$

Figure $10.4.3$ illustrates this relationship, along with some examples of various solutions. Because hydrogen ion concentrations are generally less than one (for example $1.3\times10^{-3}\ M$), the log of the number will be a negative number. To make pH even easier to work with, pH is defined as the ***negative* log of** $[H_3O^+]$, which will give a positive value for pH.

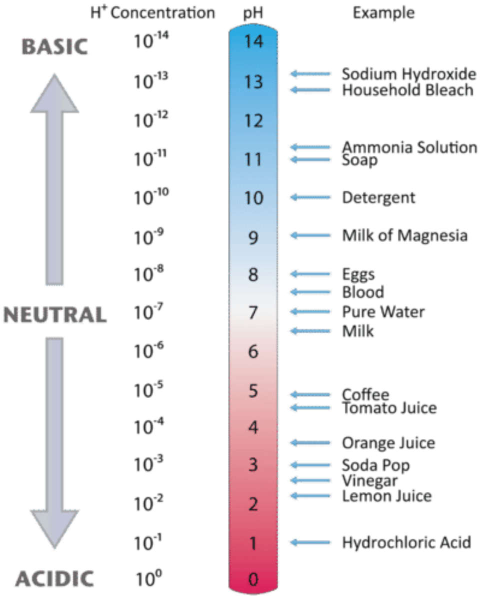


Figure 10.4.3: The relationaship between $[H^+]$ and pH *values for several common materials.*

A neutral (neither acidic nor basic) solution has a pH of 7. A pH below 7 means that a solution is acidic, with lower values of pH corresponding to increasingly acidic solutions. A pH greater than 7 indicates a basic solution, with higher values of pH corresponding to increasingly basic solutions. Thus, given the pH of several solutions, you can state which ones are acidic, which ones are basic, and which are more acidic or basic than others. These are summarized in Table \(\PageIndex{4}.

Table 10.4.4: Acidic, Basic and Neutral pH Values

Acidic, Basic and Neutral pH Values

Classification	Relative Ion Concentrations	pH at 25 °C
acidic	$[H^+] > [OH^-]$	pH < 7
neutral	$[H^+] = [OH^-]$	pH = 7
basic	$[H^+] < [OH^-]$	pH > 7

✓ Example 10.4.3

Find the pH, given the $[H^+]$ of the following:

a. 1×10^{-3} M
b. 2.5×10^{-11} M
c. 4.7×10^{-9} M

Solution

$\text{pH} = -\log[H_3O^+]$

Substitute the known quantity into the equation and solve. Use a scientific calculator for b and c.

a. $\text{pH} = -\log[\underline{1} \times 10^{-3}] = 3.\underline{0}$ (1 decimal place since 1 has 1 significant figure)
b. $\text{pH} = -\log[\underline{2.5} \times 10^{-11}] = 10.\underline{60}$ (2 decimal places since 2.5 has 2 significant figures)
c. $\text{pH} = -\log[\underline{4.7} \times 10^{-9}] = 8.\underline{33}$ (2 decimal places since 4.7 has 2 significant figures)

Note on significant figures:

Because the number(s) before the decimal point in the pH value relate to the power on 10, the number of digits *after* the decimal point (underlined) is what determines the number of significant figures in the final answer.

cise

Find the pH, given $[H^+]$ of the following:

a. 5.8×10^{-4} M
b. 1.0×10^{-7} M

Answer

a. 3.24

b. 7.00

Table 10.4.5 lists the pH of several common solutions. The most acidic among the listed solutions is battery acid with the lowest pH value (0.3). The most basic is 1M NaOH solution with the highest pH value of 14.0. Notice that some biological fluids (stomach acid and urine) are nowhere near neutral. You may also notice that many food products are slightly acidic. They are acidic because they contain solutions of weak acids. If the acid components of these foods were strong acids, the food would likely be inedible.

Table 10.4.5: The pH Values of Some Common Solutions

Solution	pH
battery acid	0.3
stomach acid	1–2
lemon or lime juice	2.1

Solution	pH
vinegar	2.8–3.0
Coca-Cola	3
wine	2.8–3.8
beer	4–5
coffee	5
milk	6
urine	6
pure H_2O	7
(human) blood	7.3–7.5
sea water	8
antacid (milk of magnesia)	10.5
NH_3 (1 M)	11.6
bleach	12.6
NaOH (1 M)	14.0

Example 10.4.4

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.

cise

Identify each substance as acidic, basic, or neutral based only on the stated pH.

a. human blood with $pH = 7.4$
b. household ammonia with $pH = 11.0$
c. cherries with $pH = 3.6$

Answer

a. slightly basic

b. basic

c. acidic

Acid Rain

Normal rainwater has a pH between 5 and 6 due to the presence of dissolved CO_2 which forms carbonic acid:

$$\mathrm{H_2O(l) + CO_2(g) \longrightarrow H_2CO_3(aq)} \tag{10.4.10}$$

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \tag{10.4.11}$$

Acid rain is rainwater that has a pH of less than 5, due to a variety of nonmetal oxides, including CO_2, SO_2, SO_3, NO, and NO_2 being dissolved in the water and reacting with it to form not only carbonic acid, but sulfuric acid and nitric acid. The formation and subsequent ionization of sulfuric acid are shown here:

$$H_2O(l) + SO_3(g) \longrightarrow H_2SO_4(aq) \tag{10.4.12}$$

$$H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4^-(aq) \tag{10.4.13}$$

Carbon dioxide is naturally present in the atmosphere because we and most other organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or when we burn wood or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also stems from burning fossil fuels, which have traces of sulfur, and from the process of "roasting" ores of metal sulfides in metal-refining processes. Oxides of nitrogen are formed in internal combustion engines where the high temperatures make it possible for the nitrogen and oxygen in air to chemically combine.

Acid rain is a particular problem in industrial areas where the products of combustion and smelting are released into the air without being stripped of sulfur and nitrogen oxides. In North America and Europe until the 1980s, it was responsible for the destruction of forests and freshwater lakes, when the acidity of the rain actually killed trees, damaged soil, and made lakes uninhabitable for all but the most acid-tolerant species. Acid rain also corrodes statuary and building facades that are made of marble and limestone (Figure 10.4.4). Regulations limiting the amount of sulfur and nitrogen oxides that can be released into the atmosphere by industry and automobiles have reduced the severity of acid damage to both natural and manmade environments in North America and Europe. It is now a growing problem in industrial areas of China and India.

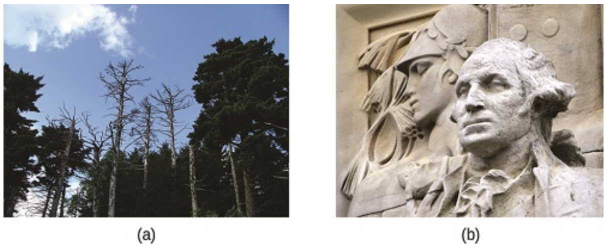


Figure 10.4.4: (a) Acid rain makes trees more susceptible to drought and insect infestation, and depletes nutrients in the soil. (b) It also is corrodes statues that are carved from marble or limestone. (credit a: modification of work by Chris M Morris; credit b: modification of work by "Eden, Janine and Jim"/Flickr)

Two photos are shown. Photograph a on the left shows the upper portion of trees against a bright blue sky. The tops of several trees at the center of the photograph have bare branches and appear to be dead. Image b shows a statue of a man that appears to from the revolutionary war era in either marble or limestone.

Key Takeaways

- Acids and bases can be strong or weak depending on the extent of ionization in solution.
- Most chemical reactions reach equilibrium at which point there is no net change.
- The ion-product of $[H^+][OH^-]$ in an aqueous solution remains constant.
- A ***pH*** value is simply the *negative* of the logarithm of the H^+ ion concentration ($-\log[H^+]$).
- The pH scale is used to succinctly communicate the acidity or basicity of a solution.
- A solution is **acidic** if $pH < 7$.
- A solution is **basic** if $pH > 7$.
- A solution is **neutral** if $pH = 7$.

10.5: Buffers

Learning Objectives

- To define *buffer* and describe how it reacts with an acid or a base.

Weak acids are relatively common, even in the foods we eat. But we occasionally come across a strong acid or base, such as stomach acid, that has a strongly acidic pH of 1–2. By definition, strong acids and bases can produce a relatively large amount of hydrogen or hydroxide ions and, as a consequence, have a marked chemical activity. In addition, very small amounts of strong acids and bases can change the pH of a solution very quickly. If 1 mL of stomach acid [which we will approximate as 0.05 M HCl(aq)] is added to the bloodstream, and if no correcting mechanism is present, the pH of the blood would go from about 7.4 to about 4.9—a pH that is not conducive to continued living. Fortunately, the body has a mechanism for minimizing such dramatic pH changes.

The mechanism involves a **buffer**, a solution that resists dramatic changes in pH. A *buffer* (or *buffered*) solution is one that resists a change in its pH when H^+ or OH^- ions are added or removed owing to some other reaction taking place in the same solution. Buffers do so by being composed of certain pairs of solutes: either a **weak acid plus its conjugate base** or a **weak base plus its conjugate acid**.

For example, a buffer can be composed of dissolved **acetic acid ($HC_2H_3O_2$, a weak acid) and sodium acetate** (**$NaC_2H_3O_2$**). Sodium acetate is a salt that dissociates into sodium ions and acetate ions in solution. For as long as acetic acid and acetate ions are present in significant amounts a solution, this can resist dramatic pH changes. Another example of a buffer is a solution containing **ammonia (NH_3, a weak base) and ammonium chloride** (**NH_4Cl).** Ammonium acetate is also a salt that dissociates into ammonium ions and chloride ions in solution. The presence of ammonium ions with ammonia molecules satisfies the requisite condition for a buffer solution.

How Buffers Work

The essential component of a buffer system is a **conjugate acid-base pair** whose concentration is fairly high in relation to the concentrations of added H^+ or OH^- it is expected to buffer against. Let us use an acetic acid–sodium acetate buffer to demonstrate how buffers work. If a strong base—a source of $OH^-(aq)$ ions—is added to the buffer solution, those hydroxide ions will react with the acetic acid in an acid-base reaction:

$$HC_2H_3O_{2(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(\ell)} + C_2H_3O^-_{2(aq)} \tag{10.5.1}$$

Rather than changing the pH dramatically by making the solution basic, the added hydroxide ions react to make water, and the pH does not change much.

> Many people are aware of the concept of buffers from *buffered aspirin*, which is aspirin that also has magnesium carbonate, calcium carbonate, magnesium oxide, or some other salt. The salt acts like a base, while aspirin is itself a weak acid.

If a strong acid—a source of H^+ ions—is added to the buffer solution, the H^+ ions will react with the anion from the salt. Because $HC_2H_3O_2$ is a weak acid, it is not ionized much. This means that if lots of hydrogen ions and acetate ions (from sodium acetate) are present in the same solution, they will come together to make acetic acid:

$$H^+_{(aq)} + C_2H_3O^-_{2(aq)} \rightarrow HC_2H_3O_{2(aq)} \tag{10.5.2}$$

Rather than changing the pH dramatically and making the solution acidic, the added hydrogen ions react to make molecules of a weak acid. Figure $10.5.1$ illustrates both actions of a buffer.

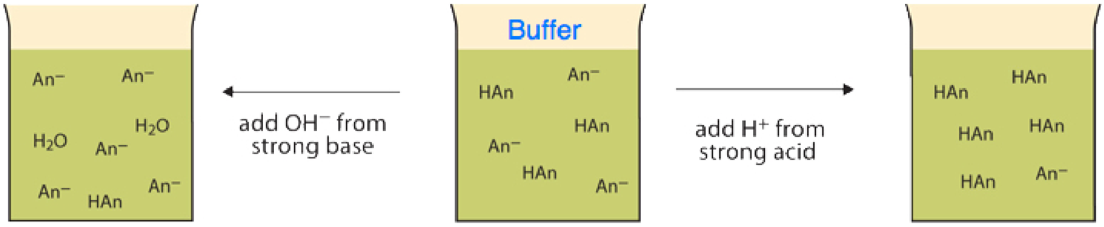


Figure 10.5.1: The Action of Buffers. Buffers can react with both strong acids (top) and strong bases (bottom) to minimize large changes in pH.

A simple buffer system might be a 0.2 *M* solution of sodium acetate; the conjugate pair here is acetic acid HAc and its conjugate base, the acetate ion Ac^{-}. The idea is that this conjugate pair "pool" will be available to gobble up any small ($\leq 10^{-3}$ *M*) addition of H+ or OH^{-} that may result from other processes going on in the solution.

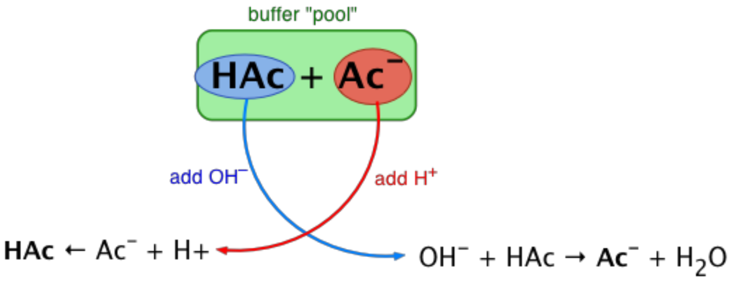


Figure 10.5.2: How HAc/Ac buffer works

Buffers work well only for limited amounts of added strong acid or base. Once either solute is all reacted, the solution is no longer a buffer, and rapid changes in pH may occur. We say that a buffer has a certain capacity. Buffers that have more solute dissolved in them to start with have larger capacities, as might be expected.

Buffers made from weak bases and salts of weak bases act similarly. For example, in a buffer containing NH_3 and NH_4Cl, ammonia molecules can react with any excess hydrogen ions introduced by strong acids:

$$NH_{3(aq)} + H^{+}_{(aq)} \rightarrow NH^{+}_{4(aq)} \tag{10.5.3}$$

while the ammonium ion [NH_4^{+}(aq)] can react with any hydroxide ions introduced by strong bases:

$$NH^{+}_{4(aq)} + OH^{-}_{(aq)} \rightarrow NH_{3(aq)} + H_2O_{(\ell)} \tag{10.5.4}$$

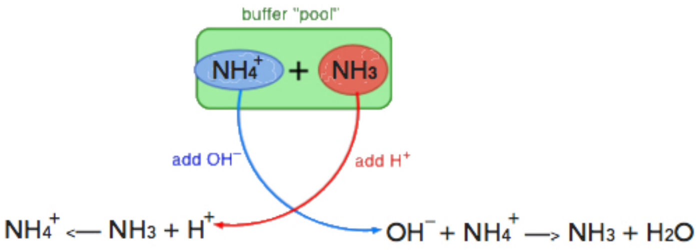


Figure 10.5.3: How NH_4^{+}/NH_3 buffer works

✓ Example 10.5.1

Which solute combinations can make a buffer solution? Assume all are aqueous solutions.

a. $HCHO_2$ and $NaCHO_2$
b. HCl and NaCl
c. CH_3NH_2 and CH_3NH_3Cl
d. NH_3 and NaOH

Solution

a. Formic acid ($HCHO_2$) is a weak acid, while $NaCHO_2$ is a salt supplying —formate ion (CHO_2^-), the conjugate base of $HCHO_2$. The combination of these two solutes would make a buffer solution.
b. Hydrochloric acid (HCl) is a strong acid, not a weak acid, so the combination of these two solutes would not make a buffer solution.
c. Methylamine (CH_3NH_2) is like ammonia, a weak base. The compound CH_3NH_3Cl is a salt supplying $CH_3NH_3^+$, the conjugate acid of CH_3NH_2. The combination of these two solutes would make a buffer solution.
d. Ammonia (NH_3) is a weak base, but NaOH is a strong base. The combination of these two solutes would not make a buffer solution.

? Exercise 10.5.1

Which solute combinations can make a buffer solution? Assume all are aqueous solutions.

a. $NaHCO_3$ and NaCl
b. H_3PO_4 and NaH_2PO_4
c. NH_3 and $(NH_4)_3PO_4$
d. NaOH and NaCl

Answer

b. H_3PO_4 (weak acid) and $H_2PO_4^-$ (conjugate base of H_3PO_4) make a buffer.

c. NH_3 (weak base) and NH_4^+ (conjugate acid of NH_3) make a buffer

✓ Food and Drink App: The Acid That Eases Pain

Although medicines are not exactly "food and drink," we do ingest them, so let's take a look at an acid that is probably the most common medicine: acetylsalicylic acid, also known as aspirin. Aspirin is well known as a pain reliever and antipyretic (fever reducer).

The structure of aspirin is shown in the accompanying figure. The acid part is circled; it is the H atom in that part that can be donated as aspirin acts as a Brønsted-Lowry acid. Because it is not given in Table 10.5.1, acetylsalicylic acid is a weak acid. However, it is still an acid, and given that some people consume relatively large amounts of aspirin daily, its acidic nature can cause problems in the stomach lining, despite the stomach's defenses against its own stomach acid.

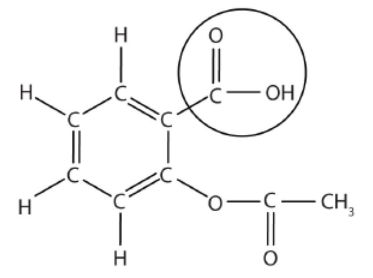


Figure 10.5.4 The Molecular Structure of Aspirin. The circled atoms are the acid part of the molecule.

Because the acid properties of aspirin may be problematic, many aspirin brands offer a "buffered aspirin" form of the medicine. In these cases, the aspirin also contains a buffering agent-usually MgO-that regulates the acidity of the aspirin to minimize its acidic side effects.

As useful and common as aspirin is, it was formally marketed as a drug starting in 1899. The US Food and Drug Administration (FDA), the governmental agency charged with overseeing and approving drugs in the United States, wasn't formed until 1906. Some have argued that if the FDA had been formed before aspirin was introduced, aspirin may never have gotten approval due to its potential for side effects-gastrointestinal bleeding, ringing in the ears, Reye's syndrome (a liver problem), and some allergic reactions. However, recently aspirin has been touted for its effects in lessening heart attacks and strokes, so it is likely that aspirin is here to stay.

Buffer solutions are essential components of all living organisms.

- Our blood is buffered to maintain a pH of 7.4 that must remain unchanged as metabolically-generated CO_2 (carbonic acid) is added and then removed by our lungs.
- Buffers in the oceans, in natural waters such as lakes and streams, and within soils help maintain their environmental stability against acid rain and increases in atmospheric CO_2.
- Many industrial processes, such as brewing, require buffer control, as do research studies in biochemistry and physiology that involve enzymes, are active only within certain pH ranges.

The pH in living systems (Figure \(\PageIndex{1}) is maintained by buffer systems.

Table 7.3.2: pH in Living Systems

Compartment	**pH**
Gastric Acid	1
Lysosomes	4.5
Granules of Chromaffin Cells	5.5
Human Skin	5.5
Urine	6
Neutral H_2O at 37 °C	6.81
Cytosol	7.2
Cerebrospinal Fluid	7.3
Blood	7.43-7.45
Mitochondrial Matrix	7.5
Pancreas Secretions	8.1

Human blood has a buffering system to minimize extreme changes in pH. One buffer in blood is based on the presence of HCO_3^- and H_2CO_3 [H_2CO_3 is another way to write CO_2(aq)]. With this buffer present, even if some stomach acid were to find its way directly into the bloodstream, the change in the pH of blood would be minimal. Inside many of the body's cells, there is a buffering system based on phosphate ions.

Medicine: The Buffer System in Blood

The normal pH of human blood is about 7.4. The carbonate buffer system in the blood uses the following equilibrium reaction:

$$\mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2CO_3}(aq) \rightleftharpoons \mathrm{HCO_3^-}(aq) + \mathrm{H_3O^+}(aq)$$

The concentration of carbonic acid, H_2CO_3 is approximately 0.0012 *M*, and the concentration of the hydrogen carbonate ion, $\mathrm{HCO_3^-}$, is around 0.024 *M*. Using the Henderson-Hasselbalch equation and the pK_a of carbonic acid at body temperature, we can calculate the pH of blood:

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{base}]}{[\mathrm{acid}]} = 6.1 + \log\frac{0.024}{0.0012} = 7.4$$

The fact that the H_2CO_3 concentration is significantly lower than that of the $\mathrm{HCO_3^-}$ ion may seem unusual, but this imbalance is due to the fact that most of the by-products of our metabolism that enter our bloodstream are acidic. Therefore, there must be a larger proportion of base than acid, so that the capacity of the buffer will not be exceeded.

Lactic acid is produced in our muscles when we exercise. As the lactic acid enters the bloodstream, it is neutralized by the $\mathrm{HCO_3^-}$ ion, producing H_2CO_3. An enzyme then accelerates the breakdown of the excess carbonic acid to carbon dioxide and water, which can be eliminated by breathing. In fact, in addition to the regulating effects of the carbonate buffering system on the pH of blood, the body uses breathing to regulate blood pH. If the pH of the blood decreases too far, an increase in breathing removes CO_2 from the blood through the lungs driving the equilibrium reaction such that [H_3O^+] is lowered. If the blood is too alkaline, a lower breath rate increases CO_2 concentration in the blood, driving the equilibrium reaction the other way, increasing $[H^+]$ and restoring an appropriate pH.

Career Focus: Blood Bank Technology Specialist

At this point in this text, you should have the idea that the chemistry of blood is fairly complex. Because of this, people who work with blood must be specially trained to work with it properly.

A blood bank technology specialist is trained to perform routine and special tests on blood samples from blood banks or transfusion centers. This specialist measures the pH of blood, types it (according to the blood's ABO+/− type, Rh factors, and other typing schemes), tests it for the presence or absence of various diseases, and uses the blood to determine if a patient has any of several medical problems, such as anemia. A blood bank technology specialist may also interview and prepare donors to give blood and may actually collect the blood donation.

Blood bank technology specialists are well trained. Typically, they require a college degree with at least a year of special training in blood biology and chemistry. In the United States, training must conform to standards established by the American Association of Blood Banks.

Key Takeaway

- A buffer is a solution that resists sudden changes in pH.

Concept Review Exercise

1. Explain how a buffer prevents large changes in pH.

Answer

1. A buffer has components that react with both strong acids and strong bases to resist sudden changes in pH.

Exercises

1. Describe a buffer. What two related chemical components are required to make a buffer?
2. Can a buffer be made by combining a strong acid with a strong base? Why or why not?
3. Which solute combinations can make a buffer? Assume all are aqueous solutions.
    1. HCl and NaCl
    2. HNO_2 and $NaNO_2$
    3. NH_4NO_3 and HNO_3
    4. NH_4NO_3 and NH_3
4. Which solute combinations can make a buffer? Assume all are aqueous solutions.
    1. H_3PO_4 and Na_3PO_4
    2. $NaHCO_3$ and Na_2CO_3
    3. $NaNO_3$ and $Ca(NO_3)_2$
    4. HN_3 and NH_3
5. For each combination in Exercise 3 that is a buffer, write the chemical equations for the reactions of the buffer components when a strong acid and a strong base is added.
6. For each combination in Exercise 4 that is a buffer, write the chemical equations for the reaction of the buffer components when a strong acid and a strong base is added.
7. The complete phosphate buffer system is based on four substances: H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}. What different buffer solutions can be made from these substances?
8. Explain why NaBr cannot be a component in either an acidic or a basic buffer.
9. Explain why $Mg(NO_3)_2$ cannot be a component in either an acidic or a basic buffer.

Answers

1. A buffer resists sudden changes in pH. It has a weak acid or base and a salt of that weak acid or base.
2. No. Combining a strong acid and a strong base will produce salt and water. Excess strong acid or strong base will not act as a buffer.

3. 1. not a buffer
   2. buffer
   3. not a buffer
   4. buffer

4. 1. not a buffer

2. buffer

3. not a buffer

4. not buffer

5. 3b: strong acid: $H^+ + NO_2^- \rightarrow HNO_2$; strong base: $OH^- + HNO_2 \rightarrow H_2O + NO_2^-$; 3d: strong acid: $H^+ + NH_3 \rightarrow NH_4^+$; strong base: $OH^- + NH_4^+ \rightarrow H_2O + NH_3$
6. 4b: strong acid: $H^+ + CO_3^{2-} \rightarrow$ HCO3$^-$; strong base: $OH^- + HCO_3^- \rightarrow H_2O + CO_3^{2-}$;

7. Buffers can be made by combining H_3PO_4 and $H_2PO_4^-$, $H_2PO_4^-$ and HPO_4^{2-}, and HPO_4^{2-} and PO_4^{3-}.
8. NaBr splits up into two ions in solution, Na^+ and Br^-. Na^+ will not react with any added base knowing that NaOH is a strong base. Br- will not react with any added acid knowing that HBr is a strong acid. Because NaBr will not react with any added base or acid, it does not resist change in pH and is not a buffer.

9. $Mg(NO_3)_2$ includes two types of ions, Mg^{2+} and NO_3^-. $Mg(OH)_2$ is strong base and completely dissociates (100% falls apart), so Mg^{2+} will not react with any added base (0% combines with OH^-). HNO_3 is strong acid and completely dissociates (100% falls apart), so NO_3^- will not react with any added acid (0% combines with H^+). Because $Mg(NO_3)_2$ will not react with any added base or acid, it does not resist change in pH and is not a buffer.

10.E: Acids and Bases (Exercises)

10.1: Arrhenius Definition of Acids and Bases

Concept Review Exercises

1. Give the Arrhenius definitions of an acid and a base.
2. What is neutralization?

Answers

1. Arrhenius acid: a compound that increases the concentration of hydrogen ion (H^+) in aqueous solution; Arrhenius base: a compound that increases the concentration of hydroxide ion (OH^-) in aqueous solution.
2. the reaction of an acid and a base

Exercises

1. Give two examples of Arrhenius acids.
2. Give two examples of Arrhenius bases.
3. List the general properties of acids.
4. List the general properties of bases.
5. Name each compound. (For acids, look up the name in Table 10.1.1. For bases, use the rules for naming ionic compounds from Chapter 3.)

    a. $HBr(aq)$

    b. $Ca(OH)_2(aq)$

    c. $HNO_3(aq)$

    d. $Fe(OH)_3(aq)$

6. Name each compound.

    a. $HI(aq)$

    b. $Cu(OH)_2(aq)$

    c. $H_3PO_4(aq)$

    d. $CsOH(aq)$

7. Write a balanced chemical equation for the neutralization of $Ba(OH)_2(aq)$ with $HNO_3(aq)$.

8. Write a balanced chemical equation for the neutralization of $H_2SO_4(aq)$ with $Cr(OH)_3(aq)$.

9. Gastric juice, the digestive fluid produced in the stomach, contains hydrochloric acid, HCl. Milk of Magnesia, a suspension of solid $Mg(OH)_2$ in an aqueous medium, is sometimes used to neutralize excess stomach acid. Write a complete balanced equation for the neutralization reaction.

10. Identify the salt produced in each acid-base reaction below. Then, balance the equation.

    a. $2HCl + Sr(OH)_2 \rightarrow 2H_2O + ??$

    b. KNO_3; $HNO_3 + KOH \rightarrow ?? + H_2O$

    c. $HF + Ca(OH)_2$ ---> $?? + H_2O$

11. How many moles of sodium hydroxide (NaOH) are needed to neutralize 0.844 mol of acetic acid ($HC_2H_3O_2$)? (Hint: begin by writing a balanced chemical equation for the process.)

12. How many moles of perchloric acid ($HClO_4$) are needed to neutralize 0.052 mol of calcium hydroxide [$Ca(OH)_2$]? (Hint: begin by writing a balanced chemical equation for the process

13. Hydrazoic acid (HN_3) can be neutralized by a base.

    a. Write the balanced chemical equation for the reaction between hydrazoic acid and calcium hydroxide.

b. How many milliliters of 0.0245 M $Ca(OH)_2$ are needed to neutralize 0.564 g of HN_3?

14. Citric acid ($H_3C_6H_5O_7$) has three hydrogen atoms that can form hydrogen ions in solution.

a. Write the balanced chemical equation for the reaction between citric acid and sodium hydroxide.

b. If an orange contains 0.0675 g of $H_3C_6H_5O_7$, how many milliliters of 0.00332 M NaOH solution are needed to neutralize the acid?

15. Magnesium hydroxide [$Mg(OH)_2$] is an ingredient in some antacids. How many grams of $Mg(OH)_2$ are needed to neutralize the acid in 158 mL of 0.106 M HCl(aq)? It might help to write the balanced chemical equation first.

16. Aluminum hydroxide [$Al(OH)_3$] is an ingredient in some antacids. How many grams of $Al(OH)_3$ are needed to neutralize the acid in 96.5 mL of 0.556 M H_2SO_4(aq)? It might help to write the balanced chemical equation first.

17. Write the balanced chemical equation for the reaction between HBr and $Ca(OH)_2$. What volume of 0.010 M HBr solution is be required to neutralize 25 mL of a 0.0100*M* $Ca(OH)_2$ solution?

18. Write the balanced chemical equation for the reaction between HNO_3 and KOH. What volume of 0.5M HNO_3 is required to neutralize 60 mL of 0.4M KOH solution?

Answers

1. HCl and HNO_3 (answers will vary)
2. NaOH and $Ca(OH)_2$ (answers will vary)

3. sour taste, react with metals, react with bases, and turn litmus red
4. bitter taste, feels slippery, react with acids and turn litmus blue

5. a. hydrobromic acid

b. calcium hydroxide

c. nitric acid

d. iron(III) hydroxide

6. a. hydroiodic acid

b. cupric hydroxide

c. phosphoric acid

d. cesium hydroxide

7. $2HNO_3(aq) + Ba(OH)_2(aq) \rightarrow Ba(NO_3)_2(aq) + 2H_2O$

8. $3H_2SO_4(aq) + 2Cr(OH)_3(aq) \rightarrow Cr_2(SO_4)_3(aq) + 6H_2O$

9. $Mg(OH)_2 + 2HCl$ --> $MgCl_2 + 2H_2O$

10. a. $SrCl_{2;}$ $2HCl + Sr(OH)_2 \rightarrow 2H_2O + SrCl_2$

b. $KNO_{3;}$ $HNO_3 + KOH \rightarrow KNO_3 + H_2O$

c. $CaF_{2;}$ $2HF + Ca(OH)_2 \rightarrow CaF_2 + 2H_2O$

11. 0.844 mol

12. 0.104 mol

13. Part 1: $2HN_3(aq) + Ca(OH)_2 \rightarrow Ca(N_3)_2 + 2H_2O$

Part 2: 268 mL

14. Part 1: $H_3C_6H_5O_7(aq) + 3NaOH(aq) \rightarrow Na_3C_6H_5O_7(aq) + 3H_2O$

Part 2: 317.5 mL

15. 0.488 g

16. 2.79 g

17. $2HBr + Ca(OH)_2 \rightarrow CaBr_2 + 2H_2O$; 50 mL HBr

18. $HNO_3 + KOH \rightarrow KNO_3 + H_2O$; 48 mL HNO_3

10.2: Brønsted-Lowry Definition of Acids and Bases

Concept Review Exercise

1. Give the definitions of a Brønsted-Lowry acid and a Brønsted-Lowry base.

Answer

1. A Brønsted-Lowry acid is a proton donor, while a Brønsted-Lowry base is a proton acceptor.

Exercises

1. Label each reactant as a Brønsted-Lowry acid or a Brønsted-Lowry base.

   $HCl(aq) + NH_3(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$

2. Label each reactant as a Brønsted-Lowry acid or a Brønsted-Lowry base.

   $H_2O(\ell) + N_2H_4(aq) \rightarrow N_2H_5^+(aq) + OH^-(aq)$

3. Explain why a Brønsted-Lowry acid can be called a proton donor.
4. Explain why a Brønsted-Lowry base can be called a proton acceptor.
5. Write the chemical equation of the reaction of ammonia in water and label the Brønsted-Lowry acid and base.
6. Write the chemical equation of the reaction of methylamine (CH_3NH_2) in water and label the Brønsted-Lowry acid and base.
7. Demonstrate that the dissolution of HNO_3 in water is actually a Brønsted-Lowry acid-base reaction by describing it with a chemical equation and labeling the Brønsted-Lowry acid and base.
8. Identify the Brønsted-Lowry acid and base in the following chemical equation:

   $C_3H_7NH_2(aq) + H_3O^+(aq) \rightarrow C_3H_7NH_3^+(aq) + H_2O(\ell)$

9. Identify the Brønsted-Lowry acid and the Brønsted-Lowry base in each of the following equations
   1. $NO_2^- + H_2O \longrightarrow HNO_2 + OH^-$
   2. $HBr + H_2O \longrightarrow H_3O^+ + Br^-$
   3. $HS^- + H_2O \longrightarrow H_2S + OH^-$
   4. $H_2PO_4^- + OH^- \longrightarrow HPO_4^{2-} + H_2O$
   5. $H_2PO_4^- + HCl \longrightarrow H_3PO_4 + Cl^-$

10. Write the chemical equation for the reaction that occurs when cocaine hydrochloride ($C_{17}H_{22}ClNO_4$) dissolves in water and donates a proton to a water molecule. (When hydrochlorides dissolve in water, they separate into chloride ions and the appropriate cation.)

11. If codeine hydrobromide has the formula $C_{18}H_{22}BrNO_3$, what is the formula of the parent compound codeine?

Answers

1. HCl: Brønsted-Lowry acid; NH_3: Brønsted-Lowry base
2. H_2O: Brønsted-Lowry acid; N_2H_4: Brønsted-Lowry base
3. A Brønsted-Lowry acid gives away an H^+ ion—nominally, a proton—in an acid-base reaction.
4. A Brønsted-Lowry base accepts an H^+ ion (a proton) in an acid-base reaction.
5. $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$ (here NH_3 = Brønsted-Lowry base; H_2O = Brønsted-Lowry acid)
6. $CH_3NH_2 + H_2O \rightarrow CH_3NH_3^+ + OH^-$ (here CH_3NH_2 = Brønsted-Lowry base; H_2O = Brønsted-Lowry acid)
7. $HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$ (here HNO_3 = Brønsted-Lowry acid; H_2O = Brønsted-Lowry base)
8. $C_3H_7NH_2(aq) + H_3O^+(aq) \rightarrow C_3H_7NH_3^+(aq) + H_2O(\ell)$ (here H_3O^+ = Brønsted-Lowry acid; $C_3H_7NH_2$ = Brønsted-Lowry base)

10.3: Water - Both an Acid and a Base

Concept Review Exercises

1. Explain how water can act as an acid.
2. Explain how water can act as a base.

Answers

1. Under the right conditions, H_2O can donate a proton, making it a Brønsted-Lowry acid.
2. Under the right conditions, H_2O can accept a proton, making it a Brønsted-Lowry base.

Exercises

1. Is $H_2O(\ell)$ acting as an acid or a base?

   $H_2O(\ell) + NH_4^+(aq) \rightarrow H_3O^+(aq) + NH_3(aq)$

2. Is $H_2O(\ell)$ acting as an acid or a base?

   $CH_3^-(aq) + H_2O(\ell) \rightarrow CH_4(aq) + OH^-(aq)$

3. In the aqueous solutions of some salts, one of the ions from the salt can react with water molecules. In some $C_2H_3O_2^-$ solutions, the following reaction can occur:

   $C_2H_3O_2^-(aq) + H_2O(\ell) \rightarrow HC_2H_3O_2(aq) + OH^-(aq)$

   Is H_2O acting as an acid or a base in this reaction?

4. In the aqueous solutions of some salts, one of the ions from the salt can react with water molecules. In some NH_4^+ solutions, the following reaction can occur:

   $NH_4^+(aq) + H_2O \rightarrow NH_3(aq) + H_3O^+(aq)$

   Is H_2O acting as an acid or a base in this reaction?

5. Why is pure water considered neutral?

Answers

1. base
2. acid

3. acid
4. base

5. When water ionizes, equal amounts of H^+ (acid) and OH^- (base) are formed, so the solution is neither acidic nor basic: $H_2O(\ell) \rightarrow H^+(aq) + OH^-(aq)$

10.4: The Strengths of Acids and Bases

Concept Review Exercises

1. Explain the difference between a strong acid or base and a weak acid or base.
2. Explain what is occurring when a chemical reaction reaches equilibrium.
3. Define *pH*.

AnswerS

1. A strong acid or base is 100% ionized in aqueous solution; a weak acid or base is less than 100% ionized.
2. The overall reaction progress stops because the reverse process balances out the forward process.
3. pH is a measure of the hydrogen ion concentration.

Exercises

1. Name a strong acid and a weak acid. (Hint: use Table 10.4.1.)
2. Name a strong base and a weak base. (Hint: use Table 10.4.1.)
3. Is each compound a strong acid or a weak acid? Assume all are in aqueous solution. (Hint: use Table 10.4.1.)
    1. HF
    2. $HC_2H_3O_2$
    3. HCl
    4. $HClO_4$
4. Is each compound a strong acid or a weak acid? Assume all are in aqueous solution. (Hint: use Table 10.4.1.)
    1. H_2SO_4
    2. HSO_4^-
    3. HPO_4^{2-}
    4. HNO_3
5. Is each compound a strong base or a weak base? Assume all are in aqueous solution. (Hint: use Table 10.4.1.)
    1. NH_3
    2. NaOH
    3. $Mg(OH)_2$
    4. $Cu(OH)_2$
6. Is each compound a strong base or a weak base? Assume all are in aqueous solution. (Hint: use Table 10.4.1.)
    1. KOH
    2. H_2O
    3. $Fe(OH)_2$
    4. $Fe(OH)_3$
7. Write the chemical equation for the equilibrium process for each weak acid in Exercise 3.
8. Write the chemical equation for the equilibrium process for each weak acid in Exercise 4.
9. Write the chemical equation for the equilibrium process for each weak base in Exercise 5.
10. Write the chemical equation for the equilibrium process for each weak base in Exercise 6.
11. Which is the stronger acid—HCl(aq) or HF(aq)?
12. Which is the stronger base—KOH(aq) or $Ni(OH)_2(aq)$?
13. Consider the two acids in Exercise 11. For solutions that have the same concentration, which one would you expect to have a lower pH?
14. Consider the two bases in Exercise 12. For solutions that have the same concentration, which one would you expect to have a higher pH?
15. Consider the list of substances in Table \PageIndex3\PageIndex3.2"The pH Values of Some Common Solutions". What is the most acidic substance on the list that you have encountered recently?
16. Consider the list of substances in Table \PageIndex3\PageIndex3.2"The pH Values of Some Common Solutions". What is the most basic substance on the list that you have encountered recently?
17. Indicate whether solutions with the following pH values are acidic, basic, or neutral:
    1. pH = 9.4
    2. pH = 7.0
    3. pH = 1.2
    4. pH = 6.5

Answers

1. strong acid: HCl; weak acid: $HC_2H_3O_2$ (answers will vary)
2. strong base: NaOH; weak base: NH_3 (answers will vary)
3.
    1. weak
    2. weak
    3. strong
    4. strong

4. 1. strong
   2. weak
   3. weak
   4. strong
5. 1. weak
   2. strong
   3. strong
   4. weak
6. 1. strong
   2. weak
   3. weak
   4. weak

7. 3a: $HF(aq) \leftrightarrows H^+(aq) + F^-(aq)$; 3b: $HC_2H_3O_2(aq) \leftrightarrows H^+(aq) + C_2H_3O_2^-(aq)$

8. 4b: $HSO_4^-(aq) \leftrightarrows H^+(aq) + SO_4^{2-}(aq)$; 4c: $HPO_4^{2-}(aq) \leftrightarrows H^+(aq) + PO_4^{3-}(aq)$

9. 5a: $NH_3(aq) + H_2O \leftrightarrows NH_4^+(aq) + OH^-(aq)$; 5d: $Cu(OH)_2(aq) \leftrightarrows Cu^{2+}(aq) + 2OH^-(aq)$

10. 6b: $H_2O + H_2O \leftrightarrows H_3O^+(aq) + OH^-(aq)$; 6c: $Fe(OH)_2(aq) \leftrightarrows Fe^{2+}(aq) + 2OH^-(aq)$; 6d: $Fe(OH)3(aq) \leftrightarrows Fe^{3+}(aq) + 3OH^-(aq)$

11. $HCl(aq)$

12. $KOH(aq)$

13. $HCl(aq)$

14. $KOH(aq)$

15. (answers will vary)

16. (answers will vary)

17. 1. basic

2. neutral

3. acidic (strongly)

4. acidic (mildly)

10.5: Buffers

Concept Review Exercise

1. Explain how a buffer prevents large changes in pH.

Answer

1. A buffer has components that react with both strong acids and strong bases to resist sudden changes in pH.

Exercises

1. Describe a buffer. What two related chemical components are required to make a buffer?
2. Can a buffer be made by combining a strong acid with a strong base? Why or why not?
3. Which solute combinations can make a buffer? Assume all are aqueous solutions.
   1. HCl and $NaCl$
   2. HNO_2 and $NaNO_2$
   3. NH_4NO_3 and HNO_3
   4. NH_4NO_3 and NH_3
4. Which solute combinations can make a buffer? Assume all are aqueous solutions.
   1. H_3PO_4 and Na_3PO_4
   2. $NaHCO_3$ and Na_2CO_3

   3. $NaNO_3$ and $Ca(NO_3)_2$
   4. HN_3 and NH_3
5. For each combination in Exercise 3 that is a buffer, write the chemical equations for the reactions of the buffer components when a strong acid and a strong base is added.
6. For each combination in Exercise 4 that is a buffer, write the chemical equations for the reaction of the buffer components when a strong acid and a strong base is added.
7. The complete phosphate buffer system is based on four substances: H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}. What different buffer solutions can be made from these substances?
8. Explain why NaBr cannot be a component in either an acidic or a basic buffer.
9. Explain why $Mg(NO_3)_2$ cannot be a component in either an acidic or a basic buffer.

Answers

1. A buffer resists sudden changes in pH. It has a weak acid or base and a salt of that weak acid or base.
2. No. Combining a strong acid and a strong base will produce salt and water. Excess strong acid or strong base will not act as a buffer.

3. 1. not a buffer
   2. buffer
   3. not a buffer
   4. buffer

4. 1. not a buffer

2. buffer

3. not a buffer

4. not buffer

5. 3b: strong acid: $H^+ + NO_2^- \rightarrow HNO_2$; strong base: $OH^- + HNO_2 \rightarrow H_2O + NO_2^-$; 3d: strong acid: $H^+ + NH_3 \rightarrow NH_4^+$; strong base: $OH^- + NH_4^+ \rightarrow H_2O + NH_3$
6. 4b: strong acid: $H^+ + CO_3^{2-} \rightarrow HCO3^-$; strong base: $OH^- + HCO_3^- \rightarrow H_2O + CO_3^{2-}$;

7. Buffers can be made by combining H_3PO_4 and $H_2PO_4^-$, $H_2PO_4^-$ and HPO_4^{2-}, and HPO_4^{2-} and PO_4^{3-}.
8. NaBr splits up into two ions in solution, Na^+ and Br^-. Na^+ will not react with any added base knowing that NaOH is a strong base. Br- will not react with any added acid knowing that HBr is a strong acid. Because NaBr will not react with any added base or acid, it does not resist change in pH and is not a buffer.

9. $Mg(NO_3)_2$ includes two types of ions, Mg^{2+} and NO_3^-. $Mg(OH)_2$ is strong base and completely dissociates (100% falls apart), so Mg^{2+} will not react with any added base (0% combines with OH^-). HNO_3 is strong acid and completely dissociates (100% falls apart), so NO_3^- will not react with any added acid (0% combines with H^+). Because $Mg(NO_3)_2$ will not react with any added base or acid, it does not resist change in pH and is not a buffer.

Additional Exercises

1. The properties of a 1.0 M HCl solution and a 1.0 M $HC_2H_3O_2$ solution are compared. Measurements show that the hydrochloric acid solution has a higher osmotic pressure than the acetic acid solution. Explain why.
2. Of a 0.50 M HNO_3 solution and a 0.50 M $HC_2H_3O_2$ solution, which should have the higher boiling point? Explain why.
3. The reaction of sulfuric acid [$H_2SO_4(aq)$] with sodium hydroxide [NaOH(aq)] can be represented by two separate steps, with only one hydrogen ion reacting in each step. Write the chemical equation for each step.
4. The reaction of aluminum hydroxide [$Al(OH)_3(aq)$] with hydrochloric acid [HCl(aq)] can be represented by three separate steps, with only one hydroxide ion reacting in each step. Write the chemical equation for each step.
5. A friend brings you a small sample of an unknown chemical. Assuming that the chemical is soluble in water, how would you determine if the chemical is an acid or a base?
6. A neutral solution has a hydrogen ion concentration of about 1×10^{-7} M. What is the concentration of the hydroxide ion in a neutral solution?
7. The Lewis definitions of an acid and a base are based on electron pairs, not protons. A Lewis acid is an electron pair acceptor, while a Lewis base is an electron pair donor. Use Lewis diagrams to show that

$H^+(aq) + OH^-(aq) \rightarrow H_2O(\ell)$

is an acid-base reaction in the Lewis sense as well as in the Arrhenius and Brønsted-Lowry senses.

8. Given the chemical reaction

   $NH_3(g) + BF_3(g) \rightarrow NH_3—BF_3(s)$

   show that the reaction illustrated by this equation is an acid-base reaction if we use the Lewis definitions of an acid and a base (see Exercise 7). The product contains a bond between the N and B atoms.

Answers

1. HCl is a strong acid and yields more ions in solution. $HC_2H_3O_2$ is a weak acid and undergoes partial ionization in solution.
2. HNO_3 is a strong acid while $HC_2H_3O_2$ is a weak acid. HNO_3 dissociates 100% and its solution contains more ions. The more ions the solution contains the lower is its vapor pressure; the higher temperature is required for it to boil.
3. $H_2SO_4 + NaOH \rightarrow NaHSO_4 + H_2O$; $NaHSO_4 + NaOH \rightarrow Na_2SO_4 + H_2O$
4. $Al(OH)_3 + HCl \rightarrow Al(OH)_2Cl + H_2O$; $Al(OH)_2Cl + HCl \rightarrow Al(OH)Cl_2 + H_2O$; $Al(OH)Cl_2 + HCl \rightarrow AlCl3 + H_2O$
5. One way is to add it to $NaHCO_3$; if it bubbles, it is an acid. Alternatively, add the sample to litmus and look for a characteristic color change (red for acid, blue for base).
6. In a neutral solution, $[OH^-] = [H^+] = 1.0 \times 10^{-7}$ M
7. The O atom is donating an electron pair to the H^+ ion, making the base an electron pair donor and the acid an electron pair acceptor.
8. The N atom is donating a lone pair to B in BF_3, Hence NH_3 is the Lewis base and BF_3 is the Lewis acid.

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10.S: Acids and Bases (Summary)

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

The earliest chemical definition of an acid, the **Arrhenius definition**, says that an **acid** is a compound that increases the amount of hydrogen ion (H^+) in aqueous solution. An **Arrhenius base** is a compound that increases the amount of hydroxide ion (OH^-) in aqueous solution. While most bases are named as ionic hydroxide compounds, aqueous acids have a naming system unique to acids. Acids and bases react together in a characteristic chemical reaction called **neutralization**, in which the products are water and a salt. The principles of stoichiometry, along with the balanced chemical equation for a reaction between an acid and a base, can be used to determine how much of one compound will react with a given amount of the other.

A **Brønsted-Lowry acid** is any substance that donates a proton to another substance. A **Brønsted-Lowry base** is any substance that accepts a proton from another substance. The reaction of ammonia with water to make ammonium ions and hydroxide ions can be used to illustrate Brønsted-Lowry acid and base behavior.

Some compounds can either donate or accept protons, depending on the circumstances. Such compounds are called **amphiprotic**. Water is one example of an amphiprotic compound. One result of water being amphiprotic is that a water molecule can donate a proton to another water molecule to make a hydronium ion and a hydroxide ion. This process is called the **autoionization of water** and occurs in any sample of water.

Not all acids and bases are equal in chemical strength. A **strong acid** is an acid whose molecules are all dissociated into ions in aqueous solution. Hydrochloric acid is an example of a strong acid. Similarly, a **strong base** is a base whose molecules are dissociated into ions in aqueous solution. Sodium hydroxide is an example of a strong base. Any acid or base whose molecules are not all dissociated into ions in aqueous solution is a **weak acid** or a **weak base**. Solutions of weak acids and weak bases reach a **chemical equilibrium** between the un-ionized form of the compound and the dissociated ions. It is a dynamic equilibrium because acid and base molecules are constantly dissociating into ions and reassociating into neutral molecules.

The **pH** scale is a scale used to express the concentration of hydrogen ions in solution. A neutral solution, neither acidic nor basic, has a pH of 7. Acidic solutions have a pH lower than 7, while basic solutions have a pH higher than 7.

Buffers are solutions that resist dramatic changes in pH when an acid or a base is added to them. They contain a weak acid and a salt of that weak acid, or a weak base and a salt of that weak base. When a buffer is present, any strong acid reacts with the anion of the salt, forming a weak acid and minimizing the presence of hydrogen ions in solution. Any strong base reacts with the weak acid, minimizing the amount of additional hydroxide ions in solution. However, buffers only have limited **capacity**; there is a limit to the amount of strong acid or strong base any given amount of buffer will react with.

CHAPTER OVERVIEW

11: Nuclear Chemistry

Most chemists pay little attention to the nucleus of an atom except to consider the number of protons it contains because that determines an element's identity. However, in nuclear chemistry, the composition of the nucleus and the changes that occur there are very important. Applications of nuclear chemistry may be more widespread than you realize. Many people are aware of nuclear power plants and nuclear bombs, but nuclear chemistry also has applications ranging from smoke detectors to medicine, from the sterilization of food to the analysis of ancient artifacts. In this chapter, we will examine some of the basic concepts of nuclear chemistry and some of the nuclear reactions that are important in our everyday lives.

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11.0: Prelude to Nuclear Chemistry

Most of us may not be aware of a device in our homes that guards our safety and, at the same time, depends on radioactivity to operate properly. This device is a smoke detector.

A typical smoke detector contains an electric circuit that includes two metal plates about 1 cm apart. A battery in the circuit creates a voltage between the plates. Next to the plates is a small disk containing a tiny amount (∼0.0002 g) of the radioactive element americium (Am). The radioactivity of the americium ionizes the air between the plates, causing a tiny current to constantly flow between them. (This constant drain on the battery explains why the batteries in smoke detectors should be replaced on a regular basis, whether the alarm has been triggered or not.)

Figure 11.0.1: Many people think of nuclear chemistry in connection with the nuclear power industry and atomic bombs but do not realize that most smoke detectors rely on nuclear chemistry and save countless lives every year. The applications of nuclear chemistry may be more widespread than you think. (CC BY-SA 3.0; Wile e2005).

When particles of smoke from a fire enter the smoke detector, they interfere with the ions between the metal plates, interrupting the tiny flow of current. When the current drops beneath a set value, another circuit triggers a loud alarm, warning of the possible presence of fire.

Although radioactive, the americium in a smoke detector is embedded in plastic and is not harmful unless the plastic package is taken apart, which is unlikely. Although many people experience an unfounded fear of radioactivity, smoke detectors provide an application of radioactivity that saves thousands of lives every year.

11.1: Radioactivity

Learning Objectives

- To define and give examples of the major types of radioactivity.

Atoms are composed of subatomic particles—protons, neutrons, and electrons. Protons and neutrons are located in the nucleus and provide most of the mass of the atom, while electrons circle the nucleus in shells and subshells and account for an atom's size. Remember, the notation for succinctly representing an isotope of a particular atom:

$$^{12}_{6}\mathrm{C} \tag{11.1.1}$$

The element in this example, represented by the symbol *C*, is carbon. Its atomic number, 6, is the lower left subscript on the symbol and is the number of protons in the atom. The mass number, the superscript to the upper left of the symbol, is the sum of the number of protons and neutrons in the nucleus of this particular isotope. In this case, the mass number is 12, which means that the number of neutrons in the atom is 12 − 6 = 6 (that is, the mass number of the atom minus the number of protons in the nucleus equals the number of neutrons). Occasionally, the atomic number is omitted in this notation because the symbol of the element itself conveys its characteristic atomic number. The two isotopes of hydrogen, $^{2}\mathrm{H}$ and $^{3}\mathrm{H}$, are given their own names: deuterium (D) and tritium (T), respectively. Another way of expressing a particular isotope is to list the mass number after the element name, like carbon-12 or hydrogen-3.

Atomic theory in the 19th century presumed that nuclei had fixed compositions. But in 1896, the French scientist Henri Becquerel found that a uranium compound placed near a photographic plate made an image on the plate, even if the compound was wrapped in black cloth. He reasoned that the uranium compound was emitting some kind of radiation that passed through the cloth to expose the photographic plate. Further investigations showed that the radiation was a combination of particles and electromagnetic rays, with its ultimate source as the atomic nucleus. These emanations were ultimately called, collectively, **radioactivity**.

There are three main forms of radioactive emissions. The first is called an alpha particle, which is symbolized by the Greek letter α. An alpha particle is composed of two protons and two neutrons, and so it is the same as a helium nucleus. (We often use $^{4}_{2}\mathrm{He}$ to represent an alpha particle.) It has a 2+ charge. When a radioactive atom emits an alpha particle, the original atom's atomic number decreases by two (because of the loss of two protons), and its mass number decreases by four (because of the loss of four nuclear particles). We can represent the emission of an alpha particle with a chemical equation—for example, the alpha-particle emission of uranium-235 is as follows:

$$^{235}_{92}\mathrm{U} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{231}_{90}\mathrm{Th} \tag{11.1.2}$$

How do we know that a product of the reaction is $^{231}_{90}\mathrm{Th}$? We use the law of conservation of matter, which says that matter cannot be created or destroyed. This means we must have the same number of protons and neutrons on both sides of the chemical equation. If our uranium nucleus loses 2 protons, there are 90 protons remaining, identifying the element as thorium. Moreover, if we lose 4 nuclear particles of the original 235, there are 231 remaining. Thus, we use subtraction to identify the isotope of the thorium atom—in this case, $^{231}_{90}\mathrm{Th}$.

Chemists often use the names *parent isotope* and *daughter isotope* to represent the original atom and the product other than the alpha particle. In the previous example, $^{235}_{92}\mathrm{U}$ is the parent isotope, and $^{231}_{90}\mathrm{Th}$ is the daughter isotope. When one element changes into another in this manner, it undergoes *radioactive decay*.

Example 11.1.1

Write the nuclear equation that represents the radioactive decay of radon-222 by alpha particle emission and identify the daughter isotope.

Solution

Radon has an atomic number of 86, so the parent isotope is represented as $^{222}_{86}\mathrm{Rn}$. We represent the alpha particle as $^{4}_{2}\mathrm{He}$ and use subtraction (222 − 4 = 218 and 86 − 2 = 84) to identify the daughter isotope as an isotope of polonium, $^{218}_{84}\mathrm{Po}$:

$$^{222}_{86}\mathrm{Rn} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{218}_{84}\mathrm{Po}$$

Exercise 11.1.1

Write the nuclear equation that represents the radioactive decay of polonium-209 by alpha particle emission and identify the daughter isotope.

Answer

$${}^{209}_{84}\text{Po} \rightarrow {}^{4}_{2}\text{He} + {}^{205}_{82}\text{Pb}$$

The second major type of radioactive emission is called a beta particle, symbolized by the Greek letter β. A beta particle is an electron ejected from the nucleus (not from the shells of electrons about the nucleus) and has a 1− charge. We can also represent a beta particle as ${}^{0}_{-1}\text{e}$ or β^-. The net effect of beta particle emission on a nucleus is that a neutron is converted to a proton. The overall mass number stays the same, but because the number of protons increases by one, the atomic number goes up by one. Carbon-14 decays by emitting a beta particle:

$${}^{14}_{6}\text{C} \rightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}\text{e} \tag{11.1.3}$$

Again, the sum of the atomic numbers is the same on both sides of the equation, as is the sum of the mass numbers. (Note that the electron is assigned an “atomic number” of 1−, equal to its charge.)

The third major type of radioactive emission is not a particle but rather a very energetic form of electromagnetic radiation called gamma rays, symbolized by the Greek letter γ. Gamma rays themselves do not carry an overall electrical charge, but they may knock electrons out of atoms in a sample of matter and make it electrically charged (for which gamma rays are termed *ionizing radiation*). For example, in the radioactive decay of radon-222, both alpha and gamma radiation are emitted, with the latter having an energy of 8.2×10^{-14} J per nucleus decayed:

$${}^{222}_{86}\text{Rn} \rightarrow {}^{218}_{84}\text{Po} + {}^{4}_{2}\text{He} + \gamma \tag{11.1.4}$$

This may not seem like much energy, but if 1 mol of radon atoms were to decay, the gamma ray energy would be 49 million kJ!

Example 11.1.2

Write the nuclear equation that represents the radioactive decay of boron-12 by beta particle emission and identify the daughter isotope. A gamma ray is emitted simultaneously with the beta particle.

Solution

The parent isotope is ${}^{12}_{5}\text{B}$ while one of the products is an electron, ${}^{0}_{-1}\text{e}$. So that the mass and atomic numbers have the same value on both sides, the mass number of the daughter isotope must be 12, and its atomic number must be 6. The element having an atomic number of 6 is carbon. Thus, the complete nuclear equation is as follows:

$${}^{12}_{5}\text{B} \rightarrow {}^{12}_{6}\text{C} + {}^{0}_{-1}\text{e} + \gamma$$

The daughter isotope is ${}^{12}_{6}\text{C}$.

Exercise 11.1.2

Write the nuclear equation that represents the radioactive decay of iodine-131 by beta particle emission and identify the daughter isotope. A gamma ray is emitted simultaneously with the beta particle.

Answer

$${}^{131}_{53}\text{I} \rightarrow {}^{131}_{54}\text{Xe} + {}^{0}_{-1}\text{e} + \gamma$$

Alpha, beta, and gamma emissions have different abilities to penetrate matter. The relatively large alpha particle is easily stopped by matter (although it may impart a significant amount of energy to the matter it contacts). Beta particles penetrate slightly into matter, perhaps a few centimeters at most. Gamma rays can penetrate deeply into matter and can impart a large amount of energy into the surrounding matter. Table 11.1.1 summarizes the properties of the three main types of radioactive emissions.

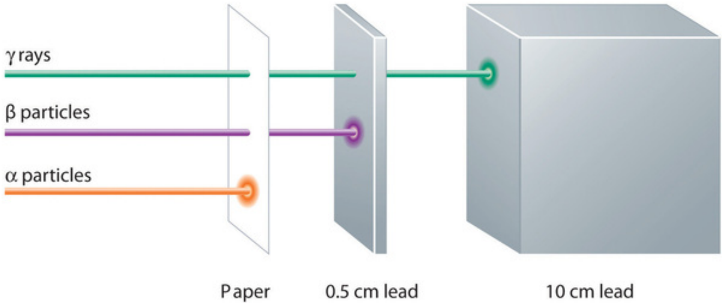


Figure 11.1.2: Different emissions exhibit different pentration powers. (CC BY-NC-SA 3.0; anonymous)

Table 11.1.1: The Three Main Forms of Radioactive Emissions

Characteristic	Alpha Particles	Beta Particles	Gamma Rays
symbols	α, $^{4}_{2}\mathrm{He}$	β, $^{0}_{-1}\mathrm{e}$	γ
identity	helium nucleus	electron	electromagnetic radiation
charge	2+	1−	none
mass number	4	0	0
penetrating power	minimal (will not penetrate skin)	short (will penetrate skin and some tissues slightly)	deep (will penetrate tissues deeply)

Occasionally, an atomic nucleus breaks apart into smaller pieces in a radioactive process called *spontaneous fission* (or fission). Typically, the daughter isotopes produced by fission are a varied mix of products, rather than a specific isotope as with alpha and beta particle emission. Often, fission produces excess neutrons that will sometimes be captured by other nuclei, possibly inducing additional radioactive events. Uranium-235 undergoes spontaneous fission to a small extent. One typical reaction is

$$^{235}_{92}\mathrm{U} \rightarrow\ ^{139}_{56}\mathrm{Ba} +\ ^{94}_{36}\mathrm{Kr} + 2\,^{1}_{0}\mathrm{n} \tag{11.1.5}$$

where $^{1}_{0}\mathrm{n}$ is a neutron. As with any nuclear process, the sums of the atomic numbers and the mass numbers must be the same on both sides of the equation. Spontaneous fission is found only in large nuclei. The smallest nucleus that exhibits spontaneous fission is lead-208.

> *Fission is the radioactive process used in nuclear power plants and one type of nuclear bomb.*

Key Takeaway

The major types of radioactivity include alpha particles, beta particles, and gamma rays.

11.2: Half-Life

Learning Objectives

- To define *half-life*.
- To determine the amount of radioactive substance remaining after a given number of half-lives.

Whether or not a given isotope is radioactive is a characteristic of that particular isotope. Some isotopes are stable indefinitely, while others are radioactive and decay through a characteristic form of emission. As time passes, less and less of the radioactive isotope will be present, and the level of radioactivity decreases. An interesting and useful aspect of radioactive decay is the **half-life**. The half-life of a radioactive isotope is the amount of time it takes for one-half of the radioactive isotope to decay. The half-life of a specific radioactive isotope is constant; it is unaffected by conditions and is independent of the initial amount of that isotope.

Consider the following example. Suppose we have 100.0 g of ^{3}H (tritium, a radioactive isotope of hydrogen). It has a half-life of 12.3 y. After 12.3 y, half of the sample will have decayed to ^{3}He by emitting a beta particle, so that only 50.0 g of the original ^{3}H remains. After another 12.3 y—making a total of 24.6 y—another half of the remaining ^{3}H will have decayed, leaving 25.0 g of ^{3}H. After another 12.3 y—now a total of 36.9 y—another half of the remaining ^{3}H will have decayed, leaving 12.5 g of ^{3}H. This sequence of events is illustrated in Figure $11.2.1$.

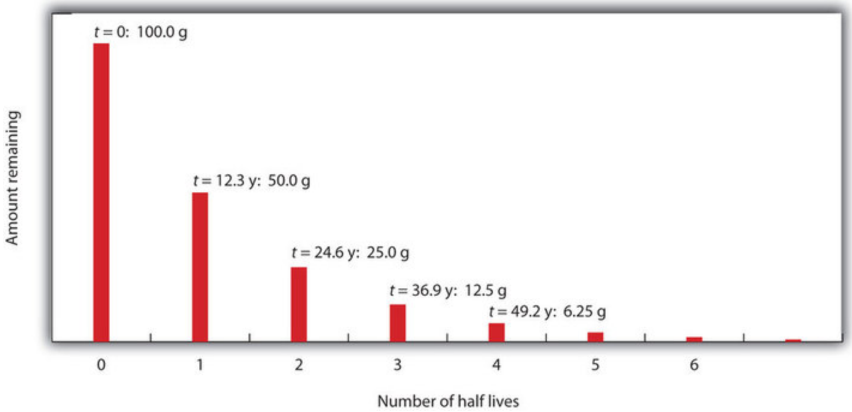


Figure 11.2.1: Radioactive Decay. During each successive half-life, half of the initial amount will radioactively decay.

We can determine the amount of a radioactive isotope remaining after a given number half-lives by using the following expression:

$$\text{amount remaining} = \text{initial amount} \times \left(\frac{1}{2}\right)^{n} \tag{11.2.1}$$

where *n* is the number of half-lives. This expression works even if the number of half-lives is not a whole number.

Example 11.2.1

The half-life of ^{20}F is 11.0 s. If a sample initially contains 5.00 g of ^{20}F, how much ^{20}F remains after 44.0 s?

Solution

If we compare the time that has passed to the isotope's half-life, we note that 44.0 s is exactly 4 half-lives, so we can use Equation ??? with $n = 4$. Substituting and solving results in the following:

$$\begin{aligned} \text{amount remaining } &= 5.00\ g \times \left(\frac{1}{2}\right)^{4} \\ &= 5.00\ g \times \frac{1}{16} \\ &= 0.313\ g \end{aligned}$$

Less than one-third of a gram of ^{20}F remains.

Exercise 11.2.2

The half-life of ^{44}Ti is 60.0 y. A sample initially contains 0.600 g of ^{44}Ti. How much ^{44}Ti remains after 180.0 y?

Answer

0.075 g.

Half-lives of isotopes range from fractions of a microsecond to billions of years. Table $11.2.1$ lists the half-lives of some isotopes.

Table 11.2.1: Half-Lives of Various Isotopes

Isotope	Half-Life
^{3}H	12.3 y
^{14}C	5,730 y
^{40}K	1.26 × 10^{9} y
^{51}Cr	27.70 d
^{90}Sr	29.1 y
^{131}I	8.04 d
^{222}Rn	3.823 d
^{235}U	7.04 × 10^{8} y
^{238}U	4.47 × 10^{9} y
^{241}Am	432.7 y
^{248}Bk	23.7 h
^{260}Sg	4 ms

Example 11.2.2

The isotope I-125 is used in certain laboratory procedures and has a half-life of 59.4 days. If the initial activity of a sample of I-125 is $32,000$ counts per minute (cpm), how much activity will be present in 178.2 days?

Solution

We begin by determining how many half-lives are represented by 178.2 days:

$$\frac{178.2 \text{ days}}{59.4 \text{ days/half-life}} = 3 \text{ half-lives}$$

Then we simply count activity:

$$\begin{aligned} \text{initial activity } (t_0) &= 32,000 \text{ cpm} \\ \text{after one half-life } &= 16,000 \text{ cpm} \\ \text{after two half-lives } &= 8,000 \text{ cpm} \\ \text{after three half-lives } &= 4,000 \text{ cpm} \end{aligned}$$

Be sure to keep in mind that the initial count is at time zero (t_0) and we subtract from that count at the first half-life. The second half-life has an activity of half the previous count (not the initial count).

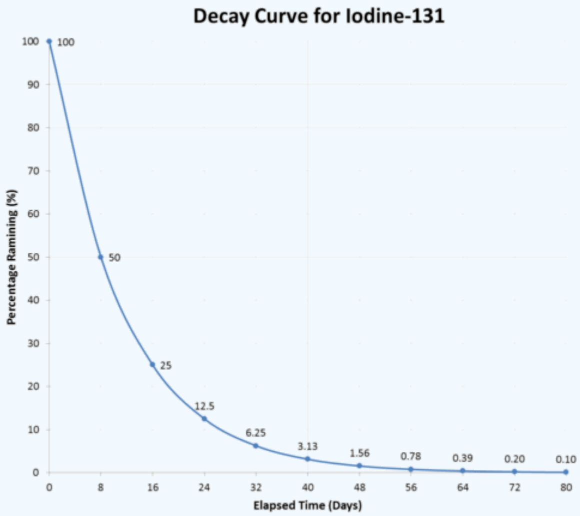
Equation 11.2.1 can be used to calculate the amount of radioactivity remaining after a given time:

$$N_t = N_0 \times (0.5)^{\text{number of half-lives}}$$

where $N_t =$ activity at time t and $N_0 =$ initial activity at time $t = 0$.

If we have an initial activity of $42,000$ cpm, what will the activity be after four half-lives?

$$\begin{aligned} N_t &= N_0 (0.5)^4 \\ &= (42,000)\,(0.5)\,(0.5)\,(0.5)\,(0.5) \\ &= 2625 \text{ cpm} \end{aligned}$$



Typical radioactive decay curve.

The graph above illustrates a typical decay curve for $\mathrm{I}-125$. The activity decreases by one-half during each succeeding half-life.

cise

A sample of Ac-225 originally contained 80 grams and after 50 days only 2.5 grams of the original Ac-225 remain. What is the half life of Ac-225?

Answer

10 days

Looking Closer: Half-Lives of Radioactive Elements

Many people think that the half-life of a radioactive element represents the amount of time an element is radioactive. In fact, it is the time required for half—not all—of the element to decay radioactively. Occasionally, however, the daughter element is also radioactive, so its radioactivity must also be considered.

The expected working life of an ionization-type smoke detector (described in the opening essay) is about 10 years. In that time, americium-241, which has a half-life of about 432 y, loses less than 4% of its radioactivity. A half-life of 432 y may seem long to us, but it is not very long as half-lives go. Uranium-238, the most common isotope of uranium, has a half-life of about 4.5 × 10^9 y, while thorium-232 has a half-life of 14 × 10^9 y.

On the other hand, some nuclei have extremely short half-lives, presenting challenges to the scientists who study them. The longest-lived isotope of lawrencium, ^{262}Lr, has a half-life of 3.6 h, while the shortest-lived isotope of lawrencium, ^{252}Lr, has a half-life of 0.36 s. As of this writing, the largest atom ever detected has atomic number 118, mass number 293, and a half-life of 120 ns. Can you imagine how quickly an experiment must be done to determine the properties of elements that exist for so short a time?

Key Takeaways

- Natural radioactive processes are characterized by a half-life, the time it takes for half of the material to decay radioactively.
- The amount of material left over after a certain number of half-lives can be easily calculated.

11.3: Units of Radioactivity

Learning Objectives

- To express amounts of radioactivity in a variety of units.

Previously, we used mass to indicate the amount of radioactive substance present. This is only one of several units used to express amounts of radiation. Some units describe the number of radioactive events occurring per unit time, while others express the amount of a person's exposure to radiation.

Perhaps the direct way of reporting radioactivity is the number of radioactive decays per second. One decay per second is called one becquerel (Bq). Even in a small mass of radioactive material, however, there are many thousands of decays or disintegrations per second. The unit curie (Ci), now defined as 3.7×10^{10} decays per second, was originally defined as the number of decays per second in 1 g of radium. Many radioactive samples have activities that are on the order of microcuries (µCi) or more. Both the becquerel and curie can be used in place of grams to describe quantities of radioactive material. As an example, the amount of americium in an average smoke detector has an activity of 0.9 µCi.

> *The unit becquerel is named after Henri Becquerel, who discovered radioactivity in 1896. The unit curie is named after Polish scientist Marie Curie, who performed some of the initial investigations into radioactive phenomena and discovered the elements, polonium (Po) and radium (Ra) in the early 1900s.*

Example 11.3.1

A sample of radium has an activity of 16.0 mCi (millicuries). If the half-life of radium is 1,600 y, how long before the sample's activity is 1.0 mCi?

Solution

The following table shows the activity of the radium sample over multiple half-lives:

Solutions to Example 11.3.1

Time in Years	Activity
0	16.0 mCi
1,600	8.0 mCi
3,200	4.0 mCi
4,800	2.0 mCi
6,400	1.0 mCi

Over a period of 4 half-lives, the activity of the radium will be halved four times, at which point its activity will be 1.0 mCi. Thus, it takes 4 half-lives, or 4 × 1,600 y = 6,400 y, for the activity to decrease to 1.0 mCi.

Exercise 11.3.1

A sample of radon has an activity of 60,000 Bq. If the half-life of radon is 15 h, how long before the sample's activity is 3,750 Bq?

Answer

60 hrs.

Other measures of radioactivity are based on the effects it has on living tissue. Radioactivity can transfer energy to tissues in two ways: through the kinetic energy of the particles hitting the tissue and through the electromagnetic energy of the gamma rays being absorbed by the tissue. Either way, the transferred energy—like thermal energy from boiling water—can damage the tissue.

The rad (an acronym for radiation absorbed dose) is a unit equivalent to a gram of tissue absorbing 0.01 J:

$$1 \text{ rad} = 0.01 \text{ J/g}$$

Another unit of radiation absorption is the gray (Gy):

$$1 \text{ Gy} = 100 \text{ rad}$$

The rad is more common. To get an idea of the amount of energy this represents, consider that the absorption of 1 rad by 70,000 g of H_2O (approximately the same mass as a 150 lb person) would increase its temperature by only 0.002°C. This may not seem like a lot, but it is enough energy to break about 1×10^{21} molecular C–C bonds in a person's body. That amount of damage would not be desirable.

Predicting the effects of radiation is complicated by the fact that various tissues are affected differently by different types of emissions. To quantify these effects, the unit **rem** (an acronym for roentgen equivalent, man) is defined as

$$\text{rem} = \text{rad} \times \text{RBE}$$

where RBE is the *relative biological effectiveness factor* is a number greater than or equal to 1 that takes into account the type of radioactive emission and sometimes the type of tissue being exposed. For beta particles, RBE factor equals 1. For alpha particles striking most tissues, the factor is 10, but for eye tissue, the factor is 30. Most radioactive emissions that people are exposed to are on the order of a few dozen millirems (mrem) or less; a medical X ray is about 20 mrem. A sievert (Sv) is a related unit and is defined as 100 rem.

What is a person's annual exposure to radioactivity and radiation? Table $11.3.1$ lists the sources and annual amounts of radiation exposure. It may surprise you to learn that fully 82% of the radioactivity and radiation exposure we receive is from natural sources —sources we cannot avoid. Fully 10% of the exposure comes from our own bodies—largely from ^{14}C and ^{40}K.

Table 11.3.1: Average Annual Radiation Exposure (Approximate)

Source	Amount (mrem)
radon gas	200
medical sources	53
radioactive atoms in the body naturally	39
terrestrial sources	28
cosmic sources	28
consumer products	10
nuclear energy	0.05
Total	358

> *Flying from New York City to San Francisco adds 5 mrem to your overall radiation exposure because the plane flies above much of the atmosphere, which protects us from most cosmic radiation.*

The actual effects of radioactivity and radiation exposure on a person's health depend on the type of radioactivity, the length of exposure, and the tissues exposed. Table $11.3.2$ lists the potential threats to health at various amounts of exposure over short periods of time (hours or days).

Table 11.3.2: Effects of Short-Term Exposure to Radioactivity and Radiation

Exposure (rem)	Effect
1 (over a full year)	no detectable effect
∼20	increased risk of some cancers

Exposure (rem)	Effect
∼100	damage to bone marrow and other tissues; possible internal bleeding; decrease in white blood cell count
200–300	visible “burns” on skin, nausea, vomiting, and fatigue
>300	loss of white blood cells; hair loss
∼600	death

One of the simplest ways of detecting radioactivity is by using a piece of photographic film embedded in a badge or a pen. On a regular basis, the film is developed and checked for exposure. A comparison of the exposure level of the film with a set of standard exposures indicates the amount of radiation a person was exposed to.

Figure 11.3.1: Detecting Radioactivity. A Geiger counter is a common instrument used to detect radioactivity.

Another means of detecting radioactivity is an electrical device called a Geiger counter (Figure 11.3.1). It contains a gas-filled chamber with a thin membrane on one end that allows radiation emitted from radioactive nuclei to enter the chamber and knock electrons off atoms of gas (usually argon). The presence of electrons and positively charged ions causes a small current, which is detected by the Geiger counter and converted to a signal on a meter or, commonly, an audio circuit to produce an audible “click.”

Key Takeaway

- Radioactivity can be expressed in a variety of units, including rems, rads, and curies.

11.4: Uses of Radioactive Isotopes

Learning Objectives

- To learn some applications of radioactivity.

Radioactive isotopes have a variety of applications. Generally, however, they are useful either because we can detect their radioactivity or we can use the energy they release.

Radioactive isotopes are effective tracers because their radioactivity is easy to detect. A tracer is a substance that can be used to follow the pathway of that substance through some structure. For instance, leaks in underground water pipes can be discovered by running some tritium-containing water through the pipes and then using a Geiger counter to locate any radioactive tritium subsequently present in the ground around the pipes. (Recall that tritium, ^{3}H, is a radioactive isotope of hydrogen.)

Tracers can also be used to follow the steps of a complex chemical reaction. After incorporating radioactive atoms into reactant molecules, scientists can track where the atoms go by following their radioactivity. One excellent example of this is the use of radioactive carbon-14 to determine the steps involved in the photosynthesis in plants. We know these steps because researchers followed the progress of the radioactive carbon-14 throughout the process.

Radioactive isotopes are useful for establishing the ages of various objects. The half-life of radioactive isotopes is unaffected by any environmental factors, so the isotope acts like an internal clock. For example, if a rock is analyzed and is found to contain a certain amount of uranium-235 and a certain amount of its daughter isotope, we can conclude that a certain fraction of the original uranium-235 has radioactively decayed. If half of the uranium has decayed, then the rock has an age of one half-life of uranium-235, or about 4.5×10^{9} y. Many analyses like this, using a wide variety of isotopes, have indicated that the age of Earth itself is over 4×10^{9} y. In another interesting example of radioactive dating, ^{3}H dating has been used to verify the stated vintages of some old fine wines.

Carbon-14 (half-life is 5,370 y) is particularly useful in determining the age of once-living artifacts (e.g., animal or plant matter). A tiny amount of carbon-14 is produced naturally in the upper reaches of the atmosphere, and living things incorporate some of it into their tissues, building up to a constant, although very low, level. Once a living thing dies, however, it no longer acquires carbon-14, and as time passes, the carbon-14 that was in the tissues decays. If a once-living artifact is discovered and analyzed many years after its death, with the remaining carbon-14 compared to the known constant level, an approximate age of the artifact can be determined. Using such methods, scientists determined that the age of the Shroud of Turin (made of linen, which comes from the flax plant, and purported by some to be the burial cloth of Jesus Christ; Figure 11.4.1) is about 600–700 y, not 2,000 y as claimed by some. Scientists were also able to use radiocarbon dating to show that the age of a mummified body found in the ice of the Alps was 5,300 y.

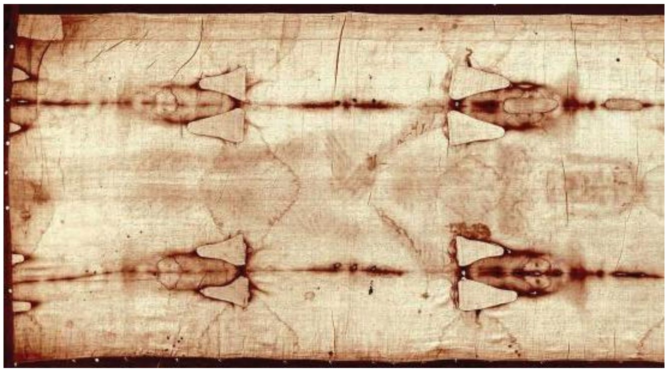


Figure 11.4.1: Shroud of Turin. In 1989, several groups of scientists used carbon-14 dating to demonstrate that the age of the Shroud of Turin was only 600–700 y. Many people still cling to a different notion, despite the scientific evidence.

The radiation emitted by some radioactive substances can be used to kill microorganisms on a variety of foodstuffs, which extends the shelf life of these products. Produce such as tomatoes, mushrooms, sprouts, and berries are irradiated with the emissions from coba . This exposure kills a lot of the bacteria that cause spoilage, so the produce stays fresh longer. Eggs and some meat, such as beef, pork, and poultry, can also be irradiated. Contrary to the belief of some people, irradiation of food *does not* make the food itself radioactive.

Radioactive isotopes have numerous medical applications—diagnosing and treating illnesses and diseases. One example of a diagnostic application is using radioactive iodine-131 to test for thyroid activity (Figure 11.4.2). The thyroid gland in the neck is one of the few places in the body with a significant concentration of iodine. To evaluate thyroid activity, a measured dose of iodine-131 is administered to a patient, and the next day a scanner is used to measure the amount of radioactivity in the thyroid gland. The amount of radioactive iodine that collects there is directly related to the activity of the thyroid, allowing trained physicians to diagnose both hyperthyroidism and hypothyroidism. Iodine-131 has a half-life of only 8 d, so the potential for damage due to exposure is minimal. Technetium-99 can also be used to test thyroid function. Bones, the heart, the brain, the liver, the lungs, and many other organs can be imaged in similar ways by using the appropriate radioactive isotope.

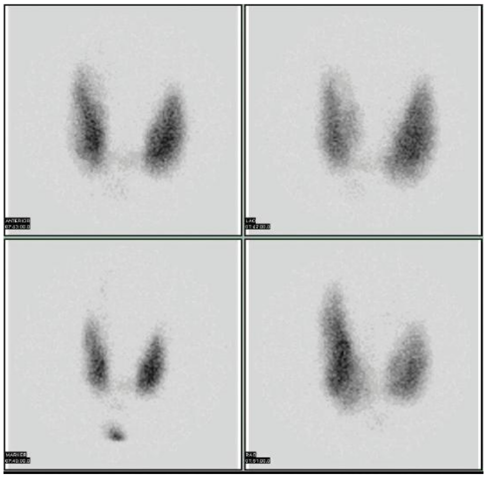


Figure 11.4.2: Medical Diagnostics. Radioactive iodine can be used to image the thyroid gland for diagnostic purposes. Source: Scan courtesy of Myo Han, Wikipedia, Thyroid Scan(opens in new window) [en.Wikipedia.org].

Very little radioactive material is needed in these diagnostic techniques because the radiation emitted is so easy to detect. However, therapeutic applications usually require much larger doses because their purpose is to preferentially kill diseased tissues. For example, if a thyroid tumor is detected, a much larger infusion (thousands of rem, as opposed to a diagnostic dose of less then 40 rem) of iodine-131 could help destroy the tumor cells. Similarly, radioactive strontium is used to not only detect but also ease the pain of bone cancers. Table 11.4.1 lists several radioactive isotopes and their medical uses.

Table 11.4.1: Some Radioactive Isotopes That Have Medical Applications

Isotope	Use
^{32}P	cancer detection and treatment, especially in eyes and skin
^{59}Fe	anemia diagnosis
^{60}Co	gamma ray irradiation of tumors
^{99m}Tc	brain, thyroid, liver, bone marrow, lung, heart, and intestinal scanning; blood volume determination
^{131}I	diagnosis and treatment of thyroid function
^{133}Xe	lung imaging
^{198}Au	liver disease diagnosis

In addition to the direct application of radioactive isotopes to diseased tissue, the gamma ray emissions of some isotopes can be directed toward the tissue to be destroyed. Cobalt-60 is a useful isotope for this kind of procedure.

To Your Health: Positron Emission Tomography Scans

One relatively rare form of radioactivity is called *positron emission*. It is similar to beta particle emission, except that instead of emitting an electron, a nucleus emits a positively charged electron, called a *positron*. A positron is actually a piece of antimatter; therefore, when a positron encounters an electron, both particles are converted into high-energy gamma radiation.

Isotopes that emit positrons can be employed in a medical imaging technique called *positron emission tomography* (*PET*). A patient receives a compound containing a positron-emitting isotope, either intravenously or by ingestion. The radioactive compound travels throughout the body, and the patient is then pushed slowly through a ring of sensors that detect the gamma radiation given off by the annihilation of positrons and electrons. A computer connected to the sensors constructs a three-dimensional image of the interior of part or all of the patient's body, allowing doctors to see organs or tumors or regulate the function of various organs (such as the brain or the heart) to diagnose the medical condition of the patient.

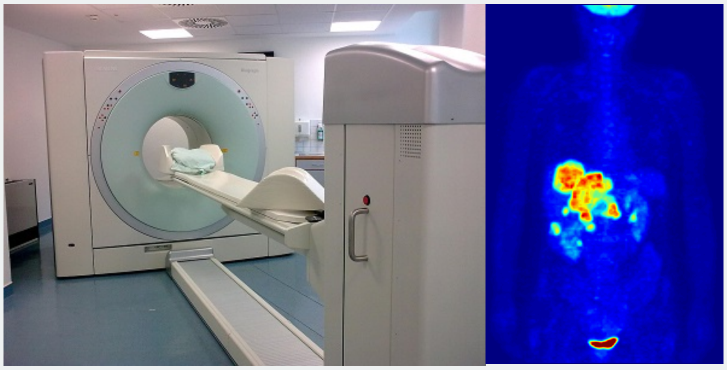


Figure 11.4.3: (left) Combined apparatus for positron emission tomography (PET) and X-ray computer tomography (CT), Siemens Biograph (right) Whole-body PET scan using 18F-FDG. Images used with permission from Wikipedia.

Two isotopes that undergo positron emission are carbon-11 and fluorine-18, with half-lives of 20.4 and 110 min, respectively. Both isotopes can be incorporated into sugar molecules and introduced into the body. Doctors can use the intensity of gamma ray emission to find tissues that metabolize the sugar faster than other tissues; fast-metabolizing tissue is one sign of a malignant (i.e., cancerous) tumor. Researchers use similar techniques to map areas of the brain that are most active during specific tasks, such as reading or speaking.

PET is one of many diagnostic and treatment methods that physicians use to improve the quality of our lives. It is one of the many positive uses of radioactivity in society.

Key Takeaway

- Radioactivity has several practical applications, including tracers, medical applications, dating once-living objects, and the preservation of food.

11.5: Nuclear Energy

Learning Objectives

- Explain where nuclear energy comes from.
- Describe the difference between fission and fusion.

Nuclear changes occur with a simultaneous release of energy. Where does this energy come from? If we could precisely measure the masses of the reactants and the products of a nuclear reaction, we would notice that the amount of mass drops slightly in the conversion from reactants to products. Consider the following nuclear reaction, in which the molar mass of each species is indicated to four decimal places:

$$\underbrace{{}^{235}\text{U}}_{235.0439} \rightarrow \underbrace{{}^{139}\text{Ba}}_{138.9088} + \underbrace{{}^{94}\text{Kr}}_{93.9343} + \underbrace{2\,{}^{1}\text{n}}_{2\times 1.0087}$$

If we compare the mass of the reactant (235.0439) to the masses of the products (sum = 234.8605), we notice a mass difference of −0.1834 g, or −0.0001834 kg. Where did this mass go?

According to Albert Einstein's theory of relativity, energy (*E*) and mass (*m*) are related by the following equation:

$$E = mc^2 \tag{11.5.1}$$

where *c* is the speed of light, or 3.00×10^8 m/s. In the course of the uranium nuclear chemical reaction, the mass difference is converted to energy, which is given off by the reaction:

$$\begin{aligned} E &= (-0.0001834\ kg)(3.00 \times 10^8\ m/s)^2 \\ &= -1.65 \times 10^{13}\ J \\ &= -1.65 \times 10^{10}\ kJ \end{aligned}$$

That is, 16.5 billion kJ of energy are given off every time 1 mol of uranium-235 undergoes this nuclear reaction. This is an extraordinary amount of energy. Compare it to combustion reactions of hydrocarbons, which give off about 650 kJ/mol of energy for every CH_2 unit in the hydrocarbon—on the order of *hundreds* of kilojoules per mole. Nuclear reactions give off *billions* of kilojoules per mole.

If this energy could be properly harvested, it would be a significant source of energy for our society. Nuclear energy involves the controlled harvesting of energy from fission reactions. The reaction can be controlled because the fission of uranium-235 (and a few other isotopes, such as plutonium-239) can be artificially initiated by injecting a neutron into a uranium nucleus. The overall nuclear equation, with energy included as a product, is then as follows:

$${}^{235}\text{U} + {}^{1}\text{n} \longrightarrow {}^{139}\text{Ba} + {}^{94}\text{Kr} + 3\,{}^{1}\text{n} + \text{energy}$$

Thus, by the careful addition of extra neutrons into a sample of uranium, we can control the fission process and obtain energy that can be used for other purposes.

The Curie Family

Artificial or induced radioactivity was first demonstrated in 1934 by Irène Joliot-Curie and Frédéric Joliot, the daughter and son-in-law of Marie Curie.

Example 11.5.1

Plutonium-239 can absorb a neutron and undergo a fission reaction to produce an atom of gold-204 and an atom of phosphorus-31. Write the balanced nuclear equation for the process and determine the number of neutrons given off as part of the reaction.

Solution

Using the data given, we can write the following initial equation:

$$^{1}_{0}\mathrm{n}+\,^{239}_{94}\mathrm{Pu}\rightarrow\,^{204}_{79}\mathrm{Au}+\,^{31}_{15}\mathrm{P}+?^{1}_{0}\mathrm{n}$$

In balanced nuclear equations, the sums of the subscripts on each sides of the equation are the same, as are the sums of the superscripts. The subscripts are already balanced: 0 + 94 = 94 and 79 + 15 = 94. The superscripts on the left equal 240 (1 + 239) but equal 235 (204 + 31) on the right. We need five more mass number units on the right. Five neutrons should be the products of the process for the mass numbers to balance. (Because the atomic number of a neutron is zero, including five neutrons on the right does not change the overall sum of the subscripts.) Thus, the balanced nuclear equation is as follows:

$$^{1}_{0}\mathrm{n}+\,^{239}_{94}\mathrm{Pu}\rightarrow\,^{204}_{79}\mathrm{Au}+\,^{31}_{15}\mathrm{P}+5^{1}_{0}\mathrm{n}$$

We predict that the overall process will give off five neutrons.

Exercise 11.5.1

Uranium-238 can absorb a neutron and undergo a fission reaction to produce an atom of cesium-135 and an atom of rubidium-96. Write the balanced nuclear equation for the process and determine the number of neutrons given off as part of the reaction.

Answer

$$^{1}_{0}\mathrm{n}+\,^{238}_{92}\mathrm{U}\rightarrow\,^{135}_{55}\mathrm{Cs}+\,^{96}_{37}\mathrm{Rb}+8^{1}_{0}\mathrm{n}$$

We predict that the overall process will give off eight neutrons.

A nuclear reactor is an apparatus designed to carefully control the progress of a nuclear reaction and extract the resulting energy for useful purposes. Figure 11.5.1 shows a simplified diagram of a nuclear reactor. The energy from the controlled nuclear reaction converts liquid water into high-pressure steam, which is used to run turbines that generate electricity.

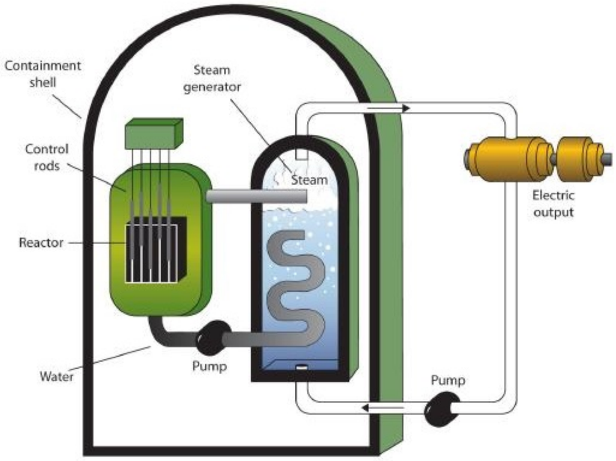


Figure 11.5.1: A Diagram of a Nuclear Power Plant for Generating Electricity. The two main components of the power plant are the nuclear reactor itself and the steam-driven turbine and electricity generator.

Notice that the fission of uranium produces two more free neutrons than were present to begin with. These neutrons can themselves stimulate other uranium nuclei to undergo fission, releasing yet more energy and even more neutrons, which can in turn induce even more uranium fission. A single neutron can thus begin a process that grows exponentially in a phenomenon called a chain reaction:

1 → 2 → 4 → 8 → 16 → 32 → 64 → 128 → 256 → 512 → 1,024 → 2,048 → 4,096 → 8,192 → 16,384 →…

Because energy is produced with each fission event, energy is also produced exponentially and in an uncontrolled fashion. The quick production of energy creates an explosion. This is the mechanism behind the atomic bomb.

> The first controlled chain reaction was achieved on December 2, 1942, in an experiment supervised by Enrico Fermi in a laboratory underneath the football stadium at the University of Chicago.

Although fairly simple in theory, an atomic bomb is difficult to produce, in part because uranium-235, the isotope that undergoes fission, makes up only 0.7% of natural uranium; the rest is mostly uranium-238, which does not undergo fission. (Remember that the radioactive process that a nucleus undergoes is characteristic of the isotope.) To make uranium useful for nuclear reactors, the uranium in uranium-235 must be *enriched* to about 3%. Enrichment of uranium is a laborious and costly series of physical and chemical separations. To be useful in an atomic bomb, the uranium in uranium-235 must be enriched to 70% or more. At lesser concentrations, the chain reaction cannot sustain itself, so no explosion is produced.

Fusion is another nuclear process that can be used to produce energy. In this process, smaller nuclei are combined to make larger nuclei, with an accompanying release of energy. One example is the hydrogen fusion, which makes helium. While the steps of the process are complicated, the net reaction is:

$$4\,{}^{1}\mathrm{H} \rightarrow {}^{4}\mathrm{He} + 2.58 \times 10^{12}\ J$$

Notice that the amount of energy given off per mole of reactant is only a fraction of the amount given off by the fission of 1 mol of uranium-235. On a mass (per gram) basis, however, the hydrogen fusion emits many times more energy than fission does. In addition, the product of fission is helium gas, not a wide range of isotopes (some of which are also radioactive) produced by fission.

The practical problem is that to perform fusion, extremely high pressures and temperatures are necessary. Currently, the only known stable systems undergoing fusion are the interiors of stars. The conditions necessary for fusion can be created using an atomic bomb, but the resulting fusion is uncontrollable (and the basis for another type of bomb, a hydrogen bomb). Currently, researchers are looking for safe, controlled ways of producing useful energy using fusion.

Career Focus: Nuclear Medicine Technologist

Generally speaking, a radiological technician deals with X ray equipment and procedures. A *nuclear medicine technologist* has similar responsibilities, using compounds containing radioactive isotopes to help diagnose and treat disease.

Nuclear medicine technologists administer the substances containing the radioactive isotope and subsequently operate the apparatus that detects the radiation produced by radioactive decay. The apparatus may be as simple as a piece of photographic film or as complex as a series of computer-controlled electronic detectors. The images obtained by the technologist are interpreted by a specially trained physician.

One of the chief responsibilities of a nuclear medicine technologist is safety. Improper exposure to radioactivity can be harmful to both patient and technologist alike. Therefore, the technologist must adhere to strict safety standards to keep unnecessary exposure as low as possible. The technologist must also know how to dispose of waste materials safely and appropriately.

Key Takeaways

- Nuclear energy comes from tiny mass changes in nuclei as radioactive processes occur.
- In fission, large nuclei break apart and release energy; in fusion, small nuclei merge together and release energy.

11.E: Nuclear Chemistry (Exercises)

11.1 Radioactivity

Concept Review Exercise

1. What are the major types of radioactivity? Write chemical equations demonstrating each type.

Answer

1. The major types of radioactivity are alpha decay, beta decay, and gamma ray emission; alpha decay with gamma emission: $^{222}_{86}\mathrm{Rn} \rightarrow {}^{218}_{84}\mathrm{Po} + {}^{4}_{2}\mathrm{He} + \gamma$; beta decay: $^{14}_{6}\mathrm{C} \rightarrow {}^{14}_{7}\mathrm{N} + {}^{0}_{-1}\mathrm{e}$ (answers will vary)

Exercises

1. Define *radioactivity*.
2. Give an example of a radioactive isotope.
3. How many protons and neutrons are in each isotope?
    a. $^{11}_{5}\mathrm{B}$
    b. $^{27}_{13}\mathrm{Al}$
    c. $^{56}\mathrm{Fe}$
    d. $^{224}\mathrm{Rn}$
4. How many protons and neutrons are in each isotope?
    a. $^{2}_{1}\mathrm{H}$
    b. $^{112}_{48}\mathrm{Cd}$
    c. $^{252}\mathrm{Es}$
    d. $^{40}\mathrm{K}$
5. Describe an alpha particle. What nucleus is it equivalent to?
6. Describe a beta particle. What subatomic particle is it equivalent to?
7. Explain what gamma rays are.
8. Explain why it is inappropriate to refer to gamma rays as gamma “particles.”
9. Plutonium has an atomic number of 94. Write the chemical equation for the alpha particle emission of $^{244}\mathrm{Pu}$. What is the daughter isotope?
10. Francium has an atomic number of 87. Write the chemical equation for the alpha particle emission of $^{212}\mathrm{Fr}$. What is the daughter isotope?
11. Tin has an atomic number of 50. Write the chemical equation for the beta particle emission of $^{121}\mathrm{Sn}$. What is the daughter isotope?
12. Technetium has an atomic number of 43. Write the chemical equation for the beta particle emission of $^{99}\mathrm{Tc}$. What is the daughter isotope?
13. Energies of gamma rays are typically expressed in units of megaelectron volts (MeV), where 1 MeV = 1.602×10^{-13} J. Using data provided in the text, calculate the energy, in megaelectron volts, of the gamma ray emitted when radon-222 decays.
14. The gamma ray emitted when oxygen-19 gives off a beta particle is 0.197 MeV. What is its energy in joules? (See Exercise 13 for the definition of a megaelectron volt.)
15. Which penetrates matter more deeply—alpha particles or beta particles? Suggest ways to protect yourself against both particles.
16. Which penetrates matter more deeply—alpha particles or gamma rays? Suggest ways to protect yourself against both emissions.
17. Define *nuclear fission*.
18. What general characteristic is typically necessary for a nucleus to undergo spontaneous fission?

Answers

1. Radioactivity is the spontaneous emission of particles and radiation from atomic nuclei.
2. C-14 or ^{14}C is an example of radioactive isotope (answers may vary).
3.
   a. 5 protons; 6 neutrons
   b. 13 protons; 14 neutrons
   c. 26 protons; 30 neutrons
   d. 86 protons; 138 neutrons
4.
   a. 1 proton; 1 neutron
   b. 48 protons; 64 neutrons
   c. 99 protons;153 neutrons
   d. 19 protons; 21 neutrons
5. An alpha particle is a combination of two protons and two neutrons and is equivalent to a helium nucleus.
6. A beta particle is an electron.
7. Gamma rays are high-energy electromagnetic radiation given off in radioactive decay.
8. Gamma rays have no mass. Hence not a particle.
9. $^{244}_{94}\text{Pu} \rightarrow {}^{4}_{2}\text{He} + {}^{240}_{92}\text{U}$; the daughter isotope is $^{240}_{92}\text{U}$, an atom of uranium.
10. $^{212}_{87}\text{Fr} \rightarrow {}^{4}_{2}\text{He} + {}^{208}_{85}\text{At}$; the daughter isotope is $^{208}_{85}\text{At}$, an atom of astatine.
11. $^{121}_{50}\text{Sn} \rightarrow {}^{0}_{-1}\text{e} + {}^{121}_{51}\text{Sb}$; the daughter isotope is $^{121}_{51}\text{Sb}$, an atom of antimony.
12. $^{99}_{43}\text{Tc} \rightarrow {}^{0}_{-1}\text{e} + {}^{99}_{44}\text{Mo}$; the daughter isotope is $^{99}_{44}\text{Mo}$, an atom of antimony.
13. 0.512 MeV
14. 3.16 x 10^{-14} J
15. Beta particles; shielding of the appropriate thickness can protect against both alpha and beta particles.
16. Gamma rays; can be shielded by thick, dense material such as lead (Pb). Alpha particles has low energy; can shielded by a piece of paper.
17. Nuclear fission is when large nuclei break down into smaller nuclei.
18. A nucleus must be very large. Examples are Th-232 and U-235.

11.2 Half-Life

Concept Review Exercises

1. Define *half-life*.
2. Describe a way to determine the amount of radioactive isotope remaining after a given number of half-lives.

Answers

1. Half-life is the amount of time needed for half of a radioactive material to decay.
2. take half of the initial amount for each half-life of time elapsed

Exercises

1. Do all isotopes have a half-life? Explain.

2. Which is more radioactive—an isotope with a long half-life or an isotope with a short half-life?

3. What percent of a sample remains after one half-life? Three half-lives?

4. The half-life of polonium-218 is 3.0 min. How much of a 0.540 mg sample would remain after 9.0 minutes have passed?

5. The half-life of protactinium-234 is 6.69 hours. If a 0.812 mg sample of Pa-239 decays for 40.14 hours, what mass of the isotope remains?

6. How long does it take for 1.00 g of ^{103}Pd to decay to 0.125 g if its half-life is 17.0 d?

7. How long does it take for 2.00 g of ^{94}Nb to decay to 0.0625 g if its half-life is 20,000 y?

8. It took 75 y for 10.0 g of a radioactive isotope to decay to 1.25 g. What is the half-life of this isotope?

9. It took 49.2 s for 3.000 g of a radioactive isotope to decay to 0.1875 g. What is the half-life of this isotope?

Answers

1. Only radioactive isotopes have half-lives.

2. An isotope with a shorter half-life decay more rapidly is more radioactive.

3. 1 half-life: 50%; 3 half-lives: 12.5%

4. 9.0 min = 3 half-lives (make 3 arrows): 0.540 mg --> 0.270 mg --> 0.135 mg --> 0.0675 mg

5. 0.0127 mg

6. 51.0 d

7. 100 000 y

8. 25 y

9. 12.3 s

11.3 Units of Radioactivity

Concept Review Exercise

1. What units are used to quantify radioactivity?

Answer

1. the curie, the becquerel, the rad, the gray, the sievert, and the rem

Exercises

1. Define *rad*.
2. Define *rem*.
3. How does a becquerel differ from a curie?
4. How is the curie defined?
5. A sample of radon gas has an activity of 140.0 mCi. If the half-life of radon is 1,500 y, how long before the activity of the sample is 8.75 mCi?
6. A sample of curium has an activity of 1,600 Bq. If the half-life of curium is 24.0 s, how long before its activity is 25.0 Bq?
7. If a radioactive sample has an activity of 65 µCi, how many disintegrations per second are occurring?

8. If a radioactive sample has an activity of 7.55 × 10^5 Bq, how many disintegrations per second are occurring?
9. Describe how a radiation exposure in rems is determined.
10. Which contributes more to the rems of exposure—alpha or beta particles? Why?
11. Use Table 11.3.2 to determine which sources of radiation exposure are inescapable and which can be avoided. What percentage of radiation is unavoidable?
12. What percentage of the approximate annual radiation exposure comes from radioactive atoms that are in the body naturally?
13. Explain how a film badge works to detect radiation.
14. Explain how a Geiger counter works to detect radiation.

Answers

1. Known as the radiation absorbed dose, a rad is the absorption of 0.01 J/g of tissue.

2. Known as roentgen equivalent man, a rem is an absorption of one rad times a factor. The factor is variable depending on the type of emission and the type of irradiated tissue.

3. A becquerel is smaller and equals 1 decay per second. A curie is 3.7 × 10^{10} Bq.

4. A curie is defined as 3.7 × 10^{10} decays per second.

5. 6000 y

6. 144 s

7. 2.41 × 10^6 disintegrations per second

8. 7.55 × 10^5 disintegrations per second

9. The radiation exposure is determined by the number of rads times the quality factor of the radiation.

10. Alpha contributes more than beta because of its bigger size and electrical charge.

11. At least 16% (terrestrial and cosmic sources) of radioactivity is unavoidable; the rest depends on what else a person is exposed to.

12. About 11% come from radioactive atoms that are in the body naturally.

13. A film badge uses film, which is exposed as it is subjected to radiation.

14. The Geiger counter consists of a tube with electrodes and is filled with an inert (argon) gas. Radiation entering the tube ionizes the gas, and the ions are attracted to the electrodes and produce an electric pulse (clicking sound).

11.4 Uses of Radioactive Isotopes

Concept Review Exercise

1. Describe some of the different ways that amounts of radioactivity are applied in society.

Answer

1. Radioactive isotopes are used in dating, as tracers, and in medicine as diagnostic and treatment tools.

Exercises

1. Define *tracer* is and give an example of how tracers work.
2. Name two isotopes that have been used as tracers.
3. Explain how radioactive dating works.
4. Name an isotope that has been used in radioactive dating.
5. The current disintegration rate for carbon-14 is 14.0 Bq. A sample of burnt wood discovered in an archaeological excavation is found to have a carbon-14 decay rate of 3.5 Bq. If the half-life of carbon-14 is 5,700 y, approximately how old is the wood sample?
6. A small asteroid crashes to Earth. After chemical analysis, it is found to contain 1 g of technetium-99 to every 3 g of ruthenium-99, its daughter isotope. If the half-life of technetium-99 is 210,000 y, approximately how old is the asteroid?
7. What do you think are some of the positive aspects of irradiation of food?
8. What do you think are some of the negative aspects of irradiation of food?
9. Describe how iodine-131 is used to both diagnose and treat thyroid problems.
10. List at least five organs that can be imaged using radioactive isotopes.
11. Which radioactive emissions can be used therapeutically?
12. Which isotope is used in therapeutics primarily for its gamma ray emissions?
13. What volume of a radioisotope should be given if a patient needs 125 mCi of a solution which contains 45 mCi in 5.0 mL?

14. Sodium-24 is used to treat leukemia. A 36-kg patient is prescribed 145 μCi/kg and it is supplied to the hospital in a vial containing 250 μCi/mL. What volume should be given to the patient?

15. Lead-212 is one of the radioisotopes used in the treatment of breast cancer. A patient needs a 15 μCi dose and it is supplied as a solution with a concentration of 2.5 μCi/mL. What volume does the patient need? Given the half-life of lead is 10.6 hours, what will be the radioactivity of the sample after approximately four days?

Answers

1. A tracer follows the path of a chemical or a physical process. One of the uses of a tracer is following the path of water underground (answers will vary).

2. Tritium (^3H) and Carbon-14 (^{14}C) (answers will vary)

3. Radioactive dating works by comparing the amounts of parent and daughter isotopes and calculating back to how long ago all of the material was just the parent isotope.

4. Carbon-14 (^{14}C) and Uranium-235 (^{235}U) (answers will vary)

5. about 11,400 y

6. about 420,000 y

7. increased shelf life (answers will vary)

8. reduction in the food's vitamin content and cost

9. Iodine-131 is preferentially absorbed by the thyroid gland and can be used to measure the gland’s activity or destroy bad cells in the gland.

10. brain, bone, heart, thyroid, lung (answers will vary)

11. gamma rays, beta particles, or alpha particles

12. cobalt-60

13. 125mCi x (5.0mL/45mCi)=14mL

14. 36kg x (145μCi/kg) x (1mL/250μCi)=21mL

15. Volume given: 15μCi x (1mL/2.5μCi) = 6.0mL

Elapsed time in hours: 4 days x (24 hr/day) = 96 hr

Number of half-lives: 96 hrs/10.6 hours = 9

Radioactivity remaining after 9 half-lives: 0.029 μCi

11.5 Nuclear Energy

Concept Review Exercises

1. How is nuclear energy produced?
2. What is the difference between fission and fusion?

Answers

1. Nuclear energy is produced by carefully controlling the speed of a fission reaction.
2. In fission, large nuclei break down into small ones; in fusion, small nuclei combine to make larger ones. In both cases, a lot of energy is emitted.

Exercises

1. In the spontaneous fission of uranium-233, the following reaction occurs:

   $^{233}U + {}^{1}n \rightarrow {}^{142}Ce + {}^{82}Se + 10{}^{1}n$

   For every mole of ^{233}U that decays, 0.1355 g of mass is lost. How much energy is given off per mole of ^{233}U reacted?
2. In the spontaneous fission of plutonium-241, the following reaction occurs:

   $^{241}Pu + {}^{1}n \rightarrow {}^{104}Ru + {}^{124}Sn + 14{}^{1}n$

   For every mole of ^{241}Pu that decays, 0.1326 g of mass is lost. How much energy is given off per mole of ^{241}Pu reacted?
3. The two rarer isotopes of hydrogen—deuterium and tritium—can also be fused to make helium by the following reaction:

   $^{2}H + {}^{3}H \rightarrow {}^{4}He + {}^{1}n$

   In the course of this reaction, 0.01888 g of mass is lost. How much energy is emitted in the reaction of 1 mol of deuterium and tritium?
4. A process called *helium burning* is thought to occur inside older stars, forming carbon:

   $3{}^{4}He \rightarrow {}^{12}C$

   If the reaction proceeds with 0.00781 g of mass lost on a molar basis, how much energy is given off?
5. Briefly describe how a nuclear reactor generates electricity.
6. Briefly describe the difference between how a nuclear reactor works and how a nuclear bomb works.

7. What is a chain reaction?
8. Why must uranium be enriched to supply nuclear energy?

Answers

1. 1.22×10^{13} J
2. 1.19×10^{13} J
3. 1.70×10^{12} J
4. 7.03×10^{11} J
5. A nuclear reactor generates heat, which is used to generate steam that turns a turbine to generate electricity.
6. Both nuclear reactor and nuclear bomb are powered by fission reaction however, in a nuclear reactor, the fission is monitored and controlled to occur continuously for a much longer time. In a nuclear bomb, the reaction is uncontrolled to explode in one event.
7. A chain reaction is an ever-expanding series of processes that, if left unchecked, can cause a runaway reaction and possibly an explosion.
8. Natural uranium ores contain only 0.7% U-235. Most nuclear reactors require enriched U-235 for their fuel.

11.6: Chapter Summary

Additional Exercises

1. Given that many elements are metals, suggest why it would be unsafe to have radioactive materials in contact with acids.
2. Many alpha-emitting radioactive substances are relatively safe to handle, but inhaling radioactive dust can be very dangerous. Why?
3. Uranium can be separated from its daughter isotope thorium by dissolving a sample in acid and adding sodium iodide, which precipitates thorium(III) iodide:

   $Th^{3+}(aq) + 3I^{-}(aq) \rightarrow ThI_3(s)$

   If 0.567 g of Th^{3+} were dissolved in solution, how many milliliters of 0.500 M NaI(aq) would have to be added to precipitate all the thorium?
4. Thorium oxide can be dissolved in an acidic solution:

   $ThO_2(s) + 4H^{+} \rightarrow Th^{4+}(aq) + 2H_2O(\ell)$

   How many milliliters of 1.55 M HCl(aq) are needed to dissolve 10.65 g of ThO_2?
5. Radioactive strontium is dangerous because it can chemically replace calcium in the human body. The bones are particularly susceptible to radiation damage. Write the nuclear equation for the beta emission of strontium-90.
6. Write the nuclear equation for the beta emission of iodine-131, the isotope used to diagnose and treat thyroid problems.
7. A common uranium compound is uranyl nitrate hexahydrate $[UO_2(NO_3)_2\_6H_2O]$. What is the formula mass of this compound?
8. Plutonium forms three oxides: PuO, PuO_2, and Pu_2O_3. What are the formula masses of these three compounds?
9. A banana contains 600 mg of potassium, 0.0117% of which is radioactive potassium-40. If 1 g of potassium-40 has an activity of 2.626×10^5 Bq, what is the activity of a banana?

10. Smoke detectors typically contain about 0.25 mg of americium-241 as part of the smoke detection mechanism. If the activity of 1 g of americium-241 is 1.26×10^{11} Bq, what is the activity of americium-241 in the smoke detector?
11. Uranium hexafluoride (UF_6) reacts with water to make uranyl fluoride (UO_2F_2) and hydrogen fluoride (HF). Balance the following chemical equation:

    $UF_6 + H_2O \rightarrow UO_2F_2 + HF$
12. The cyclopentadienyl anion ($C_5H_5^-$) is an organic ion that can make ionic compounds with positive ions of radioactive elements, such as Np^{3+}. Balance the following chemical equation:

    $NpCl_3 + Be(C_5H_5)_2 \rightarrow Np(C_5H_5)_3 + BeCl_2$

Answers

1. Acids can dissolve metals, making aqueous solutions.

2. Alpha rays are dangerous only when the alpha emitter is in direct contact with tissue cells inside the body.

3. 14.7 mL

4. 104 mL

5. $^{90}_{38}\text{Sr} \rightarrow\ ^{0}_{-1}\text{e} +\ ^{90}_{39}\text{Y}$

6. $^{131}_{53}\text{I} \rightarrow\ ^{0}_{-1}\text{e} +\ ^{131}_{54}\text{Xe}$

7. 502 g/mol

8. PuO = 260.06 g/mol; PuO_2 = 276.06 g/mol; Pu_2O_3 = 536.12 g/mol

9. about 18 Bq

10. 3.15×10^7 Bq

11. $UF_6 + 2H_2O \rightarrow UO_2F_2 + 4HF$

12. $2NpCl_3 + 3Be(C_5H_5)_2 \rightarrow 2Np(C_5H_5)_3 + 3BeCl_2$

11.S: Nuclear Chemistry (Summary)

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

Some atoms have unstable nuclei that emit particles and high-energy electromagnetic radiation to form new elements that are more stable. This emission of particles and electromagnetic radiation is called **radioactivity**. There are three main types of spontaneous radioactive emission: **alpha particles**, which are equivalent to helium nuclei; **beta particles**, which are electrons; and **gamma radiation**, which is high-energy electromagnetic radiation. Another type of radioactive process is **spontaneous fission**, in which large nuclei spontaneously break apart into smaller nuclei and, often, neutrons. In all forms of radioactivity, new elements are formed from the radioactive reactants.

Radioactive isotopes decay at different rates. The rate of an isotope's decay is expressed as a **half-life**, which is the amount of time required for half of the original material to decay. The length of its half-life is a characteristic of the particular isotope and can range from less than microseconds to billions of years.

Amounts of radioactivity are measured in several different ways. A **becquerel** is equal to one radioactive decay per second. A **curie** represents 3.7×10^{10} decays per second. Other units describe the amount of energy absorbed by body tissues. One **rad** is equivalent to 0.01 joule of energy absorbed per gram of tissue. Different tissues react differently to different types of radioactivity. The **rem** unit takes into account not only the energy absorbed by the tissues, but also includes a numerical multiplication factor to account for the type of radioactivity and the type of tissue. The average annual radiation exposure of a person is less than 360 millirem, over 80% of which is from natural sources. Radioactivity can be detected using photographic film or other devices such as **Geiger counters**.

Radioactive isotopes have many useful applications. They can be used as **tracers** to follow the journey of a substance through a system, like an underground waterway or a metabolic pathway. Radioactive isotopes can be used to date objects, since the amount of parent and daughter isotopes can sometimes be measured very accurately. Radioactive emission can be used to sterilize food for a longer edible lifetime. There are also a number of diagnostic and therapeutic medical applications for radioactive isotopes.

Radioactive processes occur with simultaneous changes in energy. This **nuclear energy** can be used to generate power for human use. **Nuclear reactors** use the energy released by fission of large isotopes to generate electricity. When carefully controlled, fission can produce a **chain reaction** that facilitates the continuous production of energy. If not carefully controlled, a very quick production of energy can result, as in an **atomic bomb**. Natural uranium does not contain enough of the proper isotope of uranium to work in a nuclear reactor, so it must first be **enriched** in uranium-235. Forcing small nuclei together to make larger nuclei, a process called **fusion**, also gives off energy; however, scientists have yet to achieve a controlled fusion process.

CHAPTER OVERVIEW

12: Organic Chemistry - Alkanes and Halogenated Hydrocarbons

We begin our study of organic chemistry with the alkanes, compounds containing only two elements, carbon and hydrogen, and having only single bonds. There are several other kinds of hydrocarbons, distinguished by the types of bonding between carbon atoms and by the properties that result from that bonding. We will first examine hydrocarbons with double bonds, with triple bonds, and with a special kind of bonding called aromaticity. Then we will study some compounds considered to be derived from hydrocarbons by replacing one or more hydrogen atoms with an oxygen-containing group. Finally, we focuse on organic acids and bases, after which we will be ready to look at the chemistry of life itself—biochemistry—in the remaining five chapters.

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12.0: Prelude to Organic Chemistry - Alkanes and Halogenated Hydrocarbons

Hydrocarbons are the simplest organic compounds, but they have interesting physiological effects. These effects depend on the size of the hydrocarbon molecules and where on or in the body they are applied. Alkanes of low molar mass—those with from 1 to approximately 10 or so carbon atoms—are gases or light liquids that act as anesthetics. Inhaling ("sniffing") these hydrocarbons in gasoline or aerosol propellants for their intoxicating effect is a major health problem that can lead to liver, kidney, or brain damage or to immediate death by asphyxiation by excluding oxygen.

Swallowed, liquid alkanes do little harm while in the stomach. In the lungs, however, they cause "chemical" pneumonia by dissolving fatlike molecules from cell membranes in the tiny air sacs (alveoli). The lungs become unable to expel fluids, just as in pneumonia caused by bacteria or viruses. People who swallow gasoline or other liquid alkane mixtures should not be made to vomit, as this would increase the chance of getting alkanes into the lungs. (There is no home-treatment antidote for gasoline poisoning; call a poison control center.)

Figure 12.0.1: Butane is a hydrocarbon with the formula C_4H_{10} and is a gas at room temperature and atmospheric pressure. Under excess pressures, it can be liquidized like the fuel shown in this butane lighters. (CC BY 3.0Unported; Frank Vincentz)

Liquid alkanes with approximately 5–16 carbon atoms per molecule wash away natural skin oils and cause drying and chapping of the skin, while heavier liquid alkanes (those with approximately 17 or more carbon atoms per molecule) act as emollients (skin softeners). Such alkane mixtures as mineral oil and petroleum jelly can be applied as a protective film. Water and aqueous solutions such as urine will not dissolve such a film, which explains why petroleum jelly protects a baby's tender skin from diaper rash.

12.1: Organic Chemistry

Learning Objectives

- To recognize the composition and properties typical of organic and inorganic compounds.

Scientists of the 18th and early 19th centuries studied compounds obtained from plants and animals and labeled them *organic* because they were isolated from “organized” (living) systems. Compounds isolated from nonliving systems, such as rocks and ores, the atmosphere, and the oceans, were labeled *inorganic*. For many years, scientists thought organic compounds could be made by only living organisms because they possessed a vital force found only in living systems. The vital force theory began to decline in 1828, when the German chemist Friedrich Wöhler synthesized urea from inorganic starting materials. He reacted silver cyanate ($AgOCN$) and ammonium chloride (NH_4Cl), expecting to get ammonium cyanate (NH_4OCN). What he expected is described by the following equation.

$$AgOCN + NH_4Cl \rightarrow AgCl + NH_4OCN \tag{12.1.1}$$

Instead, he found the product to be urea (NH_2CONH_2), a well-known organic material readily isolated from urine. This result led to a series of experiments in which a wide variety of organic compounds were made from inorganic starting materials. The vital force theory gradually went away as chemists learned that they could make many organic compounds in the laboratory.

Today organic chemistry is the study of the chemistry of the carbon compounds, and inorganic chemistry is the study of the chemistry of all other elements. It may seem strange that we divide chemistry into two branches—one that considers compounds of only one element and one that covers the 100-plus remaining elements. However, this division seems more reasonable when we consider that of tens of millions of compounds that have been characterized, the overwhelming majority are carbon compounds.

> The word *organic* has different meanings. Organic fertilizer, such as cow manure, is organic in the original sense; it is derived from living organisms. Organic foods generally are foods grown without synthetic pesticides or fertilizers. Organic chemistry is the chemistry of compounds of carbon.

Carbon is unique among the other elements in that its atoms can form stable covalent bonds with each other and with atoms of other elements in a multitude of variations. The resulting molecules can contain from one to millions of carbon atoms. We previously surveyed organic chemistry by dividing its compounds into families based on functional groups. We begin with the simplest members of a family and then move on to molecules that are organic in the original sense—that is, they are made by and found in living organisms. These complex molecules (all containing carbon) determine the forms and functions of living systems and are the subject of biochemistry.

Organic compounds, like inorganic compounds, obey all the natural laws. Often there is no clear distinction in the chemical or physical properties among organic and inorganic molecules. Nevertheless, it is useful to compare typical members of each class, as in Table 12.1.1.

Table 12.1.1: General Contrasting Properties and Examples of Organic and Inorganic Compounds

Organic	Hexane		Inorganic	NaCl
low melting points	−95°C		high melting points	801°C
low boiling points	69°C		high boiling points	1,413°C
low solubility in water; high solubility in nonpolar solvents	insoluble in water; soluble in gasoline		greater solubility in water; low solubility in nonpolar solvents	soluble in water; insoluble in gasoline
flammable	highly flammable		nonflammable	nonflammable
aqueous solutions do not conduct electricity	nonconductive		aqueous solutions conduct electricity	conductive in aqueous solution
exhibit covalent bonding	covalent bonds		exhibit ionic bonding	ionic bonds

Keep in mind, however, that there are exceptions to every category in this table. To further illustrate typical differences among organic and inorganic compounds, Table $12.1.1$ also lists properties of the inorganic compound sodium chloride (common table salt, NaCl) and the organic compound hexane (C_6H_{14}), a solvent that is used to extract soybean oil from soybeans (among other uses). Many compounds can be classified as organic or inorganic by the presence or absence of certain typical properties, as illustrated in Table $12.1.1$.

12.2: Structures and Names of Alkanes

Learning Objectives

- To identify and name simple (straight-chain) alkanes given formulas and write formulas for straight-chain alkanes given their names.

We begin our study of organic chemistry with the hydrocarbons, the simplest organic compounds, which are composed of carbon and hydrogen atoms only. As we noted, there are several different kinds of hydrocarbons. They are distinguished by the types of bonding between carbon atoms and the properties that result from that bonding. Hydrocarbons with only carbon-to-carbon single bonds (C–C) and existing as a continuous chain of carbon atoms also bonded to hydrogen atoms are called alkanes (or saturated hydrocarbons). *Saturated*, in this case, means that each carbon atom is bonded to four other atoms (hydrogen or carbon)—the most possible; there are no double or triple bonds in the molecules.

> The word *saturated* has the same meaning for hydrocarbons as it does for the dietary fats and oils: the molecule has no carbon-to-carbon double bonds (C=C).

We previously introduced the three simplest alkanes—methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) and they are shown again in Figure 12.2.1.

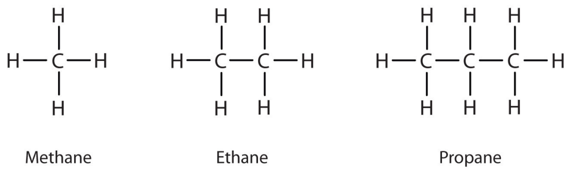


Figure 12.2.1: The Three Simplest Alkanes

The flat representations shown do not accurately portray bond angles or molecular geometry. Methane has a tetrahedral shape that chemists often portray with wedges indicating bonds coming out toward you and dashed lines indicating bonds that go back away from you. An ordinary solid line indicates a bond in the plane of the page. Recall that the VSEPR theory correctly predicts a tetrahedral shape for the methane molecule (Figure 12.2.2).

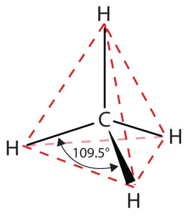


Figure 12.2.2: The Tetrahedral Methane Molecule

Methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) are the beginning of a series of compounds in which any two members in a sequence differ by one carbon atom and two hydrogen atoms—namely, a CH_2 unit. The first 10 members of this series are given in Table 12.2.1.

Table 12.2.1: The First 10 Straight-Chain Alkanes

Name	Molecular Formula (C_nH_{2n+2})	Condensed Structural Formula	Number of Possible Isomers
methane	CH_4	CH_4	—
ethane	C_2H_6	CH_3CH_3	—
propane	C_3H_8	$CH_3CH_2CH_3$	—
butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$	2
pentane	C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	3

Name	Molecular Formula (C_nH_{2n+2})	Condensed Structural Formula	Number of Possible Isomers
hexane	C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$	5
heptane	C_7H_{16}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	9
octane	C_8H_{18}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	18
nonane	C_9H_{20}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	35
decane	$C_{10}H_{22}$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	75

Consider the series in Figure 12.2.3. The sequence starts with C_3H_8, and a CH_2 unit is added in each step moving up the series. Any family of compounds in which adjacent members differ from each other by a definite factor (here a CH_2 group) is called a homologous series. The members of such a series, called *homologs*, have properties that vary in a regular and predictable manner. The principle of *homology* gives organization to organic chemistry in much the same way that the periodic table gives organization to inorganic chemistry. Instead of a bewildering array of individual carbon compounds, we can study a few members of a homologous series and from them deduce some of the properties of other compounds in the series.

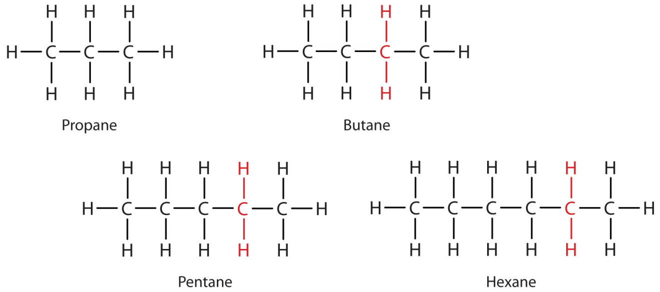


Figure 12.2.3: Members of a Homologous Series. Each succeeding formula incorporates one carbon atom and two hydrogen atoms more than the previous formula.

The principle of homology allows us to write a general formula for alkanes: C_nH_{2n+2}. Using this formula, we can write a molecular formula for any alkane with a given number of carbon atoms. For example, an alkane with eight carbon atoms has the molecular formula $C_8H_{(2 \times 8)+2} = C_8H_{18}$.

Key Takeaway

- Simple alkanes exist as a homologous series, in which adjacent members differ by a CH_2 unit.

12.3: Branched-Chain Alkanes

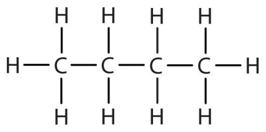
Learning Objectives

- To learn how alkane molecules can have branched chains and recognize compounds that are isomers.

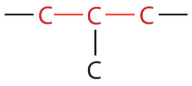
We can write the structure of butane (C_4H_{10}) by stringing four carbon atoms in a row,

–C–C–C–C–

and then adding enough hydrogen atoms to give each carbon atom four bonds:



The compound butane has this structure, but there is another way to put 4 carbon atoms and 10 hydrogen atoms together. Place 3 of the carbon atoms in a row and then branch the fourth one off the middle carbon atom:



Now we add enough hydrogen atoms to give each carbon four bonds.

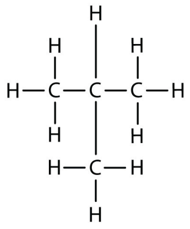


Figure 12.3.1).

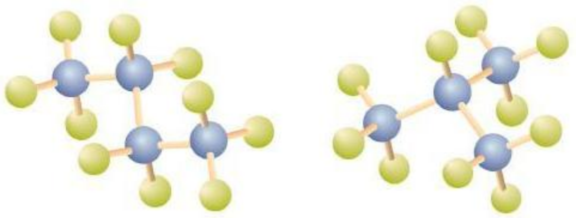
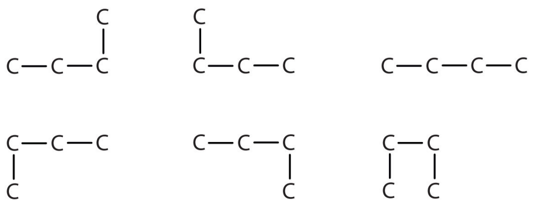


Figure 12.3.1: Butane and Isobutane. The ball-and-stick models of these two compounds show them to be isomers; both have the molecular formula C_4H_{10}.

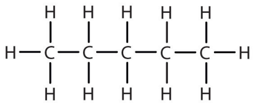
Notice that C_4H_{10} is depicted with a bent chain in Figure 12.3.1. The four-carbon chain may be bent in various ways because the groups can rotate freely about the C–C bonds. However, this rotation does not change the identity of the compound. It is important to realize that bending a chain does *not* change the identity of the compound; all of the following represent the same compound, butane:



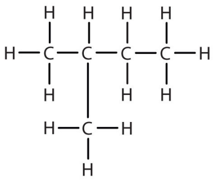
The structure of isobutane shows a continuous chain of three carbon atoms only, with the fourth attached as a branch off the middle carbon atom of the continuous chain, which is different from the structures of butane (compare the two structures in Figure 12.3.1

Unlike C_4H_{10}, the compounds methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) do not exist in isomeric forms because there is only one way to arrange the atoms in each formula so that each carbon atom has four bonds.

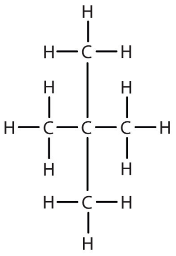
Next beyond C_4H_{10} in the homologous series is pentane. Each compound has the same molecular formula: C_5H_{12}. (Table 12.1.1 from the previous section has a column identifying the number of possible isomers for the first 10 straight-chain alkanes.) The compound at the far left is pentane because it has all five carbon atoms in a continuous chain. The compound in the middle is isopentane; like isobutane, it has a one CH_3 branch off the second carbon atom of the continuous chain. The compound at the far right, discovered after the other two, was named neopentane (from the Greek *neos*, meaning “new”). Although all three have the same molecular formula, they have different properties, including boiling points: pentane, 36.1°C; isopentane, 27.7°C; and neopentane, 9.5°C.



Pentane



Isopentane



Neopentane

> A continuous (unbranched) chain of carbon atoms is often called a *straight chain* even though the tetrahedral arrangement about each carbon gives it a zigzag shape. Straight-chain alkanes are sometimes called *normal alkanes*, and their names are given the prefix *n*-. For example, butane is called *n*-butane. We will not use that prefix here because it is not a part of the system established by the International Union of Pure and Applied Chemistry.

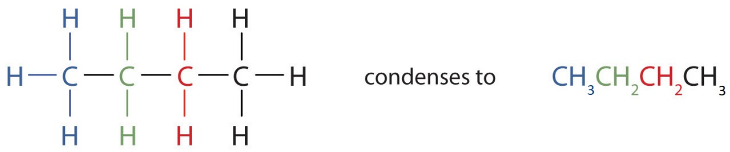
12.4: Condensed Structural and Line-Angle Formulas

Learning Objectives

- Write condensed structural formulas for alkanes given complete structural formulas.
- Draw line-angle formulas given structural formulas.

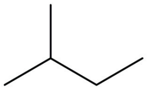
We use several kinds of formulas to describe organic compounds. A *molecular formula* shows only the kinds and numbers of atoms in a molecule. For example, the molecular formula C_4H_{10} tells us there are 4 carbon atoms and 10 hydrogen atoms in a molecule, but it doesn't distinguish between butane and isobutane. A structural formula shows all the carbon and hydrogen atoms and the bonds attaching them. Thus, structural formulas identify the specific isomers by showing the order of attachment of the various atoms.

Unfortunately, structural formulas are difficult to type/write and take up a lot of space. Chemists often use condensed structural formulas to alleviate these problems. The condensed formulas show hydrogen atoms right next to the carbon atoms to which they are attached, as illustrated for butane:



The ultimate condensed formula is a line-angle formula, in which carbon atoms are implied at the corners and ends of lines, and each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds. For example, we can represent pentane ($CH_3CH_2CH_2CH_2CH_3$) and isopentane [$(CH_3)_2CHCH_2CH_3$] as follows:

Pentane



Isopentane

> Parentheses in condensed structural formulas indicate that the enclosed grouping of atoms is attached to the adjacent carbon atom.

Key Takeaways

- Condensed chemical formulas show the hydrogen atoms (or other atoms or groups) right next to the carbon atoms to which they are attached.
- Line-angle formulas imply a carbon atom at the corners and ends of lines. Each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds.

12.5: IUPAC Nomenclature

Learning Objectives

- To name alkanes by the IUPAC system and write formulas for alkanes given IUPAC names

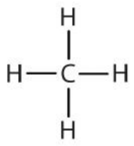
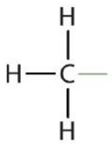
As noted in previously, the number of isomers increases rapidly as the number of carbon atoms increases. There are 3 pentanes, 5 hexanes, 9 heptanes, and 18 octanes. It would be difficult to assign unique individual names that we could remember. A systematic way of naming hydrocarbons and other organic compounds has been devised by the International Union of Pure and Applied Chemistry (IUPAC). These rules, used worldwide, are known as the IUPAC System of Nomenclature. (Some of the names we used earlier, such as isobutane, isopentane, and neopentane, do not follow these rules and are called *common names*.) A stem name (Table 12.5.1) indicates the number of carbon atoms in the longest continuous chain (LCC). Atoms or groups attached to this carbon chain, called *substituents*, are then named, with their positions indicated by numbers. For now, we will consider only those substituents called alkyl groups.

Table 12.5.1: Stems That Indicate the Number of Carbon Atoms in Organic Molecules

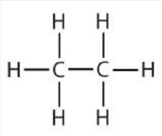
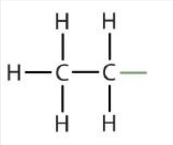
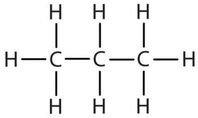
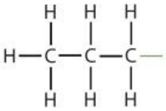
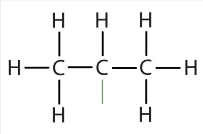
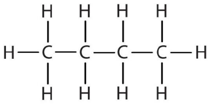
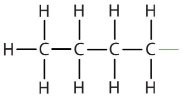
Stem	Number
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7
oct-	8
non-	9
dec-	10

An alkyl group is a group of atoms that results when one hydrogen atom is removed from an alkane. The group is named by replacing the *-ane* suffix of the parent hydrocarbon with *-yl*. For example, the -CH_3 group derived from methane (CH_4) results from subtracting one hydrogen atom and is called a *methyl group*. The alkyl groups we will use most frequently are listed in Table 12.5.2. Alkyl groups are not independent molecules; they are parts of molecules that we consider as a unit to name compounds systematically.

Table 12.5.2: Common Alkyl Groups

Parent Alkane		Alkyl Group		Condensed Structural Formula
methane		methyl		CH_3–

*There are four butyl groups, two derived from butane and two from isobutane. We will introduce the other three where appropriate.

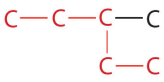
Parent Alkane		Alkyl Group		Condensed Structural Formula
ethane		ethyl		$CH_3CH_2–$
propane		propyl		$CH_3CH_2CH_2–$
		isopropyl		$(CH_3)_2CH–$
butane		butyl*		$CH_3CH_2CH_2CH_2–$

*There are four butyl groups, two derived from butane and two from isobutane. We will introduce the other three where appropriate.

Simplified IUPAC rules for naming alkanes are as follows (demonstrated in Example 12.5.1).

1. **Name alkanes according to the LCC (longest continuous chain) of carbon atoms in the molecule (rather than the total number of carbon atoms).** This LCC, considered the parent chain, determines the base name, to which we add the suffix *-ane* to indicate that the molecule is an alkane.

2. **If the hydrocarbon is branched, number the carbon atoms of the LCC.** Numbers are assigned in the direction that gives the lowest numbers to the carbon atoms with attached substituents. Hyphens are used to separate numbers from the names of substituents; commas separate numbers from each other. (The LCC need not be written in a straight line; for example, the LCC in the following has five carbon atoms.)

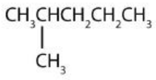


3. **Place the names of the substituent groups in alphabetical order before the name of the parent compound.** If the same alkyl group appears more than once, the numbers of all the carbon atoms to which it is attached are expressed. If the same group appears more than once on the same carbon atom, the number of that carbon atom is repeated as many times as the group appears. Moreover, the number of identical groups is indicated by the Greek prefixes *di-*, *tri-*, *tetra-*, and so on. These prefixes are *not* considered in determining the alphabetical order of the substituents. For example, ethyl is listed before dimethyl; the di- is simply ignored. The last alkyl group named is prefixed to the name of the parent alkane to form one word.

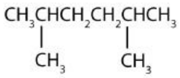
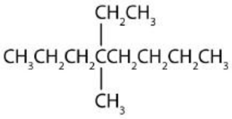
When these rules are followed, every unique compound receives its own exclusive name. The rules enable us to not only name a compound from a given structure but also draw a structure from a given name. The best way to learn how to use the IUPAC system is to put it to work, not just memorize the rules. It's easier than it looks.

Example 12.5.1

Name each compound.

1. 

$CH_3CHCH_2CH_2CH_3$ with CH_3 on C2

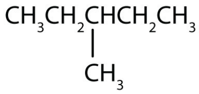
- 
  $CH_3\underset{CH_3}{CH}CH_2CH_2\underset{CH_3}{CH}CH_3$
- 
  $CH_3CH_2CH_2\overset{CH_2CH_3}{\underset{CH_3}{C}}CH_2CH_2CH_2CH_3$

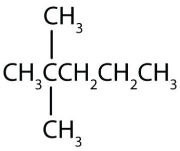
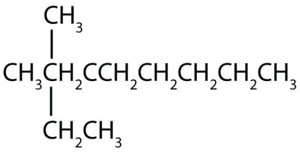
Solution

1. The LCC has five carbon atoms, and so the parent compound is pentane (rule 1). There is a methyl group (rule 2) attached to the second carbon atom of the pentane chain. The name is therefore 2-methylpentane.
2. The LCC has six carbon atoms, so the parent compound is hexane (rule 1). Methyl groups (rule 2) are attached to the second and fifth carbon atoms. The name is 2,5-dimethylhexane.
3. The LCC has eight carbon atoms, so the parent compound is octane (rule 1). There are methyl and ethyl groups (rule 2), both attached to the fourth carbon atom (counting from the *right* gives this carbon atom a lower number; rule 3). The correct name is thus 4-ethyl-4-methyloctane.

? Exercise 12.5.1

Name each compound.

1. 
   $CH_3CH_2\underset{CH_3}{CH}CH_2CH_3$

- 
  $CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2CH_2CH_3$
- 
  $CH_3CH_2\overset{CH_3}{\underset{CH_2CH_3}{C}}CH_2CH_2CH_2CH_3$

✓ Example 12.5.2

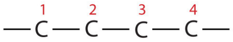
Draw the structure for each compound.

a. 2,3-dimethylbutane
b. 4-ethyl-2-methylheptane

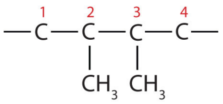
Solution

In drawing structures, always start with the parent chain.

a. The parent chain is butane, indicating four carbon atoms in the LCC.

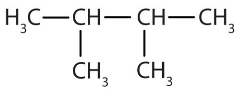


Then add the groups at their proper positions. You can number the parent chain from either direction as long as you are consistent; just don’t change directions before the structure is done. The name indicates two methyl (CH_3) groups, one on the second carbon atom and one on the third.



$-C-C(CH_3)-C(CH_3)-C-$

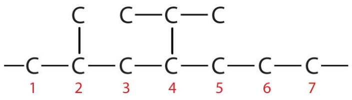
Finally, fill in all the hydrogen atoms, keeping in mind that each carbon atom must have four bonds.



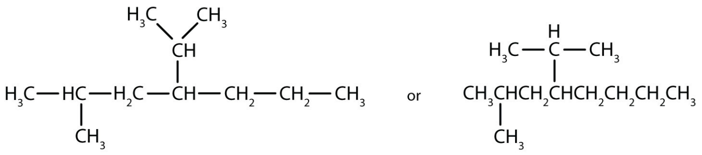
$H_3C-CH(CH_3)-CH(CH_3)-CH_3$

- The parent chain is heptane in this case, indicating seven carbon atoms in the LCC. –C–C–C–C–C–C–C–

  Adding the groups at their proper positions gives



  Filling in all the hydrogen atoms gives the following condensed structural formulas:



  Note that the bonds (dashes) can be shown or not; sometimes they are needed for spacing.

Exercise 12.5.2

Draw the structure for each compound.

a. 4-ethyloctane
b. 3-ethyl-2-methylpentane
c. 3,3,5-trimethylheptane

Key Takeaway

- Alkanes have both common names and systematic names, specified by IUPAC.

12.6: Physical Properties of Alkanes

Learning Objectives

- To identify the physical properties of alkanes and describe trends in these properties.

Because alkanes have relatively predictable physical properties and undergo relatively few chemical reactions other than combustion, they serve as a basis of comparison for the properties of many other organic compound families. Let's consider their physical properties first.

Table $12.6.1$ describes some of the properties of some of the first 10 straight-chain alkanes. Because alkane molecules are nonpolar, they are insoluble in water, which is a polar solvent, but are soluble in nonpolar and slightly polar solvents. Consequently, alkanes themselves are commonly used as solvents for organic substances of low polarity, such as fats, oils, and waxes. Nearly all alkanes have densities less than 1.0 g/mL and are therefore less dense than water (the density of H_2O is 1.00 g/mL at 20°C). These properties explain why oil and grease do not mix with water but rather float on its surface.

Table $12.6.1$: Physical Properties of Some Alkanes

Molecular Name	Formula	Melting Point (°C)	Boiling Point (°C)	Density (20°C)*	Physical State (at 20°C)
methane	CH_4	–182	–164	0.668 g/L	gas
ethane	C_2H_6	–183	–89	1.265 g/L	gas
propane	C_3H_8	–190	–42	1.867 g/L	gas
butane	C_4H_{10}	–138	–1	2.493 g/L	gas
pentane	C_5H_{12}	–130	36	0.626 g/mL	liquid
hexane	C_6H_{14}	–95	69	0.659 g/mL	liquid
octane	C_8H_{18}	–57	125	0.703 g/mL	liquid
decane	$C_{10}H_{22}$	–30	174	0.730 g/mL	liquid

*Note the change in units going from gases (grams per liter) to liquids (grams per milliliter). Gas densities are at 1 atm pressure.

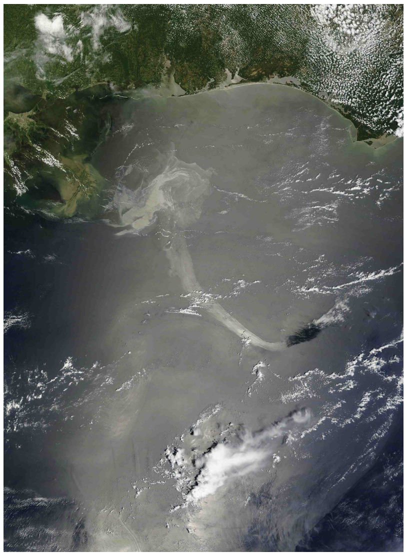


Figure $12.6.1$: Oil Spills. Crude oil coats the water's surface in the Gulf of Mexico after the *Deepwater Horizon* oil rig sank following an explosion. The leak was a mile below the surface, making it difficult to estimate the size of the spill. One liter of oil can create a slick 2.5 hectares (6.3 acres) in size. This and similar spills provide a reminder that hydrocarbons and water don't mix. Source: Photo courtesy of NASA Goddard / MODIS Rapid Response Team, NASA.gov, Topics, Earth Features, Oil Spill(opens in new window) [www.nasa.gov].

Looking Closer: Gas Densities and Fire Hazards

Table 12.6.1 indicates that the first four members of the alkane series are gases at ordinary temperatures. Natural gas is composed chiefly of methane, which has a density of about 0.67 g/L. The density of air is about 1.29 g/L. Because natural gas is less dense than air, it rises. When a natural-gas leak is detected and shut off in a room, the gas can be removed by opening an upper window. On the other hand, bottled gas can be either propane (density 1.88 g/L) or butanes (a mixture of butane and isobutane; density about 2.5 g/L). Both are much heavier than air (density 1.2 g/L). If bottled gas escapes into a building, it collects near the floor. This presents a much more serious fire hazard than a natural-gas leak because it is more difficult to rid the room of the heavier gas.

Also shown in Table 12.6.1 are the boiling points of the straight-chain alkanes increase with increasing molar mass. This general rule holds true for the straight-chain homologs of all organic compound families. Larger molecules have greater surface areas and consequently interact more strongly; more energy is therefore required to separate them. For a given molar mass, the boiling points of alkanes are relatively low because these nonpolar molecules have only weak dispersion forces to hold them together in the liquid state.

Looking Closer: An Alkane Basis for Properties of Other Compounds

An understanding of the physical properties of the alkanes is important in that petroleum and natural gas and the many products derived from them—gasoline, bottled gas, solvents, plastics, and more—are composed primarily of alkanes. This understanding is also vital because it is the basis for describing the properties of other organic and biological compound families. For example, large portions of the structures of lipids consist of nonpolar alkyl groups. Lipids include the dietary fats and fatlike compounds called phospholipids and sphingolipids that serve as structural components of living tissues. These compounds have both polar and nonpolar groups, enabling them to bridge the gap between water-soluble and water-insoluble phases. This characteristic is essential for the selective permeability of cell membranes.

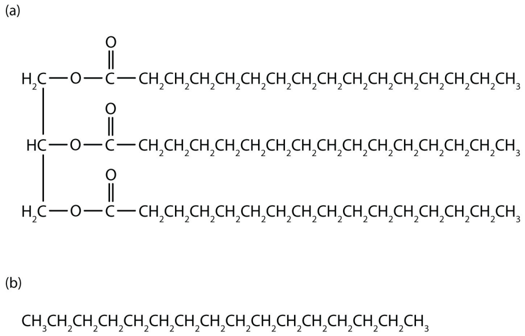


Figure 12.6.2: Tripalmitin (a), a typical fat molecule, has long hydrocarbon chains typical of most lipids. Compare these chains to hexadecane (b), an alkane with 16 carbon atoms.

Key Takeaway

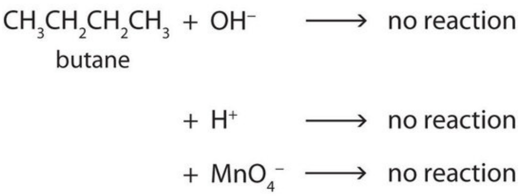
- Alkanes are nonpolar compounds that are low boiling and insoluble in water.

12.7: Chemical Properties of Alkanes

Learning Objectives

- To identify the main chemical properties of alkanes.

Alkane molecules are nonpolar and therefore generally do not react with ionic compounds such as most laboratory acids, bases, oxidizing agents, or reducing agents. Consider butane as an example:



Butane plus O H superscript negative sign yields no reaction. There is also no reaction of butane with H superscript positive sign and Mn O subscript 4 superscript negative sign.

Neither positive ions nor negative ions are attracted to a nonpolar molecule. In fact, the alkanes undergo so few reactions that they are sometimes called *paraffins*, from the Latin *parum affinis*, meaning “little affinity.”

Two important reactions that the alkanes do undergo are combustion and halogenation. Nothing happens when alkanes are merely mixed with oxygen (O_2) at room temperature, but when a flame or spark provides the activation energy, a highly exothermic combustion reaction proceeds vigorously. For methane (CH_4), the reaction is as follows:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + \text{heat} \tag{12.7.1}$$

If the reactants are adequately mixed and there is sufficient oxygen, the only products are carbon dioxide (CO_2), water (H_2O), and heat—heat for cooking foods, heating homes, and drying clothes. Because conditions are rarely ideal, however, other products are frequently formed. When the oxygen supply is limited, carbon monoxide (CO) is a by-product:

$$2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O \tag{12.7.2}$$

This reaction is responsible for dozens of deaths each year from unventilated or improperly adjusted gas heaters. (Similar reactions with similar results occur with kerosene heaters.)

Alkanes also react with the halogens chlorine (Cl_2) and bromine (Br_2) in the presence of ultraviolet light or at high temperatures to yield chlorinated and brominated alkanes. For example, chlorine reacts with excess methane (CH_4) to give methyl chloride (CH_3Cl).

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl \tag{12.7.3}$$

With more chlorine, a mixture of products is obtained: CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4. Fluorine (F_2), the lightest halogen, combines explosively with most hydrocarbons. Iodine (I_2) is relatively unreactive. Fluorinated and iodinated alkanes are produced by indirect methods.

Key Takeaway

- Alkanes react with oxygen (combustion) and with halogens (halogenation).

12.8: Halogenated Hydrocarbons

Learning Objectives

- To name halogenated hydrocarbons given formulas and write formulas for these compounds given names.

Many organic compounds are closely related to the alkanes. As we noted previously, alkanes react with halogens to produce halogenated hydrocarbons, the simplest of which have a single halogen atom substituted for a hydrogen atom of the alkane. Even more closely related are the cycloalkanes, compounds in which the carbon atoms are joined in a ring, or cyclic fashion.

The reactions of alkanes with halogens produce halogenated hydrocarbons, compounds in which one or more hydrogen atoms of a hydrocarbon have been replaced by halogen atoms:

CH_3CH_2Cl $CH_3CHBrCH_2Br$ CH_3CHICH_2Cl

The replacement of only one hydrogen atom gives an alkyl halide (or haloalkane). The *common names* of alkyl halides consist of two parts: the name of the alkyl group plus the stem of the name of the halogen, with the ending *-ide*. The IUPAC system uses the name of the parent alkane with a prefix indicating the halogen substituents, preceded by number indicating the substituent's location. The prefixes are *fluoro*-, *chloro*-, *bromo*-, and *iodo*-. Thus CH_3CH_2Cl has the common name ethyl chloride and the IUPAC name chloroethane. Alkyl halides with simple alkyl groups (one to four carbon atoms) are often called by common names. Those with a larger number of carbon atoms are usually given IUPAC names.

Example 12.8.1

Give the common and IUPAC names for each compound.

a. $CH_3CH_2CH_2Br$
b. $(CH_3)_2CHCl$

Solution

a. The alkyl group ($CH_3CH_2CH_2$–) is a propyl group, and the halogen is bromine (Br). The common name is therefore propyl bromide. For the IUPAC name, the prefix for bromine (bromo) is combined with the name for a three-carbon chain (propane), preceded by a number identifying the carbon atom to which the Br atom is attached, so the IUPAC name is 1-bromopropane.
b. The alkyl group [$(CH_3)_2CH$–] has three carbon atoms, with a chlorine (Cl) atom attached to the middle carbon atom. The alkyl group is therefore isopropyl, and the common name of the compound is isopropyl chloride. For the IUPAC name, the Cl atom (prefix *chloro*-) attached to the middle (second) carbon atom of a propane chain results in 2-chloropropane.

Exercise 12.8.1

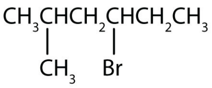
Give common and IUPAC names for each compound.

a. CH_3CH_2I
b. $CH_3CH_2CH_2CH_2F$

Example 12.8.2

Give the IUPAC name for each compound.

1. 
$CH_3\underset{\underset{Br}{|}}{CH}CH_2CH_2CH_3$

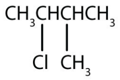
- 
$CH_3\underset{\underset{CH_3}{|}}{CH}CH_2\underset{\underset{Br}{|}}{CH}CH_2CH_3$

Solution

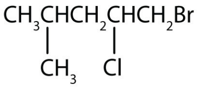
1. The parent alkane has five carbon atoms in the longest continuous chain; it is pentane. A bromo (Br) group is attached to the second carbon atom of the chain. The IUPAC name is 2-bromopentane.
2. The parent alkane is hexane. Methyl ($CH_{3)}$ and bromo (Br) groups are attached to the second and fourth carbon atoms, respectively. Listing the substituents in alphabetical order gives the name 4-bromo-2-methylhexane.

? Exercise 12.8.2

Give the IUPAC name for each compound.

a. 

$CH_3\underset{Cl}{CH}\underset{CH_3}{CH}CH_3$

- 

$CH_3\underset{CH_3}{CH}CH_2\underset{Cl}{CH}CH_2Br$

A wide variety of interesting and often useful compounds have one or more halogen atoms per molecule. For example, methane (CH_4) can react with chlorine (Cl_2), replacing one, two, three, or all four hydrogen atoms with Cl atoms. Several halogenated products derived from methane and ethane (CH_3CH_3) are listed in Table 12.8.1, along with some of their uses.

Table 12.8.1: Some Halogenated Hydrocarbons

Formula	Common Name	IUPAC Name	Some Important Uses
Derived from CH_4			
CH_3Cl	methyl chloride	chloromethane	refrigerant; the manufacture of silicones, methyl cellulose, and synthetic rubber
CH_2Cl_2	methylene chloride	dichloromethane	laboratory and industrial solvent
$CHCl_3$	chloroform	trichloromethane	industrial solvent
CCl_4	carbon tetrachloride	tetrachloromethane	dry-cleaning solvent and fire extinguishers (but no longer recommended for use)
$CBrF_3$	halon-1301	bromotrifluoromethane	fire extinguisher systems
CCl_3F	chlorofluorocarbon-11 (CFC-11)	trichlorofluoromethane	foaming plastics
CCl_2F_2	chlorofluorocarbon-12 (CFC-12)	dichlorodifluoromethane	refrigerant
Derived from CH_3CH_3			
CH_3CH_2Cl	ethyl chloride	chloroethane	local anesthetic
$ClCH_2CH_2Cl$	ethylene dichloride	1,2-dichloroethane	solvent for rubber
CCl_3CH_3	methylchloroform	1,1,1-trichloroethane	solvent for cleaning computer chips and molds for shaping plastics

To Your Health: Halogenated Hydrocarbons

Once widely used in consumer products, many chlorinated hydrocarbons are suspected carcinogens (cancer-causing substances) and also are known to cause severe liver damage. An example is carbon tetrachloride (CCl_4), once used as a dry-cleaning solvent and in fire extinguishers but no longer recommended for either use. Even in small amounts, its vapor can cause serious illness if exposure is prolonged. Moreover, it reacts with water at high temperatures to form deadly phosgene ($COCl_2$) gas, which makes the use of CCl_4 in fire extinguishers particularly dangerous.

Ethyl chloride, in contrast, is used as an external local anesthetic. When sprayed on the skin, it evaporates quickly, cooling the area enough to make it insensitive to pain. It can also be used as an emergency general anesthetic.

Bromine-containing compounds are widely used in fire extinguishers and as fire retardants on clothing and other materials. Because they too are toxic and have adverse effects on the environment, scientists are engaged in designing safer substitutes for them, as for many other halogenated compounds.

To Your Health: Chlorofluorocarbons and the Ozone Layer

Alkanes substituted with both fluorine (F) and chlorine (Cl) atoms have been used as the dispersing gases in aerosol cans, as foaming agents for plastics, and as refrigerants. Two of the best known of these chlorofluorocarbons (CFCs) are listed in Table $12.8.1$.

Chlorofluorocarbons contribute to the greenhouse effect in the lower atmosphere. They also diffuse into the stratosphere, where they are broken down by ultraviolet (UV) radiation to release Cl atoms. These in turn break down the ozone (O_3) molecules that protect Earth from harmful UV radiation. Worldwide action has reduced the use of CFCs and related compounds. The CFCs and other Cl- or bromine (Br)-containing ozone-destroying compounds are being replaced with more benign substances. Hydrofluorocarbons (HFCs), such as CH_2FCF_3, which have no Cl or Br to form radicals, are one alternative. Another is hydrochlorofluorocarbons (HCFCs), such as $CHCl_2CF_3$. HCFC molecules break down more readily in the troposphere, and fewer ozone-destroying molecules reach the stratosphere.

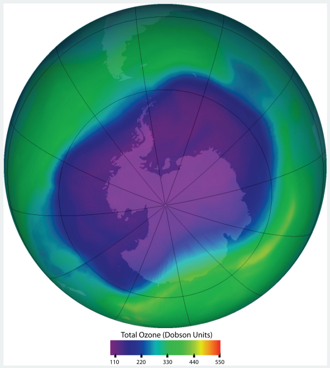


Figure 12.8.1: Ozone in the upper atmosphere shields Earth's surface from UV radiation from the sun, which can cause skin cancer in humans and is also harmful to other animals and to some plants. Ozone "holes" in the upper atmosphere (the gray, pink, and purple areas at the center) are large areas of substantial ozone depletion. They occur mainly over Antarctica from late August through early October and fill in about mid-November. Ozone depletion has also been noted over the Arctic regions. The largest ozone hole ever observed occurred on 24 September 2006. Source: Image courtesy of NASA, Ozone watch (opens in new window) [ozonewatch.gsfc.nasa.gov].

Key Takeaway

- The replacement of an hydrogen atom on an alkane by a halogen atom—F, Cl, Br, or I—forms a halogenated compound.

12.9: Cycloalkanes

Learning Objectives

- To name cycloalkanes given their formulas and write formulas for these compounds given their names.

The hydrocarbons we have encountered so far have been composed of molecules with open-ended chains of carbon atoms. When a chain contains three or more carbon atoms, the atoms can join to form *ring* or *cyclic* structures. The simplest of these cyclic hydrocarbons has the formula C_3H_6. Each carbon atom has two hydrogen atoms attached (Figure 12.9.1) and is called cyclopropane.

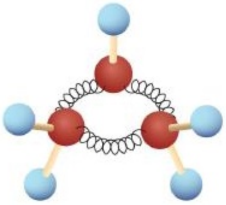
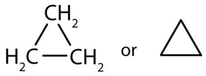


Figure 12.9.1: Ball-and-Spring Model of Cyclopropane. The springs are bent to join the carbon atoms.

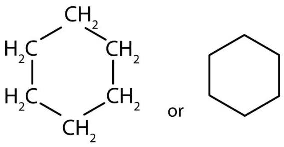
To Your Health: Cyclopropane as an Anesthetic

With its boiling point of −33°C, cyclopropane is a gas at room temperature. It is also a potent, quick-acting anesthetic with few undesirable side effects in the body. It is no longer used in surgery, however, because it forms explosive mixtures with air at nearly all concentrations.

The cycloalkanes—cyclic hydrocarbons with only single bonds—are named by adding the prefix *cyclo-* to the name of the open-chain compound having the same number of carbon atoms as there are in the ring. Thus the name for the cyclic compound C_4H_8 is cyclobutane. The carbon atoms in cyclic compounds can be represented by *line-angle formulas* that result in regular geometric figures. Keep in mind, however, that each corner of the geometric figure represents a carbon atom plus as many hydrogen atoms as needed to give each carbon atom four bonds.



cyclopropane



cyclohexane

Some cyclic compounds have substituent groups attached. Example 12.9.1 interprets the name of a cycloalkane with a single substituent group.

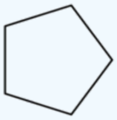
Example 12.9.1

Draw the structure for each compound.

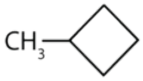
a. cyclopentane
b. methylcyclobutane

Solution

a. The name *cyclopentane* indicates a cyclic (cyclo) alkane with five (pent-) carbon atoms. It can be represented as a pentagon.



- The name *methylcyclobutane* indicates a cyclic alkane with four (but-) carbon atoms in the cyclic part. It can be represented as a square with a CH_3 group attached.



? Exercise 12.9.1

Draw the structure for each compound.

a. cycloheptane
b. ethylcyclohexane

The properties of cyclic hydrocarbons are generally quite similar to those of the corresponding open-chain compounds. So cycloalkanes (with the exception of cyclopropane, which has a highly strained ring) act very much like noncyclic alkanes. Cyclic structures containing five or six carbon atoms, such as cyclopentane and cyclohexane, are particularly stable. We will see later that some carbohydrates (sugars) form five- or six-membered rings in solution.

> The cyclopropane ring is strained because the C–C–C angles are 60°, and the preferred (tetrahedral) bond angle is 109.5°. (This strain is readily evident when you try to build a ball-and-stick model of cyclopropane; see Figure 12.9.1) Cyclopentane and cyclohexane rings have little strain because the C–C–C angles are near the preferred angles.

Key Takeaway

- Many organic compounds have cyclic structures.

12.E: Organic Chemistry- Alkanes and Halogenated Hydrocarbons (Exercises)

12.1: Organic Chemistry

Concept Review Exercises

1. Classify each compound as organic or inorganic.
   a. C_3H_8O
   b. $CaCl_2$
   c. $Cr(NH_3)_3Cl_3$
   d. $C_{30}H_{48}O_3N$
2. Which compound is likely organic and which is likely inorganic?
   a. a flammable compound that boils at 80°C and is insoluble in water
   b. a compound that does not burn, melts at 630°C, and is soluble in water

Answers

1.
   a. organic
   b. inorganic
   c. inorganic
   d. organic
2.
   a. organic
   b. inorganic

1. Classify each compound as organic or inorganic.
   a. C_6H_{10}
   b. $CoCl_2$
   c. $C_{12}H_{22}O_{11}$
2. Classify each compound as organic or inorganic.
   a. CH_3NH_2
   b. $NaNH_2$
   c. $Cu(NH_3)_6Cl_2$
3. Which member of each pair has a higher melting point?
   a. CH_3OH and NaOH
   b. CH_3Cl and KCl
4. Which member of each pair has a higher melting point?
   a. C_2H_6 and $CoCl_2$
   b. CH_4 and LiH

Answers

1.
   a. organic
   b. inorganic
   c. organic

3.

a. NaOH
b. KCl

12.2: Structures and Names of Alkanes

Concept Review Exercises

1. In the homologous series of alkanes, what is the molecular formula for the member just above C_8H_{18}?
2. Use the general formula for alkanes to write the molecular formula of the alkane with 12 carbon atoms.

Answers

1. C_9H_{20}
2. $C_{12}H_{26}$

Exercises

1. What compounds contain fewer carbon atoms than C_3H_8 and are its homologs?
2. What compounds contain five to eight carbon atoms and are homologs of C_4H_{10}?

Answer

1. CH_4 and C_2H_6

12.3: Branched-Chain Alkanes

Concept Review Exercises

1. In alkanes, can there be a two-carbon branch off the second carbon atom of a four-carbon chain? Explain.
2. A student is asked to write structural formulas for two different hydrocarbons having the molecular formula C_5H_{12}. She writes one formula with all five carbon atoms in a horizontal line and the other with four carbon atoms in a line, with a CH_3 group extending down from the first attached to the third carbon atom. Do these structural formulas represent different molecular formulas? Explain why or why not.

Answers

1. No; the branch would make the longest continuous chain of five carbon atoms.
2. No; both are five-carbon continuous chains.

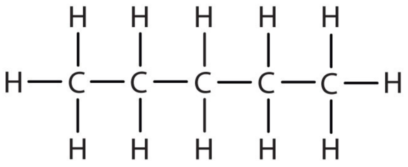
Key Takeaway

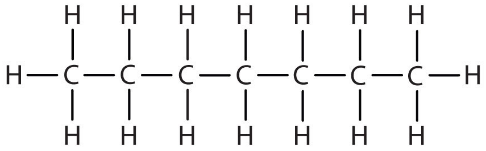
- Alkanes with four or more carbon atoms can exist in isomeric forms.

Exercises

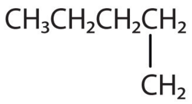
1. Briefly identify the important distinctions between a straight-chain alkane and a branched-chain alkane.
2. How are butane and isobutane related? How do they differ?
3. Name each compound.

a.



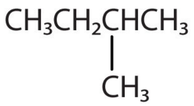
b. 

4. Write the structural formula for each compound.
   - a. hexane
   - b. octane
5. Indicate whether the structures in each set represent the same compound or isomers.
   - a. $CH_3CH_2CH_2CH_3$ and



$$\begin{array}{l} CH_3CH_2CH_2CH_2 \\ \qquad\qquad\quad | \\ \qquad\qquad\quad CH_2 \end{array}$$

   - b. $CH_3CH_2CH_2CH_2CH_3$ and



$$\begin{array}{l} CH_3CH_2CHCH_3 \\ \qquad\quad\; | \\ \qquad\quad\; CH_3 \end{array}$$

Answers

1. Straight-chain alkanes and branched-chain alkanes have different properties as well as different structures.

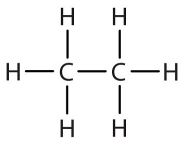
3.
   - a. pentane
   - b. heptane

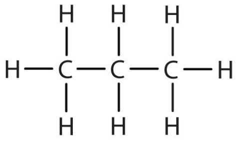
5.
   - a. no
   - b. yes

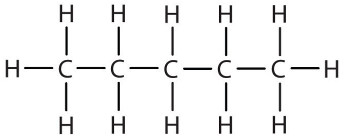
12.4: Condensed Structural and Line-Angle Formulas

Exercises

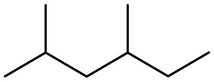
1. Write the condensed structural formula for each structural formula.

a. 

b. 

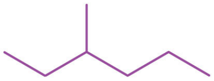
c. 

2. A condensed structural formula for isohexane can be written as $(CH_3)_2CHCH_2CH_2CH_3$. Draw the line-angle formula for isohexane.
3. Draw a line-angle formula for the compound $CH_3CH_2CH(CH_3)CH_2CH_2CH_3$.
4. Give the structural formula for the compound represented by this line-angle formula:



Answers

1.
   a. CH_3CH_3
   b. $CH_3CH_2CH_3$
   c. $CH_3CH_2CH_2CH_2CH_3$

3. 

12.5: IUPAC Nomenclature

Concept Review Exercises

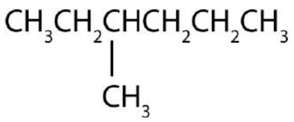
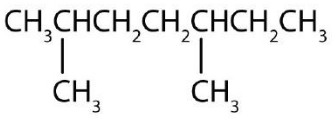
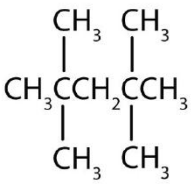
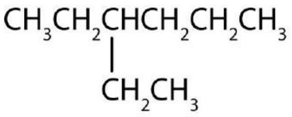
1. What is a CH_3 group called when it is attached to a chain of carbon atoms—a substituent or a functional group?
2. Which type of name uses numbers to locate substituents—common names or IUPAC names?

Answers

1. substituent
2. IUPAC names

Exercises

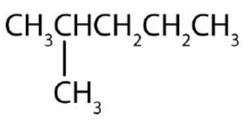
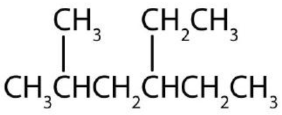
1. Briefly identify the important distinctions between an alkane and an alkyl group.
2. How many carbon atoms are present in each molecule?
   a. 2-methylbutane
   b. 3-ethylpentane
3. How many carbon atoms are present in each molecule?
   a. 2,3-dimethylbutane
   b. 3-ethyl-2-methylheptane
4. Draw the structure for each compound.
   a. 3-methylpentane
   b. 2,2,5-trimethylhexane
   c. 4-ethyl-3-methyloctane

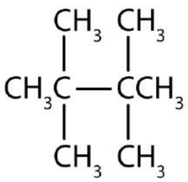
5. Draw the structure for each compound.
   a. 2-methylpentane
   b. 4-ethyl-2-methylhexane
   c. 2,2,3,3-tetramethylbutane
6. Name each compound according to the IUPAC system.
   a. 
   $CH_3CH_2\underset{CH_3}{CH}CH_2CH_2CH_3$
   b. 
   $CH_3\underset{CH_3}{CH}CH_2CH_2\underset{CH_3}{CH}CH_2CH_3$
7. Name each compound according to the IUPAC system.
   a. 
   $CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2\overset{CH_3}{\underset{CH_3}{C}}CH_3$
   b. 
   $CH_3CH_2\underset{CH_2CH_3}{CH}CH_2CH_2CH_3$
8. What is a substituent? How is the location of a substituent indicated in the IUPAC system?
9. Briefly identify the important distinctions between a common name and an IUPAC name.

Answers

1. An alkane is a molecule; an alkyl group is not an independent molecule but rather a part of a molecule that we consider as a unit.

3.
   a. 6
   b. 10

5.
   a. 
   $CH_3\underset{CH_3}{CH}CH_2CH_2CH_3$
   b. 
   $CH_3\overset{CH_3}{CH}CH_2\overset{CH_2CH_3}{CH}CH_2CH_3$

c. 

7.

   a. 2,2,4,4-tetramethylpentane
   b. 3-ethylhexane

9. Common names are widely used but not very systematic; IUPAC names identify a parent compound and name other groups as substituents.

12.6: Physical Properties of Alkanes

Concept Review Exercises

1. Without referring to a table, predict which has a higher boiling point—hexane or octane. Explain.
2. If 25 mL of hexane were added to 100 mL of water in a beaker, which of the following would you expect to happen? Explain.
   a. Hexane would dissolve in water.
   b. Hexane would not dissolve in water and would float on top.
   c. Hexane would not dissolve in water and would sink to the bottom of the container.

Answers

1. octane because of its greater molar mass
2. b; hexane is insoluble in water and less dense than water.

Exercises

1. Without referring to a table or other reference, predict which member of each pair has the higher boiling point.
   a. pentane or butane
   b. heptane or nonane
2. For which member of each pair is hexane a good solvent?
   a. pentane or water
   b. sodium chloride or soybean oil

Answer

1. a. pentane
   b. nonane

12.7: Chemical Properties of Alkanes

Concept Review Exercises

1. Why are alkanes sometimes called paraffins?
2. Which halogen reacts most readily with alkanes? Which reacts least readily?

Answers

1. Alkanes do not react with many common chemicals. They are sometimes called paraffins, from the Latin parum affinis, meaning “little affinity.”
2. most readily: F_2; least readily: I_2

Exercises

1. Why do alkanes usually not react with ionic compounds such as most laboratory acids, bases, oxidizing agents, or reducing agents?
2. Write an equation for the complete combustion of methane (CH_4), the main component of natural gas).
3. What is the most important reaction of alkanes?
4. Name some substances other than oxygen that react readily with alkanes.

Answers

1. Alkanes are nonpolar; they do not attract ions.

12.8: Halogenated Hydrocarbons

Concept Review Exercises

1. What is the IUPAC name for the HFC that has the formula CH_2FCF_3? (Hint: you must use a number to indicate the location of each substituent F atom.)
2. What is the IUPAC name for the HCFC that has the formula $CHCl_2CF_3$?

Answers

1. 1,1,1,2-tetrafluoroethane
2. 1,1,1-trifluoro-2,2-dichloroethane

Exercises

1. Write the condensed structural formula for each compound.
    a. methyl chloride
    b. chloroform
2. Write the condensed structural formula for each compound.
    a. ethyl bromide
    b. carbon tetrachloride
3. Write the condensed structural formulas for the two isomers that have the molecular formula C_3H_7Br. Give the common name and the IUPAC name of each.
4. Write the condensed structural formulas for the four isomers that have the molecular formula C_4H_9Br. Give the IUPAC name of each.
5. What is a CFC? How are CFCs involved in the destruction of the ozone layer?
6. Explain why each compound is less destructive to the ozone layer than are CFCs.
    a. fluorocarbons
    b. HCFCs

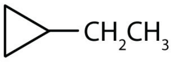
Answers

1. a. CH_3Cl
    b. $CHCl_3$
3. $CH_3CH_2CH_2Br$, propyl bromide, 1-bromopropane; $CH_3CHBrCH_3$, isopropyl bromide, 2-bromopropane
5. compounds containing Cl, F, and C; by releasing Cl atoms in the stratosphere

12.9: Cycloalkanes

Concept Review Exercises

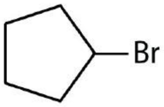
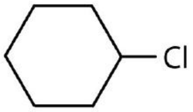
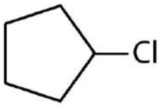
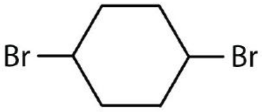
1. What is the molecular formula of cyclooctane?
2. What is the IUPAC name for this compound?



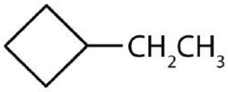
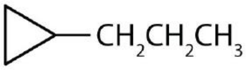
Answers

1. C_8H_{16}
2. ethylcyclopropane

Exercises

1. Draw the structure for each compound.
   a. ethylcyclobutane
   b. propylcyclopropane
2. Draw the structure for each compound.
   a. methylcyclohexane
   b. butylcyclobutane
3. Cycloalkyl groups can be derived from cycloalkanes in the same way that alkyl groups are derived from alkanes. These groups are named as cyclopropyl, cyclobutyl, and so on. Name each cycloalkyl halide.
   a. 
   b. 
4. Halogenated cycloalkanes can be named by the IUPAC system. As with alkyl derivatives, monosubstituted derivatives need no number to indicate the position of the halogen. To name disubstituted derivatives, the carbon atoms are numbered starting at the position of one substituent (C1) and proceeding to the second substituted atom by the shortest route. Name each compound.
   a. 
   b. 

Answers

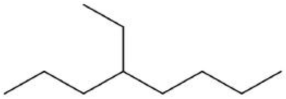
1. a. 
   b. 

3. a. cyclopentyl bromide
   b. cyclohexyl chloride

12.10: Chapter Summary

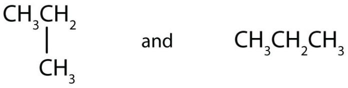
Additional Exercises

1. You find an unlabeled jar containing a solid that melts at 48°C. It ignites readily and burns readily. The substance is insoluble in water and floats on the surface. Is the substance likely to be organic or inorganic?
2. Give the molecular formulas for methylcyclopentane, 2-methylpentane, and cyclohexane. Which are isomers?
3. What is wrong with each name? (Hint: first write the structure *as if* it were correct.) Give the correct name for each compound.
   a. 2-dimethylpropane
   b. 2,3,3-trimethylbutane
   c. 2,4-diethylpentane
   d. 3,4-dimethyl-5-propylhexane
4. What is the danger in swallowing a liquid alkane?
5. Distinguish between lighter and heavier liquid alkanes in terms of their effects on the skin.
6. Following is the line formula for an alkane. Draw its structure and give its name.



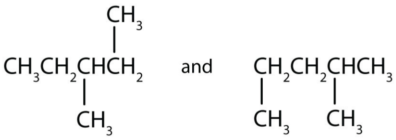
7. Write equations for the complete combustion of each compound.
   a. propane (a bottled gas fuel)
   b. octane (a typical hydrocarbon in gasoline).
8. The density of a gasoline sample is 0.690 g/mL. On the basis of the complete combustion of octane, calculate the amount in grams of carbon dioxide (CO_2) and water (H_2O) formed per gallon (3.78 L) of the gasoline when used in an automobile.
9. Draw the structures for the five isomeric hexanes (C_6H_{14}). Name each by the IUPAC system.
10. Indicate whether the structures in each set represent the same compound or isomers.

a.



$\underset{\displaystyle CH_3}{CH_3CH_2}$ and $CH_3CH_2CH_3$

b.



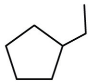
$CH_3CH_2\underset{\displaystyle CH_3}{CH}\overset{\displaystyle CH_3}{CH_2}$ and $\underset{\displaystyle CH_3}{CH_2}CH_2\underset{\displaystyle CH_3}{CH}CH_3$

c.

$CH_3CH_2\underset{\displaystyle CH_3}{CH}CH_2CH_3$ and $CH_3\underset{\displaystyle CH_3}{CH}CH_2CH_2CH_3$

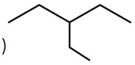
11. Consider the line-angle formulas shown here and answer the questions.

(i)

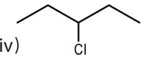


(ii)

(iii)



(iv)



a. Which pair of formulas represents isomers? Draw each structure.
b. Which formula represents an alkyl halide? Name the compound and write its condensed structural formula.
c. Which formula represents a cyclic alkane? Name the compound and draw its structure.
d. What is the molecular formula of the compound represented by (i)?

Answers

1. organic

3.

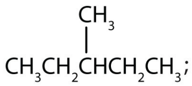
a. Two numbers are needed to indicate two substituents; 2,2-dimethylpropane.
b. The lowest possible numbers were not used; 2,2,3-trimethylbutane.
c. An ethyl substituent is not possible on the second carbon atom; 3,5-dimethylheptane.
d. A propyl substituent is not possible on the fifth carbon atom; 3,4,5-trimethyloctane.

5. Lighter alkanes wash away protective skin oils; heavier alkanes form a protective layer.

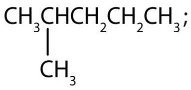
7.

a. $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$
b. $2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$

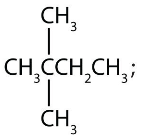
9. $CH_3CH_2CH_2CH_2CH_2CH_3$; hexane



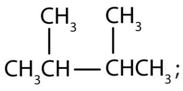
$CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_3$; 3-methylpentane



$CH_3\underset{\underset{CH_3}{|}}{C}HCH_2CH_2CH_3$; 2-methylpentane



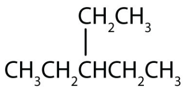
$CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_2CH_3$; 2,2-dimethylbutane



$CH_3\overset{\overset{CH_3}{|}}{C}H-\overset{\overset{CH_3}{|}}{C}HCH_3$; 2,3-dimethylbutane

11.

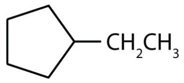
a. ii and iii; $CH_3CH_2CH_2CH_2CH_2CH_2CH_3$ and



$$\begin{array}{c} CH_2CH_3 \\ | \\ CH_3CH_2CHCH_2CH_3 \end{array}$$

b. iv; 3-chloropentane; $CH_3CH_2CHClCH_2CH_3$

c. i; ethylcyclopentane;



d. C_7H_{14}

12.S: Organic Chemistry- Alkanes and Halogenated Hydrocarbons (Summary)

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

Organic chemistry is the chemistry of carbon compounds, and **inorganic chemistry** is the chemistry of all the other elements. Carbon atoms can form stable covalent bonds with other carbon atoms and with atoms of other elements, and this property allows the formation the tens of millions of organic compounds. **Hydrocarbons** contain only hydrogen and carbon atoms.

Hydrocarbons in which each carbon atom is bonded to four other atoms are called **alkanes** or **saturated hydrocarbons**. They have the general formula C_nH_{2n+2}. Any given alkane differs from the next one in a series by a CH_2 unit. Any family of compounds in which adjacent members differ from each other by a definite factor is called a **homologous series**.

Carbon atoms in alkanes can form straight chains or branched chains. Two or more compounds having the same molecular formula but different structural formulas are **isomers** of each other. There are no isomeric forms for the three smallest alkanes; beginning with C_4H_{10}, all other alkanes have isomeric forms.

A **structural formula** shows all the carbon and hydrogen atoms and how they are attached to one another. A **condensed structural formula** shows the hydrogen atoms right next to the carbon atoms to which they are attached. A **line-angle formula** is a formula in which carbon atoms are implied at the corners and ends of lines. Each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds.

The **IUPAC System of Nomenclature** provides rules for naming organic compounds. An **alkyl group** is a unit formed by removing one hydrogen atom from an alkane.

The physical properties of alkanes reflect the fact that alkane molecules are nonpolar. Alkanes are insoluble in water and less dense than water.

Alkanes are generally unreactive toward laboratory acids, bases, oxidizing agents, and reducing agents. They do burn (undergo **combustion reactions**).

Alkanes react with halogens by substituting one or more halogen atoms for hydrogen atoms to form **halogenated hydrocarbons**. An **alkyl halide (haloalkane)** is a compound resulting from the replacement of a hydrogen atom of an alkane with a halogen atom.

Cycloalkanes are hydrocarbons whose molecules are closed rings rather than straight or branched chains. A **cyclic hydrocarbon** is a hydrocarbon with a ring of carbon atoms

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CHAPTER OVERVIEW

13: Unsaturated and Aromatic Hydrocarbons

Our modern society is based to a large degree on the chemicals we discuss in this chapter. Most are made from petroleum. Alkanes—saturated hydrocarbons—have relatively few important chemical properties other than that they undergo combustion and react with halogens. Unsaturated hydrocarbons—hydrocarbons with double or triple bonds—on the other hand, are quite reactive. In fact, they serve as building blocks for many familiar plastics—polyethylene, vinyl plastics, acrylics—and other important synthetic materials (e.g., alcohols, antifreeze, and detergents). Aromatic hydrocarbons have formulas that can be drawn as cyclic alkenes, making them appear unsaturated, but their structure and properties are generally quite different, so they are not considered to be alkenes. Aromatic compounds serve as the basis for many drugs, antiseptics, explosives, solvents, and plastics (e.g., polyesters and polystyrene). The two simplest unsaturated compounds—ethylene (ethene) and acetylene (ethyne)—were once used as anesthetics and were introduced to the medical field in 1924. However, it was discovered that acetylene forms explosive mixtures with air, so its medical use was abandoned in 1925. Ethylene was thought to be safer, but it too was implicated in numerous lethal fires and explosions during anesthesia. Even so, it remained an important anesthetic into the 1960s, when it was replaced by nonflammable anesthetics such as halothane ($\mathrm{CHBrClCF_3}$).

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13.0: Prelude to Unsaturated and Aromatic Hydrocarbons

Our modern society is based to a large degree on the chemicals we discuss in this chapter. Most are made from petroleum. Alkanes—saturated hydrocarbons—have relatively few important chemical properties other than that they undergo combustion and react with halogens. Unsaturated hydrocarbons—hydrocarbons with double or triple bonds—on the other hand, are quite reactive. In fact, they serve as building blocks for many familiar plastics—polyethylene, vinyl plastics, acrylics—and other important synthetic materials (e.g., alcohols, antifreeze, and detergents). Aromatic hydrocarbons have formulas that can be drawn as cyclic alkenes, making them appear unsaturated, but their structure and properties are generally quite different, so they are not considered to be alkenes. Aromatic compounds serve as the basis for many drugs, antiseptics, explosives, solvents, and plastics (e.g., polyesters and polystyrene).

The two simplest unsaturated compounds—ethylene (ethene) and acetylene (ethyne)—were once used as anesthetics and were introduced to the medical field in 1924. However, it was discovered that acetylene forms explosive mixtures with air, so its medical use was abandoned in 1925. Ethylene was thought to be safer, but it too was implicated in numerous lethal fires and explosions during anesthesia. Even so, it remained an important anesthetic into the 1960s, when it was replaced by nonflammable anesthetics such as halothane ($\mathrm{CHBrClCF_3}$).

13.1: Alkenes- Structures and Names

Learning Objectives

- To name alkenes given formulas and write formulas for alkenes given names.

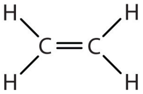
As noted before, alkenes are hydrocarbons with carbon-to-carbon double bonds ($R_2C{=}CR_2$) and alkynes are hydrocarbons with carbon-to-carbon triple bonds ($R{-}C{\equiv}C{-}R$). Collectively, they are called unsaturated hydrocarbons because they have fewer hydrogen atoms than does an alkane with the same number of carbon atoms, as is indicated in the following general formulas:

Some representative alkenes—their names, structures, and physical properties—are given in Table 13.1.1.

Table 13.1.1: Physical Properties of Some Selected Alkenes

IUPAC Name	Molecular Formula	Condensed Structural Formula	Melting Point (°C)	Boiling Point (°C)
ethene	C_2H_4	$CH_2{=}CH_2$	–169	–104
propene	C_3H_6	$CH_2{=}CHCH_3$	–185	–47
1-butene	C_4H_8	$CH_2{=}CHCH_2CH_3$	–185	–6
1-pentene	C_5H_{10}	$CH_2{=}CH(CH_2)_2CH_3$	–138	30
1-hexene	C_6H_{12}	$CH_2{=}CH(CH_2)_3CH_3$	–140	63
1-heptene	C_7H_{14}	$CH_2{=}CH(CH_2)_4CH_3$	–119	94
1-octene	C_8H_{16}	$CH_2{=}CH(CH_2)_5CH_3$	–102	121

We used only condensed structural formulas in Table 13.1.1. Thus, $CH_2{=}CH_2$ stands for



The double bond is shared by the two carbons and does not involve the hydrogen atoms, although the condensed formula does not make this point obvious. Note that the molecular formula for ethene is C_2H_4, whereas that for ethane is C_2H_6.

The first two alkenes in Table 13.1.1, ethene and propene, are most often called by their common names—ethylene and propylene, respectively (Figure 13.1.1). Ethylene is a major commercial chemical. The US chemical industry produces about 25 billion kilograms of ethylene annually, more than any other synthetic organic chemical. More than half of this ethylene goes into the manufacture of polyethylene, one of the most familiar plastics. Propylene is also an important industrial chemical. It is converted to plastics, isopropyl alcohol, and a variety of other products.

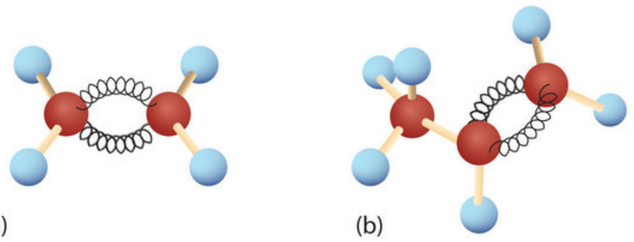
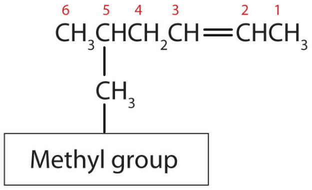


Figure 13.1.1: Ethene and Propene. The ball-and-spring models of ethene/ethylene (a) and propene/propylene (b) show their respective shapes, especially bond angles.

> Although there is only one alkene with the formula C_2H_4 (ethene) and only one with the formula C_3H_6 (propene), there are several alkenes with the formula C_4H_8.

Here are some basic rules for naming alkenes from the International Union of Pure and Applied Chemistry (IUPAC):

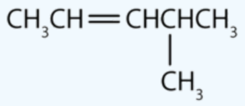
1. The longest chain of carbon atoms *containing the double bond* is considered the parent chain. It is named using the same stem as the alkane having the same number of carbon atoms but ends in *-ene* to identify it as an alkene. Thus the compound $CH_2{=}CHCH_3$ is *propene*.
2. If there are four or more carbon atoms in a chain, we must indicate the position of the double bond. The carbons atoms are numbered so that the first of the two that are doubly bonded is given the lower of the two possible numbers.The compound $CH_3CH{=}CHCH_2CH_3$, for example, has the double bond between the second and third carbon atoms. Its name is 2-pentene (not 3-pentene).
3. Substituent groups are named as with alkanes, and their position is indicated by a number. Thus, the structure below is 5-methyl-2-hexene. Note that the numbering of the parent chain is always done in such a way as to give the double bond the lowest number, even if that causes a substituent to have a higher number. *The double bond always has priority in numbering.*



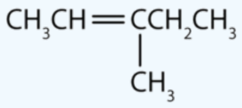
$$\overset{6}{CH_3}\underset{\displaystyle CH_3}{\overset{5}{C}H}\overset{4}{CH_2}\overset{3}{CH}{=}\overset{2}{CH}\overset{1}{CH_3}$$

Example 13.1.1

Name each compound.

a. 

$$CH_3CH{=}CH\underset{\displaystyle CH_3}{C}HCH_3$$

b. 

$$CH_3CH{=}\underset{\displaystyle CH_3}{C}CH_2CH_3$$

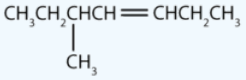
Solution

a. The longest chain containing the double bond has five carbon atoms, so the compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the fourth carbon atom (rule 3), so the compound's name is 4-methyl-2-pentene.
b. The longest chain containing the double bond has five carbon atoms, so the parent compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the third carbon atom (rule 3), so the compound's name is 3-methyl-2-pentene.

Exercise 13.1.1

Name each compound.

a. $CH_3CH_2CH_2CH_2CH_2CH{=}CHCH_3$

b. 

$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}H}CH{=}CHCH_2CH_3$

Answer

Just as there are cycloalkanes, there are *cycloalkenes*. These compounds are named like alkenes, but with the prefix *cyclo-* attached to the beginning of the parent alkene name.

Example 13.1.2

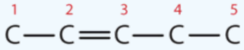
Draw the structure for each compound.

a. 3-methyl-2-pentene
b. cyclohexene

Solution

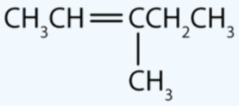
a.

First write the parent chain of five carbon atoms: C–C–C–C–C. Then add the double bond between the second and third carbon atoms:



$\overset{1}{C}-\overset{2}{C}=\overset{3}{C}-\overset{4}{C}-\overset{5}{C}$

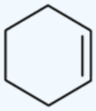
Now place the methyl group on the third carbon atom and add enough hydrogen atoms to give each carbon atom a total of four bonds.



$CH_3CH{=}\underset{\displaystyle CH_3}{\underset{|}{C}}CH_2CH_3$

b

First, consider what each of the three parts of the name means. *Cyclo* means a ring compound, *hex* means 6 carbon atoms, and -*ene* means a double bond.



Exercise 13.1.2

Draw the structure for each compound.

a. 2-ethyl-1-hexene
b. cyclopentene

Key Takeaway

- Alkenes are hydrocarbons with a carbon-to-carbon double bond.

13.2: Cis-Trans Isomers (Geometric Isomers)

Learning Objectives

- Recognize that alkenes that can exist as cis-trans isomers.
- Classify isomers as cis or trans.
- Draw structures for cis-trans isomers given their names.

There is free rotation about the carbon-to-carbon single bonds (C–C) in alkanes. In contrast, the structure of alkenes requires that the carbon atoms of a double bond and the two atoms bonded to each carbon atom all lie in a single plane, and that each doubly bonded carbon atom lies in the center of a triangle. This part of the molecule's structure is rigid; rotation about doubly bonded carbon atoms is *not* possible without rupturing the bond. Look at the two chlorinated hydrocarbons in Figure 13.2.1.

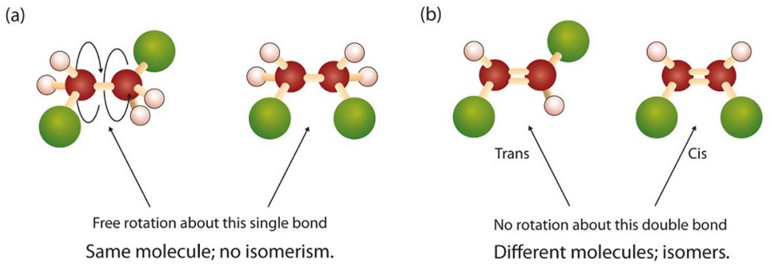
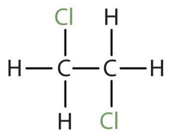
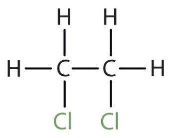


Figure 13.2.1: *Rotation about Bonds. In 1,2-dichloroethane (a), free rotation about the C–C bond allows the two structures to be interconverted by a twist of one end relative to the other. In 1,2-dichloroethene (b), restricted rotation about the double bond means that the relative positions of substituent groups above or below the double bond are significant.*

In 1,2-dichloroethane (part (a) of Figure 13.2.1), there is free rotation about the C–C bond. The two models shown represent exactly the same molecule; they are *not* isomers. You can draw structural formulas that look different, but if you bear in mind the possibility of this free rotation about single bonds, you should recognize that these two structures represent the same molecule:



$$\begin{array}{ccccc} & \text{Cl} & & \text{H} & \\ & | & & | & \\ \text{H}- & \text{C} & - & \text{C} & -\text{H} \\ & | & & | & \\ & \text{H} & & \text{Cl} & \end{array}$$



$$\begin{array}{ccccc} & \text{H} & & \text{H} & \\ & | & & | & \\ \text{H}- & \text{C} & - & \text{C} & -\text{H} \\ & | & & | & \\ & \text{Cl} & & \text{Cl} & \end{array}$$

In 1,2-dichloroethene (Figure 13.2.1b), however, restricted rotation about the double bond means that the relative positions of substituent groups above or below the double bond become significant. This leads to a special kind of isomerism. The isomer in which the two chlorine (Cl) atoms lie on the same side of the molecule is called the cis isomer (Latin *cis*, meaning "on this side") and is named cis-1,2-dichloroethene. The isomer with the two Cl atoms on opposite sides of the molecule is the trans isomer (Latin *trans*, meaning "across") and is named *trans*-1,2-dichloroethene. These two compounds are cis-trans isomers (or geometric isomers), compounds that have different configurations (groups permanently in different places in space) because of the presence of a rigid structure in their molecule.

Consider the alkene with the condensed structural formula $CH_3CH{=}CHCH_3$. We could name it 2-butene, but there are actually two such compounds; the double bond results in cis-trans isomerism (Figure 13.2.2).

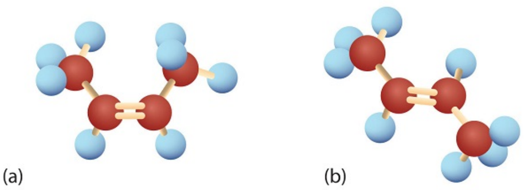


Figure 13.2.2: Ball-and-Spring Models of (a) Cis-2-Butene and (b) Trans-2-Butene. Cis-trans isomers have different physical, chemical, and physiological properties.

Cis-2-butene has both methyl groups on the same side of the molecule. *Trans*-2-butene has the methyl groups on opposite sides of the molecule. Their structural formulas are as follows:

cis-2-butene *trans*-2-butene

***Figure 13.2.3**: Models of (left) Cis-2-Butene and (right) Trans-2-Butene.*

Note, however, that the presence of a double bond does **not** necessarily lead to cis-trans isomerism (Figure 13.2.4). We can draw two *seemingly* different propenes:

***Figure 13.2.4**: Different views of the propene molecule (flip vertically). These are not isomers.*

However, these two structures are not really different from each other. If you could pick up either molecule from the page and flip it over top to bottom, you would see that the two formulas are identical. Thus there are two requirements for cis-trans isomerism:

1. Rotation must be restricted in the molecule.
2. There must be **two nonidentical groups** on **each** doubly bonded carbon atom.

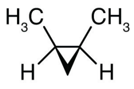
In these propene structures, the second requirement for cis-trans isomerism is not fulfilled. One of the doubly bonded carbon atoms does have two different groups attached, but the rules require that *both* carbon atoms have two different groups. In general, the following statements hold true in cis-trans isomerism:

- Alkenes with a C=CH$_2$ unit do not exist as cis-trans isomers.
- Alkenes with a C=CR$_2$ unit, where the two R groups are the same, do not exist as cis-trans isomers.
- Alkenes of the type R–CH=CH–R can exist as cis and trans isomers; cis if the two R groups are on the same side of the carbon-to-carbon double bond, and trans if the two R groups are on opposite sides of the carbon-to-carbon double bond.

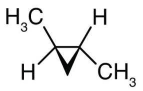
Advanced Note: E/Z Isomerization

If a molecule has a C=C bond with one non-hydrogen group attached to each of the carbons, cis/trans nomenclature descried above is enough to describe it. However, if you have three different groups (or four), then the cis/trans approach is insufficient to describe the different isomers, since we do not know which two of the three groups are being described. For example, if you have a C=C bond, with a methyl group and a bromine on one carbon , and an ethyl group on the other, it is neither trans nor cis, since it is not clear whether the ethyl group is trans to the bromine or the methyl. This is addressed with a more advanced E,Z Convention [E] [E] [E] discussed elsewhere.

Cis-trans isomerism also occurs in cyclic compounds. In ring structures, groups are unable to rotate about any of the ring carbon–carbon bonds. Therefore, groups can be either on the same side of the ring (cis) or on opposite sides of the ring (trans). For our purposes here, we represent all cycloalkanes as planar structures, and we indicate the positions of the groups, either above or below the plane of the ring.



Cis-1,2-dimethylcyclopropane



Trans-1,2-dimethylcyclopropane

Example 13.2.1

Which compounds can exist as cis-trans (geometric) isomers? Draw them.

1. CHCl=CHBr
2. CH$_2$=CBrCH$_3$
3. (CH$_3$)$_2$C=CHCH$_2$CH$_3$

4. $CH_3CH{=}CHCH_2CH_3$

Solution

All four structures have a double bond and thus meet rule 1 for cis-trans isomerism.

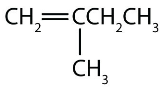
1. This compound meets rule 2; it has two nonidentical groups on *each* carbon atom (H and Cl on one and H and Br on the other). It exists as both cis and trans isomers:

2. This compound has two hydrogen atoms on one of its doubly bonded carbon atoms; it fails rule 2 and does not exist as cis and trans isomers.
3. This compound has two methyl (CH_3) groups on one of its doubly bonded carbon atoms. It fails rule 2 and does not exist as cis and trans isomers.
4. This compound meets rule 2; it has two nonidentical groups on *each* carbon atom and exists as both cis and trans isomers:

? Exercise 13.2.1

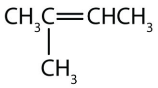
Which compounds can exist as cis-trans isomers? Draw them.

a. $CH_2{=}CHCH_2CH_2CH_3$
b. $CH_3CH{=}CHCH_2CH_3$
c. $CH_3CH_2CH{=}CHCH_2CH_3$
d.



$$\begin{array}{l} CH_2{=}CCH_2CH_3 \\ \quad\quad\;\, | \\ \quad\quad\; CH_3 \end{array}$$

e.



$$\begin{array}{l} CH_3C{=}CHCH_3 \\ \quad\;\;\, | \\ \quad\; CH_3 \end{array}$$

Key Takeaway

- Cis-trans (geometric) isomerism exists when there is restricted rotation in a molecule and there are two nonidentical groups on *each* doubly bonded carbon atom.

13.3: Physical Properties of Alkenes

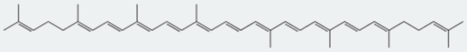
Learning Objectives

- To identify the physical properties of alkenes and describe trends in these properties.

The physical properties of alkenes are similar to those of the alkanes. The table at the start of the chapter shows that the boiling points of straight-chain alkenes increase with increasing molar mass, just as with alkanes. For molecules with the same number of carbon atoms and the same general shape, the boiling points usually differ only slightly, just as we would expect for substances whose molar mass differs by only 2 u (equivalent to two hydrogen atoms). Like other hydrocarbons, the alkenes are insoluble in water but soluble in organic solvents.

Looking Closer: Environmental Note

Alkenes occur widely in nature. Ripening fruits and vegetables give off ethylene, which triggers further ripening. Fruit processors artificially introduce ethylene to hasten the ripening process; exposure to as little as 0.1 mg of ethylene for 24 h can ripen 1 kg of tomatoes. Unfortunately, this process does not exactly duplicate the ripening process, and tomatoes picked green and treated this way don't taste much like vine-ripened tomatoes fresh from the garden.



The bright red color of tomatoes is due to lycopene—a polyene.

Other alkenes that occur in nature include 1-octene, a constituent of lemon oil, and octadecene ($C_{18}H_{36}$) found in fish liver. Dienes (two double bonds) and polyenes (three or more double bonds) are also common. Butadiene (CH_2=CHCH=CH_2) is found in coffee. Lycopene and the carotenes are isomeric polyenes ($C_{40}H_{56}$) that give the attractive red, orange, and yellow colors to watermelons, tomatoes, carrots, and other fruits and vegetables. Vitamin A, essential to good vision, is derived from a carotene. The world would be a much less colorful place without alkenes.

Key Takeaway

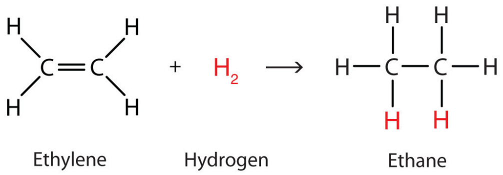
- The physical properties of alkenes are much like those of the alkanes: their boiling points increase with increasing molar mass, and they are insoluble in water.

13.4: Chemical Properties of Alkenes

Learning Objectives

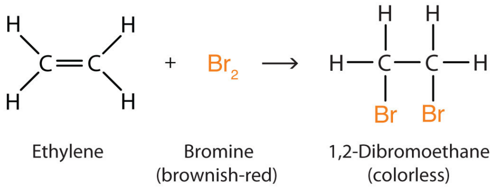
- To write equations for the addition reactions of alkenes with hydrogen, halogens, and water

Alkenes are valued mainly for addition reactions, in which one of the bonds in the double bond is broken. Each of the carbon atoms in the bond can then attach another atom or group while remaining joined to each other by a single bond. Perhaps the simplest addition reaction is hydrogenation—a reaction with hydrogen (H_2) in the presence of a catalyst such as nickel (Ni) or platinum (Pt).

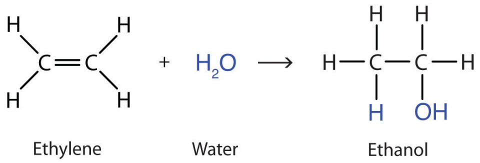


The product is an alkane having the same carbon skeleton as the alkene.

Alkenes also readily undergo halogenation—the addition of halogens. Indeed, the reaction with bromine (Br_2) can be used to test for alkenes. Bromine solutions are brownish red. When we add a Br_2 solution to an alkene, the color of the solution disappears because the alkene reacts with the bromine:



Another important addition reaction is that between an alkene and water to form an alcohol. This reaction, called hydration, requires a catalyst—usually a strong acid, such as sulfuric acid (H_2SO_4):



The hydration reaction is discussed later, where we deal with this reaction in the synthesis of alcohols.

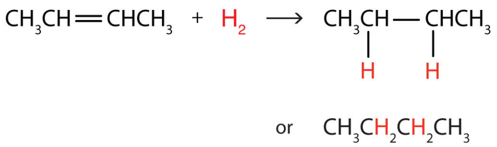
Example 13.4.1

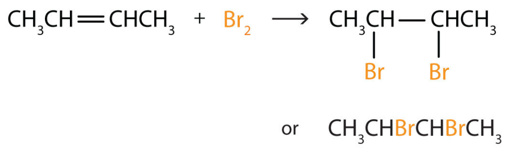
Write the equation for the reaction between $CH_3CH{=}CHCH_3$ and each substance.

a. H_2 (Ni catalyst)
b. Br_2
c. H_2O (H_2SO_4 catalyst)

Solution

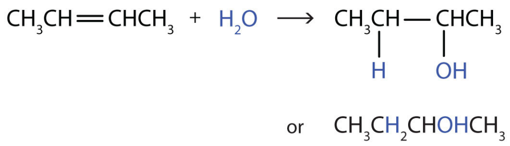
In each reaction, the reagent adds across the double bond.

a. 

b. 

$$CH_3CH{=}CHCH_3 + Br_2 \longrightarrow CH_3\underset{Br}{CH}{-}\underset{Br}{CH}CH_3$$

or $CH_3CHBrCHBrCH_3$

c. 

$$CH_3CH{=}CHCH_3 + H_2O \longrightarrow CH_3\underset{H}{CH}{-}\underset{OH}{CH}CH_3$$

or $CH_3CH_2CHOHCH_3$

? Exercise 13.4.1

Write the equation for each reaction.

a. $CH_3CH_2CH{=}CH_2$ with H_2 (Ni catalyst)
b. $CH_3CH{=}CH_2$ with Cl_2
c. $CH_3CH_2CH{=}CHCH_2CH_3$ with H_2O (H_2SO_4 catalyst)

Key Takeaway

- Alkenes undergo addition reactions, adding such substances as hydrogen, bromine, and water across the carbon-to-carbon double bond.

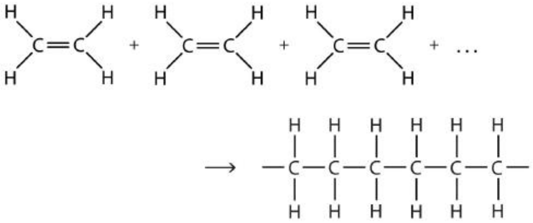
13.5: Polymers

Learning Objectives

- To draw structures for monomers that can undergo addition polymerization and for four-monomer-unit sections of an addition polymer.

The most important commercial reactions of alkenes are *polymerizations*, reactions in which small molecules, referred to in general as monomers (from the Greek *monos*, meaning "one," and *meros*, meaning "parts"), are assembled into giant molecules referred to as polymers (from the Greek *poly*, meaning "many," and *meros*, meaning "parts"). A polymer is as different from its monomer as a long strand of spaghetti is from a tiny speck of flour. For example, polyethylene, the familiar waxy material used to make plastic bags, is made from the monomer ethylene—a gas.

There are two general types of polymerization reactions: addition polymerization and condensation polymerization. In addition polymerization, the monomers add to one another in such a way that the polymer contains all the atoms of the starting monomers. Ethylene molecules are joined together in long chains. The polymerization can be represented by the reaction of a few monomer units:



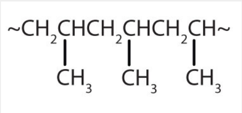
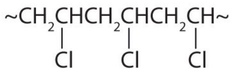
The bond lines extending at the ends in the formula of the product indicate that the structure extends for many units in each direction. Notice that all the atoms—two carbon atoms and four hydrogen atoms—of each monomer molecule are incorporated into the polymer structure. Because displays such as the one above are cumbersome, the polymerization is often abbreviated as follows:

$$n\mathrm{CH_2{=}CH_2} \rightarrow \left[\mathrm{CH_2CH_2}\right]_n$$

> Many natural materials—such as proteins, cellulose and starch, and complex silicate minerals—are polymers. Artificial fibers, films, plastics, semisolid resins, and rubbers are also polymers. More than half the compounds produced by the chemical industry are synthetic polymers.

Some common addition polymers are listed in Table 13.5.1. Note that all the monomers have carbon-to-carbon double bonds. Many polymers are mundane (e.g., plastic bags, food wrap, toys, and tableware), but there are also polymers that conduct electricity, have amazing adhesive properties, or are stronger than steel but much lighter in weight.

Table 13.5.1: *Some Addition Polymers*

Monomer	Polymer	Polymer Name	Some Uses
$\mathrm{CH_2{=}CH_2}$	$\sim\mathrm{CH_2CH_2CH_2CH_2CH_2CH_2}\sim$	polyethylene	plastic bags, bottles, toys, electrical insulation
$\mathrm{CH_2{=}CHCH_3}$	 $\sim\mathrm{CH_2\underset{CH_3}{CH}CH_2\underset{CH_3}{CH}CH_2\underset{CH_3}{CH}}\sim$	polypropylene	carpeting, bottles, luggage, exercise clothing
$\mathrm{CH_2{=}CHCl}$	 $\sim\mathrm{CH_2\underset{Cl}{CH}CH_2\underset{Cl}{CH}CH_2\underset{Cl}{CH}}\sim$	polyvinyl chloride	bags for intravenous solutions, pipes, tubing, floor coverings
$\mathrm{CF_2{=}CF_2}$	$\sim\mathrm{CF_2CF_2CF_2CF_2CF_2CF_2}\sim$	polytetrafluoroethylene	nonstick coatings, electrical insulation

Medical Uses of Polymers

An interesting use of polymers is the replacement of diseased, worn out, or missing parts in the body. For example, about a 250,000 hip joints and 500,000 knees are replaced in US hospitals each year. The artificial ball-and-socket hip joints are made of a special steel (the ball) and plastic (the socket). People crippled by arthritis or injuries gain freedom of movement and relief from pain. Patients with heart and circulatory problems can be helped by replacing worn out heart valves with parts based on synthetic polymers. These are only a few of the many biomedical uses of polymers.

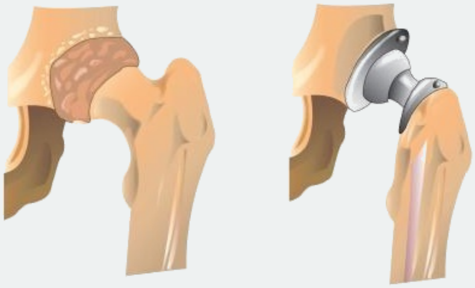


Figure 13.5.1: Hip Joint Replacement. Synthetic polymers are an important part of a hip joint replacement. The hip is much like a ball-and-socket joint, and total hip replacements mimic this with a metal ball that fits in a plastic cup.

Key Takeaway

- Molecules having carbon-to-carbon double bonds can undergo addition polymerization.

13.6: Alkynes

Learning Objectives

- Describe the general physical and chemical properties of alkynes.
- Name alkynes given formulas and write formulas for alkynes given names.

The simplest alkyne—a hydrocarbon with carbon-to-carbon triple bond—has the molecular formula C_2H_2 and is known by its common name—acetylene (Figure 13.6.1). Its structure is H–C≡C–H.

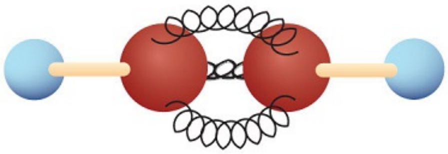


Figure 13.6.1: Ball-and-Spring Model of Acetylene. Acetylene (ethyne) is the simplest member of the alkyne family.

> Acetylene is used in oxyacetylene torches for cutting and welding metals. The flame from such a torch can be very hot. Most acetylene, however, is converted to chemical intermediates that are used to make vinyl and acrylic plastics, fibers, resins, and a variety of other products.

Alkynes are similar to alkenes in both physical and chemical properties. For example, alkynes undergo many of the typical addition reactions of alkenes. The International Union of Pure and Applied Chemistry (IUPAC) names for alkynes parallel those of alkenes, except that the family ending is *-yne* rather than *-ene*. The IUPAC name for acetylene is ethyne. The names of other alkynes are illustrated in the following exercises.

Key Takeaway

- Alkynes are hydrocarbons with carbon-to-carbon triple bonds and properties much like those of alkenes.

13.7: Aromatic Compounds- Benzene

Learning Objectives

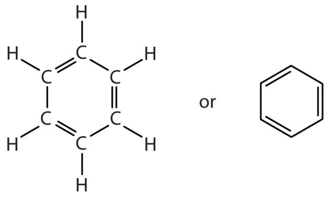
- To describe the bonding in benzene and the way typical reactions of benzene differ from those of the alkenes.

Next we consider a class of hydrocarbons with molecular formulas like those of unsaturated hydrocarbons, but which, unlike the alkenes, do not readily undergo addition reactions. These compounds comprise a distinct class, called aromatic hydrocarbons, with unique structures and properties. We start with the simplest of these compounds. Benzene (C_6H_6) is of great commercial importance, but it also has noteworthy health effects.

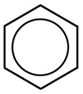
The formula C_6H_6 seems to indicate that benzene has a high degree of unsaturation. (Hexane, the saturated hydrocarbon with six carbon atoms has the formula C_6H_{14}—eight more hydrogen atoms than benzene.) However, despite the seeming low level of saturation, benzene is rather unreactive. It does not, for example, react readily with bromine, which, is a test for unsaturation.

> Benzene is a liquid that smells like gasoline, boils at 80°C, and freezes at 5.5°C. It is the aromatic hydrocarbon produced in the largest volume. It was formerly used to decaffeinate coffee and was a significant component of many consumer products, such as paint strippers, rubber cements, and home dry-cleaning spot removers. It was removed from many product formulations in the 1950s, but others continued to use benzene in products until the 1970s when it was associated with leukemia deaths. Benzene is still important in industry as a precursor in the production of plastics (such as Styrofoam and nylon), drugs, detergents, synthetic rubber, pesticides, and dyes. It is used as a solvent for such things as cleaning and maintaining printing equipment and for adhesives such as those used to attach soles to shoes. Benzene is a natural constituent of petroleum products, but because it is a known carcinogen, its use as an additive in gasoline is now limited.

To explain the surprising properties of benzene, chemists suppose the molecule has a cyclic, hexagonal, planar structure of six carbon atoms with one hydrogen atom bonded to each. We can write a structure with alternate single and double bonds, either as a full structural formula or as a line-angle formula:



However, these structures do not explain the unique properties of benzene. Furthermore, experimental evidence indicates that all the carbon-to-carbon bonds in benzene are equivalent, and the molecule is unusually stable. Chemists often represent benzene as a hexagon with an inscribed circle:



The inner circle indicates that the valence electrons are shared equally by all six carbon atoms (that is, the electrons are *delocalized*, or spread out, over all the carbon atoms). It is understood that each corner of the hexagon is occupied by one carbon atom, and each carbon atom has one hydrogen atom attached to it. Any other atom or groups of atoms substituted for a hydrogen atom must be shown bonded to a particular corner of the hexagon. We use this modern symbolism, but many scientists still use the earlier structure with alternate double and single bonds.

To Your Health: Benzene and Us

Most of the benzene used commercially comes from petroleum. It is employed as a starting material for the production of detergents, drugs, dyes, insecticides, and plastics. Once widely used as an organic solvent, benzene is now known to have both short- and long-term toxic effects. The inhalation of large concentrations can cause nausea and even death due to respiratory or

> heart failure, while repeated exposure leads to a progressive disease in which the ability of the bone marrow to make new blood cells is eventually destroyed. This results in a condition called *aplastic anemia*, in which there is a decrease in the numbers of both the red and white blood cells.

Key Takeaway

- Aromatic hydrocarbons appear to be unsaturated, but they have a special type of bonding and do not undergo addition reactions.

13.8: Structure and Nomenclature of Aromatic Compounds

Learning Objectives

- Recognize aromatic compounds from structural formulas.
- Name aromatic compounds given formulas.
- Write formulas for aromatic compounds given their names.

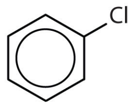
Historically, benzene-like substances were called aromatic hydrocarbons because they had distinctive aromas. Today, an aromatic compound is any compound that contains a benzene ring or has certain benzene-like properties (but not necessarily a strong aroma). You can recognize the aromatic compounds in this text by the presence of one or more benzene rings in their structure. Some representative aromatic compounds and their uses are listed in Table 13.8.1, where the benzene ring is represented as C_6H_5.

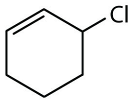
Table 13.8.1: Some Representative Aromatic Compounds

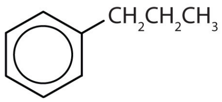
Name	Structure	Typical Uses
aniline	$C_6H_5-NH_2$	starting material for the synthesis of dyes, drugs, resins, varnishes, perfumes; solvent; vulcanizing rubber
benzoic acid	C_6H_5-COOH	food preservative; starting material for the synthesis of dyes and other organic compounds; curing of tobacco
bromobenzene	C_6H_5-Br	starting material for the synthesis of many other aromatic compounds; solvent; motor oil additive
nitrobenzene	$C_6H_5-NO_2$	starting material for the synthesis of aniline; solvent for cellulose nitrate; in soaps and shoe polish
phenol	C_6H_5-OH	disinfectant; starting material for the synthesis of resins, drugs, and other organic compounds
toluene	$C_6H_5-CH_3$	solvent; gasoline octane booster; starting material for the synthesis of benzoic acid, benzaldehyde, and many other organic compounds

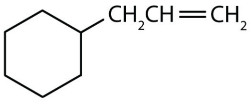
Example 13.8.1

Which compounds are aromatic?

1. 

2. 

3. 

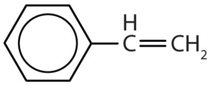
4. 

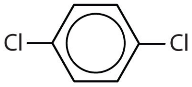
Solution

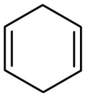
1. The compound has a benzene ring (with a chlorine atom substituted for one of the hydrogen atoms); it is aromatic.
2. The compound is cyclic, but it does not have a benzene ring; it is not aromatic.
3. The compound has a benzene ring (with a propyl group substituted for one of the hydrogen atoms); it is aromatic.
4. The compound is cyclic, but it does not have a benzene ring; it is not aromatic.

? Exercise 13.8.1

Which compounds are aromatic?

1. 

2. 

3. 

In the International Union of Pure and Applied Chemistry (IUPAC) system, aromatic hydrocarbons are named as derivatives of benzene. Figure 13.8.1 shows four examples. In these structures, it is immaterial whether the single substituent is written at the top, side, or bottom of the ring: a hexagon is symmetrical, and therefore all positions are equivalent.

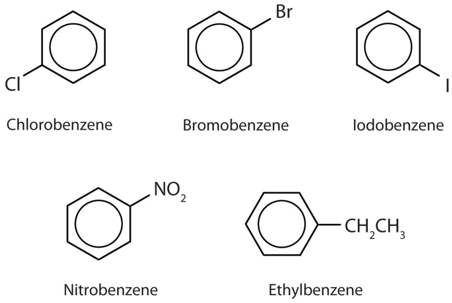
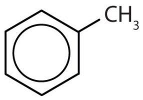
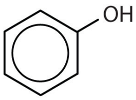


Figure 13.8.1: Some Benzene Derivatives. These compounds are named in the usual way with the group that replaces a hydrogen atom named as a substituent group: Cl as chloro, Br as bromo, I as iodo, NO_2 as nitro, and CH_3CH_2 as ethyl.

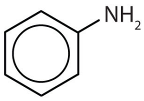
Although some compounds are referred to exclusively by IUPAC names, some are more frequently denoted by common names, as is indicated in Table 13.8.1.



Toluene

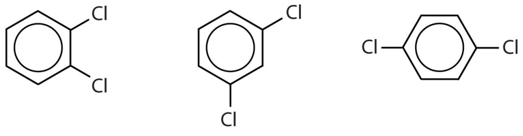


Phenol



Aniline

When there is more than one substituent, the corners of the hexagon are no longer equivalent, so we must designate the relative positions. There are three possible disubstituted benzenes, and we can use numbers to distinguish them (Figure 13.8.2). We start numbering at the carbon atom to which one of the groups is attached and count toward the carbon atom that bears the other substituent group by the shortest path.



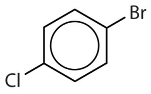
1,2-dichlorobenzene
o-dichlorobenzene

1,3-dichlorobenzene
m-dichlorobenzene

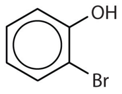
1,4-dichlorobenzene
p-dichlorobenzene

Figure 13.8.2: The Three Isomeric Dichlorobenzenes

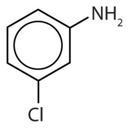
In Figure 13.8.2, common names are also used: the prefix *ortho* (*o*-) for 1,2-disubstitution, *meta* (*m*-) for 1,3-disubstitution, and *para* (*p*-) for 1,4-disubstitution. The substituent names are listed in alphabetical order. The first substituent is given the lowest number. When a common name is used, the carbon atom that bears the group responsible for the name is given the number 1:



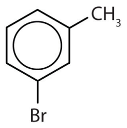
1-Bromo-4-chlorobenzene
p-Bromochlorobenzene



2-Bromophenol
o-Bromophenol



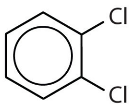
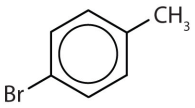
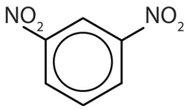
3-Chloroaniline
m-Chloroaniline



3-Bromotoluene
m-Bromotoluene

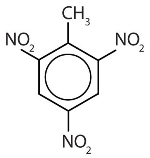
Example 13.8.2

Name each compound using both the common name and the IUPAC name.

1. 
2. 
3. 

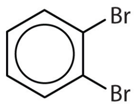
Solution

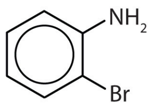
1. The benzene ring has two chlorine atoms (dichloro) in the first and second positions. The compound is *o*-dichlorobenzene or 1,2-dichlorobenzene.
2. The benzene ring has a methyl (CH_3) group. The compound is therefore named as a derivative of toluene. The bromine atom is on the fourth carbon atom, counting from the methyl group. The compound is *p*-bromotoluene or 4-bromotoluene.
3. The benzene ring has two nitro (NO_2) groups in the first and third positions. It is *m*-dinitrobenzene or 1,3-dinitrobenzene.
4. Note: The nitro (NO_2) group is a common substituent in aromatic compounds. Many nitro compounds are explosive, most notably 2,4,6-trinitrotoluene (TNT).

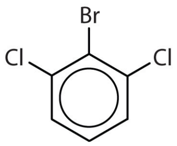


? Exercise 13.8.2

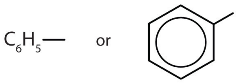
Name each compound using both the common name and the IUPAC name.

1. 

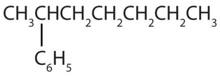
2. 

3. 

- Sometimes an aromatic group is found as a substituent bonded to a nonaromatic entity or to another aromatic ring. The group of atoms remaining when a hydrogen atom is removed from an aromatic compound is called an aryl group. The most common aryl group is derived from benzene (C_6H_6) by removing one hydrogen atom (C_6H_5) and is called a *phenyl* group, from *pheno*, an old name for benzene.



Phenyl group

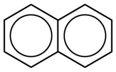


$$CH_3\underset{\displaystyle C_6H_5}{\underset{|}{C}}HCH_2CH_2CH_2CH_2CH_3$$

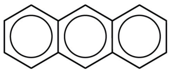
2-Phenylheptane

Polycyclic Aromatic Hydrocarbons

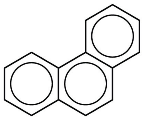
Some common aromatic hydrocarbons consist of fused benzene rings—rings that share a common side. These compounds are called polycyclic aromatic hydrocarbons (PAHs).



Naphthalene



Anthracene



Phenanthrene

The three examples shown here are colorless, crystalline solids generally obtained from coal tar. Naphthalene has a pungent odor and is used in mothballs. Anthracene is used in the manufacture of certain dyes. Steroids, a large group of naturally occurring substances, contain the phenanthrene structure.

To Your Health: Polycyclic Aromatic Hydrocarbons and Cancer

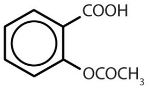
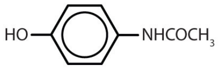
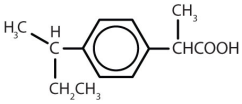
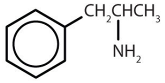
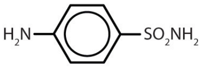
The intense heating required for distilling coal tar results in the formation of PAHs. For many years, it has been known that workers in coal-tar refineries are susceptible to a type of skin cancer known as tar cancer. Investigations have shown that a number of PAHs are carcinogens. One of the most active carcinogenic compounds, benzopyrene, occurs in coal tar and has also been isolated from cigarette smoke, automobile exhaust gases, and charcoal-broiled steaks. It is estimated that more than 1,000 t of benzopyrene are emitted into the air over the United States each year. Only a few milligrams of benzopyrene per kilogram of body weight are required to induce cancer in experimental animals.

Biologically Important Compounds with Benzene Rings

Substances containing the benzene ring are common in both animals and plants, although they are more abundant in the latter. Plants can synthesize the benzene ring from carbon dioxide, water, and inorganic materials. Animals cannot synthesize it, but they are dependent on certain aromatic compounds for survival and therefore must obtain them from food. Phenylalanine, tyrosine, and tryptophan (essential amino acids) and vitamins K, B_2 (riboflavin), and B_9 (folic acid) all contain the benzene ring. Many important drugs, a few of which are shown in Table 13.8.2, also feature a benzene ring.

> So far we have studied only aromatic compounds with carbon-containing rings. However, many cyclic compounds have an element other than carbon atoms in the ring. These compounds, called *heterocyclic compounds*, are discussed later. Some of these are heterocyclic aromatic compounds.

Table 13.8.2: Some Drugs That Contain a Benzene Ring

Name	Structure
aspirin	
acetaminophen	
ibuprofen	
amphetamine	
sulfanilamide	

Key Takeaway

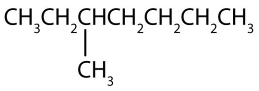
- Aromatic compounds contain a benzene ring or have certain benzene-like properties; for our purposes, you can recognize aromatic compounds by the presence of one or more benzene rings in their structure.

13.E: Unsaturated and Aromatic Hydrocarbons (Exercises)

13.1: Alkenes- Structures and Names

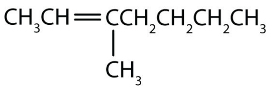
Concept Review Exercises

1. Briefly identify the important distinctions between a saturated hydrocarbon and an unsaturated hydrocarbon.
2. Briefly identify the important distinctions between an alkene and an alkane.
3. Classify each compound as saturated or unsaturated. Identify each as an alkane, an alkene, or an alkyne.

    a. 

    $CH_3CH_2\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_2CH_2CH_2CH_3$

    b. CH3CH2C≡CCH3

    c. 

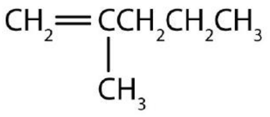
    $CH_3CH{=}\underset{\underset{\displaystyle CH_3}{|}}{C}CH_2CH_2CH_2CH_3$

Answers

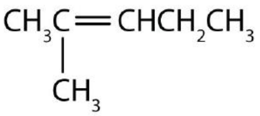
1. Unsaturated hydrocarbons have double or triple bonds and are quite reactive; saturated hydrocarbons have only single bonds and are rather unreactive.
2. An alkene has a double bond; an alkane has single bonds only.
3. a. saturated; alkane
    b. unsaturated; alkyne
    c. unsaturated; alkene

Exercises

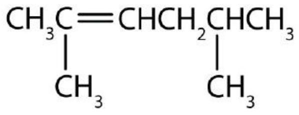
1. Draw the structure for each compound.
    a. 2-methyl-2-pentene
    b. 2,3-dimethyl-1-butene
    c. cyclohexene
2. Draw the structure for each compound.
    a. 5-methyl-1-hexene
    b. 3-ethyl-2-pentene
    c. 4-methyl-2-hexene
3. Name each compound according to the IUPAC system.

    a. 

    $CH_2{=}\underset{\underset{\displaystyle CH_3}{|}}{C}CH_2CH_2CH_3$

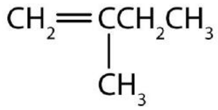
    b. 

    $CH_3\underset{\underset{\displaystyle CH_3}{|}}{C}{=}CHCH_2CH_3$

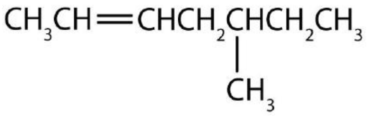
    c. 

    $CH_3\underset{\underset{\displaystyle CH_3}{|}}{C}{=}CHCH_2\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_3$

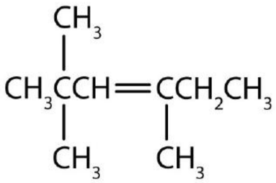
4. Name each compound according to the IUPAC system.

a. 

$CH_2{=}\underset{\underset{CH_3}{|}}{C}CH_2CH_3$

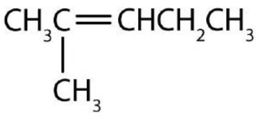
b. 

$CH_3CH{=}CHCH_2\underset{\underset{CH_3}{|}}{C}HCH_2CH_3$

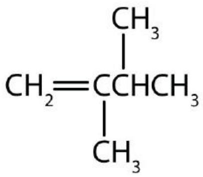
c. 

$CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}CH{=}\underset{\underset{CH_3}{|}}{C}CH_2CH_3$

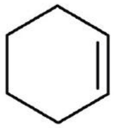
Answers

1. a. 

$CH_3\underset{\underset{CH_3}{|}}{C}{=}CHCH_2CH_3$

   b. 

$CH_2{=}\underset{\underset{CH_3}{|}}{C}\overset{\overset{CH_3}{|}}{C}HCH_3$

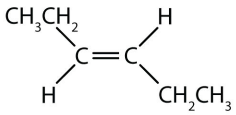
   c. 

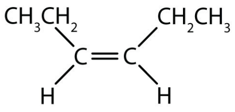
3. a. 2-methyl-1-pentene
   b. 2-methyl-2-pentene
   c. 2,5-dimethyl-2-hexene

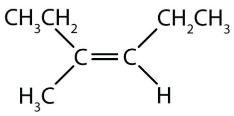
13.2: Cis-Trans Isomers (Geometric Isomers)

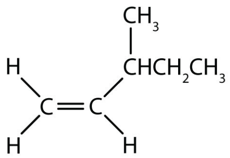
Concept Review Exercises

1. What are cis-trans (geometric) isomers? What two types of compounds can exhibit cis-trans isomerism?
2. Classify each compound as a cis isomer, a trans isomer, or neither.

a. 

b. 

c. 

d. 

Answers

1. Cis-trans isomers are compounds that have different configurations (groups permanently in different places in space) because of the presence of a rigid structure in their molecule. Alkenes and cyclic compounds can exhibit cis-trans isomerism.
2. a. trans (the two hydrogen atoms are on opposite sides)
   b. cis (the two hydrogen atoms are on the same side, as are the two ethyl groups)
   c. cis (the two ethyl groups are on the same side)
   d. neither (flipping the bond does not change the molecule. There are no isomers for this molecule)

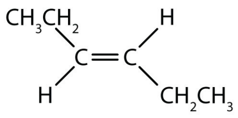
Exercises

1. Draw the structures of the cis-trans isomers for each compound. Label them cis and trans. If no cis-trans isomers exist, write none.
   a. 2-bromo-2-pentene
   b. 3-hexene
   c. 4-methyl-2-pentene
   d. 1,1-dibromo-1-butene
   e. 2-butenoic acid ($CH_3CH=CHCOOH$)
2. Draw the structures of the cis-trans isomers for each compound. Label them cis and trans. If no cis-trans isomers exist, write none.
   a. 2,3-dimethyl-2-pentene
   b. 1,1-dimethyl-2-ethylcyclopropane
   c. 1,2-dimethylcyclohexane
   d. 5-methyl-2-hexene
   e. 1,2,3-trimethylcyclopropane

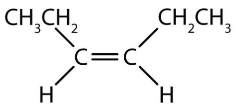
Answer

1. a: none. There are two distinct geometric isomers, but since there are there are four different groups off the double bond, these are both cis/trans isomers (they are technically E/Z isomers discussed elsewhere).

b:



cis



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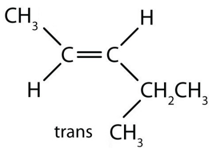

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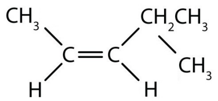

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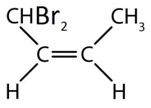
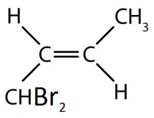


cis



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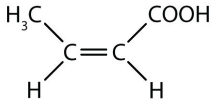
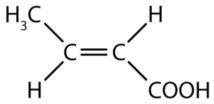
e:



cis



trans

13.3: Physical Properties of Alkenes

Concept Review Exercises

1. Briefly describe the physical properties of alkenes. How do these properties compare to those of the alkanes?
2. Without consulting tables, arrange the following alkenes in order of increasing boiling point: 1-butene, ethene, 1-hexene, and propene.

Answers

1. Alkenes have physical properties (low boiling points, insoluble in water) quite similar to those of their corresponding alkanes.
2. ethene < propene < 1-butene < 1-hexene

Exercises

1. Without referring to a table or other reference, predict which member of each pair has the higher boiling point.
   a. 1-pentene or 1-butene
   b. 3-heptene or 3-nonene
2. Which is a good solvent for cyclohexene, pentane or water?

Answer

1. a. 1-pentene
   b. 3-nonene

13.4: Chemical Properties of Alkenes

Concept Review Exercises

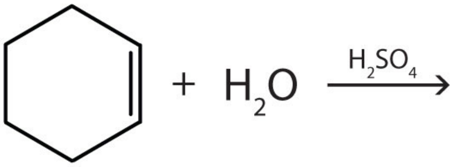
1. What is the principal difference in properties between alkenes and alkanes? How are they alike?
2. If $C_{12}H_{24}$ reacts with HBr in an addition reaction, what is the molecular formula of the product?

Answers

1. Alkenes undergo addition reactions; alkanes do not. Both burn.
2. $C_{12}H_{24}Br_2$

Exercises

1. Complete each equation.
   a. $(CH_3)\ _2C{=}CH_2 + Br_2 \rightarrow$
   b. $CH_2{=}C(CH_3)CH_2CH_3 + H_2 \xrightarrow{Ni}$

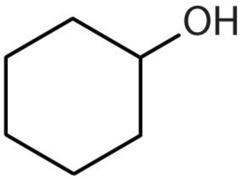


   c.
2. Complete each equation.
   a. $CH_2{=}CHCH{=}CH_2 + 2H_2 \xrightarrow{Ni}$

b. $(CH_3)_2C{=}C(CH_3)_2 + H_2O \xrightarrow{H_2SO_4}$

c. 

Answer

1. a. $(CH_3)_2CBrCH_2Br$
   b. $CH_3CH(CH_3)CH_2CH_3$
   c. 

13.5: Polymers

Concept Review Exercises

1. What is a monomer? What is a polymer? How do polymer molecules differ from the molecules we have discussed in earlier sections of this chapter?
2. What is addition polymerization? What structural feature usually characterizes molecules used as monomers in addition polymerization?
3. What is the molecular formula of a polymer molecule formed by the addition polymerization of 175 molecules of vinyl chloride ($CH_2{=}CHCl$)?

Answers

1. Monomers are small molecules that can be assembled into giant molecules referred to as polymers, which are much larger than the molecules we discussed earlier in this chapter.
2. In addition polymerization, the monomers add to one another in such a way that the polymer contains all the atoms of the starting monomers.
3. $C_{350}H_{525}Cl_{175}$

Exercises

1. Write the condensed structural formula of the monomer from which Saran is formed. A segment of the Saran molecule has the following structure: $CH_2CCl_2CH_2CCl_2CH_2CCl_2CH_2CCl_2$.
2. Write the condensed structural formula for the section of a molecule formed from four units of the monomer $CH_2{=}CHF$.

Answer

1. $H_2C{=}CCl_2$

13.6: Alkynes

Concept Review Exercises

1. Briefly identify the important differences between an alkene and an alkyne. How are they similar?
2. The alkene $(CH_3)_2CHCH_2CH{=}CH_2$ is named 4-methyl-1-pentene. What is the name of $(CH_3)_2CHCH_2C{\equiv}CH$?
3. Do alkynes show cis-trans isomerism? Explain.

Answers

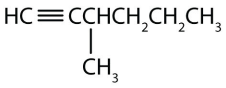
1. Alkenes have double bonds; alkynes have triple bonds. Both undergo addition reactions.
2. 4-methyl-1-pentyne

3. No; a triply bonded carbon atom can form only one other bond. It would have to have two groups attached to show cis-trans isomerism.

Exercises

1. Draw the structure for each compound.
    a. acetylene
    b. 3-methyl-1-hexyne
2. Draw the structure for each compound.
    a. 4-methyl-2-hexyne
    b. 3-octyne
3. Name each alkyne.
    a. $CH_3CH_2CH_2C{\equiv}CH$
    b. $CH_3CH_2CH_2C{\equiv}CCH_3$

Answers

1. a. H–C≡C–H
    b. 

$HC{\equiv}C\underset{\substack{|\\ CH_3}}{C}HCH_2CH_2CH_3$

3. a. 1-pentyne
    b. 2-hexyne

13.7: Aromatic Compounds- Benzene

Concept Review Exercises

1. How do the typical reactions of benzene differ from those of the alkenes?
2. Briefly describe the bonding in benzene.
3. What does the circle mean in the chemist’s representation of benzene?

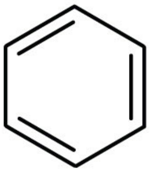
Answers

1. Benzene is rather unreactive toward addition reactions compared to an alkene.
2. Valence electrons are shared equally by all six carbon atoms (that is, the electrons are delocalized).
3. The six electrons are shared equally by all six carbon atoms.

Exercises

1. Draw the structure of benzene as if it had alternate single and double bonds.
2. Draw the structure of benzene as chemists usually represent it today.

Answer

1. 

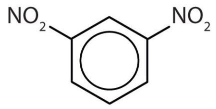
13.8: Structure and Nomenclature of Aromatic Compounds

Concept Review Exercises

1. Briefly identify the important characteristics of an aromatic compound.
2. What is meant by the prefixes *meta*, *ortho*, or *para*? Give the name and draw the structure for a compound that illustrates each.
3. What is a phenyl group? Give the structure for 3-phenyloctane.

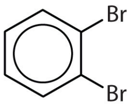
Answers

1. An aromatic compound is any compound that contains a benzene ring or has certain benzene-like properties.
2. meta = 1,3 disubstitution; (answers will vary)



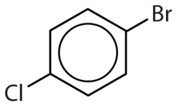
m-dinitrobenzene or 1,3-dinitrobenzene

ortho = 1,2 disubstitution



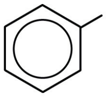
o-dibromobenzene or 1,2-dibromobenzene

para = 1,4 disubstitution or 1-bromo-4-chlorobenzene

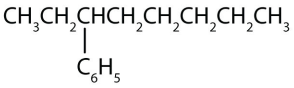


p-bromochlorobenzene or 1-bromo-2-chlorobenzene

3. phenyl group: C_6H_5 or



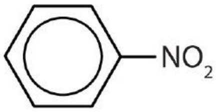
3-phenyloctane:

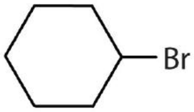


$$\mathrm{CH_3CH_2\underset{\underset{C_6H_5}{|}}{CH}CH_2CH_2CH_2CH_2CH_3}$$

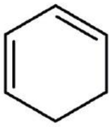
Exercises

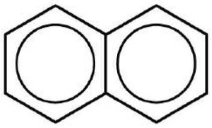
1. Is each compound aromatic?

a. 

b. 

2. Is each compound aromatic?

   a. 

   b. 

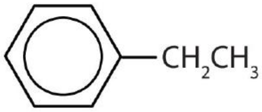
3. Draw the structure for each compound.

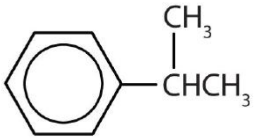
   a. toluene
   b. *m*-diethylbenzene
   c. 3,5-dinitrotoluene

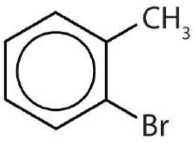
4. Draw the structure for each compound.

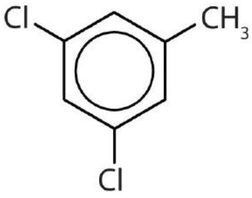
   a. *p*-dichlorobenzene
   b. naphthalene
   c. 1,2,4-trimethylbenzene

5. Name each compound with its IUPAC name.

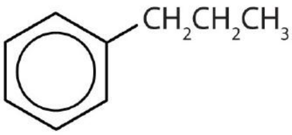
   a. 

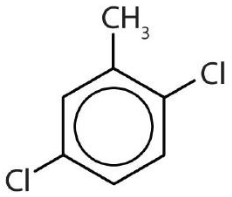
   b. 

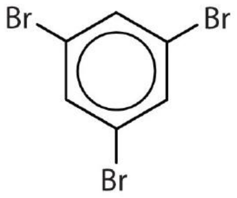
   c. 

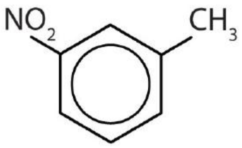
   d. 

6. Name each compound with its IUPAC name.

   a. 

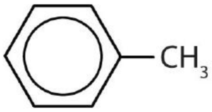
b. 

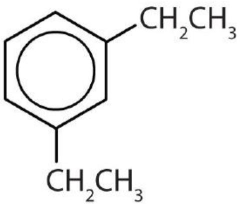
c. 

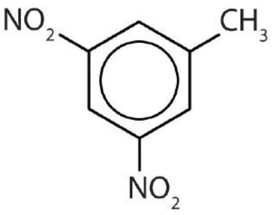
d. 

Answers

1. a. yes
   b. no

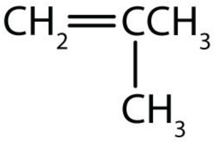
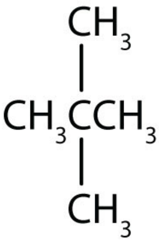
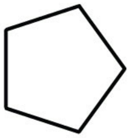
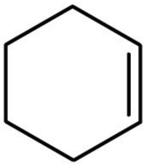
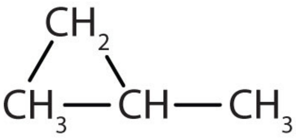
3. a. 

   b. 

   c. 

5. a. ethylbenzene
   b. isopropylbenzene
   c. *o*-bromotoluene
   d. 3,5-dichlorotoluene

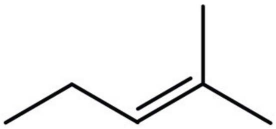
Additional Exercises

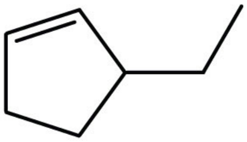
1. Classify each compound as saturated or unsaturated.
    a. 
    $CH_2{=}C(CH_3)CH_3$
    b. $CH_3C{\equiv}CCH_3$
2. Classify each compound as saturated or unsaturated.
    a. 
    $CH_3C(CH_3)_2CH_3$
    b. 
3. Give the molecular formula for each compound.
    a. 
    b. 
4. When three isomeric pentenes—X, Y, and Z—are hydrogenated, all three form 2-methylbutane. The addition of Cl_2 to Y gives 1,2-dichloro-3-methylbutane, and the addition of Cl_2 to Z gives 1,2-dichloro-2-methylbutane. Draw the original structures for X, Y, and Z.
5. Pentane and 1-pentene are both colorless, low-boiling liquids. Describe a simple test that distinguishes the two compounds. Indicate what you would observe.
6. Draw and name all the alkene cis-trans isomers corresponding to the molecular formula C_5H_{10}. (Hint: there are only two.)

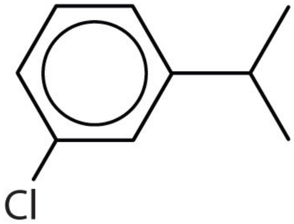
7. The complete combustion of benzene forms carbon dioxide and water:

   $C_6H_6 + O_2 \rightarrow CO_2 + H_2O$

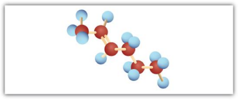
   Balance the equation. What mass, in grams, of carbon dioxide is formed by the complete combustion of 39.0 g of benzene?
8. Describe a physiological effect of some PAHs.
9. What are some of the hazards associated with the use of benzene?
10. What is wrong with each name? Draw the structure and give the correct name for each compound.
    a. 2-methyl-4-heptene
    b. 2-ethyl-2-hexene
    c. 2,2-dimethyl-3-pentene
11. What is wrong with each name?
    a. 2-bromobenzene
    b. 3,3-dichlorotoluene
    c. 1,4-dimethylnitrobenzene
12. Following are line-angle formulas for three compounds. Draw the structure and give the name for each.

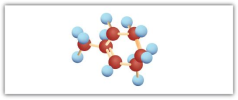
a. 

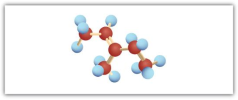
b. 

c. 

13. Following are ball-and-stick molecular models for three compounds (blue balls represent H atoms; red balls are C atoms). Write the condensed structural formula and give the name for each.

a. 

b. 

c. 

Answers

1.

   a. unsaturated
   b. unsaturated

3.

   a. C_6H_{10}
   b. C_4H_8

5. Add bromine solution (reddish-brown) to each. Pentane will not react, and the reddish-brown color persists; 1-pentene will react, leaving a colorless solution.

7. $2C_6H_6 + 15O_2 \rightarrow 12CO_2 + 6H_2O$; 132 g

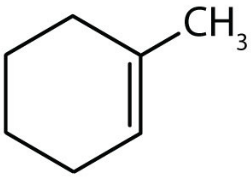
9. carcinogenic, flammable

11.

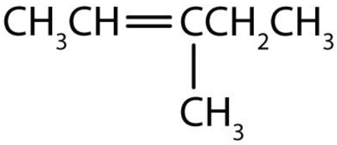
   a. number not needed
   b. can’t have two groups on one carbon atom on a benzene ring
   c. can’t have a substituent on the same carbon atom as the nitro group

13.

   a. $CH_3CH{=}CHCH_2CH_2CH_3$; 2-hexene
   b.



   c.



$$CH_3CH{=}\underset{\displaystyle CH_3}{\underset{|}{C}}CH_2CH_3$$

13.S: Unsaturated and Aromatic Hydrocarbons (Summary)

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

Any hydrocarbon containing either a double or triple bond is an **unsaturated hydrocarbon**. **Alkenes** have a carbon-to-carbon double bond. The general formula for alkenes with one double bond is C_nH_{2n}. Alkenes can be straight chain, branched chain, or cyclic. Simple alkenes often have common names, but all alkenes can be named by the system of the International Union of Pure and Applied Chemistry.

Cis-trans isomers (or geometric isomers) are characterized by molecules that differ only in their configuration around a rigid part of the structure, such as a carbon–to-carbon double bond or a ring. The molecule having two identical (or closely related) atoms or groups on the same side is the **cis isomer**; the one having the two groups on opposite sides is the **trans isomer**.

The physical properties of alkenes are quite similar to those of alkanes. Like other hydrocarbons, alkenes are insoluble in water but soluble in organic solvents.

More reactive than alkanes, alkenes undergo **addition reactions** across the double bond:

- Addition of hydrogen (**hydrogenation**):

$$CH_2{=}CH_2 + H_2 \rightarrow CH_3CH_3$$

- Addition of halogen (**halogenation**):

$$CH_2{=}CH_2 + X_2 \rightarrow XCH_2CH_2X$$

where X = F, Cl, Br, or I.

- Addition of water (**hydration**):

$$CH_2{=}CH_2 + HOH \rightarrow HCH_2CH_2OH$$

Alkenes also undergo **addition polymerization**, molecules joining together to form long-chain molecules.

$$\ldots CH_2{=}CH_2 + CH_2{=}CH_2 + CH_2{=}CH_2 + \ldots \rightarrow \ldots CH_2CH_2–CH_2CH_2–CH_2CH_2– \ldots$$

The reactant units are **monomers**, and the product is a **polymer**.

Alkynes have a carbon-to-carbon triple bond. The general formula for alkynes is C_nH_{2n-2}. The properties of alkynes are quite similar to those of alkenes. They are named much like alkenes but with the ending *-yne*.

The cyclic hydrocarbon *benzene* (C_6H_6) has a ring of carbon atoms. The molecule seems to be unsaturated, but it does not undergo the typical reactions expected of alkenes. The electrons that might be fixed in three double bonds are instead *delocalized* over all six carbon atoms.

A hydrocarbon containing one or more benzene rings (or other similarly stable electron arrangements) is an **aromatic hydrocarbon**, and any related substance is an **aromatic compound**. One or more of the hydrogen atoms on a benzene ring can be replaced by other atoms. When two hydrogen atoms are replaced, the product name is based on the relative position of the replacement atoms (or atom groups). A 1,2-disubstituted benzene is designated as an *ortho* (*o*-) isomer; 1,3-, a *meta* (*m*-) isomer; and 1,4-, a *para* (*p*-) isomer. An aromatic group as a substituent is called an **aryl** group.

A **polycyclic aromatic hydrocarbon (PAH)** has fused benzene rings sharing a common side.

CHAPTER OVERVIEW

14: Organic Compounds of Oxygen

Ethanol and resveratrol, a phenol, are representatives of two of the families of oxygen-containing compounds that we consider in this chapter. Two other classes, aldehydes and ketones, are formed by the oxidation of alcohols. Ethers, another class, are made by the dehydration of alcohols.

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14.0: Prelude to Organic Compounds of Oxygen

One of the more familiar chemical compounds on Earth is ethyl alcohol (ethanol). As the intoxicant in alcoholic beverages, ethanol is often simply called alcohol. If ethanol is diluted, as it is in wine, beer, or mixed drinks with about 1 oz of liquor, and if it is consumed in small quantities, it is relatively safe. In excess—four or more drinks in a few hours—it causes intoxication, which is characterized by a loss of coordination, nausea and vomiting, and memory blackouts.

Excessive ingestion of ethanol over a long period of time leads to cirrhosis of the liver, alteration of brain cell function, nerve damage, and strong physiological addiction. Alcoholism—an addiction to ethanol—is the most serious drug problem in the United States. Heavy drinking shortens a person's life span by contributing to diseases of the liver, the cardiovascular system, and virtually every other organ of the body.

In small quantities—one or two drinks a day—ethanol might promote health. In addition to the possible benefits of modest amounts of ethanol, a chemical in red wines, resveratrol, is thought to lower the risk of heart disease. Resveratrol, found in red grapes, is an antioxidant. It inhibits the oxidation of cholesterol and subsequent clogging of the arteries. One need not drink wine to get the benefits of resveratrol, however. It can be obtained by eating the grapes or drinking red grape juice.

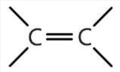
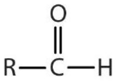
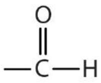
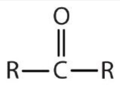
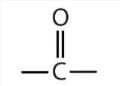
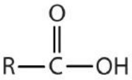
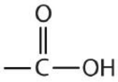
14.1: Organic Compounds with Functional Groups

Learning Objectives

- to describe functional groups and explain why they are useful in the study of organic chemistry.

Previously, we considered several kinds of hydrocarbons. Now we examine some of the many organic compounds that contain functional groups. We first introduced the idea of the functional group, a specific structural arrangement of atoms or bonds that imparts a characteristic chemical reactivity to the molecule. If you understand the behavior of a particular functional group, you will know a great deal about the general properties of that class of compounds. In this chapter, we make a brief yet systematic study of some of organic compound families. Each family is based on a common, simple functional group that contains an oxygen atom or a nitrogen atom. Some common functional groups are listed in Table 14.1.1.

Table 14.1.1: Selected Organic Functional Groups

Name of Family	General Formula	Functional Group	Suffix*
alkane	RH	none	*-ane*
alkene	$R_2C{=}CR_2$		*-ene*
alkyne	RC≡CR	–C≡C–	*-yne*
alcohol	ROH	–OH	*-ol*
thiol	RSH	–SH	*-thiol*
ether	ROR	–O–	ether
aldehyde	 $R-\overset{\overset{O}{\|}}{C}-H$	 $-\overset{\overset{O}{\|}}{C}-H$	*-al*
ketone	 $R-\overset{\overset{O}{\|}}{C}-R$	 $-\overset{\overset{O}{\|}}{C}-$	*-one*
carboxylic acid	 $R-\overset{\overset{O}{\|}}{C}-OH$	 $-\overset{\overset{O}{\|}}{C}-OH$	*-oic acid*

*Ethers do not have a suffix in their common name; all ethers end with the word *ether*.

Summary

The functional group, a structural arrangement of atoms and/or bonds, is largely responsible for the properties of organic compound families.

14.2: Alcohols - Nomenclature and Classification

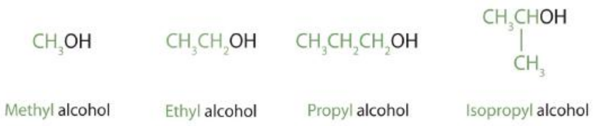
Learning Objectives

- Identify the general structure for an alcohol.
- Identify the structural feature that classifies alcohols as primary, secondary, or tertiary.
- Name alcohols with both common names and IUPAC names

An alcohol is an organic compound with a hydroxyl (OH) functional group on an aliphatic carbon atom. Because OH is the functional group of all alcohols, we often represent alcohols by the general formula ROH, where R is an alkyl group. Alcohols are common in nature. Most people are familiar with ethyl alcohol (ethanol), the active ingredient in alcoholic beverages, but this compound is only one of a family of organic compounds known as alcohols. The family also includes such familiar substances as cholesterol and the carbohydrates. Methanol (CH_3OH) and ethanol (CH_3CH_2OH) are the first two members of the homologous series of alcohols.

Nomenclature of Alcohols

Alcohols with one to four carbon atoms are frequently called by common names, in which the name of the alkyl group is followed by the word *alcohol*:



Structural formula of methyl alcohol, ethyl alcohol, propyl alcohol, and isopropyl alcohol with the methyl, ethyl propyl, and isopropyl groups highlighted in green.

According to the International Union of Pure and Applied Chemistry (IUPAC), alcohols are named by changing the ending of the parent alkane name to *-ol*. Here are some basic IUPAC rules for naming alcohols:

1. The longest continuous chain (LCC) of carbon atoms containing the OH group is taken as the parent compound—an alkane with the same number of carbon atoms. The chain is numbered from the end nearest the OH group.
2. The number that indicates the position of the OH group is prefixed to the name of the parent hydrocarbon, and the *-e* ending of the parent alkane is replaced by the suffix *-ol*. (In cyclic alcohols, the carbon atom bearing the OH group is designated C1, but the 1 is not used in the name.) Substituents are named and numbered as in alkanes.
3. If more than one OH group appears in the same molecule (polyhydroxy alcohols), suffixes such as *-diol* and *-triol* are used. In these cases, the *-e* ending of the parent alkane is retained.

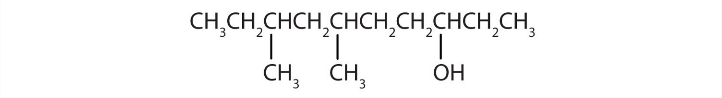
Figure 14.2.1 shows some examples of the application of these rules.

Structures of 2 methylbutan-2-ol, 3 5-dimethylhexan-1-ol, 6 methylheptan-3-ol, 2 bromo 5 chlorocyclopentanol are shown to highlight rules 1 and 2. 1 2 ethanediol and propane 1 2 3 triol are shown to highlight rule 3
Figure 14.2.1: IUPAC Rules for Alcohols. The names and structures of some alcohols demonstrate the use of IUPAC rules.

Example 14.2.1

Give the IUPAC name for each compound.

a.



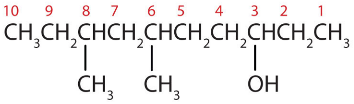
$$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CH_3$$

From left to right, there are ten carbon on the alkane straight chain with methyl groups emerging from carbon 3 and 5 and a hydroxyl group on carbon 8.

- $HOCH_2CH_2CH_2CH_2CH_2OH$

Solution

a. Ten carbon atoms in the LCC makes the compound a derivative of decane (rule 1), and the OH on the third carbon atom makes it a 3-decanol (rule 2).



$CH_3CH_2\underset{CH_3}{CH}CH_2\underset{CH_3}{CH}CH_2CH_2\underset{OH}{CH}CH_2CH_3$

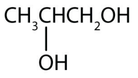
The carbon atoms are numbered from the end closest to the OH group. That fixes the two methyl (CH_3) groups at the sixth and eighth positions. The name is 6,8-dimethyl-3-decanol (not 3,5-dimethyl-8-decanol).

b. Five carbon atoms in the LCC make the compound a derivative of pentane. Two OH groups on the first and fifth carbon atoms make the compound a diol and give the name 1,5-pentanediol (rule 3).

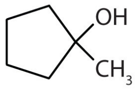
$$HO\overset{1}{C}H_2\overset{2}{C}H_2\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_2OH$$

Exercise 14.2.1

Give the IUPAC name for each compound.

a. 

$CH_3\underset{OH}{CH}CH_2OH$

- 

Example 14.2.2

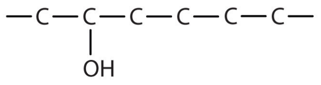
Draw the structure for each compound.

a. 2-hexanol
b. 3-methyl-2-pentanol

Solution

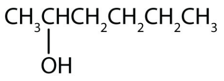
a. The ending *-ol* indicates an alcohol (the OH functional group), and the *hex-* stem tells us that there are six carbon atoms in the LCC. We start by drawing a chain of six carbon atoms: –C–C–C–C–C–C–.

The 2 indicates that the OH group is attached to the second carbon atom.



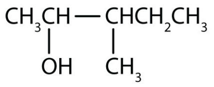
$—C—\underset{OH}{C}—C—C—C—C—$

Finally, we add enough hydrogen atoms to give each carbon atom four bonds.



$CH_3\underset{OH}{CH}CH_2CH_2CH_2CH_3$

- The numbers indicate that there is a methyl (CH_3) group on the third carbon atom and an OH group on the second carbon atom.



$CH_3\underset{OH}{CH}—\underset{CH_3}{CH}CH_2CH_3$

Exercise 14.2.2

Draw the structure for each compound.

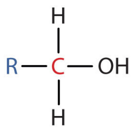
a. 3-heptanol

- 2-methyl-3-hexanol

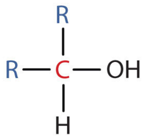
Classification of Alcohols

Some of the properties of alcohols depend on the number of carbon atoms attached to the specific carbon atom that is attached to the OH group. Alcohols can be grouped into three classes on this basis.

- A primary (1°) alcohol is one in which the carbon atom (in red) with the OH group is attached to *one* other carbon atom (in blue). Its general formula is RCH_2OH.



- A secondary (2°) alcohol is one in which the carbon atom (in red) with the OH group is attached to *two* other carbon atoms (in blue). Its general formula is R_2CHOH.



- A tertiary (3°) alcohol is one in which the carbon atom (in red) with the OH group is attached to *three* other carbon atoms (in blue). Its general formula is R_3COH.

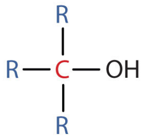
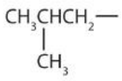
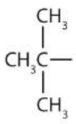


Table 14.2.1 names and classifies some of the simpler alcohols. Some of the common names reflect a compound's classification as secondary (*sec*-) or tertiary (*tert*-). These designations are not used in the IUPAC nomenclature system for alcohols. Note that there are four butyl alcohols in the table, corresponding to the four butyl groups: the butyl group ($CH_3CH_2CH_2CH_2$) discussed before, and three others:



Isobutyl group

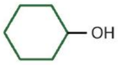
Sec-butyl group



Tert-butyl group

Table 14.2.1: Classification and Nomenclature of Some Alcohols

Condensed Structural Formula	Class of Alcohol	Common Name	IUPAC Name
CH_3OH	—	methyl alcohol	methanol
CH_3CH_2OH	primary	ethyl alcohol	ethanol
$CH_3CH_2CH_2OH$	primary	propyl alcohol	1-propanol
$(CH_3)_2CHOH$	secondary	isopropyl alcohol	2-propanol
$CH_3CH_2CH_2CH_2OH$	primary	butyl alcohol	1-butanol

Condensed Structural Formula	Class of Alcohol	Common Name	IUPAC Name
$CH_3CH_2CHOHCH_3$	secondary	*sec*-butyl alcohol	2-butanol
$(CH_3)_2CHCH_2OH$	primary	isobutyl alcohol	2-methyl-1-propanol
$(CH_3)_3COH$	tertiary	*tert*-butyl alcohol	2-methyl-2-propanol
	secondary	cyclohexyl alcohol	cyclohexanol

Summary

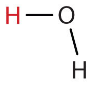
In the IUPAC system, alcohols are named by changing the ending of the parent alkane name to *-ol*. Alcohols are classified according to the number of carbon atoms attached to the carbon atom that is attached to the OH group.

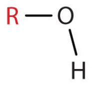
14.3: Physical Properties of Alcohols

Learning Objectives

- Explain why the boiling points of alcohols are higher than those of ethers and alkanes of similar molar masses.
- Explain why alcohols and ethers of four or fewer carbon atoms are soluble in water while comparable alkanes are not soluble.

Alcohols can be considered derivatives of water (H_2O; also written as HOH).





Like the H–O–H bond in water, the R–O–H bond is bent, and alcohol molecules are polar. This relationship is particularly apparent in small molecules and reflected in the physical and chemical properties of alcohols with low molar mass. Replacing a hydrogen atom from an alkane with an OH group allows the molecules to associate through hydrogen bonding (Figure 14.3.1).

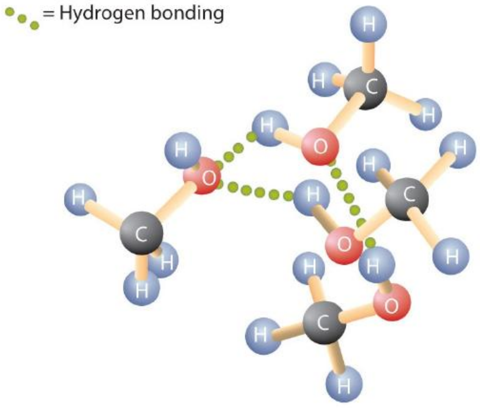


Figure 14.3.1: Intermolecular Hydrogen Bonding in Methanol. The OH groups of alcohol molecules make hydrogen bonding possible.

Recall that physical properties are determined to a large extent by the type of intermolecular forces. Table 14.3.1 lists the molar masses and the boiling points of some common compounds. The table shows that substances with similar molar masses can have quite different boiling points.

Table 14.3.1: Comparison of Boiling Points and Molar Masses

Formula	Name	Molar Mass	Boiling Point (°C)
CH_4	methane	16	–164
HOH	water	18	100
C_2H_6	ethane	30	–89
CH_3OH	methanol	32	65
C_3H_8	propane	44	–42
CH_3CH_2OH	ethanol	46	78
C_4H_{10}	butane	58	–1
$CH_3CH_2CH_2OH$	1-propanol	60	97

Alkanes are nonpolar and are thus associated only through relatively weak dispersion forces. Alkanes with one to four carbon atoms are gases at room temperature. In contrast, even methanol (with one carbon atom) is a liquid at room temperature. Hydrogen bonding greatly increases the boiling points of alcohols compared to hydrocarbons of comparable molar mass. The boiling point is a rough measure of the amount of energy necessary to separate a liquid molecule from its nearest neighbors. If the molecules interact through hydrogen bonding, a relatively large quantity of energy must be supplied to break those intermolecular attractions. Only then can the molecule escape from the liquid into the gaseous state.

Alcohols can also engage in hydrogen bonding with water molecules (Figure 14.3.2). Thus, whereas the hydrocarbons are insoluble in water, alcohols with one to three carbon atoms are completely soluble. As the length of the chain increases, however, the solubility of alcohols in water decreases; the molecules become more like hydrocarbons and less like water. The alcohol 1-decanol ($CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2OH$) is essentially insoluble in water. We frequently find that the borderline of solubility in a family of organic compounds occurs at four or five carbon atoms.

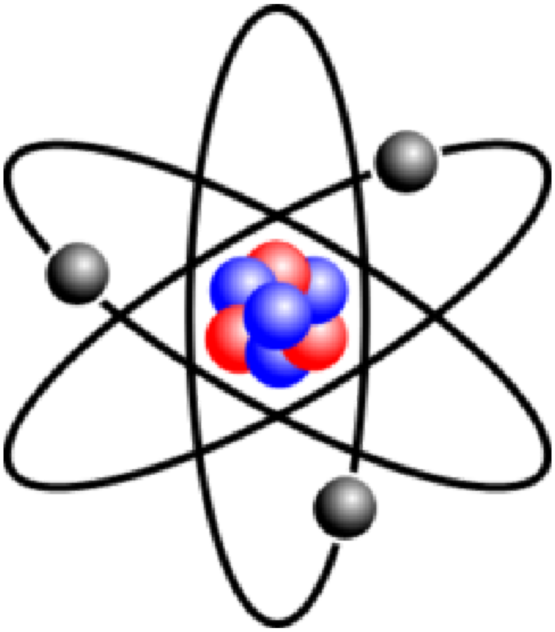


Figure 14.3.2: Hydrogen Bonding between Methanol Molecules and Water Molecules. Hydrogen bonding between the OH of methanol and water molecules accounts for the solubility of methanol in water.

Summary

Alcohols have higher boiling points than do ethers and alkanes of similar molar masses because the OH group allows alcohol molecules to engage in hydrogen bonding. Alcohols of four or fewer carbon atoms are soluble in water because the alcohol molecules engage in hydrogen bonding with water molecules; comparable alkane molecules cannot engage in hydrogen bonding.

14.4: Reactions that Form Alcohols

Learning Objectives

- To describe how to prepare alcohols from alkenes

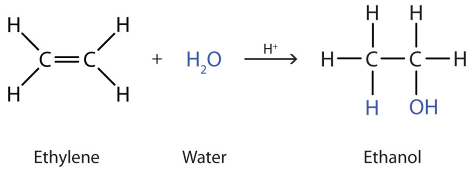
Methanol is prepared by combining hydrogen gas and carbon monoxide at high temperatures and pressures in the presence of a catalyst composed of zinc oxide (ZnO) and chromium oxide (Cr_2O_3) catalyst:

$$2H_2 + CO \xrightarrow[\text{ZnO, } Cr_2O_3]{200\text{ atm, } 350^\circ C} CH_3OH$$

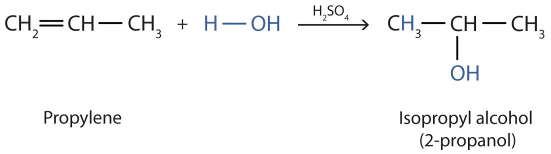
Methanol is an important solvent and is used as an automotive fuel, either as the pure liquid—as in some racing cars—or as an additive in gasoline.

> *Nearly 2 billion gallons of methanol are produced each year in the United States by the catalytic reduction of carbon monoxide with hydrogen gas.*

Many simple alcohols are made by the hydration of alkenes. Ethanol is made by the hydration of ethylene in the presence of a catalyst such as sulfuric acid (H_2SO_4).



In a similar manner, isopropyl alcohol is produced by the addition of water to propene (propylene).



$$CH_2{=}CH{-}CH_3 + H{-}OH \xrightarrow{H_2SO_4} CH_3{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_3$$

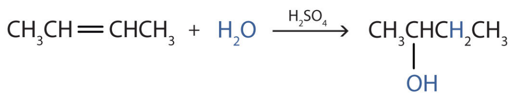
Additional Exercise 14.4.1 describes how to use a generalization called Markovnikov’s rule to predict the results when the addition of water to an alcohol has two possible products.

Example 14.4.1

Write the equation for the reaction of 2-butene with water to form 2-butanol. Indicate that sulfuric acid is used as a catalyst.

Solution

First write the condensed structural formula of 2-butene and indicate that it reacts with water. Then write the condensed structural formula of 2-butanol after the reaction arrow to indicate that it is the product. Finally, write the formula for the catalyst above the arrow.



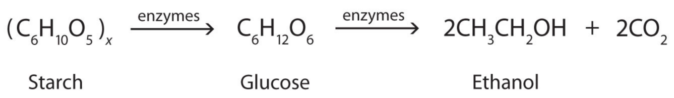
$$CH_3CH{=}CHCH_3 + H_2O \xrightarrow{H_2SO_4} CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CH_3$$

Exercise 14.4.1

Write the equation for the reaction of cyclopentene with water to form cyclopentanol. Indicate that phosphoric acid (H_3PO_4) is used as a catalyst.

> *Many OH compounds in living systems are formed by alkene hydration. Here is an example that occurs in the Krebs cycle: fumarate is hydrated to form malate.*
>
> $$^{-}OOCCH{=}CHCOO^{-} + HOH \xrightleftharpoons{\text{enzyme}} {}^{-}OOCCH_2CHOHCOO^{-}$$

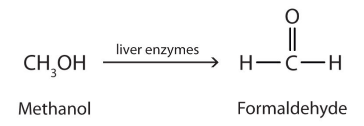
In addition to its preparation from ethylene, ethanol is made by the fermentation of sugars or starch from various sources (potatoes, corn, wheat, rice, etc.). Fermentation is catalyzed by enzymes found in yeast and proceeds by an elaborate multistep mechanism. We can represent the overall process as follows:



$$\underset{\text{Starch}}{(C_6H_{10}O_5)_x} \xrightarrow{\text{enzymes}} \underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{enzymes}} \underset{\text{Ethanol}}{2CH_3CH_2OH} + 2CO_2$$

To Your Health: The Physiological Effects of Alcohols

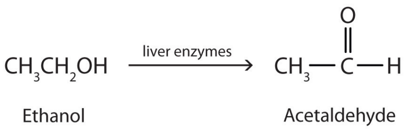
Methanol is quite poisonous to humans. Ingestion of as little as 15 mL of methanol can cause blindness, and 30 mL (1 oz) can cause death. However, the usual fatal dose is 100 to 150 mL. The main reason for methanol's toxicity is that we have liver enzymes that catalyze its oxidation to formaldehyde, the simplest member of the aldehyde family:



Formaldehyde reacts rapidly with the components of cells, coagulating proteins in much the same way that cooking coagulates an egg. This property of formaldehyde accounts for much of the toxicity of methanol.

Organic and biochemical equations are frequently written showing only the organic reactants and products. In this way, we focus attention on the organic starting material and product, rather than on balancing complicated equations.

Ethanol is oxidized in the liver to acetaldehyde:



The acetaldehyde is in turn oxidized to acetic acid ($HC_2H_3O_2$), a normal constituent of cells, which is then oxidized to carbon dioxide and water. Even so, ethanol is potentially toxic to humans. The rapid ingestion of 1 pt (about 500 mL) of pure ethanol would kill most people, and acute ethanol poisoning kills several hundred people each year—often those engaged in some sort of drinking contest. Ethanol freely crosses into the brain, where it depresses the respiratory control center, resulting in failure of the respiratory muscles in the lungs and hence suffocation. Ethanol is believed to act on nerve cell membranes, causing a diminution in speech, thought, cognition, and judgment.

Rubbing alcohol is usually a 70% aqueous solution of isopropyl alcohol. It has a high vapor pressure, and its rapid evaporation from the skin produces a cooling effect. It is toxic when ingested but, compared to methanol, is less readily absorbed through the skin.

Summary

Many alcohols are made by the hydration of alkenes. Ethanol can be made by the fermentation of sugars or starch from various sources.

14.5: Reactions of Alcohols

Learning Objectives

1. Give two major types of reactions of alcohols.
2. Describe the result of the oxidation of a primary alcohol.
3. Describe the result of the oxidation of a secondary alcohol.

Chemical reactions in alcohols occur mainly at the functional group, but some involve hydrogen atoms attached to the OH-bearing carbon atom or to an adjacent carbon atom. Of the three major kinds of alcohol reactions, which are summarized in Figure 14.5.1, two—dehydration and oxidation—are considered here. The third reaction type—esterification—is covered elsewhere.

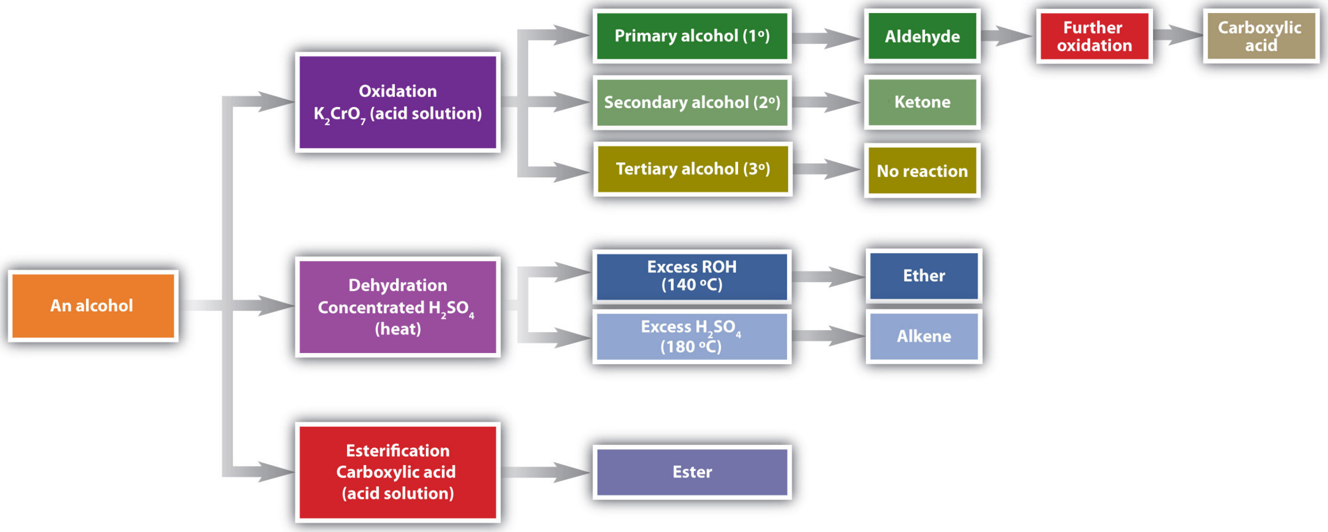
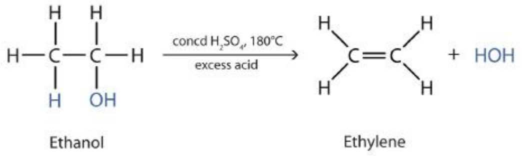


Figure 14.5.1: Reactions of Alcohols. Oxidation and dehydration of alcohols are considered here.

A flow diagram of three possible reactions of an alcohol. The final products of the reactions are also shown at the end of the flow diagram.

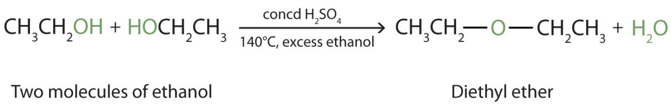
Dehydration

As noted in Figure 14.5.1, an alcohol undergoes dehydration in the presence of a catalyst to form an alkene and water. The reaction removes the OH group from the alcohol carbon atom and a hydrogen atom from an adjacent carbon atom in the same molecule:



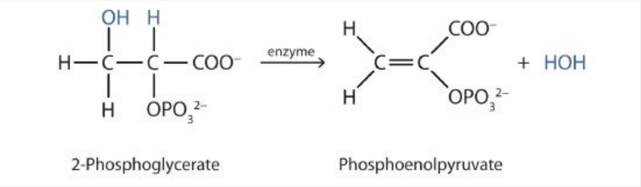
Structural formula of ethanol dehydrating under excess concentrated sulfuric acid at 180 degrees celsius. The products are ethylene and a side product of a water molecule.

Under the proper conditions, it is possible for the dehydration to occur between *two* alcohol molecules. The entire OH group of one molecule and only the hydrogen atom of the OH group of the second molecule are removed. The two ethyl groups attached to an oxygen atom form an ether molecule.



Two molecules of ethanol are dehydrated under concentrated sulfuric acid at 140 degrees celsius and excess ethanol to give a diethyl ether and a water molecule.

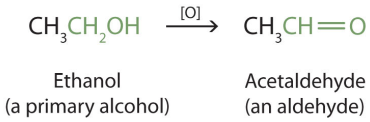
(Ethers are discussed in elsewhere) Thus, depending on conditions, one can prepare either alkenes or ethers by the dehydration of alcohols.

> Both dehydration and hydration reactions occur continuously in cellular metabolism, with enzymes serving as catalysts and at a temperature of about 37°C. The following reaction occurs in the "Embden–Meyerhof" pathway
>
> 
>
>
> Structural formula of 2 phosphoglycerate forming phosphoenolpyruvate and a water molecule with the aid of enzymes.

Although the participating compounds are complex, the reaction is the same: elimination of water from the starting material. The idea is that if you know the chemistry of a particular functional group, you know the chemistry of hundreds of different compounds.

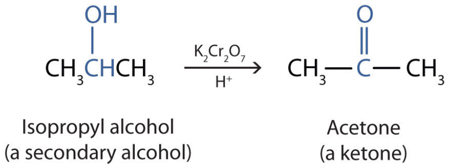
Oxidation

Primary and secondary alcohols are readily oxidized. We saw earlier how methanol and ethanol are oxidized by liver enzymes to form aldehydes. Because a variety of oxidizing agents can bring about oxidation, we can indicate an oxidizing agent without specifying a particular one by writing an equation with the symbol [O] above the arrow. For example, we write the oxidation of ethanol—a primary alcohol—to form acetaldehyde—an aldehyde—as follows:



Formula of ethanol reacting to form acetaldehyde with an O in a bracket above the right pointing arrow.

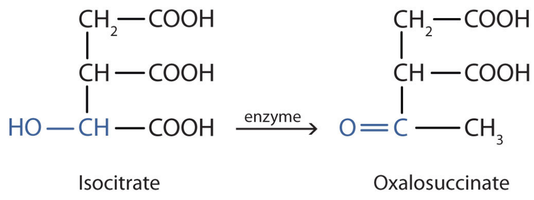
We shall see that aldehydes are even more easily oxidized than alcohols and yield carboxylic acids. Secondary alcohols are oxidized to *ketones*. The oxidation of isopropyl alcohol by potassium dichromate ($K_2Cr_2O_7$) gives acetone, the simplest ketone:



Unlike aldehydes, ketones are relatively resistant to further oxidation, so no special precautions are required to isolate them as they form. Note that in oxidation of both primary (RCH_2OH) and secondary (R_2CHOH) alcohols, two hydrogen atoms are removed from the alcohol molecule, one from the OH group and other from the carbon atom that bears the OH group.

> These reactions can also be carried out in the laboratory with chemical oxidizing agents. One such oxidizing agent is potassium dichromate. The balanced equation (showing only the species involved in the reaction) in this case is as follows:
>
> $$8\,H^{=} + Cr_2O_7^{2-} + 3\,CH_3CH_2OH \longrightarrow 3\,CH_3CHO + 2\,Cr^{3+} + 7\,H_2O$$

Alcohol oxidation is important in living organisms. Enzyme-controlled oxidation reactions provide the energy cells need to do useful work. One step in the metabolism of carbohydrates involves the oxidation of the secondary alcohol group in isocitric acid to a ketone group:



The overall type of reaction is the same as that in the conversion of isopropyl alcohol to acetone.

Tertiary alcohols (R_3COH) are resistant to oxidation because the carbon atom that carries the OH group does not have a hydrogen atom attached but is instead bonded to other carbon atoms. The oxidation reactions we have described involve the formation of a carbon-to-oxygen double bond. Thus, the carbon atom bearing the OH group must be able to release one of its attached atoms to form the double bond. The carbon-to-hydrogen bonding is easily broken under oxidative conditions, but carbon-to-carbon bonds are not. Therefore tertiary alcohols are not easily oxidized.

✓ Example 14.5.1

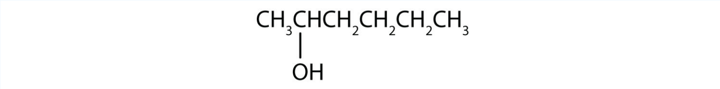
Write an equation for the oxidation of each alcohol. Use [O] above the arrow to indicate an oxidizing agent. If no reaction occurs, write “no reaction” after the arrow.

a. $CH_3CH_2CH_2CH_2CH_2OH$

b. 

$$CH_3\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large OH}{|}}{C}}CH_2CH_3$$

From left to right, there are four carbons on the alkane straight chain with a methyl and hydroxyl group on carbon 2.

c. 

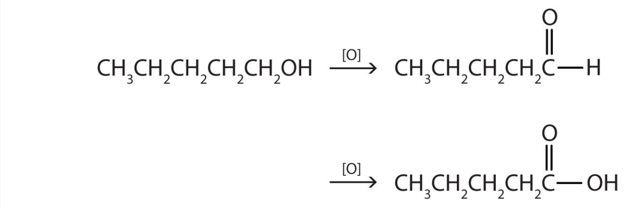
$$CH_3\underset{\underset{\large OH}{|}}{C}HCH_2CH_2CH_2CH_3$$

From left to right, there are six carbons on the alkane straight chain with a hydroxyl group on carbon 2.

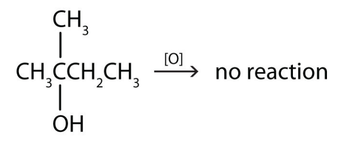
Solution

The first step is to recognize the class of each alcohol as primary, secondary, or tertiary.

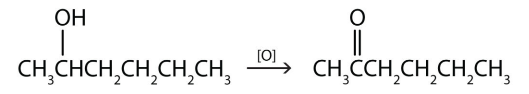
a. This alcohol has the OH group on a carbon atom that is attached to only *one* other carbon atom, so it is a primary alcohol. Oxidation forms first an aldehyde and further oxidation forms a carboxylic acid.



b. This alcohol has the OH group on a carbon atom that is attached to three other carbon atoms, so it is a tertiary alcohol. No reaction occurs.

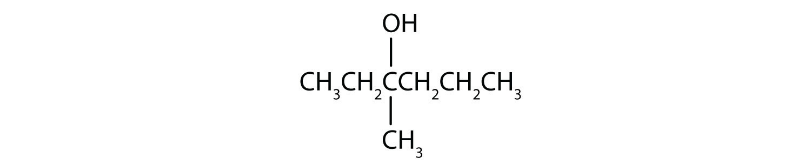


c. This alcohol has the OH group on a carbon atom that is attached to two other carbon atoms, so it is a secondary alcohol; oxidation gives a ketone.

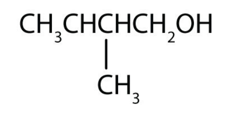

$CH_3\overset{\overset{OH}{|}}{C}HCH_2CH_2CH_2CH_3 \xrightarrow{[O]} CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2CH_2CH_3$

Exercise 14.5.1

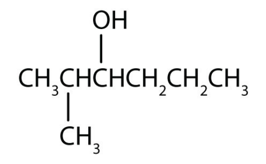
Write an equation for the oxidation of each alcohol. Use [O] above the arrow to indicate an oxidizing agent. If no reaction occurs, write “no reaction” after the arrow.

a. 
$CH_3CH_2\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_2CH_2CH_3$

From left to right, there are six carbons on the alkane straight chain with a hydroxyl group and methyl group on carbon 3.

b. 
$CH_3\underset{\underset{CH_3}{|}}{C}HCH_2OH$

From left to right, there are four carbons on the alkane straight chain with a methyl group on carbon 3 as well as a hydroxyl group on carbon 4.

c. 
$CH_3\underset{\underset{CH_3}{|}}{C}H\overset{\overset{OH}{|}}{C}HCH_2CH_2CH_3$

From left to right, there are six carbons on the alkane straight chain with a methyl group on carbon 2 and a hydroxyl group on carbon 3.

Summary

Alcohols can be dehydrated to form either alkenes (higher temperature, excess acid) or ethers (lower temperature, excess alcohol). Primary alcohols are oxidized to form aldehydes. Secondary alcohols are oxidized to form ketones. Tertiary alcohols are not readily oxidized.

14.6: Glycols and Glycerol

Learning Objectives

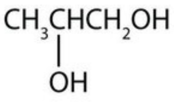
- To describe the structure and uses of some common polyhydric alcohols.

Alcohols with two OH groups on adjacent carbon atoms are commonly known as glycols. The most important of these is 1,2-ethanediol (the common name is ethylene glycol), a sweet, colorless, somewhat viscous liquid.

$HOCH_2CH_2OH$

Ethylene glycol

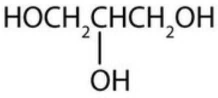
Another common glycol, 1,2-propanediol, is commonly called propylene glycol. Its physical properties are quite similar to those of ethylene glycol.



$$\underset{\displaystyle OH}{CH_3\overset{}{C}HCH_2OH}$$

Propylene glycol

Commonly called glycerol or glycerin, 1,2,3-propanetriol is the most important trihydroxy alcohol. Like the two glycols, it is a sweet, syrupy liquid. Glycerol is a product of the hydrolysis of fats and oils.



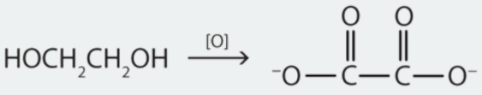
$$HOCH_2\underset{\displaystyle |\atop \displaystyle OH}{C}HCH_2OH$$

Glycerol

Ethylene glycol is the main ingredient in many antifreeze mixtures for automobile radiators. The two OH groups lead to extensive intermolecular hydrogen bonding. This results in a high boiling point—198°C; thus ethylene glycol does not boil away when it is used as an antifreeze. It is also completely miscible with water. A solution of 60% ethylene glycol in water freezes at −49°C (−56°F) and thus protects an automobile radiator down to that temperature. Ethylene glycol is also used in the manufacture of polyester fiber and magnetic film used in tapes for recorders and computers.

To Your Health: Glycols and Human Health

Ethylene glycol is quite toxic. Because it is sweet, pets often lap up spills of leaked antifreeze from a garage floor or driveway. Sometimes people, especially children, drink it. As with methanol, its toxicity is due to a metabolite. Liver enzymes oxidize ethylene glycol to oxalate ion.



$$HOCH_2CH_2OH \xrightarrow{[O]} {}^{-}O-\overset{\displaystyle O \atop \displaystyle \|}{C}-\overset{\displaystyle O \atop \displaystyle \|}{C}-O^{-}$$

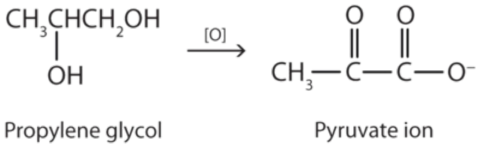
Ethylene glycol Oxalate ion

In the kidneys, the oxalate ion combines with the calcium (Ca^{2+}) ion, precipitating as calcium oxalate (CaC_2O_4).

$$\mathrm{Ca^{2+}(aq) + C_2O_4^{2-}(aq) \rightarrow CaC_2O_4(s)}$$

These crystals cause renal damage and can lead to kidney failure and death.

Although propylene glycol has physical properties much like those of ethylene glycol, its physiological properties are quite different. Propylene glycol is essentially nontoxic, and it can be used as a solvent for drugs and as a moisturizing agent for foods. Like other alcohols, propylene glycol is oxidized by liver enzymes.



In this case, however, the product is pyruvate ion, a normal intermediate in carbohydrate metabolism. Glycerol, a product of fat metabolism, is essentially nontoxic.

Summary

Glycols are alcohols with two OH groups on adjacent carbon atoms. Glycerol is the most important trihydroxy alcohol.

14.7: Phenols

Learning Objectives

- To describe the structure and uses of some phenols

Compounds in which an OH group is attached directly to an aromatic ring are designated ArOH and called phenols. Phenols differ from alcohols in that they are slightly acidic in water. They react with aqueous sodium hydroxide (NaOH) to form salts.

$$\mathrm{ArOH(aq) + NaOH(aq) \rightarrow ArONa(aq) + H_2O}$$

The parent compound, C_6H_5OH, is itself called phenol. (An old name, emphasizing its slight acidity, was *carbolic acid*.) Phenol is a white crystalline compound that has a distinctive ("hospital smell") odor.

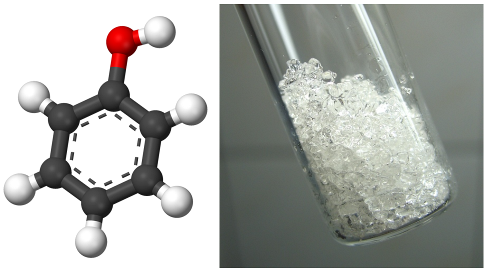


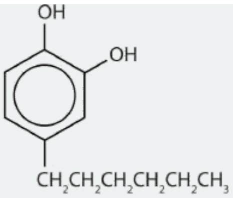
Figure 14.7.1: (Left) Structure of Phenol (right) Approximately two grams of phenol in glass vial. from Wikipedia

To Your Health: Phenols and Us

Phenols are widely used as antiseptics (substances that kill microorganisms on living tissue) and as disinfectants (substances intended to kill microorganisms on inanimate objects such as furniture or floors). The first widely used antiseptic was phenol. Joseph Lister used it for antiseptic surgery in 1867. Phenol is toxic to humans, however, and can cause severe burns when applied to the skin. In the bloodstream, it is a systemic poison—that is, one that is carried to and affects all parts of the body. Its severe side effects led to searches for safer antiseptics, a number of which have been found.

An operation in 1753, painted by Gaspare Traversi, of a surgery before antiseptics were used.

One safer phenolic antiseptic is 4-hexylresorcinol (4-hexyl-1,3-dihydroxybenzene; resorcinol is the common name for 1,3-dihydroxybenzene, and 4-hexylresorcinol has a hexyl group on the fourth carbon atom of the resorcinol ring). It is much more powerful than phenol as a germicide and has fewer undesirable side effects. Indeed, it is safe enough to be used as the active ingredient in some mouthwashes and throat lozenges.



The compound 4-hexylresorcinol is mild enough to be used as the active ingredient in antiseptic preparations for use on the skin.

The compound 4-hexylresorcinol is mild enough to be used as the active ingredient in antiseptic preparations for use on the skin.

Summary

Phenols are compounds in which an OH group is attached directly to an aromatic ring. Many phenols are used as antiseptics.

14.8: Ethers

Learning Objectives

- Describe the structural difference between an alcohol and an ether that affects physical characteristics and reactivity of each.
- Name simple ethers.
- Describe the structure and uses of some ethers.

With the general formula ROR′, an ether may be considered a derivative of water in which both hydrogen atoms are replaced by alkyl or aryl groups. It may also be considered a derivative of an alcohol (ROH) in which the hydrogen atom of the OH group is been replaced by a second alkyl or aryl group:

$$\text{HOH} \xrightarrow[\text{H atoms}]{\text{replace both}} \text{ROR}' \xleftarrow[\text{of OH group}]{\text{replace H atom}} \text{ROH}$$

Simple ethers have simple common names, formed from the names of the groups attached to oxygen atom, followed by the generic name *ether*. For example, $CH_3–O–CH_2CH_2CH_3$ is methyl propyl ether. If both groups are the same, the group name should be preceded by the prefix *di*-, as in dimethyl ether ($CH_3–O–CH_3$) and diethyl ether $CH_3CH_2–O–CH_2CH_3$.

Ether molecules have no hydrogen atom on the oxygen atom (that is, no OH group). Therefore there is no intermolecular hydrogen bonding between ether molecules, and ethers therefore have quite low boiling points for a given molar mass. Indeed, ethers have boiling points about the same as those of alkanes of comparable molar mass and much lower than those of the corresponding alcohols (Table 14.8.1).

Table 14.8.1: Comparison of Boiling Points of Alkanes, Alcohols, and Ethers

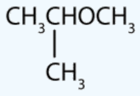
Condensed Structural Formula	Name	Molar Mass	Boiling Point (°C)	Intermolecular Hydrogen Bonding in Pure Liquid?
$CH_3CH_2CH_3$	propane	44	–42	no
CH_3OCH_3	dimethyl ether	46	–25	no
CH_3CH_2OH	ethyl alcohol	46	78	yes
$CH_3CH_2CH_2CH_2CH_3$	pentane	72	36	no
$CH_3CH_2OCH_2CH_3$	diethyl ether	74	35	no
$CH_3CH_2CH_2CH_2OH$	butyl alcohol	74	117	yes

Ether molecules do have an oxygen atom, however, and engage in hydrogen bonding with water molecules. Consequently, an ether has about the same solubility in water as the alcohol that is isomeric with it. For example, dimethyl ether and ethanol (both having the molecular formula C_2H_6O) are completely soluble in water, whereas diethyl ether and 1-butanol (both $C_4H_{10}O$) are barely soluble in water (8 g/100 mL of water).

Example 14.8.1

What is the common name for each ether?

a. $CH_3CH_2CH_2OCH_2CH_2CH_3$

b. 

$CH_3\underset{\underset{\displaystyle CH_3}{|}}{C}HOCH_3$

Solution

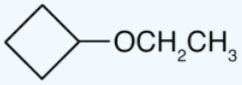
a. The carbon groups on either side of the oxygen atom are propyl ($CH_3CH_2CH_2$) groups, so the compound is dipropyl ether.

b. The three-carbon group is attached by the middle carbon atom, so it is an isopropyl group. The one-carbon group is a methyl group. The compound is isopropyl methyl ether.

? Exercise 14.8.1

What is the common name for each ether?

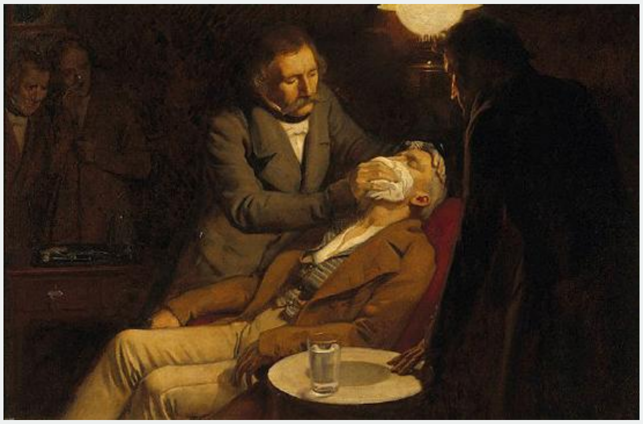
a. $CH_3CH_2CH_2CH_2OCH_2CH_2CH_2CH_3$



b.

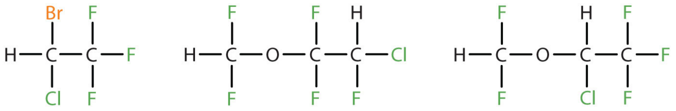
To Your Health: Ethers as General Anesthetics

A *general anesthetic* acts on the brain to produce unconsciousness and a general insensitivity to feeling or pain. Diethyl ether ($CH_3CH_2OCH_2CH_3$) was the first general anesthetic to be used.



William Morton, a Boston dentist, introduced diethyl ether into surgical practice in 1846. This painting shows an operation in Boston in 1846 in which diethyl ether was used as an anesthetic. Inhalation of ether vapor produces unconsciousness by depressing the activity of the central nervous system. Source: Painting of William Morton by Ernest Board.

Diethyl ether is relatively safe because there is a fairly wide gap between the dose that produces an effective level of anesthesia and the lethal dose. However, because it is highly flammable and has the added disadvantage of causing nausea, it has been replaced by newer inhalant anesthetics, including the fluorine-containing compounds halothane, enflurane, and isoflurane. Unfortunately, the safety of these compounds for operating room personnel has been questioned. For example, female operating room workers exposed to halothane suffer a higher rate of miscarriages than women in the general population.



Halothane Enflurane Isoflurane

These three modern, inhalant, halogen-containing, anesthetic compounds are less flammable than diethyl ether.

Summary

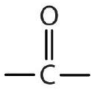
To give ethers common names, simply name the groups attached to the oxygen atom, followed by the generic name *ether*. If both groups are the same, the group name should be preceded by the prefix *di-*. Ether molecules have no OH group and thus no intermolecular hydrogen bonding. Ethers therefore have quite low boiling points for a given molar mass. Ether molecules have an oxygen atom and can engage in hydrogen bonding with water molecules. An ether molecule has about the same solubility in water as the alcohol that is isomeric with it.

14.9: Aldehydes and Ketones- Structure and Names

Learning Objectives

- Identify the general structure for an aldehyde and a ketone.
- Use common names to name aldehydes and ketones.
- Use the IUPAC system to name aldehydes and ketones.

The next functional group we consider, the carbonyl group, has a carbon-to-oxygen double bond.

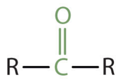


$-\overset{\overset{\displaystyle O}{\|}}{C}-$

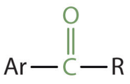
Carbonyl groups define two related families of organic compounds: the aldehydes and the ketones.

> *The carbonyl group is ubiquitous in biological compounds. It is found in carbohydrates, fats, proteins, nucleic acids, hormones, and vitamins—organic compounds critical to living systems.*

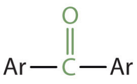
In a ketone, two carbon groups are attached to the carbonyl carbon atom. The following general formulas, in which R represents an alkyl group and Ar stands for an aryl group, represent ketones.



$R-\overset{\overset{\displaystyle O}{\|}}{C}-R$

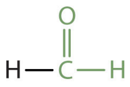


$Ar-\overset{\overset{\displaystyle O}{\|}}{C}-R$

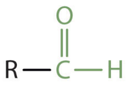


$Ar-\overset{\overset{\displaystyle O}{\|}}{C}-Ar$

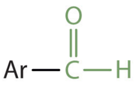
In an aldehyde, at least one of the attached groups must be a hydrogen atom. The following compounds are aldehydes:



$H-\overset{\overset{\displaystyle O}{\|}}{C}-H$



$R-\overset{\overset{\displaystyle O}{\|}}{C}-H$



$Ar-\overset{\overset{\displaystyle O}{\|}}{C}-H$

In condensed formulas, we use CHO to identify an aldehyde rather than COH, which might be confused with an alcohol. This follows the general rule that in condensed structural formulas H comes after the atom it is attached to (usually C, N, or O).

$-CHO$

An aldehyde

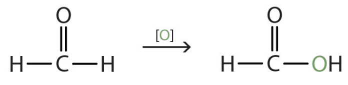
$-CO-$

A ketone

The carbon-to-oxygen double bond is not shown but understood to be present. Because they contain the same functional group, aldehydes and ketones share many common properties, but they still differ enough to warrant their classification into two families.

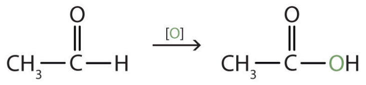
Naming Aldehydes and Ketones

Both common and International Union of Pure and Applied Chemistry (IUPAC) names are frequently used for aldehydes and ketones, with common names predominating for the lower homologs. The common names of aldehydes are taken from the names of the acids into which the aldehydes can be converted by *oxidation*.



$$H{-}\overset{\overset{\large O}{\|}}{C}{-}H \xrightarrow{[O]} H{-}\overset{\overset{\large O}{\|}}{C}{-}OH$$

Formaldehyde Formic acid

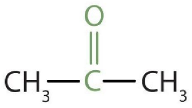


$$CH_3{-}\overset{\overset{\large O}{\|}}{C}{-}H \xrightarrow{[O]} CH_3{-}\overset{\overset{\large O}{\|}}{C}{-}OH$$

Acetaldehyde Acetic acid

> The stems for the common names of the first four aldehydes are as follows:
>
> - 1 carbon atom: *form-*
> - 2 carbon atoms: *acet-*
> - 3 carbon atoms: *propion-*
> - 4 carbon atoms: *butyr-*

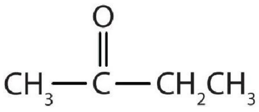
Because the carbonyl group in a ketone must be attached to two carbon groups, the simplest ketone has three carbon atoms. It is widely known as *acetone*, a unique name unrelated to other common names for ketones.



$$CH_3{-}\overset{\overset{\large O}{\|}}{C}{-}CH_3$$

Acetone

Generally, the common names of ketones consist of the names of the groups attached to the carbonyl group, followed by the word *ketone*. (Note the similarity to the naming of ethers.) Another name for acetone, then, is *dimethyl ketone*. The ketone with four carbon atoms is ethyl methyl ketone.

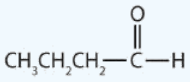


$$CH_3{-}\overset{\overset{\large O}{\|}}{C}{-}CH_2CH_3$$

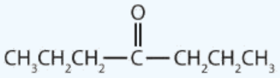
Ethyl methyl ketone

Example 14.9.1

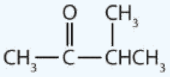
Classify each compound as an aldehyde or a ketone. Give the common name for each ketone.

a. 

$$CH_3CH_2CH_2{-}\overset{\overset{\large O}{\|}}{C}{-}H$$

b. 

$$CH_3CH_2CH_2{-}\overset{\overset{\large O}{\|}}{C}{-}CH_2CH_2CH_3$$

c. 

$$CH_3{-}\overset{\overset{\large O}{\|}}{C}{-}\overset{\overset{\large CH_3}{|}}{C}HCH_3$$

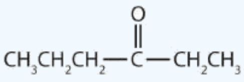
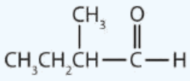
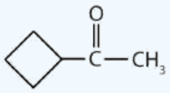
Solution

a. This compound has the carbonyl group on an end carbon atom, so it is an aldehyde.
b. This compound has the carbonyl group on an interior carbon atom, so it is a ketone. Both alkyl groups are propyl groups. The name is therefore dipropyl ketone.

c. This compound has the carbonyl group between two alkyl groups, so it is a ketone. One alkyl group has three carbon atoms and is attached by the middle carbon atom; it is an isopropyl group. A group with one carbon atom is a methyl group. The name is therefore isopropyl methyl ketone.

Exercise 14.9.1

Classify each compound as an aldehyde or a ketone. Give the common name for each ketone.

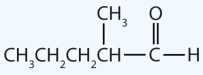
1. 
$CH_3CH_2CH_2{-}\overset{\overset{O}{\|}}{C}{-}CH_2CH_3$
2. 
$CH_3CH_2\overset{\overset{CH_3}{|}}{CH}{-}\overset{\overset{O}{\|}}{C}{-}H$
3. 

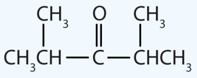
Here are some simple IUPAC rules for naming aldehydes and ketones:

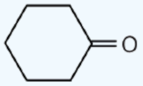
- The stem names of aldehydes and ketones are derived from those of the parent alkanes, defined by the longest continuous chain (LCC) of carbon atoms that contains the functional group.
- For an aldehyde, drop the *-e* from the alkane name and add the ending *-al*. Methanal is the IUPAC name for formaldehyde, and ethanal is the name for acetaldehyde.
- For a ketone, drop the *-e* from the alkane name and add the ending *-one*. Propanone is the IUPAC name for acetone, and butanone is the name for ethyl methyl ketone.
- To indicate the position of a substituent on an aldehyde, the carbonyl carbon atom is always considered to be C1; it is unnecessary to designate this group by number.
- To indicate the position of a substituent on a ketone, number the chain in the manner that gives the carbonyl carbon atom the lowest possible number. In cyclic ketones, it is understood that the carbonyl carbon atom is C1.

Example 14.9.2

Give the IUPAC name for each compound.

a. 
$CH_3CH_2CH_2\overset{\overset{CH_3}{|}}{CH}{-}\overset{\overset{O}{\|}}{C}{-}H$

b. 
$CH_3\overset{\overset{CH_3}{|}}{CH}{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{CH_3}{|}}{C}HCH_3$

c. 

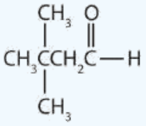
Solution

a. There are five carbon atoms in the LCC. The methyl group (CH_3) is a substituent on the second carbon atom of the chain; the aldehyde carbon atom is always C1. The name is derived from pentane. Dropping the *-e* and adding the ending *-al* gives pentanal. The methyl group on the second carbon atom makes the name 2-methylpentanal.
b. There are five carbon atoms in the LCC. The carbonyl carbon atom is C3, and there are methyl groups on C2 and C4. The IUPAC name is 2,4-dimethyl-3-pentanone.
c. There are six carbon atoms in the ring. The compound is cyclohexanone. No number is needed to indicate the position of the carbonyl group because all six carbon atoms are equivalent.

Exercise

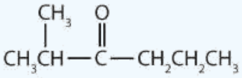
Give the IUPAC name for each compound.

a.



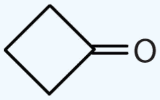
$$CH_3\underset{CH_3}{\overset{CH_3}{C}}CH_2\overset{O}{\overset{\|}{C}}-H$$

b.



$$CH_3\overset{CH_3}{CH}-\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_3$$

c.



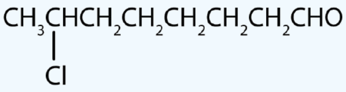
Example 14.9.3

Draw the structure for each compound.

a. 7-chlorooctanal
b. 4-methyl–3-hexanone

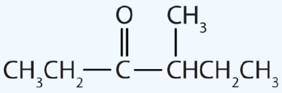
Solution

a. The *octan-* part of the name tells us that the LCC has eight carbon atoms. There is a chlorine (Cl) atom on the seventh carbon atom; numbering from the carbonyl group and counting the carbonyl carbon atom as C1, we place the Cl atom on the seventh carbon atom.



$$CH_3\underset{Cl}{CH}CH_2CH_2CH_2CH_2CH_2CHO$$

b. The *hexan-* part of the name tells us that the LCC has six carbon atoms. The 3 means that the carbonyl carbon atom is C3 in this chain, and the 4 tells us that there is a methyl (CH_3) group at C4:



$$CH_3CH_2-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{CH}CH_2CH_3$$

Exercise 14.9.3

Draw the structure for each compound.

a. 5-bromo-3-iodoheptanal
b. 5-bromo-4-ethyl-2-heptanone

Summary

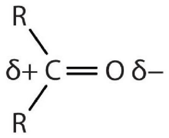
The common names of aldehydes are taken from the names of the corresponding carboxylic acids: formaldehyde, acetaldehyde, and so on. The common names of ketones, like those of ethers, consist of the names of the groups attached to the carbonyl group, followed by the word *ketone*. Stem names of aldehydes and ketones are derived from those of the parent alkanes, using an *-al* ending for an aldehydes and an *-one* ending for a ketone.

14.10: Properties of Aldehydes and Ketones

Learning Objectives

- Explain why the boiling points of aldehydes and ketones are higher than those of ethers and alkanes of similar molar masses but lower than those of comparable alcohols.
- Compare the solubilities in water of aldehydes and ketones of four or fewer carbon atoms with the solubilities of comparable alkanes and alcohols.
- Name the typical reactions take place with aldehydes and ketones.
- Describe some of the uses of common aldehydes and ketones.

The carbon-to-oxygen double bond is quite polar, more polar than a carbon-to-oxygen single bond. The electronegative oxygen atom has a much greater attraction for the bonding electron pairs than does the carbon atom. The carbon atom has a partial positive charge, and the oxygen atom has a partial negative charge:



In aldehydes and ketones, this charge separation leads to dipole-dipole interactions that are great enough to significantly affect the boiling points. Table 14.10.1shows that the polar single bonds in ethers have little such effect, whereas hydrogen bonding between alcohol molecules is even stronger.

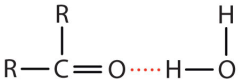
Table 14.10.1: Boiling Points of Compounds Having Similar Molar Masses but Different Types of Intermolecular Forces

Compound	Family	Molar Mass	Type of Intermolecular Forces	Boiling Point (°C)
$CH_3CH_2CH_2CH_3$	alkane	58	dispersion only	–1
$CH_3OCH_2CH_3$	ether	60	weak dipole	6
CH_3CH_2CHO	aldehyde	58	strong dipole	49
$CH_3CH_2CH_2OH$	alcohol	60	hydrogen bonding	97

Formaldehyde is a gas at room temperature. Acetaldehyde boils at 20°C; in an open vessel, it boils away in a warm room. Most other common aldehydes are liquids at room temperature.

> Although the lower members of the homologous series have pungent odors, many higher aldehydes have pleasant odors and are used in perfumes and artificial flavorings. As for the ketones, acetone has a pleasant odor, but most of the higher homologs have rather bland odors.

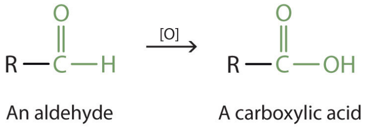
The oxygen atom of the carbonyl group engages in hydrogen bonding with a water molecule.

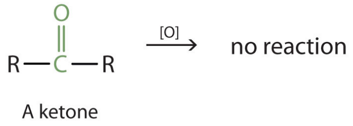


The solubility of aldehydes is therefore about the same as that of alcohols and ethers. Formaldehyde, acetaldehyde, and acetone are soluble in water. As the carbon chain increases in length, solubility in water decreases. The borderline of solubility occurs at about four carbon atoms per oxygen atom. All aldehydes and ketones are soluble in organic solvents and, in general, are less dense than water.

Oxidation of Aldehydes and Ketones

Aldehydes and ketones are much alike in many of their reactions, owing to the presence of the carbonyl functional group in both. They differ greatly, however, in one most important type of reaction: oxidation. Aldehydes are readily oxidized to carboxylic acids, whereas ketones resist oxidation.





The aldehydes are, in fact, among the most easily oxidized of organic compounds. They are oxidized by oxygen ($\mathrm{O_2}$) in air to carboxylic acids.

$$2\,\mathrm{RCHO} + \mathrm{O_2} \longrightarrow 2\,\mathrm{RCOOH}$$

The ease of oxidation helps chemists identify aldehydes. A sufficiently mild oxidizing agent can distinguish aldehydes not only from ketones but also from alcohols. Tollens' reagent, for example, is an alkaline solution of silver ($\mathrm{Ag^+}$) ion complexed with ammonia (NH_3), which keeps the $\mathrm{Ag^+}$ ion in solution.

$$\mathrm{H_3N{-}Ag^+{-}NH_3}$$

When Tollens' reagent oxidizes an aldehyde, the $\mathrm{Ag^+}$ ion is reduced to free silver (Ag).

$$\underbrace{\mathrm{RCHO(aq)}}_{\text{an aldehyde}} + 2\,\mathrm{Ag(NH_3)_2^+(aq)} \longrightarrow \mathrm{RCOO^-} + \underbrace{2\,\mathrm{Ag(s)}}_{\text{free silver}} + 4\,\mathrm{NH_3(aq)} + 2\,\mathrm{H_2O}$$

Deposited on a clean glass surface, the silver produces a mirror (Figure 14.10.1). Ordinary ketones do not react with Tollens' reagent.

Figure 14.10.1: Aldehyde Reactions. A reaction related to the Tollens' reaction is often used to silver mirrors. These ornaments were silvered by such a reaction. Glucose, a simple sugar with an aldehyde functional group, is used as the reducing agent. Source: Photo courtesy of Krebs Glas Lauscha, commons.wikimedia.org/wiki/File:Silvering.jpg.

A person wearing gloves is holding a bunch of ornaments that she has just lifted from a basin containing a solution.

Although ketones resist oxidation by ordinary laboratory oxidizing agents, they undergo combustion, as do aldehydes.

Some Common Carbonyl Compounds

Formaldehyde has an irritating odor. Because of its reactivity, it is difficult to handle in the gaseous state. For many uses, it is therefore dissolved in water and sold as a 37% to 40% aqueous solution called *formalin*. Formaldehyde denatures proteins, rendering them insoluble in water and resistant to bacterial decay. For this reason, formalin is used in embalming solutions and in preserving biological specimens.

Aldehydes are the active components in many other familiar substances. Large quantities of formaldehyde are used to make phenol-formaldehyde resins for gluing the wood sheets in plywood and as adhesives in other building materials. Sometimes the formaldehyde escapes from the materials and causes health problems in some people. While some people seem unaffected, others experience coughing, wheezing, eye irritation, and other symptoms.

> *The odor of green leaves is due in part to a carbonyl compound, cis-3-hexenal, which with related compounds is used to impart a "green" herbal odor to shampoos and other products.*

Acetaldehyde is an extremely volatile, colorless liquid. It is a starting material for the preparation of many other organic compounds. Acetaldehyde is formed as a metabolite in the fermentation of sugars and in the detoxification of alcohol in the liver. Aldehydes are the active components of many other familiar materials (Figure 14.10.2).

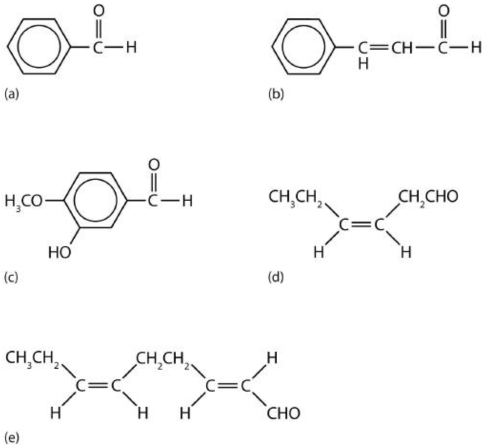


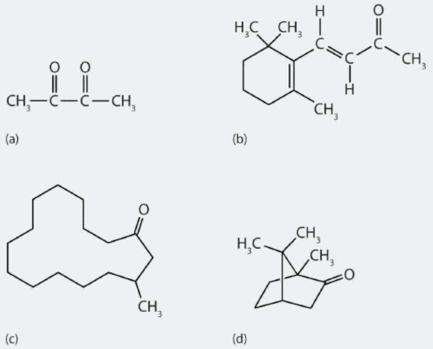
Figure 14.10.2 Some Interesting Aldehydes. (a) Benzaldehyde is an oil found in almonds; (b) cinnamaldehyde is oil of cinnamon; (c) vanillin gives vanilla its flavor; (d) *cis*-3-hexenal provides an herbal odor; and (e) *trans*-2-*cis*-6-nonadienal gives a cucumber odor.

Acetone is the simplest and most important ketone. Because it is miscible with water as well as with most organic solvents, its chief use is as an industrial solvent (for example, for paints and lacquers). It is also the chief ingredient in some brands of nail polish remover.

To Your Health: Acetone in Blood, Urine, and Breath

Acetone is formed in the human body as a by-product of lipid metabolism. Normally, acetone does not accumulate to an appreciable extent because it is oxidized to carbon dioxide and water. The normal concentration of acetone in the human body is less than 1 mg/100 mL of blood. In certain disease states, such as uncontrolled diabetes mellitus, the acetone concentration rises to higher levels. It is then excreted in the urine, where it is easily detected. In severe cases, its odor can be noted on the breath.

Ketones are also the active components of other familiar substances, some of which are noted in the accompanying figure.



Some ketones have interesting properties: (a) Butter flavoring comes from 2,3-butanedione; (b) β-ionone is responsible for the odor of violets; (c) muscone is musk oil, an ingredient in perfumes; and (d) camphor is used in some insect repellents.

Certain steroid hormones have the ketone functional group as a part of their structure. Two examples are progesterone, a hormone secreted by the ovaries that stimulates the growth of cells in the uterine wall and prepares it for attachment of a fertilized egg, and testosterone, the main male sex hormone. These and other sex hormones affect our development and our lives in fundamental ways.

Summary

The polar carbon-to-oxygen double bond causes aldehydes and ketones to have higher boiling points than those of ethers and alkanes of similar molar masses but lower than those of comparable alcohols that engage in intermolecular hydrogen bonding. Aldehydes are readily oxidized to carboxylic acids, whereas ketones resist oxidation.

14.11: Organic Sulfur Compounds

Learning Objectives

- Identify thiols (mercaptans) by the presence of an SH group.
- The mild oxidation of thiols gives disulfides.

Because sulfur is in the same group (6A) of the periodic table as oxygen, the two elements have some similar properties. We might expect sulfur to form organic compounds related to those of oxygen, and indeed it does. Thiols (also called mercaptans), which are sulfur analogs of alcohols, have the general formula RSH. Methanethiol (also called methyl mercaptan), has the formula CH_3SH. Ethanethiol (ethyl mercaptan) is the most common odorant for liquid propane (LP) gas.

The mild oxidation of thiols gives compounds called **disulfides**.

$$2RSH \xrightarrow{[O]} RSSR$$

The amino acids cysteine [$HSCH_2CH(NH_2)COOH$] and methionine [$CH_3SCH_2CH_2CH(NH_2)COOH$] contain sulfur atoms, as do all proteins that contain these amino acids. Disulfide linkages (–S–S–) between protein chains are extremely important in protein structure.

Thioethers, which are sulfur analogs of ethers, have the form general formula RSR′. An example is dimethylsulfide (CH_3SCH_3), which is responsible for the sometimes unpleasant odor of cooking cabbage and related vegetables. Note that methionine has a thioether functional group.

Career Focus: Paramedic

Paramedics are highly trained experts at providing emergency medical treatment. Their critical duties often include rescue work and emergency medical procedures in a wide variety of settings, sometimes under extremely harsh and difficult conditions. Like other science-based professions, their work requires knowledge, ingenuity, and complex thinking, as well as a great deal of technical skill. The recommended courses for preparation in this field include anatomy, physiology, medical terminology, and—not surprisingly—chemistry. An understanding of basic principles of organic chemistry, for example, is useful when paramedics have to deal with such traumas as burns from fuel (hydrocarbons) or solvent (alcohols, ethers, esters, and so on) fires and alcohol and drug overdoses.

To become a paramedic requires 2–4 y of training and usually includes a stint as an emergency medical technician (EMT). An EMT provides basic care, can administer certain medications and treatments, such as oxygen for respiratory problems and epinephrine (adrenalin) for allergic reactions, and has some knowledge of common medical conditions. A paramedic, in contrast, must have extensive knowledge of common medical problems and be trained to administer a wide variety of emergency drugs.

Paramedics usually work under the direction of a medical doctor with a title such as “medical director.” Some paramedics are employed by fire departments and may work from a fire engine that carries medical equipment as well as fire-fighting gear. Some work from hospital-sponsored ambulances and continue to care for their patients after reaching the hospital emergency room. Still other paramedics work for a government department responsible for emergency health care in a specific geographical area. Finally, some work for private companies that contract to provide service for a government body.

An experienced paramedic has a broad range of employment options, including training for mountain or ocean rescue, working with police department special weapons and tactics (SWAT) teams, or working in isolated settings such as on oil rigs. With their expertise at treating and stabilizing patients before quickly moving them to a hospital, paramedics often provide the first critical steps in saving an endangered life. The following quotation, inscribed on the Arlington National Cemetery headstone of Army Lieutenant R. Adams Cowley, who is often called the “father” of shock trauma medicine, serves as the motto for many paramedic units: “Next to creating a life the finest thing a man can do is save one.” —Abraham Lincoln

Summary

Thiols, thioethers, and disulfides are common in biological compounds.

14.E: Organic Compounds of Oxygen (Exercises)

14.1: Organic Compounds with Functional Groups

Concept Review Exercises

1. What is the functional group of an alkene? An alkyne?
2. Does $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ have a functional group? Explain.

Answers

1. carbon-to-carbon double bond; carbon-to-carbon triple bond
2. No; it has nothing but carbon and hydrogen atoms and all single bonds.

Exercises

1. What is the functional group of 1-butanol ($CH_3CH_2CH_2CH_2OH$)?
2. What is the functional group of butyl bromide, $CH_3CH_2CH_2CH_2Br$?

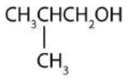
Answer

1. OH

14.2: Alcohols - Nomenclature and Classification

Concept Review Exercises

1. Is isobutyl alcohol primary, secondary, or tertiary? Explain.



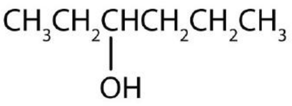
$CH_3\underset{\underset{CH_3}{|}}{C}HCH_2OH$

2. What is the LCC in 2-ethyl-1-hexanol? What is taken as the LCC in naming the compound? Explain.

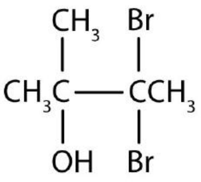
Answers

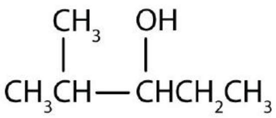
1. primary; the carbon atom bearing the OH group is attached to only one other carbon atom
2. 7 carbon atoms; the 6-atom chain includes the carbon atom bearing the OH group

Exercises

1. Name each alcohol and classify it as primary, secondary, or tertiary.
   a. $CH_3CH_2CH_2CH_2CH_2CH_2OH$
   b. 

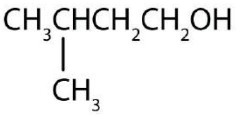
   $CH_3CH_2\underset{\underset{OH}{|}}{C}HCH_2CH_2CH_3$

   c. 

   $CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}—\overset{\overset{Br}{|}}{\underset{\underset{Br}{|}}{C}}CH_3$
2. Name each alcohol and classify it as primary, secondary, or tertiary.
   a. 

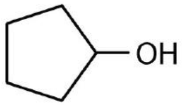
   $CH_3\overset{\overset{CH_3}{|}}{C}H—\overset{\overset{OH}{|}}{C}HCH_2CH_3$

b.



$CH_3\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_2CH_2OH$

c.

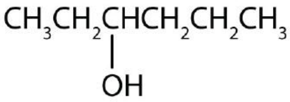


3. Draw the structure for each alcohol.
   a. 3-hexanol
   b. 3,3-dimethyl-2-butanol
   c. cyclobutanol
4. Draw the structure for each alcohol.
   a. cyclopentanol
   b. 4-methyl-2-hexanol
   c. 4,5-dimethyl-3-heptanol

Answers

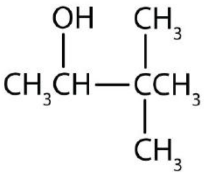
1. a. 1-hexanol; primary
   b. 3-hexanol; secondary
   c. 3,3-dibromo-2-methyl-2-butanol; tertiary

3. a.



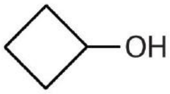
$CH_3CH_2\underset{\underset{\displaystyle OH}{|}}{C}HCH_2CH_2CH_3$

b.



$CH_3\overset{\overset{\displaystyle OH}{|}}{C}H-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}CH_3$

c.



14.3: Physical Properties of Alcohols

Concept Review Exercises

1. Why is ethanol more soluble in water than 1-hexanol?
2. Why does 1-butanol have a lower boiling point than 1-hexanol?

Answers

1. Ethanol has an OH group and only 2 carbon atoms; 1-hexanol has one OH group for 6 carbon atoms and is thus more like a (nonpolar) hydrocarbon than ethanol is.
2. The molar mass of 1-hexanol is greater than that of 1-butanol.

Exercises

Answer the following exercises without consulting tables in the text.

1. Arrange these alcohols in order of increasing boiling point: ethanol, methanol, and 1-propanol.
2. Which has the higher boiling point—butane or 1-propanol?

3. Arrange these alcohols in order of increasing solubility in water: 1-butanol, methanol, and 1-octanol.
4. Arrange these compounds in order of increasing solubility in water: 1-butanol, ethanol, and pentane.

Answers

1. methanol < ethanol < 1-propanol

3. 1-octanol < 1-butanol < methanol

14.4: Reactions that Form Alcohols

Concept Review Exercises

1. Why is methanol more toxic than ethanol?
2. How does rubbing alcohol cool a feverish patient?

Answers

1. Methanol is oxidized to formaldehyde, which destroys tissue; ethanol is oxidized to acetaldehyde and then acetic acid, a normal metabolite.
2. Evaporation removes heat.

Exercises

1. From what alkene is ethanol made? Draw its condensed structural formula.
2. Can methanol be made from an alkene? Explain.

Answer

1. ethylene; $CH_2{=}CH_2$

14.5: Reactions of Alcohols

Conceptual Questions

1. In a reaction, compound W with the molecular formula $C_4H_{10}O$ is converted to compound X with the formula C_4H_8O. Is W oxidized, reduced, dehydrated, or none of these? Explain.

2. In a reaction, 2 mol of compound Y with the molecular formula $C_4H_{10}O$ is converted to 1 mol of compound Z with the formula $C_8H_{18}O$. Is Y oxidized, reduced, or neither? Explain.

Answers

1. oxidized; H is removed

2. neither; water is removed

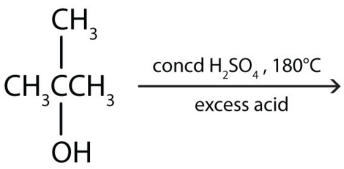
Exercises

1. Name the three major types of chemical reactions of alcohols.

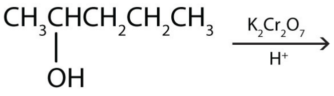
2. Why do tertiary alcohols not undergo oxidation? Can a tertiary alcohol undergo dehydration?

3. Draw the structure of the product for each reaction.

a.

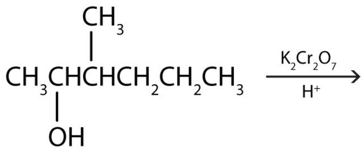


$$CH_3\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{C}}CH_3 \xrightarrow[\text{excess acid}]{\text{concd } H_2SO_4\text{, 180°C}}$$

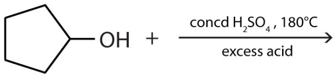
b. 

$\underset{\displaystyle\text{OH}}{\underset{|}{CH_3CH}}CH_2CH_2CH_3 \xrightarrow[H^+]{K_2Cr_2O_7}$

4. Draw the structure of the product for each reaction.

a. 

$CH_3\underset{\displaystyle\text{OH}}{\underset{|}{CH}}\overset{\displaystyle CH_3}{\overset{|}{CH}}CH_2CH_2CH_3 \xrightarrow[H^+]{K_2Cr_2O_7}$

b. 

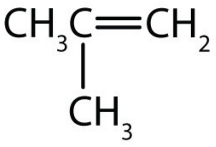
5. Write an equation for the dehydration of 2-propanol to yield each compound type.

   a. an alkene
   b. an ether

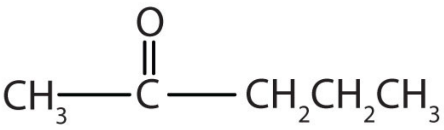
6. Draw the structure of the alkene formed by the dehydration of cyclohexanol.

Answers

1. dehydration, oxidation, and esterification

3. a. 

$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2$

   b. 

$CH_3{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_2CH_2CH_3$

5. a. $CH_3CHOHCH_3 \xrightarrow[180^\circ C, \text{ excess acid}]{\text{conc } H_2SO_4} CH_3COCH_3 + H_2O$

   b. $2CH_3CHOHCH_3 \xrightarrow[180^\circ C, \text{ excess acid}]{\text{conc } H_2SO_4} (CH_3)_2CHOCH(CH_3)_2 + H_2O$

14.6: Glycols and Glycerol

Concept Review Exercises

1. In the oxidation of propylene glycol to pyruvic acid, what functional groups in the reactant are involved? What new functional groups appear in the product?
2. Oxalate ion is formed by the oxidation of ethylene glycol. In what kind of reaction is the oxalate ion involved?

Answers

1. two OH groups; a ketone group and a carboxylic acid group
2. precipitation

Exercises

1. What is a glycol?
2. Why is ethylene glycol so much more toxic to humans than propylene glycol?

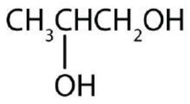
3. Draw the structure for each compound.
    a. 1,5-pentanediol
    b. propylene glycol
4. Draw the structure for each compound.
    a. 1,3-hexandiol
    b. glycerol

Answers

1. an alcohol with two OH groups on adjacent carbon atoms

3. a. $HOCH_2CH_2CH_2CH_2CH_2OH$

    b.



$$\underset{\displaystyle OH}{CH_3\underset{|}{C}HCH_2OH}$$

14.7: Phenols

Concept Review Exercises

1. How do phenols differ from alcohols in terms of structure and properties?
2. How do phenols differ in properties from aromatic hydrocarbons?

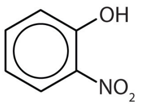
Answers

1. Phenols have an OH group attached directly to an aromatic ring. Phenols are weakly acidic.
2. Phenols have an OH group and are somewhat soluble in water.

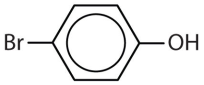
Exercises

1. Name each compound.

    a.

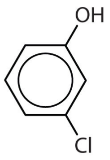


    b.

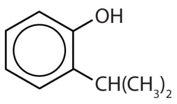


2. Name each compound.

    a.



    b.

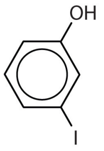


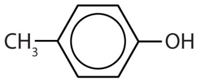
3. Draw the structure for each compound.
    a. *m*-iodophenol
    b. *p*-methylphenol (*p*-cresol)
4. Draw the structure for each compound.

   a. 2,4,6-trinitrophenol (picric acid)
   b. 3,5-diethylphenol

Answers

1. a. *o*-nitrophenol
   b. *p*-bromophenol

3. a.


   b.


14.8: Ethers

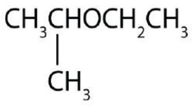
Concept Review Exercises

1. Why does diethyl ether ($CH_3CH_2OCH_2CH_3$) have a much lower boiling point than 1-butanol ($CH_3CH_2CH_2CH_2OH$)?
2. Which is more soluble in water—ethyl methyl ether ($CH_3CH_2OCH_3$) or 1-butanol ($CH_3CH_2CH_2CH_2OH$)? Explain.

Answers

1. Diethyl ether has no intermolecular hydrogen bonding because there is no OH group; 1-butanol has an OH and engages in intermolecular hydrogen bonding.
2. Ethyl methyl ether (three carbon atoms, one oxygen atom) is more soluble in water than 1-butanol (four carbon atoms, one oxygen atom), even though both can engage in hydrogen bonding with water.

Exercises

1. How can ethanol give two different products when heated with sulfuric acid? Name these products.
2. Which of these ethers is isomeric with ethanol—$CH_3CH_2OCH_2CH_3$, $CH_3OCH_2CH_3$, or CH_3OCH_3?
3. Name each compound.
   a. $CH_3OCH_2CH_2CH_3$
   b.


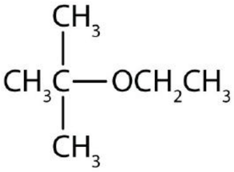
$$\underset{\displaystyle CH_3}{CH_3\underset{|}{C}HOCH_2CH_3}$$

4. Name each compound.
   a. $CH_3CH_2CH_2CH_2OCH_3$
   b. $CH_3CH_2OCH_2CH_2CH_3$
5. Draw the structure for each compound.
   a. methyl ethyl ether
   b. *tert*-butyl ethyl ether
6. Draw the structure for each compound.
   a. diisopropyl ether
   b. cyclopropyl propyl ether

Answers

1. Intramolecular (both the H and the OH come from the same molecule) dehydration gives ethylene; intermolecular (the H comes from one molecule and the OH comes from another molecule) dehydration gives diethyl ether.

3. a. methyl propyl ether
   b. ethyl isopropyl ether
5. a. $CH_3OCH_2CH_3$
   b.



$$CH_3C(CH_3)_2-OCH_2CH_3$$

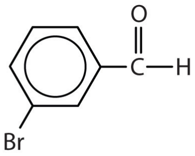
14.9: Aldehydes and Ketones- Structure and Names

Concept Review Exercises

1. Give the structure and IUPAC name for the compound that has the common name m-bromobenzaldehyde.
2. Give the IUPAC name for glyceraldehyde, (HOCH2CHOHCHO). (Hint: as a substituent, the OH group is named hydroxy.)

Answers

1.



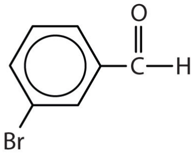
3-Bromobenzaldehyde

3-bromobenzaldehyde

2. 2,3-dihydroxypropanal

Answers

1. The stem names of aldehydes and ketones are derived from those of the parent alkanes, defined by the longest continuous chain (LCC) of carbon atoms that contains the functional group.
2. For an aldehyde, drop the *-e* from the alkane name and add the ending *-al*. Methanal is the IUPAC name for formaldehyde, and ethanal is the name for acetaldehyde.
3. For a ketone, drop the *-e* from the alkane name and add the ending *-one*. Propanone is the IUPAC name for acetone, and butanone is the name for ethyl methyl ketone.
4. To indicate the position of a substituent on an aldehyde, the carbonyl carbon atom is always considered to be C1; it is unnecessary to designate this group by number.
5. To indicate the position of a substituent on a ketone, number the chain in the manner that gives the carbonyl carbon atom the lowest possible number. In cyclic ketones, it is understood that the carbonyl carbon atom is C1.
6. Give the structure and IUPAC name for the compound that has the common name *m*-bromobenzaldehyde.
7. Give the IUPAC name for glyceraldehyde, ($HOCH_2CHOHCHO$). (Hint: as a substituent, the OH group is named *hydroxy*.)
8.

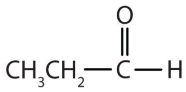


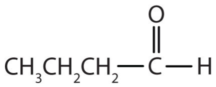
3-Bromobenzaldehyde

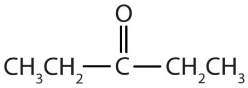
3-bromobenzaldehyde

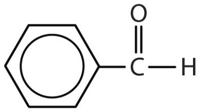
9. 2,3-dihydroxypropanal

10. Name each compound.

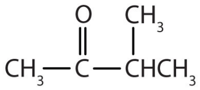
a. 
$CH_3CH_2-\overset{O}{\overset{\|}{C}}-H$

b. 
$CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-H$

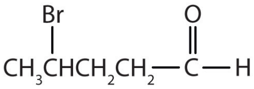
c. 
$CH_3CH_2-\overset{O}{\overset{\|}{C}}-CH_2CH_3$

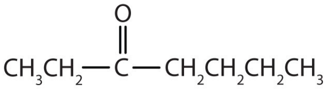
d. 

11. Name each compound.

a. 
$CH_3-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\overset{|}{C}}HCH_3$

b. $CH_3CH_2CH_2CH_2CH_2CHO$

c. 
$CH_3\overset{Br}{\overset{|}{C}}HCH_2CH_2-\overset{O}{\overset{\|}{C}}-H$

d. 
$CH_3CH_2-\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_2CH_3$

12. Draw the structure for each compound.

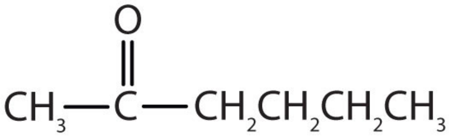
a. butyraldehyde
b. 2-hexanone
c. *p*-nitrobenzaldehyde

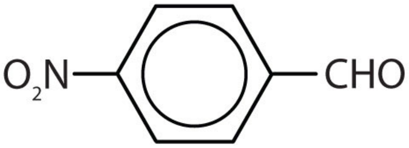
13. Draw the structure for each compound.

a. 5-ethyloctanal
b. 2-chloropropanal
c. 2-hydroxy-3-pentanone

14. a. propanal or propionaldehyde
b. butanal or butyraldehyde
c. 3-pentanone or diethyl ketone
d. benzaldehyde

15. a. $CH_3CH_2CH_2CHO$

b. 
$CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_2CH_3$

c. 

14.10: Properties of Aldehydes and Ketones

Concept Review Exercises

1. What feature of their structure makes aldehydes easier to oxidize than ketones?
2. How does the carbon-to-oxygen bond of aldehydes and ketones differ from the carbon-to-carbon bond of alkenes?

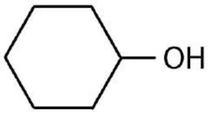
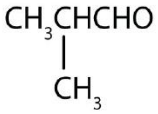
Answers

1. the H on the carbonyl carbon atom
2. The carbon-to-oxygen double bond is polar; the carbon-to-carbon double bond is nonpolar.

Exercises

1. Which compound in each pair has the higher boiling point?
   1. acetone or 2-propanol
   2. dimethyl ether or acetaldehyde
2. Which compound in each pair has the higher boiling point?
   1. butanal or 1-butanol
   2. acetone or isobutane
3. Draw the structure of the alcohol that could be oxidized to each compound.
   1. cyclohexanone
   2. 2-methyl-1-propanal
4. Draw the structure of the alcohol that could be oxidized to each compound.
   1. 2-pentanone
   2. *o*-methylbenzaldehyde
5. Acetaldehyde is treated with each substance.
   1. $Ag^+(aq)$—What inorganic product, if any, is formed?
   2. $K_2Cr_2O_7$ in an acid solution—What organic product, if any, is formed?
6. Acetone is treated with each substance.
   1. $Ag^+(aq)$ —What inorganic product, if any, is formed?
   2. $K_2Cr_2O_7$ in an acid solution—What organic product, if any, is formed?

Answers

1. 1. 2-propanol
   2. acetaldehyde
3. 1. 
   2. 

      $CH_3CH(CH_3)CHO$
5. 1. silver metal (Ag)
   2. acetic acid (CH_3COOH)

14.11: Organic Sulfur Compounds

Concept Review Exercises

1. What is the functional group of a thiol? Write the condensed structural formula for ethanethiol (ethyl mercaptan).
2. What is the functional group of a disulfide? Write the condensed structural formula for dipropyl disulfide.

Answers

1. SH; CH_3CH_2SH
2. –S–S–; $CH_3CH_2CH_2SSCH_2CH_2CH_3$

Exercises

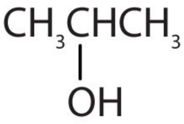
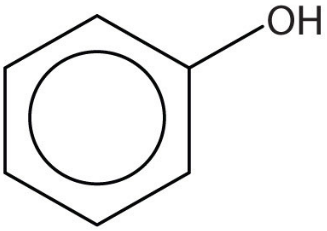
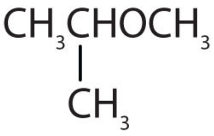
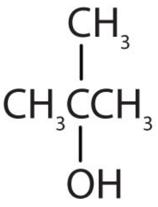
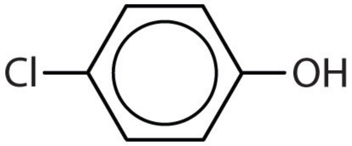
1. A common natural gas odorant is *tert*-butyl mercaptan. What is its condensed structural formula?
2. Write the equation for the oxidation of ethanethiol to diethyl disulfide.

Answer

1. $(CH_3)_3CSH$

Extra Exercises

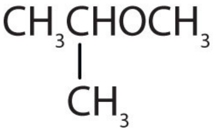
1. Describe two ways that ethanol can be prepared. Which method is used to produce alcoholic beverages?
2. Give the structure of the alkene from which isopropyl alcohol is made by reaction with water in an acidic solution.
3. Ethanol is used as a solvent for some drugs that are not soluble in water. Why is methanol not used in medicines?
4. Give the structure of the alkene that is made from *tert*-butyl alcohol [$(CH_3)_3COH$] by reaction with water in an acidic solution.
5. Classify each conversion as oxidation, dehydration, or hydration (only the organic starting material and product are shown):
   a. $CH_3OH \rightarrow HCHO$
   b. $CH_3CHOHCH_3 \rightarrow CH_3CH{=}CH_2$
   c. $CH_2{=}CHCH_2CH_3 \rightarrow CH_3CHOHCH_2CH_3$
6. Classify each conversion as oxidation, dehydration, or hydration (only the organic starting material and product are shown.):
   a. $CH_3CHOHCH_3 \rightarrow CH_3COCH_3$
   b. $HOOCCH{=}CHCOOH \rightarrow HOOCCH_2CHOHCOOH$
   c. $2\ CH_3OH \rightarrow CH_3OCH_3$

7. Why is methanol so much more toxic to humans than ethanol?
8. Each of the four isomeric butyl alcohols is treated with potassium dichromate ($K_2Cr_2O_7$) in acid. Give the product (if any) expected from each reaction.
9. Draw the structures and give IUPAC names for the four isomeric aldehydes having the formula $C_5H_{10}O$.
10. Write an equation for the reaction of phenol with aqueous NaOH.
11. Write an equation for the ionization of phenol in water.
12. Draw the structures and give the common and IUPAC names for the three isomeric ketones having the formula $C_5H_{10}O$.
13. As we shall see in Chapter 16 "Carbohydrates", 2,3-dihydroxypropanal and 1,3-dihydroxyacetone are important carbohydrates. Draw their structures.
14. Glutaraldehyde (pentanedial) is a germicide that is replacing formaldehyde as a sterilizing agent. It is less irritating to the eyes, the nose, and skin. Write the condensed structural formula of glutaraldehyde.
15. Why does the oxidation of isopropyl alcohol give a ketone, whereas the oxidation of isobutyl alcohol gives an aldehyde?
16. Identify each compound as an alcohol, a phenol, or an ether. Classify any alcohols as primary (1°), secondary (2°), or tertiary (3°).
    a. $CH_3CH_2CH_2OH$
    b. 
    $\underset{\displaystyle OH}{CH_3\underset{|}{C}HCH_3}$
    c. 
    d. 
    $\underset{\displaystyle CH_3}{CH_3\underset{|}{C}HOCH_3}$
17. Identify each compound as an alcohol, a phenol, or an ether. Classify any alcohols as primary, secondary, or tertiary.
    a. $CH_3CH_2OCH_2CH_3$
    b. 
    $\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{CH_3\overset{|}{\underset{|}{C}}CH_3}}$
    c. 

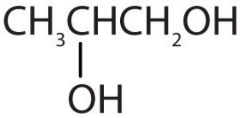
d. 

$$CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CH_2CH_3$$

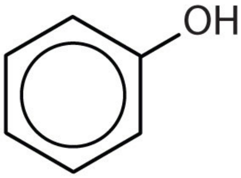
18. Tell whether each compound forms an acidic, a basic, or a neutral solution in water.

a. 

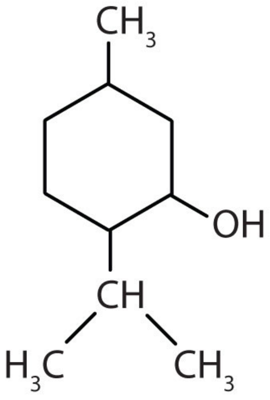
$$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HOCH_3$$

b. 

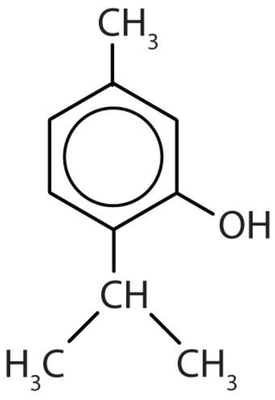
$$CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_2OH$$

c. 

19. When water is added to ethylene in the presence of an acid catalyst, only one product—ethanol—is possible. However, when water is added to propylene, two products are possible—1-propanol and 2-propanol—but only 2-propanol is formed. In 1870, the Russian chemist Vladimir V. Markovnikov proposed a rule to predict the products of such reactions: Considering water to be HOH, the hydrogen atom of water goes on the carbon atom (of the two involved in the double bond) that has the most hydrogen atoms already bonded to it. The OH group goes on the carbon atom with fewer hydrogen atoms. Use Markovnikov's rule to predict the product of the addition of water to each compound.
    a. 2-methylpropene
    b. 1-butene
    c. 2-methyl-1-pentene
    d. 2-methyl-2-pentene
20. Ethyl alcohol, like rubbing alcohol (isopropyl alcohol), is often used for sponge baths. What property of alcohols makes them useful for this purpose?
21. In addition to ethanol, the fermentation of grain produces other organic compounds collectively called fusel oils (FO). The four principal FO components are 1-propanol, isobutyl alcohol, 3-methyl-1-butanol, and 2-methyl-1-butanol. Draw a structure for each. (FO is quite toxic and accounts in part for hangovers.)
22. Draw and name the isomeric ethers that have the formula $C_5H_{12}O$.
23. Menthol is an ingredient in mentholated cough drops and nasal sprays. It produces a cooling, refreshing sensation when rubbed on the skin and so is used in shaving lotions and cosmetics. Thymol, the aromatic equivalent of menthol, is the flavoring constituent of thyme.



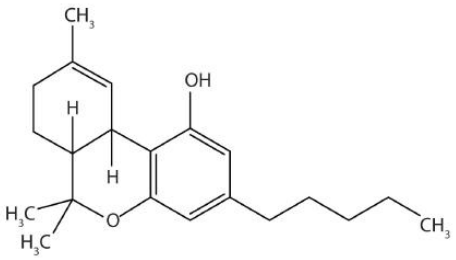
Menthol



Thymol

a. To what class of compounds does each belong?
b. Give an alternate name for thymol.

24. Write the equation for the production of ethanol by the addition of water to ethylene. How much ethanol can be made from 14.0 kg of ethylene?
25. Methanol is not particularly toxic to rats. If methanol were newly discovered and tested for toxicity in laboratory animals, what would you conclude about its safety for human consumption?
26. The amino acid cysteine has the formula $HSCH_2CH(NH_2)COOH$. What is the sulfur-containing functional group in the cysteine molecule?
27. The amino acid methionine has the formula $CH_3SCH_2CH_2CH(NH_2)COOH$. What functional groups are in methionine?
28. Tetrahydrocannabinol is the principal active ingredient in marijuana. What functional groups are present in this molecule?



Answers

1. addition of water to ethylene; fermentation (for beverages)

3. Methanol is too toxic.

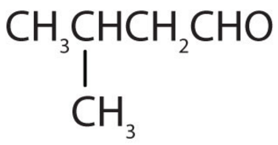
5.
   a. oxidation
   b. dehydration
   c. hydration

7. Methanol is oxidized in the body to toxic formaldehyde; ethanol is oxidized to the less toxic acetaldehyde.

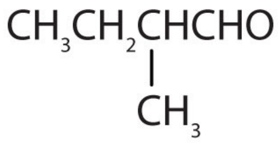
9.


$CH_3CH_2CH_2CH_2CHO$

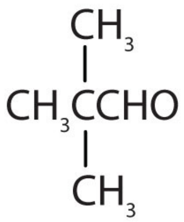
Pentanal


CH_3CHCH_2CHO with CH_3 on the second carbon

3-Methylbutanal


CH_3CH_2CHCHO with CH_3 on the third carbon

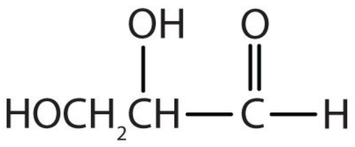
2-Methylbutanal


CH_3CCHO with CH_3 above and CH_3 below the second carbon

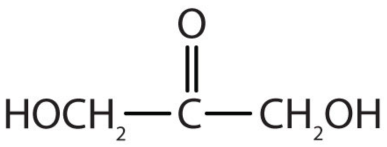
2,2-Dimethylpropanal

11. $C_6H_5OH + H_2O \rightarrow C_6H_5O^- + H_3O^+$

13.


$HOCH_2CH(OH)—C(=O)—H$

and


$HOCH_2—C(=O)—CH_2OH$

15. Isopropyl alcohol is a secondary alcohol, whereas isobutyl alcohol is a primary alcohol.

17.

a. ether
b. tertiary alcohol
c. phenol
d. secondary alcohol

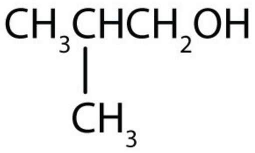
19.

a. *tert*-butyl alcohol
b. 2-butanol
c. 2-methyl-2-pentanol
d. 2-methyl-2-pentanol

21.

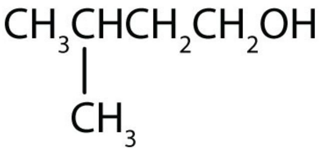
$CH_3CH_2CH_2OH$

1-Propanol



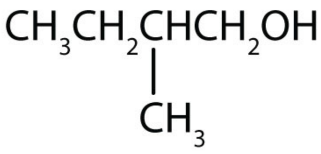
$\mathrm{CH_3\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_2OH}$

Isobutyl alcohol



$\mathrm{CH_3\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_2CH_2OH}$

3-Methyl-1-butanol



$\mathrm{CH_3CH_2\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_2OH}$

2-Methyl-1-butanol

23.

a. menthol: alcohol; thymol: phenol
b. 2-isopropyl-5-methylphenol

25. It might be ruled safe until tested on humans.

27. sulfide, amino, and carboxylic acid

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14.S: Organic Compounds of Oxygen (Summary)

CHAPTER OVERVIEW

15: Organic Acids and Bases and Some of Their Derivatives

Organic acids have been known for ages. Prehistoric people likely made acetic acid when their fermentation reactions went awry and produced vinegar instead of wine. The Sumerians (2900–1800 BCE) used vinegar as a condiment, a preservative, an antibiotic, and a detergent. Citric acid was discovered by an Islamic alchemist, Jabir Ibn Hayyan (also known as Geber), in the 8th century, and crystalline citric acid was first isolated from lemon juice in 1784 by the Swedish chemist Carl Wilhelm Scheele. Medieval scholars in Europe were aware that the crisp, tart flavor of citrus fruits is caused by citric acid. Naturalists of the 17th century knew that the sting of a red ant's bite was due to an organic acid that the ant injected into the wound. The acetic acid of vinegar, the formic acid of red ants, and the citric acid of fruits all belong to the same family of compounds—carboxylic acids. Soaps are salts of long-chain carboxylic acids. Prehistoric people also knew about organic bases—by smell if not by name; amines are the organic bases produced when animal tissue decays. The organic compounds that we consider in this chapter are organic acids and bases. We will also consider two derivatives of carboxylic acids: esters and amides. An ester is derived from a carboxylic acid and an alcohol. Fats and oils are esters, as are many important fragrances and flavors. An amide is derived from a carboxylic acid and either ammonia or an amine. Proteins, often called "the stuff of life," are polyamides.

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15.0: Prelude to Organic Acids and Bases and Some of Their Derivatives

Organic acids have been known for ages. Prehistoric people likely made acetic acid when their fermentation reactions went awry and produced vinegar instead of wine. The Sumerians (2900–1800 BCE) used vinegar as a condiment, a preservative, an antibiotic, and a detergent. Citric acid was discovered by an Islamic alchemist, Jabir Ibn Hayyan (also known as Geber), in the 8th century, and crystalline citric acid was first isolated from lemon juice in 1784 by the Swedish chemist Carl Wilhelm Scheele. Medieval scholars in Europe were aware that the crisp, tart flavor of citrus fruits is caused by citric acid. Naturalists of the 17th century knew that the sting of a red ant's bite was due to an organic acid that the ant injected into the wound. The acetic acid of vinegar, the formic acid of red ants, and the citric acid of fruits all belong to the same family of compounds—carboxylic acids. Soaps are salts of long-chain carboxylic acids.

Prehistoric people also knew about organic bases—by smell if not by name; amines are the organic bases produced when animal tissue decays.

15.1: Carboxylic Acids - Structures and Names

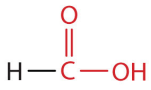
Learning Objectives

- Name carboxylic acids with common names.
- Name carboxylic acids according to IUPAC nomenclature.

Carboxylic acids occur widely in nature, often combined with alcohols or other functional groups, as in fats, oils, and waxes. They are components of many foods, medicines, and household products (Figure 15.1.1). Not surprisingly, many of them are best known by common names based on Latin and Greek words that describe their source.

Figure 15.1.1: Carboxylic Acids in the Home. Carboxylic acids occur in many common household items. (a) Vinegar contains acetic acid, (b) aspirin is acetylsalicylic acid, (c) vitamin C is ascorbic acid, (d) lemons contain citric acid, and (e) spinach contains oxalic acid. © Thinkstock

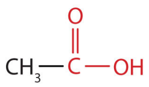
The simplest carboxylic acid, formic acid (HCOOH), was first obtained by the distillation of ants (Latin *formica*, meaning "ant"). The bites of some ants inject formic acid, and the stings of wasps and bees contain formic acid (as well as other poisonous materials).



$$H-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

Formic acid

The next higher homolog is acetic acid, which is made by fermenting cider and honey in the presence of oxygen. This fermentation produces vinegar, a solution containing 4%–10% acetic acid, plus a number of other compounds that add to its flavor. Acetic acid is probably the most familiar weak acid used in educational and industrial chemistry laboratories.



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

Acetic acid

> Pure acetic acid solidifies at 16.6°C, only slightly below normal room temperature. In the poorly heated laboratories of the late 19th and early 20th centuries in northern North America and Europe, acetic acid often "froze" on the storage shelf. For that

> reason, pure acetic acid (sometimes called concentrated acetic acid) came to be known as *glacial acetic acid*, a name that survives to this day.

The third homolog, propionic acid (CH_3CH_2COOH), is seldom encountered in everyday life. The fourth homolog, butyric acid ($CH_3CH_2CH_2COOH$), is one of the most foul-smelling substances imaginable. It is found in rancid butter and is one of the ingredients of body odor. By recognizing extremely small amounts of this and other chemicals, bloodhounds are able to track fugitives. Models of the first four carboxylic acids are shown in Figure 15.1.2

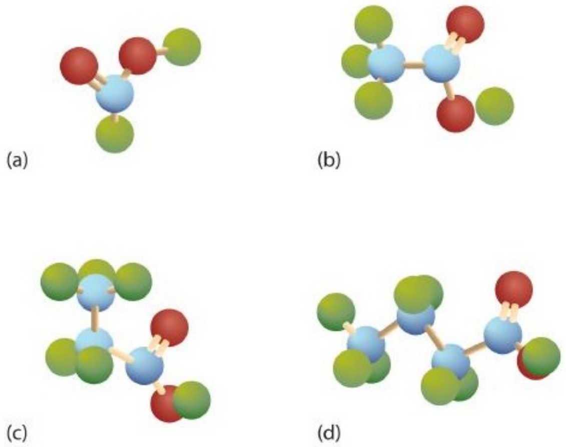
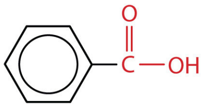


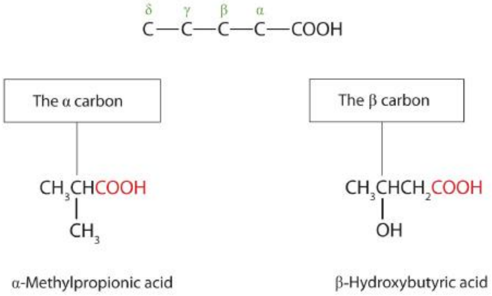
Figure 15.1.2: Ball-and-Stick Models of Carboxylic Acids. Carboxylic acids feature a carbon atom doubly bonded to an oxygen atom and also joined to an OH group. The four acids illustrated here are formic acid (a), acetic acid (b), propionic acid (c), and butyric acid (d).

The acid with the carboxyl group attached directly to a benzene ring is called benzoic acid (C_6H_5COOH).



Benzoic acid

The common names of carboxylic acids use Greek letters (α, β, γ, δ, and so forth), not numbers, to designate the position of substituent groups in acids. These letters refer to the position of the carbon atom in relation to the carboxyl carbon atom.

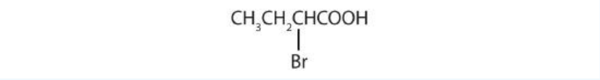


In the nomenclature system of the International Union of Pure and Applied Chemistry (IUPAC), the parent hydrocarbon is the one that corresponds to the longest continuous chain (LCC) containing the carboxyl group. The *-e* ending of the parent alkane is replaced by the suffix *-oic* and the word *acid*. For example, the carboxylic acid derived from pentane is pentanoic acid ($CH_3CH_2CH_2CH_2COOH$). As with aldehydes, the carboxyl carbon atom is counted first; numbers are used to indicate any substituted carbon atoms in the parent chain.

> Greek letters are used with common names; numbers are used with IUPAC names.

Example 15.1.1

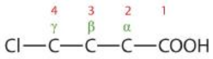
Give the common and IUPAC names for each compound.

1. $ClCH_2CH_2CH_2COOH$
2. 

$$\begin{array}{c}CH_3CH_2CHCOOH\\ \hspace{1em}|\\ \hspace{1em}Br\end{array}$$

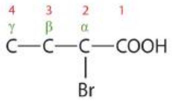
Solution

1. The LCC contains four carbon atoms; the compound is therefore named as a substituted butyric (or butanoic) acid.



The chlorine atom is attached to the γ-carbon in the common system or C4 in the IUPAC system. The compound is γ-chlorobutyric acid or 4-chlorobutanoic acid.

2. The LCC contains four carbon atoms; the compound is therefore named as a substituted butyric (or butanoic) acid.



The bromine (Br) atom is at the α-carbon in the common system or C2 in the IUPAC system. The compound is α-bromobutyric acid or 2-bromobutanoic acid.

Exercise 15.1.1

Give the IUPAC name for each compound.

a. $ClCH_2CH_2CH_2CH_2COOH$
b. $(CH_3)_2CHCH_2CHBrCOOH$

Example 15.1.2

Write the condensed structural formula for β-chloropropionic acid.

Solution

Propionic acid has three carbon atoms: C–C–COOH. Attach a chlorine (Cl) atom to the parent chain at the beta carbon atom, the second one from the carboxyl group: Cl–C–C–COOH. Then add enough hydrogen atoms to give each carbon atom four bonds: $ClCH_2CH_2COOH$.

Exercise 15.1.2

Write the condensed structural formula for 4-bromo-5-methylhexanoic acid.

Key Takeaways

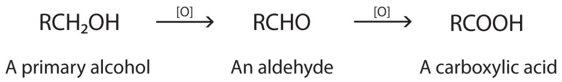
- Simple carboxylic acids are best known by common names based on Latin and Greek words that describe their source (e.g., formic acid, Latin *formica*, meaning "ant").
- Greek letters, not numbers, designate the position of substituted acids in the common naming convention.
- IUPAC names are derived from the LCC of the parent hydrocarbon with the *-e* ending of the parent alkane replaced by the suffix *-oic* and the word *acid*.

15.2: The Formation of Carboxylic Acids

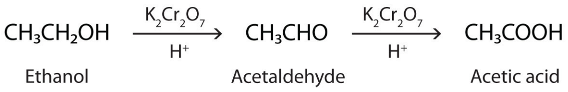
Learning Objectives

- To describe the preparation of carboxylic acids.

As we noted previously, the oxidation of aldehydes or primary alcohols forms carboxylic acids:



In the presence of an oxidizing agent, ethanol is oxidized to acetaldehyde, which is then oxidized to acetic acid.



This process also occurs in the liver, where enzymes catalyze the oxidation of ethanol to acetic acid.

$$\mathrm{CH_3CH_2OH} \xrightarrow[\text{oxidizing agent}]{\text{alcohol dehydrogenase}} \mathrm{CH_3CHO} \xrightarrow[\text{oxidizing agent}]{\text{alcohol dehydrogenase}} \mathrm{CH_3COOH}$$

Acetic acid can be further oxidized to carbon dioxide and water.

Summary

Whether in the laboratory or in the body, the oxidation of aldehydes or primary alcohols forms carboxylic acids.

15.3: Physical Properties of Carboxylic Acids

Learning Objectives

- Compare the boiling points of carboxylic acids with alcohols of similar molar mass.
- Compare the solubilities of carboxylic acids in water with the solubilities of comparable alkanes and alcohols in water.

Many carboxylic acids are colorless liquids with disagreeable odors. The carboxylic acids with 5 to 10 carbon atoms all have "goaty" odors (explaining the odor of Limburger cheese). These acids are also produced by the action of skin bacteria on human sebum (skin oils), which accounts for the odor of poorly ventilated locker rooms. The acids with more than 10 carbon atoms are waxlike solids, and their odor diminishes with increasing molar mass and resultant decreasing volatility.

Carboxylic acids exhibit strong hydrogen bonding between molecules. They therefore have high boiling points compared to other substances of comparable molar mass.

The carboxyl group readily engages in hydrogen bonding with water molecules (Figure 15.3.1). The acids with one to four carbon atoms are completely miscible with water. Solubility decreases as the carbon chain length increases because dipole forces become less important and dispersion forces become more predominant. Hexanoic acid [$CH_3(CH_2)_4COOH$] is barely soluble in water (about 1.0 g/100 g of water). Palmitic acid [$CH_3(CH_2)_{14}COOH$], with its large nonpolar hydrocarbon component, is essentially insoluble in water. The carboxylic acids generally are soluble in such organic solvents as ethanol, toluene, and diethyl ether.

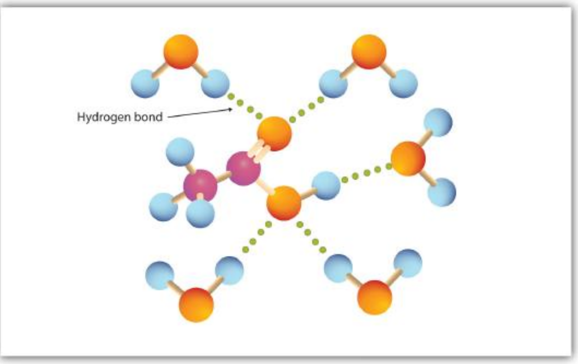


Figure 15.3.1: Hydrogen Bonding between an Acetic Acid Molecule and Water Molecules. Carboxylic acids of low molar mass are quite soluble in water.

Table 15.4.1 lists some physical properties for selected carboxylic acids. The first six are homologs. Notice that the boiling points increase with increasing molar mass, but the melting points show no regular pattern.

Table 15.3.1: Physical Constants of Carboxylic Acids

Condensed Structural Formula	Name of Acid	Melting Point (°C)	Boiling Point (°C)	Solubility (g/100 g of Water)
HCOOH	formic acid	8	100	miscible
CH_3COOH	acetic acid	17	118	miscible
CH_3CH_2COOH	propionic acid	–22	141	miscible
$CH_3(CH_2)_2COOH$	butyric acid	–5	163	miscible
$CH_3(CH_2)_3COOH$	valeric acid	–35	187	5
$CH_3(CH_2)_4COOH$	caproic acid	–3	205	1.1
C_6H_5COOH	benzoic acid	122	249	0.29

Key Takeaways

- Carboxylic acids have high boiling points compared to other substances of comparable molar mass. Boiling points increase with molar mass.
- Carboxylic acids having one to four carbon atoms are completely miscible with water. Solubility decreases with molar mass.

15.4: Chemical Properties of Carboxylic Acids- Ionization and Neutralization

Learning Objectives

- Name the typical reactions that take place with carboxylic acids.
- Describe how carboxylic acids react with basic compounds.

Water-soluble carboxylic acids ionize slightly in water to form moderately acidic solutions.

$$\mathrm{RCOOH} + \mathrm{H_2O} \rightleftharpoons \mathrm{RCOO^-} + \mathrm{H_3O^+}$$

Their aqueous solutions exhibit the typical properties of acids, such as changing litmus from blue to red.

> The anion formed when a carboxylic acid dissociates is called the *carboxylate* anion ($RCOO^-$).

Whether soluble in water or not, carboxylic acids react with aqueous solutions of sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), and sodium bicarbonate ($NaHCO_3$) to form salts:

$$\mathrm{RCOOH + NaOH(aq) \rightarrow RCOO^-Na^+(aq) + H_2O}$$

$$\mathrm{2RCOOH + Na_2CO_3(aq) \rightarrow 2RCOO^-Na^+(aq) + H_2O + CO_2(g)}$$

$$\mathrm{RCOOH + NaHCO_3(aq) \rightarrow RCOO^-Na^+(aq) + H_2O + CO_2(g)}$$

In these reactions, the carboxylic acids act like inorganic acids: they neutralize basic compounds. With solutions of carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions, they also form carbon dioxide gas.

Carboxylic acid salts are named in the same manner as inorganic salts: the name of the cation is followed by the name of the organic anion. The name of the anion is obtained by dropping the *-ic* ending of the acid name and replacing it with the suffix *-ate*. This rule applies whether we are using common names or International Union of Pure and Applied Chemistry (IUPAC) names:

$CH_3COO^-Li^+$	$CH_3CH_2CH_2COO^-K^+$	$C_6H_5COO^-Na^+$
Lithium acetate (lithium ethanoate)	Potassium butyrate (potassium butanoate)	Sodium benzoate

> The salts of long-chain carboxylic acids are called soaps. We discuss the chemistry of soaps elsewhere.
>
> $CH_3(CH_2)_{13}CH_2COO^-Na^+$
>
> Sodium palmitate (a soap)

Example 15.4.1

Write an equation for each reaction.

1. the ionization of propionic acid in water (H_2O)
2. the neutralization of propionic acid with aqueous sodium hydroxide (NaOH)

Solution

Propionic acid has three carbon atoms, so its formula is CH_2CH_2COOH.

1. Propionic acid ionizes in water to form a propionate ion and a hydronium (H_3O^+) ion. $CH_3CH_2COOH(aq) + H_2O(\ell) \rightarrow CH_3CH_2COO^-(aq) + H_3O^+(aq)$
2. Propionic acid reacts with NaOH(aq) to form sodium propionate and water. $CH_3CH_2COOH(aq) + NaOH(aq) \rightarrow CH_3CH_2COO^-Na^+(aq) + H_2O(\ell)$

Exercise 15.4.1

Write an equation for each reaction.

a. the ionization of formic acid in water
b. the ionization of *p*-chlorobenzoic acid in water

Example 15.4.2

Write an equation for the reaction of decanoic acid with each compound.

a. aqueous sodium hydoxide (NaOH)
b. aqueous sodium bicarbonate ($NaHCO_3$)

Solution

a. Decanoic acid has 10 carbon atoms. It reacts with NaOH to form a salt and water (H_2O). $CH_3(CH_2)_8COOH + NaOH(aq) \rightarrow CH_3(CH_2)_8COO^-Na^+(aq) + H_2O(\ell)$
b. With $NaHCO_3$, the products are a salt, H_2O, and carbon dioxide (CO_2). $CH_3(CH_2)_8COOH + NaHCO_3(aq) \rightarrow CH_3(CH_2)_8COO^-Na^+(aq) + H_2O(\ell) + CO_2(g)$

Exercise 15.4.3

Write an equation for the reaction of benzoic acid with each compound.

a. aqueous sodium hydroxide (NaOH)
b. aqueous sodium bicarbonate ($NaHCO_3$)

To Your Health: Organic Salts as Preservatives

Some organic salts are used as preservatives in food products. They prevent spoilage by inhibiting the growth of bacteria and fungi. Calcium and sodium propionate, for example, are added to processed cheese and bakery goods; sodium benzoate is added to cider, jellies, pickles, and syrups; and sodium sorbate and potassium sorbate are added to fruit juices, sauerkraut, soft drinks, and wine. Look for them on ingredient labels the next time you shop for groceries.

$(CH_3CH_2COO^-)_2\ Ca^{2+}$

Calcium propionate

$CH_3CH{=}CHCH{=}CHCOO^-K^+$

Potassium sorbate

Key Takeaways

- Soluble carboxylic acids are weak acids in aqueous solutions.
- Carboxylic acids neutralize bases to form salts.

15.5: Esters - Structures and Names

Learning Objectives

- Identify the general structure for an ester.
- Use common names to name esters.
- Name esters according to the IUPAC system.

Esters have the general formula RCOOR′, where R may be a hydrogen atom, an alkyl group, or an aryl group, and R′ may be an alkyl group or an aryl group but *not* a hydrogen atom. (If it were hydrogen atom, the compound would be a carboxylic acid.) Figure 15.5.1 shows models for two common esters.

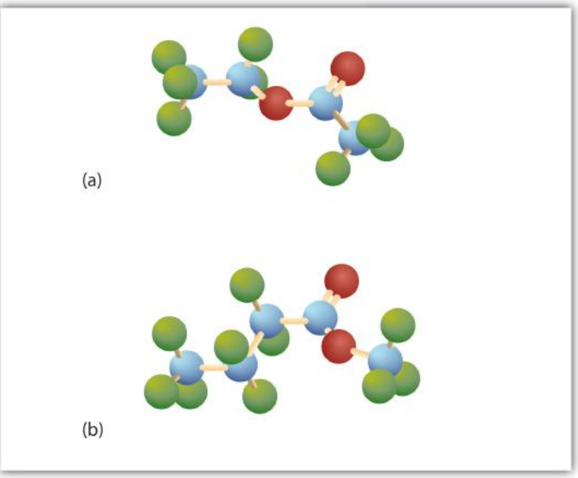


Figure 15.5.1: The Structure of Esters. Esters feature a carbon-to-oxygen double bond that is also singly bonded to a second oxygen atom, which is then joined to an alkyl or an aryl group. The esters shown here are ethyl acetate (a) and methyl butyrate (b).

Esters occur widely in nature. Unlike carboxylic acids, esters generally have pleasant odors and are often responsible for the characteristic fragrances of fruits and flowers. Once a flower or fruit has been chemically analyzed, flavor chemists can attempt to duplicate the natural odor or taste. Both natural and synthetic esters are used in perfumes and as flavoring agents.

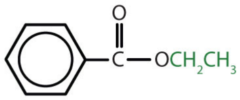
> Fats and vegetable oils are esters of long-chain fatty acids and glycerol. Esters of phosphoric acid are of the utmost importance to life.

Names of Esters

Although esters are covalent compounds and salts are ionic, esters are named in a manner similar to that used for naming salts. The group name of the alkyl or aryl portion is given first and is followed by the name of the acid portion. In both common and International Union of Pure and Applied Chemistry (IUPAC) nomenclature, the *-ic* ending of the parent acid is replaced by the suffix *-ate* (Table 15.5.1).

Table 15.5.1: Nomenclature of Esters

Condensed Structural Formula	Common Name	IUPAC Name
$HCOOCH_3$	methyl formate	methyl methanoate
CH_3COOCH_3	methyl acetate	methyl ethanoate
$CH_3COOCH_2CH_3$	ethyl acetate	ethyl ethanoate
$CH_3CH_2COOCH_2CH_3$	ethyl propionate	ethyl propanoate
$CH_3CH_2CH_2COOCH(CH_3)_2$	isopropyl butyrate	isopropyl butanoate

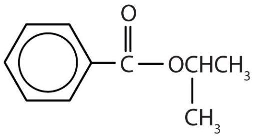
Condensed Structural Formula	Common Name	IUPAC Name
	ethyl benzoate	ethyl benzoate

Example 15.5.1

Give the common and IUPAC names for each compound.

1. 

$CH_3CH_2\overset{\overset{O}{\|}}{C}OCH_2CH_2CH_2CH_3$

2. 

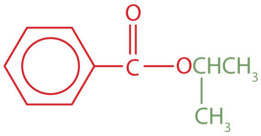
Solution

The alkyl group attached directly to the oxygen atom is a butyl group (in green).

$CH_3CH_2\overset{\overset{O}{\|}}{C}OCH_2CH_2CH_2CH_3$

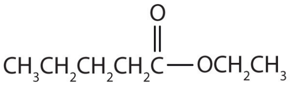
The part of the molecule derived from the carboxylic acid (in red) has three carbon atoms. It is called propionate (common) or propanoate (IUPAC). The ester is therefore butyl propionate or butyl propanoate.

1. An alkyl group (in green) is attached directly to the oxygen atom by its middle carbon atom; it is an isopropyl group. The part derived from the acid (that is, the benzene ring and the carbonyl group, in red) is benzoate. The ester is therefore isopropyl benzoate (both the common name and the IUPAC name).

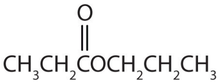


Exercise 15.5.1

Give the common and IUPAC names for each compound.

1. 

$CH_3CH_2CH_2CH_2\overset{\overset{O}{\|}}{C}—OCH_2CH_3$



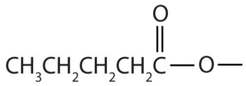
$CH_3CH_2\overset{\overset{O}{\|}}{C}OCH_2CH_3$

Example 15.5.2

Draw the structure for ethyl pentanoate.

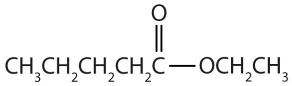
Solution

Start with the portion from the acid. Draw the pentanoate (five carbon atoms) group first; keeping in mind that the last carbon atom is a part of the carboxyl group.



$$\mathrm{CH_3CH_2CH_2CH_2}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{O}-$$

Then attach the ethyl group to the bond that ordinarily holds the hydrogen atom in the carboxyl group.



$$\mathrm{CH_3CH_2CH_2CH_2}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{OCH_2CH_3}$$

? Exercise 15.5.2

Draw the structure for phenyl pentanoate.

Key Takeaway

- An ester has an OR group attached to the carbon atom of a carbonyl group.

15.6: Physical Properties of Esters

Learning Objectives

- Compare the boiling points of esters with alcohols of similar molar mass.
- Compare the solubilities of esters in water with the solubilities of comparable alkanes and alcohols in water.

Ester molecules are polar but have no hydrogen atom attached directly to an oxygen atom. They are therefore incapable of engaging in intermolecular hydrogen bonding with one another and thus have considerably lower boiling points than their isomeric carboxylic acids counterparts. Because ester molecules can engage in hydrogen bonding with water molecules, however, esters of low molar mass are somewhat soluble in water. Borderline solubility occurs in those molecules that have three to five carbon atoms. Table 15.6.1 lists the physical properties of some common esters.

> Esters are common solvents. Ethyl acetate is used to extract organic solutes from aqueous solutions—for example, to remove caffeine from coffee. It also is used to remove nail polish and paint. Cellulose nitrate is dissolved in ethyl acetate and butyl acetate to form lacquers. The solvent evaporates as the lacquer "dries," leaving a thin film on the surface. High boiling esters are used as softeners (plasticizers) for brittle plastics.

Table 15.6.1: *Physical Properties of Some Esters*

Condensed Structural Formula	Name	Molar Mass	Melting Point (°C)	Boiling Point (°C)	Aroma
$HCOOCH_3$	methyl formate	60	−99	32	
$HCOOCH_2CH_3$	ethyl formate	74	−80	54	rum
CH_3COOCH_3	methyl acetate	74	−98	57	
$CH_3COOCH_2CH_3$	ethyl acetate	88	−84	77	
$CH_3CH_2CH_2COOCH_3$	methyl butyrate	102	−85	102	apple
$CH_3CH_2CH_2COOCH_2CH_3$	ethyl butyrate	116	−101	121	pineapple
$CH_3COO(CH_2)_4CH_3$	pentyl acetate	130	−71	148	pear
$CH_3COOCH_2CH_2CH(CH_3)_2$	isopentyl acetate	130	−79	142	banana
$CH_3COOCH_2C_6H_5$	benzyl acetate	150	−51	215	jasmine
$CH_3CH_2CH_2COO(CH_2)_4CH_3$	pentyl butyrate	158	−73	185	apricot
$CH_3COO(CH_2)_7CH_3$	octyl acetate	172	−39	210	orange

Summary

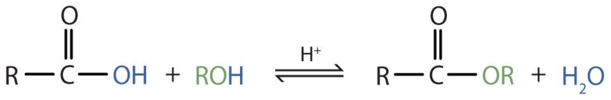
Esters have polar bonds but do not engage in hydrogen bonding and are therefore intermediate in boiling points between the nonpolar alkanes and the alcohols, which engage in hydrogen bonding. Ester molecules can engage in hydrogen bonding with water, so esters of low molar mass are therefore somewhat soluble in water.

15.7: Preparation of Esters

Learning Objectives

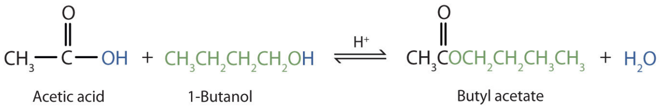
- To identify and describe the substances from which most esters are prepared.

Some esters can be prepared by esterification, a reaction in which a carboxylic acid and an alcohol, heated in the presence of a mineral acid catalyst, form an ester and water:



$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH + ROH \overset{H^+}{\rightleftharpoons} R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OR + H_2O$$

The reaction is reversible. As a specific example of an esterification reaction, butyl acetate can be made from acetic acid and 1-butanol.

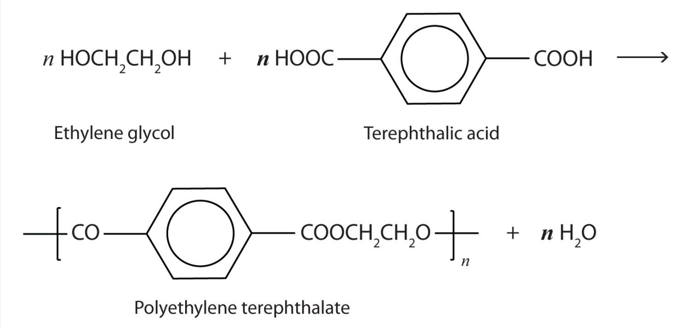


$$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH + CH_3CH_2CH_2CH_2OH \overset{H^+}{\rightleftharpoons} CH_3\overset{\overset{\displaystyle O}{\|}}{C}OCH_2CH_2CH_3CH_3 + H_2O$$

A Closer Look: Condensation Polymers

A commercially important esterification reaction is condensation polymerization, in which a reaction occurs between a dicarboxylic acid and a dihydric alcohol (diol), with the elimination of water. Such a reaction yields an ester that contains a free (unreacted) carboxyl group at one end and a free alcohol group at the other end. Further condensation reactions then occur, producing polyester polymers.

The most important polyester, polyethylene terephthalate (PET), is made from terephthalic acid and ethylene glycol monomers:



Polyester molecules make excellent fibers and are used in many fabrics. A knitted polyester tube, which is biologically inert, can be used in surgery to repair or replace diseased sections of blood vessels. PET is used to make bottles for soda pop and other beverages. It is also formed into films called Mylar. When magnetically coated, Mylar tape is used in audio- and videocassettes. Synthetic arteries can be made from PET, polytetrafluoroethylene, and other polymers.

Summary

Esters are made by the reaction of a carboxylic acid with an alcohol, a process that is called esterification.

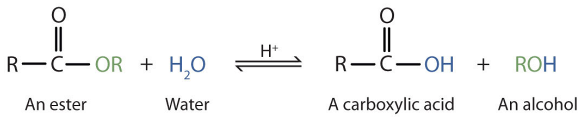
15.8: Hydrolysis of Esters

Learning Objectives

- Describe the typical reaction that takes place with esters.
- Identify the products of an acidic hydrolysis of an ester.
- Identify the products of a basic hydrolysis of an ester.

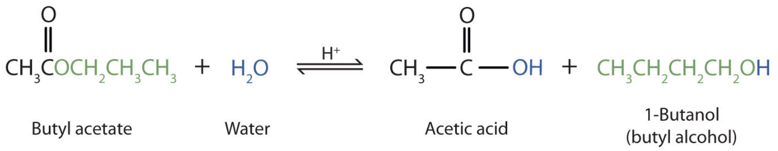
Esters are neutral compounds, unlike the acids from which they are formed. In typical reactions, the alkoxy (OR′) group of an ester is replaced by another group. One such reaction is hydrolysis, literally “splitting with water.” The hydrolysis of esters is catalyzed by either an acid or a base.

Acidic hydrolysis is simply the reverse of esterification. The ester is heated with a large excess of water containing a strong-acid catalyst. Like esterification, the reaction is reversible and does not go to completion.



$$R{-}\overset{O}{\overset{\|}{C}}{-}OR + H_2O \xrightleftharpoons{H^+} R{-}\overset{O}{\overset{\|}{C}}{-}OH + ROH$$

As a specific example, butyl acetate and water react to form acetic acid and 1-butanol. The reaction is reversible and does not go to completion.



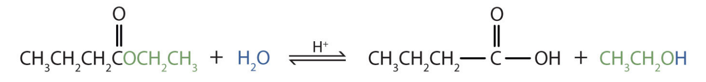
$$CH_3\overset{O}{\overset{\|}{C}}OCH_2CH_2CH_2CH_3 + H_2O \xrightleftharpoons{H^+} CH_3{-}\overset{O}{\overset{\|}{C}}{-}OH + CH_3CH_2CH_2CH_2OH$$

Example 15.8.1

Write an equation for the acidic hydrolysis of ethyl butyrate ($CH_3CH_2CH_2COOCH_2CH_3$) and name the products.

Solution

Remember that in acidic hydrolysis, water (HOH) splits the ester bond. The H of HOH joins to the oxygen atom in the OR part of the original ester, and the OH of HOH joins to the carbonyl carbon atom:



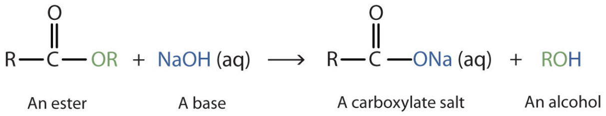
$$CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}OCH_2CH_3 + H_2O \xrightleftharpoons{H^+} CH_3CH_2CH_2{-}\overset{O}{\overset{\|}{C}}{-}OH + CH_3CH_2OH$$

The products are butyric acid (butanoic acid) and ethanol.

Exercise 15.8.1

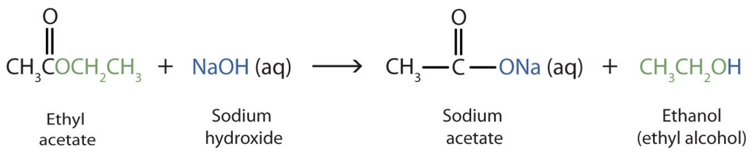
Write an equation for the acidic hydrolysis of methyl butanoate and name the products.

When a base (such as sodium hydroxide [NaOH] or potassium hydroxide [KOH]) is used to hydrolyze an ester, the products are a carboxylate salt and an alcohol. Because soaps are prepared by the alkaline hydrolysis of fats and oils, alkaline hydrolysis of esters is called saponification (Latin *sapon*, meaning “soap,” and *facere*, meaning “to make”). In a saponification reaction, the base is a reactant, not simply a catalyst. The reaction goes to completion:



$$R{-}\overset{O}{\overset{\|}{C}}{-}OR + NaOH\,(aq) \longrightarrow R{-}\overset{O}{\overset{\|}{C}}{-}ONa\,(aq) + ROH$$

As a specific example, ethyl acetate and NaOH react to form sodium acetate and ethanol:

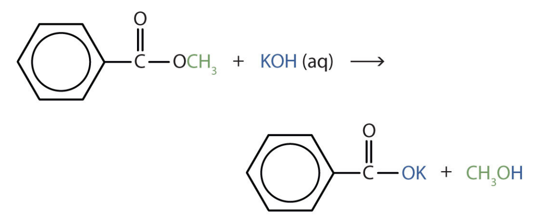


Example 15.8.2

Write an equation for the hydrolysis of methyl benzoate in a potassium hydroxide solution.

Solution

In basic hydrolysis, the molecule of the base splits the ester linkage. The acid portion of the ester ends up as the *salt* of the acid (in this case, the potassium salt). The alcohol portion of the ester ends up as the free alcohol.



Exercise 15.8.2

Write the equation for the hydrolysis of ethyl propanoate in a sodium hydroxide solution.

Summary

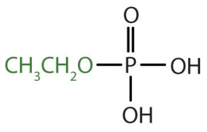
Hydrolysis is a most important reaction of esters. Acidic hydrolysis of an ester gives a carboxylic acid and an alcohol. Basic hydrolysis of an ester gives a carboxylate salt and an alcohol.

15.9: Esters of Phosphoric Acid

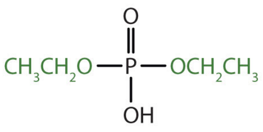
Learning Objectives

- Describe phosphate esters.
- Understand why phosphate esters are important in living cells.

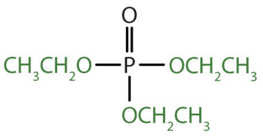
Just as carboxylic acids do, inorganic acids such as nitric acid (HNO_3), sulfuric acid (H_2SO_4), and phosphoric acid (H_3PO_4) also form esters. The esters of phosphoric acid are especially important in biochemistry. A phosphoric acid molecule can form a monoalkyl, a dialkyl, or a trialkyl ester by reaction with one, two, or three molecules of an alcohol.



Ethyl dihydrogen phosphate

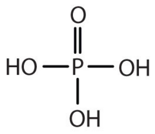


Diethyl hydrogen phosphate

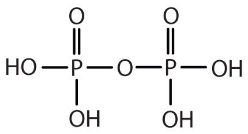


Triethyl phosphate

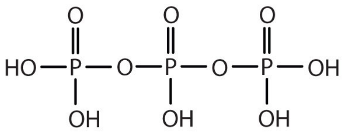
Esters of pyrophosphoric acid and triphosphoric acid are also important in biochemistry.



Phosphoric acid



Pyrophosphoric acid

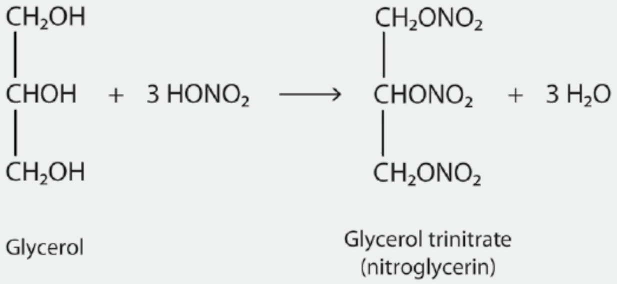


Triphosphoric acid

Esters of these acids are present in every plant and animal cell. They are biochemical intermediates in the transformation of food into usable energy. The bonds between phosphate units in adenosine triphosphate (ATP) are called **phosphoanhydride bonds**. These are high-energy bonds that store energy from the metabolism of foods. Hydrolysis of ATP releases energy as it is needed for biochemical processes (for instance, for muscle contraction). Phosphate esters are also important structural constituents of phospholipids and nucleic acids.

Nitroglycerin

The explosive nitroglycerin (glyceryl trinitrate) is an ester formed from glycerol and nitric acid. It is used in medicine to relieve chest pain in heart disease.



cise

What compounds combine to form phosphate esters?

Answer

phosphoric acids and alcohols

Summary

Inorganic acids such as H_3PO_4 form esters. The esters of phosphoric acid are especially important in biochemistry.

15.10: Amines - Structures and Names

Learning Objectives

- Identify the general structure for an amine.
- Identify the functional group for amines.
- Determine the structural feature that classifies amines as primary, secondary, or tertiary.
- Use nomenclature systems to name amines.

Amines are classified according to the number of carbon atoms bonded directly to the nitrogen atom. A primary (1°) amine has one alkyl (or aryl) group on the nitrogen atom, a secondary (2°) amine has two, and a tertiary (3°) amine has three (Figure 15.10.1).

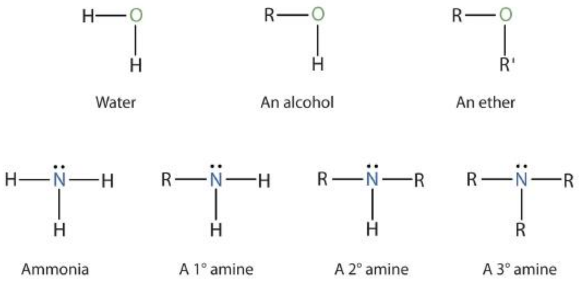


Figure 15.10.1: The Structure of Amines Compared to Water, an Alcohol, and an Ether

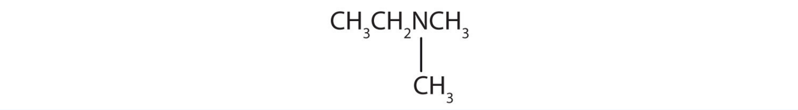
To classify alcohols, we look at the number of carbon atoms bonded to the *carbon atom* bearing the OH group, not the oxygen atom itself. Thus, although isopropylamine looks similar to isopropyl alcohol, the former is a *primary* amine, while the latter is a *secondary* alcohol.

The common names for simple aliphatic amines consist of an alphabetic list of alkyl groups attached to the nitrogen atom, followed by the suffix *-amine*. (Systematic names are often used by some chemists.) The amino group (NH_2) is named as a substituent in more complicated amines, such as those that incorporate other functional groups or in which the alkyl groups cannot be simply named.

Example 15.10.1

Name and classify each compound.

a. $CH_3CH_2CH_2NH_2$

b. 

$CH_3CH_2N(CH_3)CH_3$

c. $CH_3CH_2NHCH_2CH_3$

d. $CH_3CH_2CH_2NHCH_3$

Solution

a. There is only one alkyl group attached to the nitrogen atom, so the amine is primary. A group of three carbon atoms (a propyl group) is attached to the NH_2 group through an end carbon atom, so the name is propylamine.

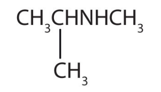
b. There are two methyl groups and one ethyl group on the nitrogen atom. The compound is ethyldimethylamine, a tertiary amine.

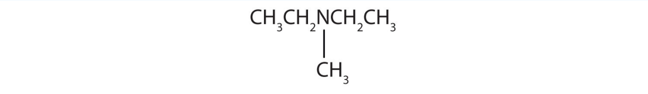
c. There are two ethyl groups attached to the nitrogen atom; the amine is secondary, so the compound is diethylamine.

d. The nitrogen atom has a methyl group and a propyl group, so the compound is methylpropylamine, a secondary amine.

Exercise 15.10.1

Name and classify each compound.

a. 
$$\underset{\displaystyle CH_3}{CH_3\underset{|}{C}HNHCH_3}$$

b. 
$$CH_3CH_2\underset{\underset{\displaystyle CH_3}{|}}{N}CH_2CH_3$$

c. $CH_3CH_2CH_2CH_2NH_2$

d. $CH_3CH_2CH_2NHCH_2CH_2\ CH_3$

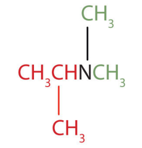
Example 15.10.2

Draw the structure for each compound and classify.

a. isopropyldimethylamine
b. dipropylamine

Solution

a. The name indicates that there are an isopropyl group (in red) and two methyl groups (in green) attached to the nitrogen atom; the amine is tertiary.


$$CH_3\underset{\underset{\displaystyle CH_3}{|}}{C}H\overset{\overset{\displaystyle CH_3}{|}}{N}CH_3$$

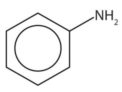
b. The name indicates that there are two propyl groups attached to the nitrogen atom; the amine is secondary. (The third bond on the nitrogen atom goes to a hydrogen atom.) $CH_3CH_2CH_2NHCH_2CH_2CH_3$

Exercise 15.10.2

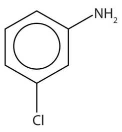
Draw the structure for each compound and classify.

a. ethylisopropylamine
b. diethylpropylamine

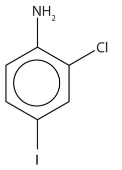
The primary amine in which the nitrogen atom is attached directly to a benzene ring has a special name—**aniline**. Aryl amines are named as derivatives of aniline.



Aniline



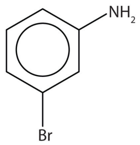
M-chloroaniline



2-Chloro-4-iodoaniline

Example 15.10.3

Name this compound.

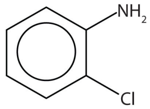


Solution

The benzene ring with an amino (NH_2) group is aniline. The compound is named as a derivative of aniline: 3-bromoaniline or *m*-bromoaniline.

Exercise 15.10.3

Name this command.

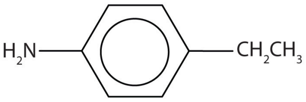


Example 15.10.4

Draw the structure for *p*-ethylaniline and classify.

Solution

The compound is a derivative of aniline. It is a primary amine having an ethyl group located *para* to the amino (NH_2) group.



Exercise 15.10.4

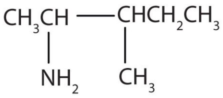
Draw the structure for *p*-isopropylaniline and classify.

Example 15.10.5

Draw the structure for 2-amino-3-methylpentane.

Solution

Always start with the parent compound: draw the pentane chain. Then attach a methyl group at the third carbon atom and an amino group at the second carbon atom.



Exercise 15.10.5

Draw the structure for 2-amino-3-ethyl-1-chloroheptane.

Ammonium (NH_4^+) ions, in which one or more hydrogen atoms are replaced with alkyl groups, are named in a manner analogous to that used for simple amines. The alkyl groups are named as substituents, and the parent species is regarded as the NH_4^+ ion. For example, $CH_3NH_3^+$ is the methylammonium ion. The ion formed from aniline ($C_6H_5NH_3^+$) is called the anilinium ion.

✓ Example 15.10.6

Name each ion.

a. $CH_3NH_3^+$
b. $(CH_3)_2NH_2^+$
c. $(CH_3)_3NH^+$
d. $(CH_3)_4N^+$

Solution

The ions have one, two, three, and four methyl (CH_3) groups attached to a nitrogen atom. Their names are as follows:

a. methylammonium ion
b. dimethylammonium ion
c. trimethylammonium ion
d. tetramethylammonium ion

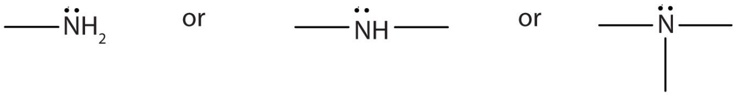
? Exercise 15.10.6

Name each ion.

a. $CH_3CH_2NH_3^+$
b. $(CH_3CH_2)_3NH^+$
c. $(CH_3CH_2CH_2)_2NH_2^+$
d. $(CH_3CH_2CH_2CH_2)_4N^+$

Summary

An amine is a derivative of ammonia in which one, two, or all three hydrogen atoms are replaced by hydrocarbon groups. The amine functional group is as follows:



Amines are classified as primary, secondary, or tertiary by the number of hydrocarbon groups attached to the nitrogen atom. Amines are named by naming the alkyl groups attached to the nitrogen atom, followed by the suffix *-amine*.

15.11: Physical Properties of Amines

Learning Objectives

- Explain why the boiling points of primary and secondary amines are higher than those of alkanes or ethers of similar molar mass but are lower than those of alcohols.
- Compare the boiling points of tertiary amines with alcohols, alkanes, and ethers of similar molar mass.
- Compare the solubilities in water of amines of five or fewer carbon atoms with the solubilities of comparable alkanes and alcohols in water.

Primary and secondary amines have hydrogen atoms bonded to an nitrogen atom and are therefore capable of hydrogen bonding (part (a) of Figure 15.11.1), although not as strongly as alcohol molecules (which have hydrogen atoms bonded to an oxygen atom, which is more electronegative than nitrogen). These amines boil at higher temperatures than alkanes but at lower temperatures than alcohols of comparable molar mass. For example, compare the boiling point of methylamine (CH_3NH_2; −6°C) with those of ethane (CH_3CH_3; −89°C) and methanol (CH_3OH; 65°C). Tertiary amines have no hydrogen atom bonded to the nitrogen atom and so cannot participate in intermolecular hydrogen bonding. They have boiling points comparable to those of ethers (Table 15.11.1).

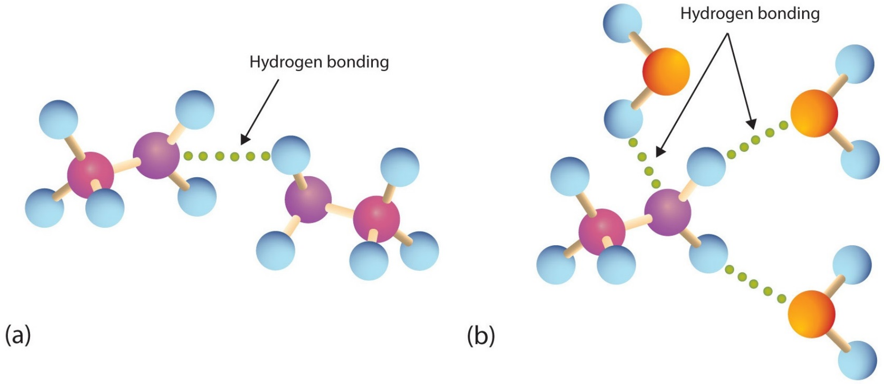


Figure 15.11.1: Hydrogen Bonding. (a) Amine molecules are associated through hydrogen bonding. (b) An amine molecule can form a hydrogen bond with water molecules.

Table 15.11.1: Physical Properties of Some Amines and Comparable Oxygen-Containing Compounds

Name	Condensed Structural Formula	Class	Molar Mass	Boiling Point (°C)	Solubility at 25°C (g/100 g Water)
butylamine	$CH_3CH_2CH_2CH_2NH_2$	1°	73	78	miscible
diethylamine	$(CH_3CH_2)_2NH$	2°	73	55	miscible
butyl alcohol	$CH_3CH_2CH_2CH_2OH$	—	74	118	8
dipropylamine	$(CH_3CH_2CH_2)_2NH$	2°	101	111	4
triethylamine	$(CH_3CH_2)_3N$	3°	101	90	14
dipropyl ether	$(CH_3CH_2CH_2)_2O$	—	102	91	0.25

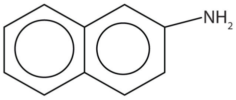
All three classes of amines can engage in hydrogen bonding with water (Figure 15.11.1b). Amines of low molar mass are quite soluble in water; the borderline of solubility in water is at five or six carbon atoms.

To Your Health: Amines in Death and Life

Amines have “interesting” odors. The simple ones smell very much like ammonia. Higher aliphatic amines smell like decaying fish. Or perhaps we should put it the other way around: Decaying fish give off odorous amines. The stench of rotting fish is due in part to two diamines: putrescine and cadaverine. They arise from the decarboxylation of ornithine and lysine, respectively, amino acids that are found in animal cells.

$$HOCH_2CH_2OH$$

Aromatic amines generally are quite toxic. They are readily absorbed through the skin, and workers must exercise caution when handling these compounds. Several aromatic amines, including β-naphthylamine, are potent carcinogens.



Key Takeaways

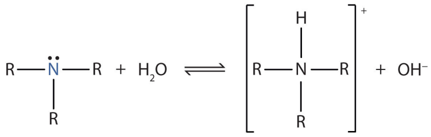
- Primary and secondary amines have higher boiling points than those of alkanes or ethers of similar molar mass because they can engage in intermolecular hydrogen bonding. Their boiling points are lower than those of alcohols because alcohol molecules have hydrogen atoms bonded to an oxygen atom, which is more electronegative.
- The boiling points of tertiary amines, which cannot engage in hydrogen bonding because they have no hydrogen atom on the nitrogen atom, are comparable to those of alkanes and ethers of similar molar mass.
- Because all three classes of amines can engage in hydrogen bonding with water, amines of low molar mass are quite soluble in water.

15.12: Amines as Bases

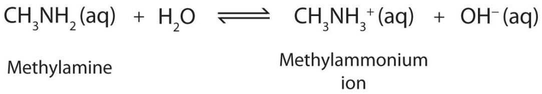
Learning Objectives

- Name the typical reactions that take place with amines.
- Describe heterocyclic amines.

Recall that ammonia (NH_3) acts as a base because the nitrogen atom has a lone pair of electrons that can accept a proton. Amines also have a lone electron pair on their nitrogen atoms and can accept a proton from water to form substituted ammonium (NH_4^+) ions and hydroxide (OH^-) ions:

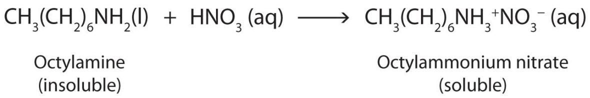


As a specific example, methylamine reacts with water to form the methylammonium ion and the OH^- ion.



$$CH_3NH_2(aq) + H_2O \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$$

Nearly all amines, including those that are not very soluble in water, will react with strong acids to form salts soluble in water.



$$CH_3(CH_2)_6NH_2(l) + HNO_3(aq) \longrightarrow CH_3(CH_2)_6NH_3^+NO_3^-(aq)$$

Amine salts are named like other salts: the name of the cation is followed by the name of the anion.

✓ Example 15.12.1

What are the formulas of the acid and base that react to form $[CH_3NH_2CH_2CH_3]^+CH_3COO^-$?

Solution

The cation has two groups—methyl and ethyl—attached to the nitrogen atom. It comes from ethylmethylamine ($CH_3NHCH_2CH_3$). The anion is the acetate ion. It comes from acetic acid (CH_3COOH).

? Exercise 15.12.1

What are the formulas of the acid and base that react to form $(CH_3CH_2CH_2)_3NH^+I^-$?

To Your Health: Amine Salts as Drugs

Salts of aniline are properly named as *anilinium* compounds, but an older system, still in use for naming drugs, identifies the salt of aniline and hydrochloric acid as "aniline hydrochloride." These compounds are ionic—they are salts—and the properties of the compounds (solubility, for example) are those characteristic of salts. Many drugs that are amines are converted to hydrochloride salts to increase their solubility in aqueous solution.

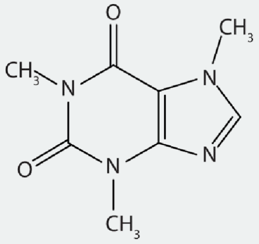
Heterocyclic Amines

Looking back at the various cyclic hydrocarbons discussed previously, we see that all the atoms in the rings of these compounds are carbon atoms. In other cyclic compounds, called **heterocyclic compounds** (Greek *heteros*, meaning "other"), nitrogen, oxygen, sulfur, or some other atom is incorporated in the ring. Many heterocyclic compounds are important in medicine and biochemistry. Some compose part of the structure of the nucleic acids, which in turn compose the genetic material of cells and direct protein synthesis.

Many heterocyclic amines occur naturally in plants. Like other amines, these compounds are basic. Such a compound is an **alkaloid**, a name that means “like alkalis.” Many alkaloids are physiologically active, including the familiar drugs caffeine, nicotine, and cocaine.

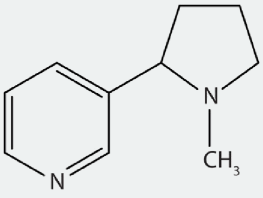
To Your Health: Three Well-Known Alkaloids

Caffeine is a stimulant found in coffee, tea, and some soft drinks. Its mechanism of action is not well understood, but it is thought to block the activity of adenosine, a heterocyclic base that acts as a neurotransmitter, a substance that carries messages across a tiny gap (synapse) from one nerve cell (neuron) to another cell. The effective dose of caffeine is about 200 mg, corresponding to about two cups of strong coffee or tea.



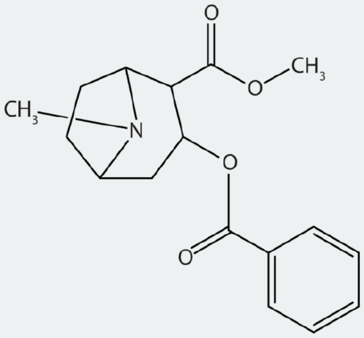
Caffeine

Nicotine acts as a stimulant by a different mechanism; it probably mimics the action of the neurotransmitter acetylcholine. People ingest this drug by smoking or chewing tobacco. Its stimulant effect seems transient, as this initial response is followed by depression. Nicotine is highly toxic to animals. It is especially deadly when injected; the lethal dose for a human is estimated to be about 50 mg. Nicotine has also been used in agriculture as a contact insecticide.



Nicotine

Cocaine acts as a stimulant by preventing nerve cells from taking up dopamine, another neurotransmitter, from the synapse. High levels of dopamine are therefore available to stimulate the pleasure centers of the brain. The enhancement of dopamine action is thought to be responsible for cocaine’s “high” and its addictive properties. After the binge, dopamine is depleted in less than an hour. This leaves the user in a pleasureless state and (often) craving more cocaine.



Cocaine

Cocaine is used as the salt cocaine hydrochloride and in the form of broken lumps of the free (unneutralized) base, which is called *crack cocaine*.

$$\underbrace{C_{17}H_{21}O_4N}_{\text{cocaine (freebase)}} + HCl \longrightarrow \underbrace{C_{17}H_{21}O_4NH^+Cl^-}_{\text{cocaine hydrochloride}}$$

> Because it is soluble in water, cocaine hydrochloride is readily absorbed through the watery mucous membranes of the nose when it is snorted. Crack cocaine is more volatile than cocaine hydrochloride. It vaporizes at the temperature of a burning cigarette. When smoked, cocaine reaches the brain in 15 s.

Summary

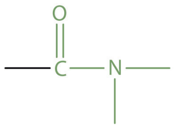
Amines are bases; they react with acids to form salts. Salts of aniline are properly named as *anilinium* compounds, but an older system is used to name drugs: the salts of amine drugs and hydrochloric acid are called “hydrochlorides.” Heterocyclic amines are cyclic compounds with one or more nitrogen atoms in the ring.

15.13: Amides- Structures and Names

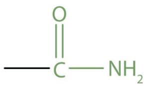
Learning Objectives

- Identify the general structure for an amide.
- Identify the functional group for an amide.
- Names amides with common names.
- Name amides according to the IUPAC system.

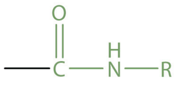
The amide functional group has an nitrogen atom attached to a carbonyl carbon atom. If the two remaining bonds on the nitrogen atom are attached to hydrogen atoms, the compound is a *simple amide*. If one or both of the two remaining bonds on the atom are attached to alkyl or aryl groups, the compound is a *substituted amide*.



The amide group



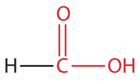
A simple amide



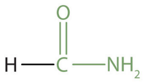
A substituted amide

> The carbonyl carbon-to-nitrogen bond is called an *amide linkage*. This bond is quite stable and is found in the repeating units of protein molecules, where it is called a *peptide linkage*.

Simple amides are named as derivatives of carboxylic acids. The *-ic* ending of the common name or the *-oic* ending of the International Union of Pure and Applied Chemistry (IUPAC) name of the carboxylic acid is replaced with the suffix *-amide*.



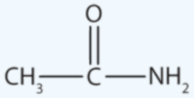
Formic acid
(methanoic acid)

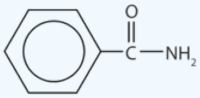


Formamide
(methanamide)

Example 15.13.1

Name each compound with the common name, the IUPAC name, or both.

a. 

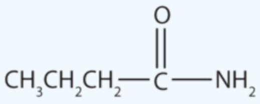
b. 

Solution

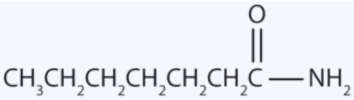
a. This amide has two carbon atoms and is thus derived from acetic acid. The OH of acetic acid is replaced by an NH_2 group. The *-ic* from *acetic* (or *-oic* from ethanoic) is dropped, and *-amide* is added to give *acetamide* (or ethanamide in the IUPAC system).
b. This amide is derived from benzoic acid. The *-oic* is dropped, and *-amide* is added to give benzamide.

Exercise 15.13.1

Name each compound with the common name, the IUPAC name, or both.

a. 

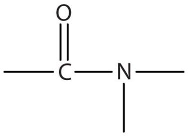
b.



$CH_3CH_2CH_2CH_2CH_2CH_2\overset{\displaystyle O}{\overset{\|}{C}}—NH_2$

Key Takeaways

- Amides have a general structure in which a nitrogen atom is bonded to a carbonyl carbon atom.
- The functional group for an amide is as follows:



- In names for amides, the *-ic acid* of the common name or the *-oic* ending of the IUPAC for the corresponding carboxylic acid is replaced by *-amide*.

15.14: Physical Properties of Amides

Learning Objectives

- Compare the boiling points of amides with alcohols of similar molar mass.
- Compare the solubilities in water of amides of five or fewer carbon atoms with the solubilities of comparable alkanes and alcohols in water.

With the exception of formamide ($HCONH_2$), which is a liquid, all simple amides are solids (Table 15.14.1). The lower members of the series are soluble in water, with borderline solubility occurring in those that have five or six carbon atoms. Like the esters, solutions of amides in water usually are neutral—neither acidic nor basic.

Table 15.14.1: *Physical Constants of Some Unsubstituted Amides*

Condensed Structural Formula	Name	Melting Point (°C)	Boiling Point (°C)	Solubility in Water
$HCONH_2$	formamide	2	193	soluble
CH_3CONH_2	acetamide	82	222	soluble
$CH_3CH_2CONH_2$	propionamide	81	213	soluble
$CH_3CH_2CH_2CONH_2$	butyramide	115	216	soluble
$C_6H_5CONH_2$	benzamide	132	290	slightly soluble

The amides generally have high boiling points and melting points. These characteristics and their solubility in water result from the polar nature of the amide group and hydrogen bonding (Figure 15.14.1). (Similar hydrogen bonding plays a critical role in determining the structure and properties of proteins, deoxyribonucleic acid [DNA], ribonucleic acid [RNA], and other giant molecules so important to life processes.

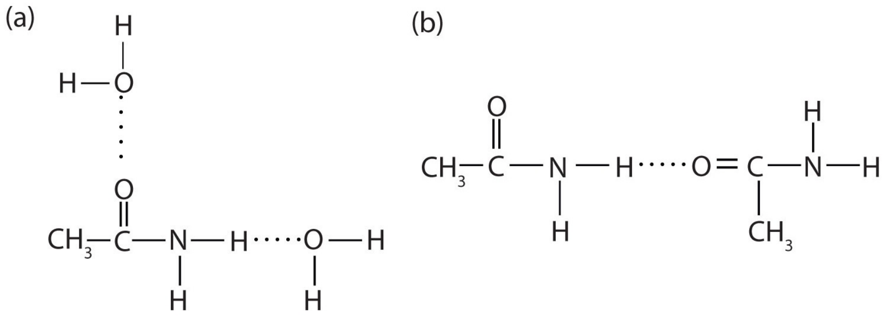


Figure 15.14.1: Hydrogen Bonding in Amides. Amide molecules can engage in hydrogen bonding with water molecules (a). Those amides with a hydrogen atom on the nitrogen atom can also engage in hydrogen bonding (b). Both hydrogen bonding networks extend in all directions.

Key Takeaways

- Most amides are solids at room temperature; the boiling points of amides are much higher than those of alcohols of similar molar mass.
- Amides of five or fewer carbon atoms are soluble in water?.

15.15: Formation of Amides

Learning Objectives

- To describe the preparation procedure for amides.

The addition of ammonia (NH_3) to a carboxylic acid forms an amide, but the reaction is very slow in the laboratory at room temperature. Water molecules are split out, and a bond is formed between the nitrogen atom and the carbonyl carbon atom.

$$\underset{\text{Acetic acid}}{CH_3COOH} + NH_3 \longrightarrow \underset{\text{Acetamide}}{CH_3CONH_2} + H_2O$$

In living cells, amide formation is catalyzed by enzymes. Proteins are polyamides; they are formed by joining amino acids into long chains. In proteins, the amide functional group is called a *peptide bond*.

Polyamides

Just as the reaction of a diol and a diacid forms a polyester, the reaction of a diacid and a diamine yields a polyamide. The two difunctional monomers often employed are adipic acid and 1,6-hexanediamine. The monomers condense by splitting out water to form a new product, which is still difunctional and thus can react further to yield a polyamide polymer.

$$n\,\underset{\text{1,6-Hexanediamine}}{H_2NCH_2CH_2CH_2CH_2CH_2CH_2NH_2} + n\,\underset{\text{Adipic acid}}{HOOCCH_2CH_2CH_2CH_2COOH} \longrightarrow$$

$$\underset{\text{Nylon 66 (a polyamide)}}{\text{—}HN[COCH_2CH_2CH_2CH_2CONHCH_2CH_2CH_2CH_2CH_2CH_2NH]_nCO\text{—}} + 2n\,H_2O$$

Some polyamides are known as *nylons*. Nylons are among the most widely used synthetic fibers—for example, they are used in ropes, sails, carpets, clothing, tires, brushes, and parachutes. They also can be molded into blocks for use in electrical equipment, gears, bearings, and valves.

Key Takeaway

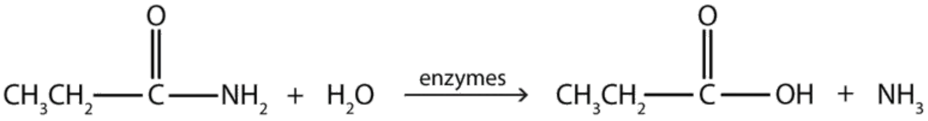
- Amides are prepared by the reaction of a carboxylic acid with ammonia or an amine.

15.16: Chemical Properties of Amides- Hydrolysis

Learning Objectives

- To identify the typical reaction that amides undergo.

Generally, amides resist hydrolysis in plain water, even after prolonged heating. In the presence of added acid or base, however, hydrolysis proceeds at a moderate rate. In living cells, amide hydrolysis is catalyzed by enzymes. Amide hydrolysis is illustrated in the following example:



$$CH_3CH_2-\overset{\overset{O}{\|}}{C}-NH_2 + H_2O \xrightarrow{\text{enzymes}} CH_3CH_2-\overset{\overset{O}{\|}}{C}-OH + NH_3$$

> *Hydrolysis of an amide in acid solution actually gives a carboxylic acid and the salt of ammonia or an amine (the ammonia or amine initially formed is neutralized by the acid). Basic hydrolysis gives a salt of the carboxylic acid and ammonia or an amine.*

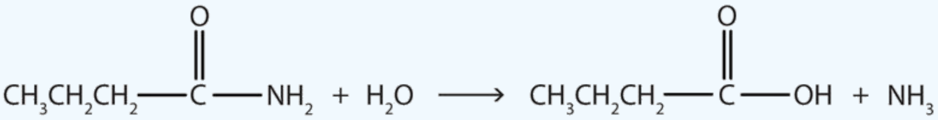
Example 15.16.1

Write the equation for the hydrolysis of each compound.

a. butyramide
b. benzamide

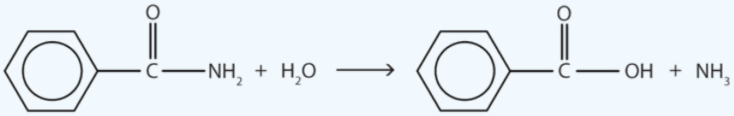
Solution

a. The hydrolysis of a simple amide produces an organic acid and ammonia. Butyramide thus yields butyric acid and ammonia.



$$CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-NH_2 + H_2O \longrightarrow CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-OH + NH_3$$

- The hydrolysis of an amide produces an organic acid and ammonia. Benzamide thus yields benzoic acid and ammonia.



Exercise 15.16.1

Write the equation for the hydrolysis of each compound.

a. propionamide (propanamide)
b. hexanamide

Career Focus: Athletic Trainer

Athletic training is an allied health-care profession recognized by the American Medical Association. The athletic trainer's role is to recognize, evaluate, and provide immediate care for athletic injuries; prevent athletic injuries by taping, bandaging, and bracing vulnerable body parts; make referrals to medical doctors when necessary; and rehabilitate injured athletes. Athletic trainers work in high schools, colleges, and other organizations where athletics programs are found. Athletic trainers usually have a degree from an accredited athletic training program whose curriculum includes such basic science courses as biology, chemistry, and physics. These studies provide the necessary background for more applied courses, such as anatomy and

> physiology, exercise physiology, kinesiology, and nutrition. Knowledge of chemistry is necessary for understanding pharmacological and medical terminology. For example, athletic trainers must understand the action of numerous drugs, many of which are esters, amines, or amides like those mentioned in this chapter.
>
> Athletic trainers may have administrative duties, such as the responsibility for ordering supplies. They also need to be able to evaluate nutritional supplements because providing the wrong one can get an athlete banned from competition and may bring sanctions against a school. In short, the athletic trainer is responsible for the overall health and well-being of the athletes in his or her charge.

Key Takeaway

- The hydrolysis of an amide produces a carboxylic acid and ammonia or an amine.

15.S: Organic Acids and Bases and Some of Their Derivatives (Summary)

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

A **carboxylic acid** (RCOOH) contains the functional group COOH, called the **carboxyl group**, which has an OH group attached to a carbonyl carbon atom. An **ester** (RCOOR′) has an OR′ group attached to a carbonyl carbon atom. An **amine** is derived from ammonia (NH_3), with one, two, or all three of the hydrogen atoms of NH_3 replaced by an alkyl (or an aryl) group. The **amide** functional group has a carbonyl group joined to a nitrogen atom from NH_3 or an amine.

There are many familiar carboxylic acids. The R group may be a hydrogen atom (as in formic acid, HCOOH), an alkyl group (as in acetic acid, CH_2COOH), or an aryl group (as in benzoic acid, C_6H_5COOH). The location of substituents along the carbon chain is indicated by a Greek letter (for common names) or a number (for names from the International Union of Pure and Applied Chemistry).

A carboxylic acid is formed by the oxidation of an aldehyde with the same number of carbon atoms. Because aldehydes are formed from primary alcohols, these alcohols are also a starting material for carboxylic acids.

Carboxylic acids have strong, often disagreeable, odors. They are highly polar molecules and readily engage in hydrogen bonding, so they have relatively high boiling points.

Carboxylic acids are weak acids. They react with bases to form salts and with carbonates and bicarbonates to form carbon dioxide gas and the salt of the acid.

Esters are pleasant-smelling compounds that are responsible for the fragrances of flowers and fruits. They have lower boiling points than comparable carboxylic acids because, even though ester molecules are somewhat polar, they cannot engage in hydrogen bonding. However, with water, esters can engage in hydrogen bonding; consequently, the low molar mass esters are soluble in water. Esters can be synthesized by **esterification**, in which a carboxylic acid and an alcohol are combined under acidic conditions. Esters are neutral compounds that undergo **hydrolysis**, a reaction with water. Under acidic conditions, hydrolysis is essentially the reverse of esterification. When carried out under basic conditions, the process is called **saponification**.

Inorganic acids also react with alcohols to form esters. Some of the most important esters in biochemistry are those formed from phosphoric acid.

Amines are nitrogen-containing organic molecules derived from ammonia (NH_3). A **primary (1°) amine** (RNH_2) has one organic group bonded to the nitrogen atom, a **secondary (2°) amine** (R_2NH) has two organic groups bonded to the nitrogen atom, and a **tertiary (3°) amine** (R_3N) has three organic groups bonded to the nitrogen atom. Amines are basic compounds that react with strong acids to produce ammonium (NH_4^+) salts. A cyclic compound in which the ring contains one or more noncarbon atoms is called a **heterocyclic compound**. There are many heterocyclic amines, including many physiologically important ones. **Alkaloids** are heterocyclic amines found in many plants. Caffeine, nicotine, and cocaine are familiar alkaloids.

Organic compounds containing a carbonyl group bonded to a nitrogen atom are amides, and the carbon-to-nitrogen bond is an amide linkage (or a peptide linkage). Most amides are colorless and odorless, and the lighter ones are soluble in water. Because they are polar molecules, amides have comparatively high boiling points and melting points. Amides are synthesized from carboxylic acids and NH_3 or amines. Amides are neutral compounds. They resist hydrolysis in water, but acids, bases, and enzymes catalyze the reaction.

CHAPTER OVERVIEW

16: Carbohydrates

Glucose is one of the carbohydrates you will learn about in this chapter as we begin the study of biochemistry—the chemistry of molecules found in living organisms. Later we will study the other three major types of macromolecules found in living organisms: lipids, proteins, and nucleic acids.

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16.0: Prelude to Carbohydrates

In the United States, 17.9 million people have been diagnosed with diabetes, and experts estimate that at least another 5.7 million people have the disease but have not been diagnosed. In 2006, diabetes was the seventh leading cause of death, listed on 72,507 death certificates. Moreover, it was a contributing factor in over 200,000 deaths in which the cause was listed as something else, such as heart or kidney disease.

People with diabetes are impaired in their ability to metabolize glucose, a sugar needed by the body for energy; as a result, excessive quantities of glucose accumulate in the blood and the urine. The characteristic symptoms of diabetes are weight loss, constant hunger, extreme thirst, and frequent urination (the kidneys excrete large amounts of water in an attempt to remove the excess sugar from the blood).

An important diagnostic test for diabetes is the oral glucose tolerance test, which measures the level of glucose in blood plasma. A first measurement is made after a fast of at least 8 h, followed by another measurement 2 h after the person drinks a flavored solution of 75 g of glucose dissolved in water. At the second measurement, the glucose plasma level should be no higher than 139 mg/dL. Individuals with a value between 140 and 199 mg/dL are diagnosed with prediabetes, while those with a value of 200 mg/dL or above are diagnosed with diabetes. Following a diagnosis of diabetes a person will need to monitor his or her blood glucose levels daily (or more often) using a glucose meter.

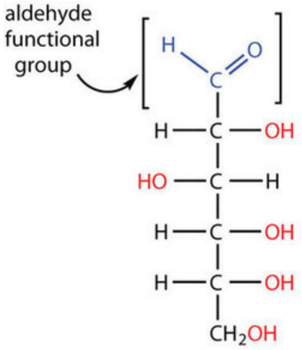
Figure 16.0.1: Using a Glucose Meter to Test Blood Glucose Level. (Public Domain; Centers for Disease Control and Prevention).

16.1: Carbohydrates

Learning Objectives

- To recognize carbohydrates and classify them as mono-, di-, or polysaccharides.

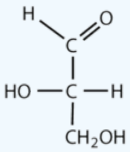
All carbohydrates consist of carbon, hydrogen, and oxygen atoms and are polyhydroxy aldehydes or ketones or are compounds that can be broken down to form such compounds. Examples of carbohydrates include starch, fiber, the sweet-tasting compounds called sugars, and structural materials such as cellulose. The term *carbohydrate* had its origin in a misinterpretation of the molecular formulas of many of these substances. For example, because its formula is $C_6H_{12}O_6$, glucose was once thought to be a “carbon hydrate” with the structure $C_6{\cdot}6H_2O$.

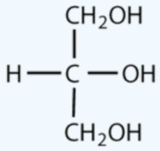


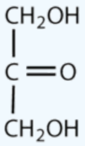
Because glucose has an aldehyde functional group and several –OH (hydroxyl) groups, it is described as a polyhydroxy aldehyde.

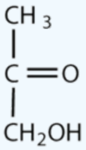
Example 16.1.1

Which compounds would be classified as carbohydrates?

a. 

b. 

c. 

d. 

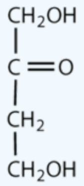
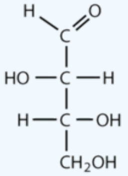
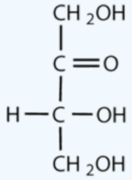
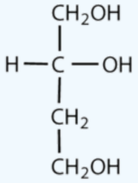
Solution

a. This is a carbohydrate because the molecule contains an aldehyde functional group with OH groups on the other two carbon atoms.
b. This is not a carbohydrate because the molecule does not contain an aldehyde or a ketone functional group.
c. This is a carbohydrate because the molecule contains a ketone functional group with OH groups on the other two carbon atoms.

d. This is not a carbohydrate; although it has a ketone functional group, one of the other carbons atoms does not have an OH group attached.

Exercise 16.1.1

Which compounds would be classified as carbohydrates?

1. 
2. 
3. 
4. 

Green plants are capable of synthesizing glucose ($C_6H_{12}O_6$) from carbon dioxide (CO_2) and water (H_2O) by using solar energy in the process known as photosynthesis:

$$6\,CO_2 + 6\,H_2O + 686\text{ kcal} \rightarrow C_6H_{12}O_6 + 6\,O_2 \tag{16.1.1}$$

(The 686 kcal come from solar energy.) Plants can use the glucose for energy or convert it to larger carbohydrates, such as starch or cellulose. Starch provides energy for later use, perhaps as nourishment for a plant’s seeds, while cellulose is the structural material of plants. We can gather and eat the parts of a plant that store energy—seeds, roots, tubers, and fruits—and use some of that energy ourselves. Carbohydrates are also needed for the synthesis of nucleic acids and many proteins and lipids.

Animals, including humans, cannot synthesize carbohydrates from carbon dioxide and water and are therefore dependent on the plant kingdom to provide these vital compounds. We use carbohydrates not only for food (about 60%–65% by mass of the average diet) but also for clothing (cotton, linen, rayon), shelter (wood), fuel (wood), and paper (wood).

The simplest carbohydrates—those that cannot be hydrolyzed to produce even smaller carbohydrates—are called monosaccharides. Two or more monosaccharides can link together to form chains that contain from two to several hundred or thousand monosaccharide units. Prefixes are used to indicate the number of such units in the chains. Disaccharide molecules have two monosaccharide units, *trisaccharide* molecules have three units, and so on. Chains with many monosaccharide units joined together are called polysaccharides. All these so-called higher saccharides can be hydrolyzed back to their constituent monosaccharides.

> *Compounds that cannot be hydrolyzed will not react with water to form two or more smaller compounds.*

Summary

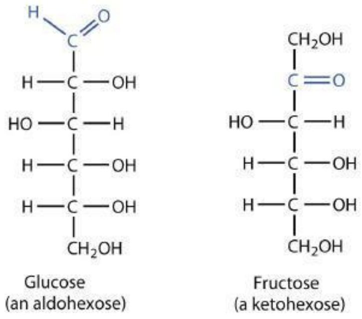
Carbohydrates are an important group of biological molecules that includes sugars and starches. Photosynthesis is the process by which plants use energy from sunlight to synthesize carbohydrates. A monosaccharide is the simplest carbohydrate and cannot be hydrolyzed to produce a smaller carbohydrate molecule. Disaccharides contain two monosaccharide units, and polysaccharides contain many monosaccharide units.

16.2: Classes of Monosaccharides

Learning Objectives

- Classify monosaccharides as aldoses or ketoses and as trioses, tetroses, pentoses, or hexoses.
- Distinguish between a D sugar and an L sugar.

The naturally occurring monosaccharides contain three to seven carbon atoms per molecule. Monosaccharides of specific sizes may be indicated by names composed of a stem denoting the number of carbon atoms and the suffix *-ose*. For example, the terms *triose*, *tetrose*, *pentose*, and *hexose* signify monosaccharides with, respectively, three, four, five, and six carbon atoms. Monosaccharides are also classified as aldoses or ketoses. Those monosaccharides that contain an aldehyde functional group are called aldoses; those containing a ketone functional group on the second carbon atom are ketoses. Combining these classification systems gives general names that indicate both the type of carbonyl group *and* the number of carbon atoms in a molecule. Thus, monosaccharides are described as aldotetroses, aldopentoses, ketopentoses, ketoheptoses, and so forth. Glucose and fructose are specific examples of an aldohexose and a ketohexose, respectively.



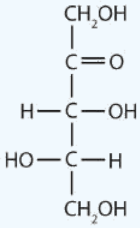
Example 16.2.1

Draw an example of each type of compound.

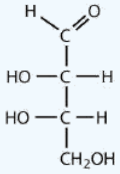
a. a ketopentose
b. an aldotetrose

Solution

a. The structure must have five carbon atoms with the second carbon atom being a carbonyl group and the other four carbon atoms each having an OH group attached. Several structures are possible, but one example is shown.



- The structure must have four carbon atoms with the first carbon atom part of the aldehyde functional group. The other three carbon atoms each have an OH group attached. Several structures are possible, but one example is shown.



Exercise 16.2.1

Draw an example of each type of compound.

a. an aldohexose
b. a ketotetrose

The simplest sugars are the trioses. The possible trioses are shown in part (a) of Figure 16.2.1; glyceraldehyde is an aldotriose, while dihydroxyacetone is a ketotriose. Notice that two structures are shown for glyceraldehyde. These structures are stereoisomers, and hence are isomers having the same structural formula but differing in the arrangement of atoms or groups of atoms in three-dimensional space. If you make models of the two stereoisomers of glyceraldehyde, you will find that you cannot place one model on top of the other and have each functional group point in the same direction. However, if you place one of the models in front of a mirror, the image in the mirror will be identical to the second stereoisomer in part (b) of Figure 16.2.1. Molecules that are nonsuperimposable (nonidentical) mirror images of each other are a type of stereoisomer called enantiomers (Greek *enantios*, meaning "opposite").

Note

These are another type of stereoisomers than the *cis-trans* (geometric) isomers previously discussed.

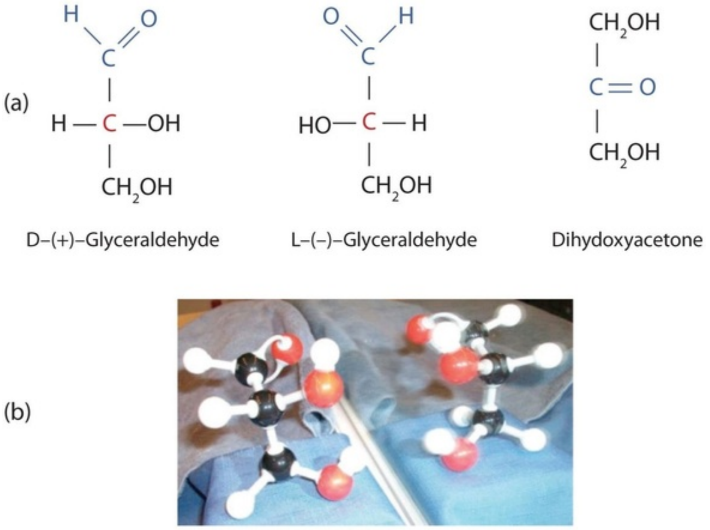


Figure 16.2.1: Structures of the Trioses. (a) D- and L-glyceraldehyde are mirror images of each other and represent a pair of enantiomers. (b) A ball-and-stick model of D-glyceraldehyde is reflected in a mirror. Note that the reflection has the same structure as L-glyceraldehyde.

A key characteristic of enantiomers is that they have a carbon atom to which four different groups are attached. Note, for example, the four different groups attached to the central carbon atom of glyceraldehyde (part (a) of Figure 16.2.1). A carbon atom that has four different groups attached is a chiral carbon. If a molecule contains one or more chiral carbons, it is likely to exist as two or more stereoisomers. Dihydroxyacetone does not contain a chiral carbon and thus does not exist as a pair of stereoisomers. Glyceraldehyde, however, has a chiral carbon and exists as a pair of enantiomers. Except for the direction in which each enantiomer rotates plane-polarized light, these two molecules have identical physical properties. One enantiomer has a specific rotation of +8.7°, while the other has a specific rotation of −8.7°.

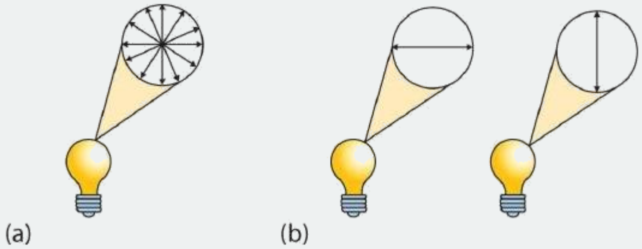
H. Emil Fischer, a German chemist, developed the convention commonly used for writing two-dimensional representations of the monosaccharides, such as those in part (a) of Figure 16.2.1. In these structural formulas, the aldehyde group is written at the top, and the hydrogen atoms and OH groups that are attached to each chiral carbon are written to the right or left. (If the monosaccharide is a ketose, the ketone functional group is the second carbon atom.) Vertical lines represent bonds pointing away from you, while horizontal lines represent bonds coming toward you. The formulas of chiral molecules represented in this manner are referred to as **Fischer projections**.

The two enantiomers of glyceraldehyde are especially important because monosaccharides with more than three carbon atoms can be considered as being derived from them. Thus, D- and L-glyceraldehyde provide reference points for designating and drawing all other monosaccharides. Sugars whose Fischer projections terminate in the same configuration as D-glyceraldehyde are designated as D sugars; those derived from L-glyceraldehyde are designated as L sugars.

> *By convention, the penultimate (next-to-last) carbon atom has been chosen as the carbon atom that determines if a sugar is D or L. It is the chiral carbon farthest from the aldehyde or ketone functional group.*

Looking Closer: Polarized Light

A beam of ordinary light can be pictured as a bundle of waves; some move up and down, some sideways, and others at all other conceivable angles. When a beam of light has been polarized, however, the waves in the bundle all vibrate in a single plane. Light altered in this way is called *plane-polarized light*. Much of what chemists know about stereoisomers comes from studying the effects they have on plane-polarized light. In this illustration, the light on the left is not polarized, while that on the right is polarized.



Sunlight, in general, is not polarized; light from an ordinary light bulb or an ordinary flashlight is not polarized. One way to polarize ordinary light is to pass it through Polaroid sheets, special plastic sheets containing carefully oriented organic compounds that permit only light vibrating in a single plane to pass through. To the eye, polarized light doesn't "look" any different from nonpolarized light. We can detect polarized light, however, by using a second sheet of polarizing material, as shown here.

In the photo on the left, two Polaroid sheets are aligned in the same direction; plane-polarized light from the first Polaroid sheet can pass through the second sheet. In the photo on the right, the top Polaroid sheet has been rotated 90° and now blocks the plane-polarized light that comes through the first Polaroid sheet.

Certain substances act on polarized light by rotating the plane of vibration. Such substances are said to be optically active. The extent of optical activity is measured by a polarimeter, an instrument that contains two polarizing lenses separated by a sample tube, as shown in the accompanying figure. With the sample tube empty, maximum light reaches the observer's eye when the two lenses are aligned so that both pass light vibrating in the same plane. When an optically active substance is placed in the sample tube, that substance rotates the plane of polarization of the light passing through it, so that the polarized light emerging from the sample tube is vibrating in a different direction than when it entered the tube. To see the maximum amount of light when the sample is in place, the observer must rotate one lens to accommodate the change in the plane of polarization.

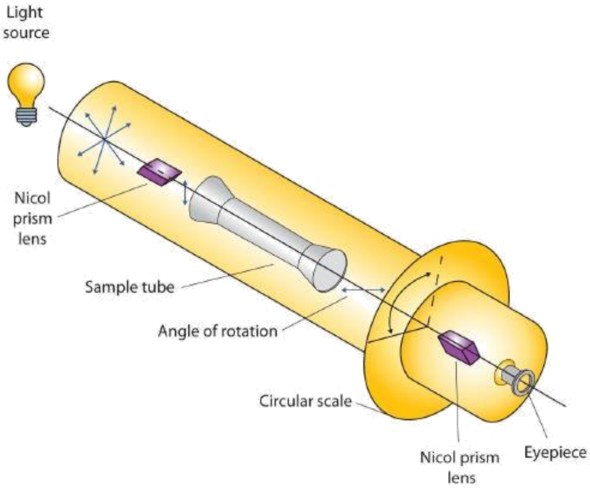


Figure 16.2.2: Diagram of a Polarimeter

Some optically active substances rotate the plane of polarized light to the right (clockwise) from the observer’s point of view. These compounds are said to be dextrorotatory; substances that rotate light to the left (counterclockwise) are levorotatory. To denote the direction of rotation, a positive sign (+) is given to dextrorotatory substances, and a negative sign (−) is given to levorotatory substances.

Summary

Monosaccharides can be classified by the number of carbon atoms in the structure and/or the type of carbonyl group they contain (aldose or ketose). Most monosaccharides contain at least one chiral carbon and can form stereoisomers. Enantiomers are a specific type of stereoisomers that are mirror images of each other.

16.3: Important Hexoses

Learning Objectives

- To identify the structures of D-glucose, D-galactose, and D-fructose and describe how they differ from each other.

Although a variety of monosaccharides are found in living organisms, three hexoses are particularly abundant: D-glucose, D-galactose, and D-fructose (Figure 16.3.1). Glucose and galactose are both aldohexoses, while fructose is a ketohexose.

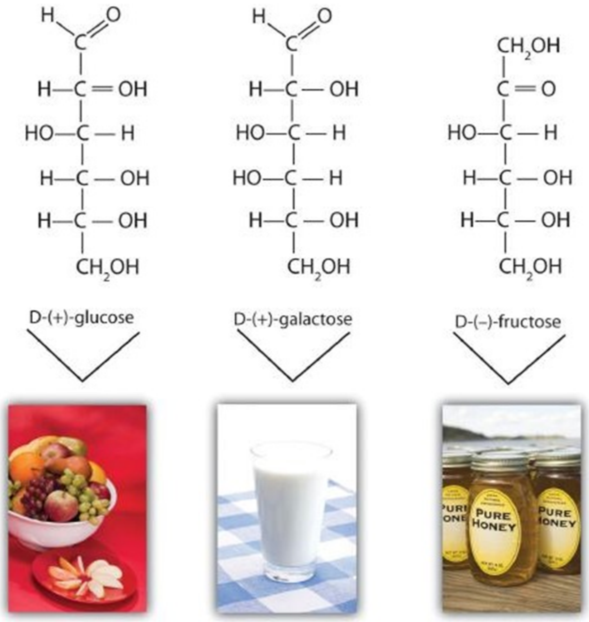


Figure 16.3.1: Structures of Three Important Hexoses. Each hexose is pictured with a food source in which it is commonly found. Source: Photos © Thinkstock.

Glucose

D-Glucose, generally referred to as simply glucose, is the most abundant sugar found in nature; most of the carbohydrates we eat are eventually converted to it in a series of biochemical reactions that produce energy for our cells. It is also known by three other names: *dextrose*, from the fact that it rotates plane-polarized light in a clockwise (dextrorotatory) direction; *corn sugar* because in the United States cornstarch is used in the commercial process that produces glucose from the hydrolysis of starch; and *blood sugar* because it is the carbohydrate found in the circulatory system of animals. Normal blood sugar values range from 70 to 105 mg glucose/dL plasma, and normal urine may contain anywhere from a trace to 20 mg glucose/dL urine.

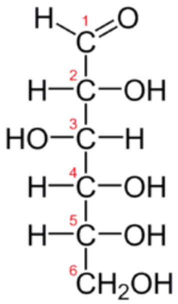


Figure 16.3.2: Fischer projection of D-glucose

The Fischer projection of D-glucose is given in Figure 16.3.2. Glucose is a D sugar because the OH group on the fifth carbon atom (the chiral center farthest from the carbonyl group) is on the right. In fact, all the OH groups except the one on the third carbon atom are to the right.

Galactose

D-Galactose does not occur in nature in the uncombined state. It is released when lactose, a disaccharide found in milk, is hydrolyzed. The galactose needed by the human body for the synthesis of lactose is obtained by the metabolic conversion of D-glucose to D-galactose. Galactose is also an important constituent of the glycolipids that occur in the brain and the myelin sheath of nerve cells. For this reason it is also known as *brain sugar*. The structure of D-galactose is shown in Figure $16.3.1$. Notice that the configuration differs from that of glucose only at the fourth carbon atom.

Fructose

D-Fructose, also shown in Figure $16.3.1$, is the most abundant ketohexose. Note that from the third through the sixth carbon atoms, its structure is the same as that of glucose. It occurs, along with glucose and sucrose, in honey (which is 40% fructose) and sweet fruits. Fructose (from the Latin *fructus*, meaning "fruit") is also referred to as *levulose* because it has a specific rotation that is strongly levorotatory (−92.4°). It is the sweetest sugar, being 1.7 times sweeter than sucrose, although many nonsugars are several hundred or several thousand times as sweet (Table $16.3.1$).

Table 16.3.1: The Relative Sweetness of Some Compounds (Sucrose = 100)

Compound	Relative Sweetness
lactose	16
maltose	32
glucose	74
sucrose	100
fructose	173
aspartame	18,000
acesulfame K	20,000
saccharin	30,000
sucralose	60,000

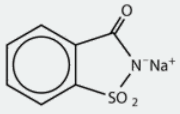
Looking Closer: Artificial Sweeteners

Although sweetness is commonly associated with mono- and disaccharides, it is not a property found only in sugars. Several other kinds of organic compounds have been synthesized that are far superior as sweetening agents. These so-called high-intensity or artificial sweeteners are useful for people with diabetes or other medical conditions that require them to control their carbohydrate intake. The synthetic compounds are noncaloric or used in such small quantities that they do not add significantly to the caloric value of food.

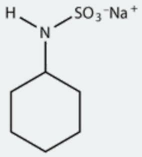
The first artificial sweetener—saccharin—was discovered by accident in 1879. It is 300 times sweeter than sucrose, but it passes through the body unchanged and thus adds no calories to the diet. After its discovery, saccharin was used until it was banned in the early 1900s. However, during the sugar-short years of World War I, the ban was lifted and was not reinstated at the war's end. One drawback to the use of saccharin is its bitter, metallic aftertaste. The initial solution to this problem was to combine saccharin with cyclamate, a second artificial sweetener discovered in 1937.

In the 1960s and 1970s, several clinical tests with laboratory animals implicated both cyclamate and saccharin as carcinogenic (cancer-causing) substances. The results from the cyclamate tests were completed first, and cyclamate was banned in the United States in 1969. Then a major study was released in Canada in 1977 indicating that saccharin increased the incidence of bladder cancer in rats. The US Food and Drug Administration (FDA) proposed a ban on saccharin that raised immediate public opposition because saccharin was the only artificial sweetener still available. In response, Congress passed the Saccharin Study and Labeling Act in 1977, permitting the use of saccharin as long as any product containing it was labeled with a consumer warning regarding the possible elevation of the risk of bladder cancer. Today this warning is no longer required; moreover, the

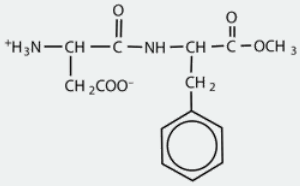
FDA is currently reviewing the ban on cyclamate, as 75 additional studies and years of usage in other countries, such as Canada, have failed to show that it has any carcinogenic effect.



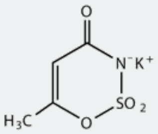
Saccharin



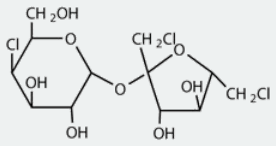
Cyclamate



Aspartame



Acesulfame K



Sucralose

A third artificial sweetener, aspartame, was discovered in 1965. This white crystalline compound is about 180 times sweeter than sucrose and has no aftertaste. It was approved for use in 1981 and is used to sweeten a wide variety of foods because it blends well with other food flavors. Aspartame is not used in baked goods, however, because it is not heat stable.

In the body (or when heated), aspartame is initially hydrolyzed to three molecules: the amino acids aspartic acid and phenylalanine and an alcohol methanol. Repeated controversy regarding the safety of aspartame arises partly from the fact that the body metabolizes the released methanol to formaldehyde. It should be noted, though, that a glass of tomato juice has six times as much methanol as a similar amount of a diet soda containing aspartame. The only documented risk connected to aspartame use is for individuals with the genetic disease *phenylketonuria* (PKU); these individuals lack the enzyme needed to metabolize the phenylalanine released when aspartame is broken down by the body. Because of the danger to people with PKU, all products containing aspartame must carry a warning label.

Acesulfame K, discovered just two years after aspartame (1967), was approved for use in the United States in 1988. It is 200 times sweeter than sugar and, unlike aspartame, is heat stable. It has no lingering aftertaste.

One of the newest artificial sweeteners to gain FDA approval (April 1998) for use in the United States is sucralose, a white crystalline solid approximately 600 times sweeter than sucrose. Sucralose is synthesized from sucrose and has three chlorine atoms substituted for three OH groups. It is noncaloric because it passes through the body unchanged. It can be used in baking because it is heat stable.

All of the extensive clinical studies completed to date have indicated that these artificial sweeteners approved for use in the United States are safe for consumption by healthy individuals in moderate amounts.

Summary

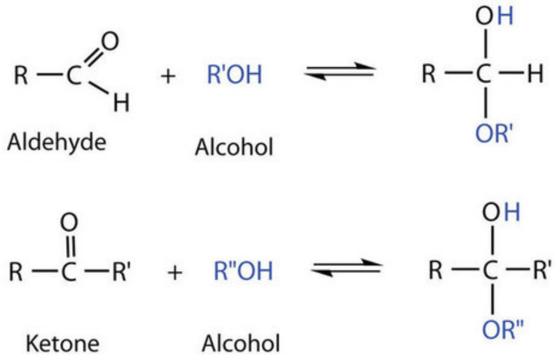
Three abundant hexoses in living organisms are the aldohexoses D-glucose and D-galactose and the ketohexose D-fructose.

16.4: Cyclic Structures of Monosaccharides

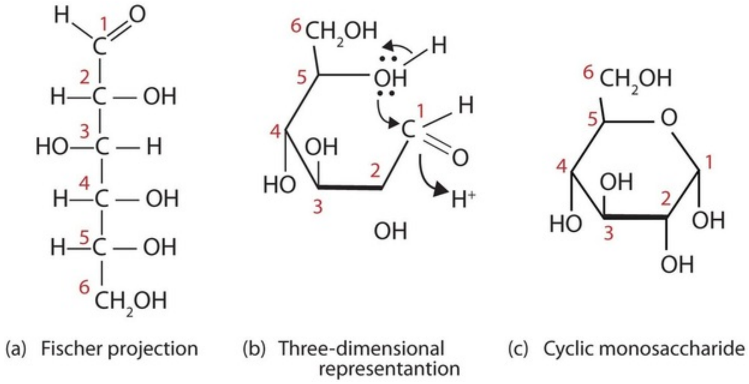
Learning Objectives

- Define what is meant by anomers and describe how they are formed.
- Explain what is meant by mutarotation.

So far we have represented monosaccharides as linear molecules, but many of them also adopt cyclic structures. This conversion occurs because of the ability of aldehydes and ketones to react with alcohols:



You might wonder why the aldehyde reacts with the OH group on the fifth carbon atom rather than the OH group on the second carbon atom next to it. Recall that cyclic alkanes containing five or six carbon atoms in the ring are the most stable. The same is true for monosaccharides that form cyclic structures: rings consisting of five or six carbon atoms are the most stable.



(a) Fischer projection (b) Three-dimensional representantion (c) Cyclic monosaccharide

Figure 16.4.1: Cyclization of D-Glucose. D-Glucose can be represented with a Fischer projection (a) or three dimensionally (b). By reacting the OH group on the fifth carbon atom with the aldehyde group, the cyclic monosaccharide (c) is produced.

When a straight-chain monosaccharide, such as any of the structures shown in Figure 16.4.1, forms a cyclic structure, the carbonyl oxygen atom may be pushed either up or down, giving rise to two stereoisomers, as shown in Figure 16.4.2. The structure shown on the left side of Figure 16.4.2, with the OH group on the first carbon atom projected downward, represent what is called the *alpha (α) form*. The structures on the right side, with the OH group on the first carbon atom pointed upward, is the *beta (β) form*. These two stereoisomers of a cyclic monosaccharide are known as anomers; they differ in structure around the anomeric carbon—that is, the carbon atom that was the carbonyl carbon atom in the straight-chain form.

It is possible to obtain a sample of crystalline glucose in which all the molecules have the α structure or all have the β structure. The α form melts at 146°C and has a specific rotation of +112°, while the β form melts at 150°C and has a specific rotation of +18.7°. When the sample is dissolved in water, however, a mixture is soon produced containing both anomers as well as the straight-chain form, in dynamic equilibrium (part (a) of Figure 16.4.2). You can start with a pure crystalline sample of glucose consisting entirely of either anomer, but as soon as the molecules dissolve in water, they open to form the carbonyl group and then reclose to form either the α or the β anomer. The opening and closing repeats continuously in an ongoing interconversion between anomeric forms and is referred to as mutarotation (Latin *mutare*, meaning “to change”). At equilibrium, the mixture consists of about 36% α-D-glucose, 64% β-D-glucose, and less than 0.02% of the open-chain aldehyde form. The observed rotation of this solution is +52.7°.

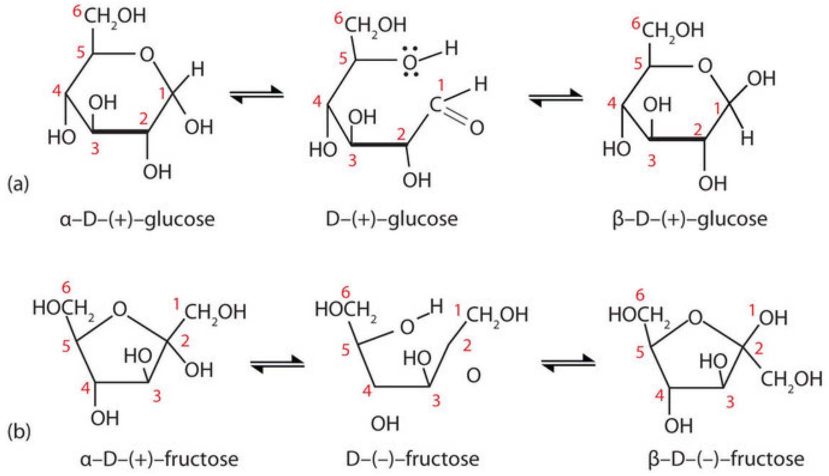


Figure 16.4.2: Monosaccharides. In an aqueous solution, monosaccharides exist as an equilibrium mixture of three forms. The interconversion between the forms is known as *mutarotation*, which is shown for D-glucose (a) and D-fructose (b).

Even though only a small percentage of the molecules are in the open-chain aldehyde form at any time, the solution will nevertheless exhibit the characteristic reactions of an aldehyde. As the small amount of free aldehyde is used up in a reaction, there is a shift in the equilibrium to yield more aldehyde. Thus, *all* the molecules may eventually react, even though very little free aldehyde is present at a time.

Commonly, (e.g., in Figures 16.4.1 and 16.4.2) the cyclic forms of sugars are depicted using a convention first suggested by Walter N. Haworth, an English chemist. The molecules are drawn as planar hexagons with a darkened edge representing the side facing toward the viewer. The structure is simplified to show only the functional groups attached to the carbon atoms. Any group written to the right in a Fischer projection appears below the plane of the ring in a Haworth projection, and any group written to the left in a Fischer projection appears above the plane in a Haworth projection.

The difference between the α and the β forms of sugars may seem trivial, but such structural differences are often crucial in biochemical reactions. This explains why we can get energy from the starch in potatoes and other plants but not from cellulose, even though both starch and cellulose are polysaccharides composed of glucose molecules linked together.

Summary

Monosaccharides that contain five or more carbons atoms form cyclic structures in aqueous solution. Two cyclic stereoisomers can form from each straight-chain monosaccharide; these are known as anomers. In an aqueous solution, an equilibrium mixture forms between the two anomers and the straight-chain structure of a monosaccharide in a process known as mutarotation.

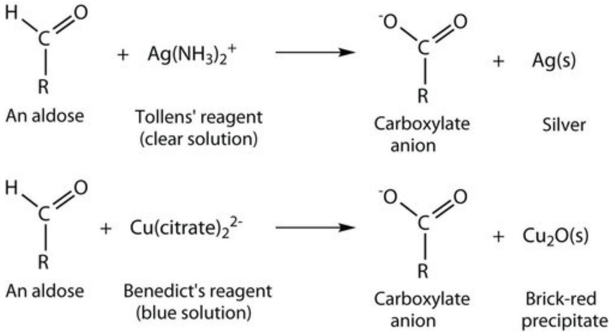
16.5: Properties of Monosaccharides

Learning Objectives

- To identify the physical and chemical properties of monosaccharides.

Monosaccharides such as glucose and fructose are crystalline solids at room temperature, but they are quite soluble in water, each molecule having several OH groups that readily engage in hydrogen bonding. The chemical behavior of these monosaccharides is likewise determined by their functional groups.

An important reaction of monosaccharides is the oxidation of the aldehyde group, one of the most easily oxidized organic functional groups. Aldehyde oxidation can be accomplished with any mild oxidizing agent, such as Tollens' reagent or Benedict's reagent. With the latter, complexed copper(II) ions are reduced to copper(I) ions that form a brick-red precipitate [copper(I) oxide; Figure 16.5.1].



Any carbohydrate capable of reducing either Tollens' or Benedict's reagents without first undergoing hydrolysis is said to be a reducing sugar. Because both the Tollens' and Benedict's reagents are basic solutions, ketoses (such as fructose) also give positive tests due to an equilibrium that exists between ketoses and aldoses in a reaction known as *tautomerism*.

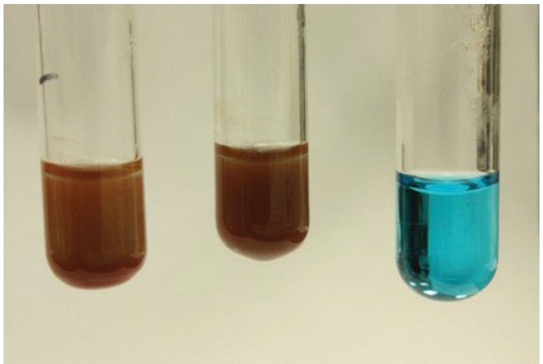


Figure 16.5.1: Benedict's Test. Benedict's test was performed on three carbohydrates, depicted from left to right: fructose, glucose, and sucrose. The solution containing sucrose remains blue because sucrose is a nonreducing sugar.

These reactions have been used as simple and rapid diagnostic tests for the presence of glucose in blood or urine. For example, Clinitest tablets, which are used to test for sugar in the urine, contain copper(II) ions and are based on Benedict's test. A green color indicates very little sugar, whereas a brick-red color indicates sugar in excess of 2 g/100 mL of urine.

Summary

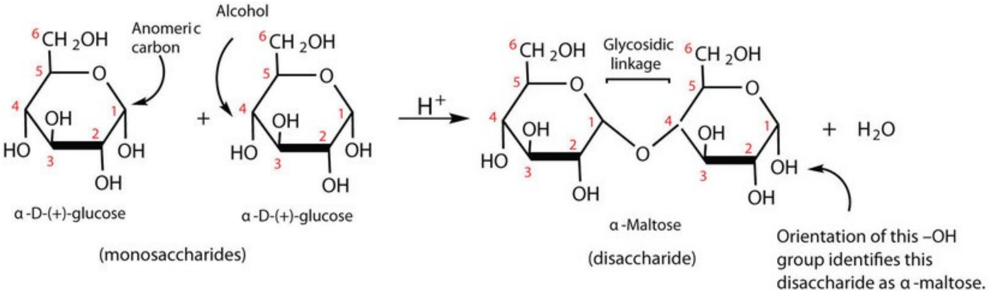
Monosaccharides are crystalline solids at room temperature and quite soluble in water. Monosaccharides are reducing sugars; they reduce mild oxidizing agents, such as Tollens' or Benedict's reagents.

16.6: Disaccharides

Learning Objectives

- Identify the structures of sucrose, lactose, and maltose.
- Identify the monosaccharides that are needed to form sucrose, lactose, and maltose

Previously, you learned that monosaccharides can form cyclic structures by the reaction of the carbonyl group with an OH group. These cyclic molecules can in turn react with another alcohol. Disaccharides ($C_{12}H_{22}O_{11}$) are sugars composed of two monosaccharide units that are joined by a carbon–oxygen-carbon linkage known as a glycosidic linkage. This linkage is formed from the reaction of the anomeric carbon of one cyclic monosaccharide with the OH group of a second monosaccharide.



The disaccharides differ from one another in their monosaccharide constituents and in the specific type of glycosidic linkage connecting them. There are three common disaccharides: maltose, lactose, and sucrose. All three are white crystalline solids at room temperature and are soluble in water. We’ll consider each sugar in more detail.

Maltose

Maltose occurs to a limited extent in sprouting grain. It is formed most often by the partial hydrolysis of starch and glycogen. In the manufacture of beer, maltose is liberated by the action of malt (germinating barley) on starch; for this reason, it is often referred to as *malt sugar*. Maltose is about 30% as sweet as sucrose. The human body is unable to metabolize maltose or any other disaccharide directly from the diet because the molecules are too large to pass through the cell membranes of the intestinal wall. Therefore, an ingested disaccharide must first be broken down by hydrolysis into its two constituent monosaccharide units.

In the body, such hydrolysis reactions are catalyzed by enzymes such as *maltase*. The same reactions can be carried out in the laboratory with dilute acid as a catalyst, although in that case the rate is much slower, and high temperatures are required. Whether it occurs in the body or a glass beaker, the hydrolysis of maltose produces two molecules of D-glucose.

$$\text{maltose} \xrightarrow{\text{H}^+ \text{ or maltase}} 2 \text{ D-glucose}$$

Maltose is a reducing sugar. Thus, its two glucose molecules must be linked in such a way as to leave one anomeric carbon that can open to form an aldehyde group. The glucose units in maltose are joined in a *head-to-tail* fashion through an α-linkage from the first carbon atom of one glucose molecule to the fourth carbon atom of the second glucose molecule (that is, an α-1,4-glycosidic linkage; see Figure $16.6.1$). The bond from the anomeric carbon of the first monosaccharide unit is directed downward, which is why this is known as an α-glycosidic linkage. The OH group on the anomeric carbon of the second glucose can be in either the α or the β position, as shown in Figure $16.6.1$.

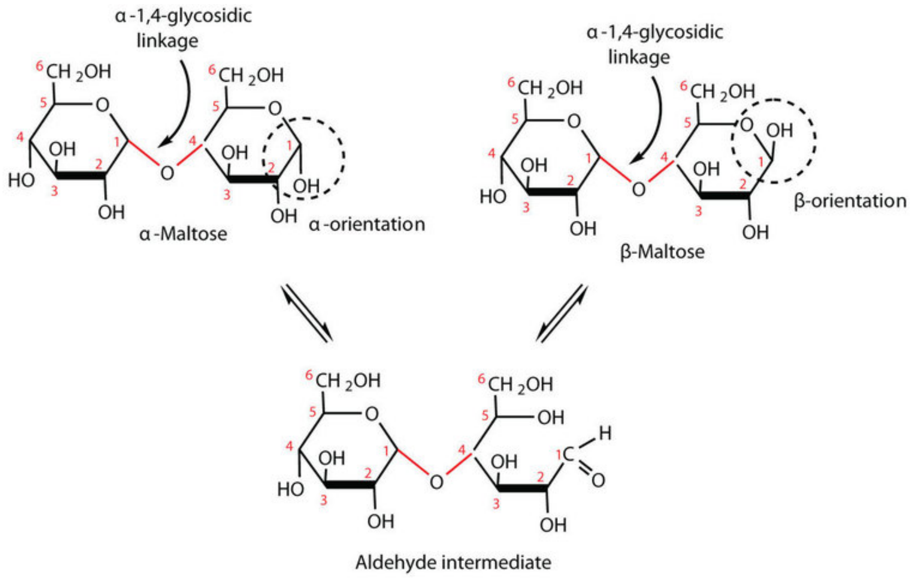
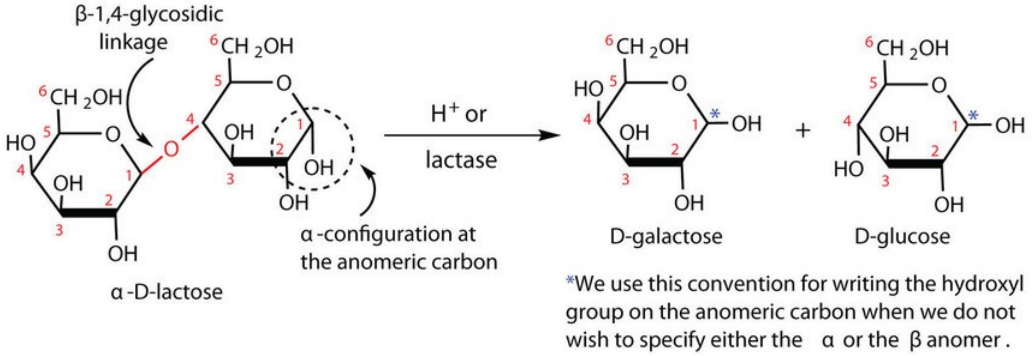


Figure 16.6.1: An Equilibrium Mixture of Maltose Isomers

Lactose

Lactose is known as *milk sugar* because it occurs in the milk of humans, cows, and other mammals. In fact, the natural synthesis of lactose occurs only in mammary tissue, whereas most other carbohydrates are plant products. Human milk contains about 7.5% lactose, and cow's milk contains about 4.5%. This sugar is one of the lowest ranking in terms of sweetness, being about one-sixth as sweet as sucrose. Lactose is produced commercially from whey, a by-product in the manufacture of cheese. It is important as an infant food and in the production of penicillin.

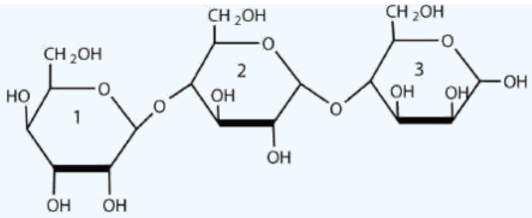
Lactose is a reducing sugar composed of one molecule of D-galactose and one molecule of D-glucose joined by a β-1,4-glycosidic bond (the bond from the anomeric carbon of the first monosaccharide unit being directed upward). The two monosaccharides are obtained from lactose by acid hydrolysis or the catalytic action of the enzyme *lactase*:



Many adults and some children suffer from a deficiency of lactase. These individuals are said to be lactose intolerant because they cannot digest the lactose found in milk. A more serious problem is the genetic disease galactosemia, which results from the absence of an enzyme needed to convert galactose to glucose. Certain bacteria can metabolize lactose, forming lactic acid as one of the products. This reaction is responsible for the "souring" of milk.

✓ Example 16.6.1

For this trisaccharide, indicate whether each glycosidic linkage is α or β.

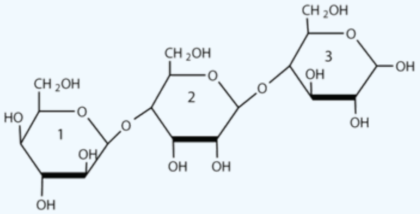


Solution

The glycosidic linkage between sugars 1 and 2 is β because the bond is directed up from the anomeric carbon. The glycosidic linkage between sugars 2 and 3 is α because the bond is directed down from the anomeric carbon.

Exercise 16.6.1

For this trisaccharide, indicate whether each glycosidic linkage is α or β.



To Your Health: Lactose Intolerance and Galactosemia

Lactose makes up about 40% of an infant's diet during the first year of life. Infants and small children have one form of the enzyme lactase in their small intestines and can digest the sugar easily; however, adults usually have a less active form of the enzyme, and about 70% of the world's adult population has some deficiency in its production. As a result, many adults experience a reduction in the ability to hydrolyze lactose to galactose and glucose in their small intestine. For some people the inability to synthesize sufficient enzyme increases with age. Up to 20% of the US population suffers some degree of lactose intolerance.

In people with lactose intolerance, some of the unhydrolyzed lactose passes into the colon, where it tends to draw water from the interstitial fluid into the intestinal lumen by osmosis. At the same time, intestinal bacteria may act on the lactose to produce organic acids and gases. The buildup of water and bacterial decay products leads to abdominal distention, cramps, and diarrhea, which are symptoms of the condition.

The symptoms disappear if milk or other sources of lactose are excluded from the diet or consumed only sparingly. Alternatively, many food stores now carry special brands of milk that have been pretreated with lactase to hydrolyze the lactose. Cooking or fermenting milk causes at least partial hydrolysis of the lactose, so some people with lactose intolerance are still able to enjoy cheese, yogurt, or cooked foods containing milk. The most common treatment for lactose intolerance, however, is the use of lactase preparations (e.g., Lactaid), which are available in liquid and tablet form at drugstores and grocery stores. These are taken orally with dairy foods—or may be added to them directly—to assist in their digestion.

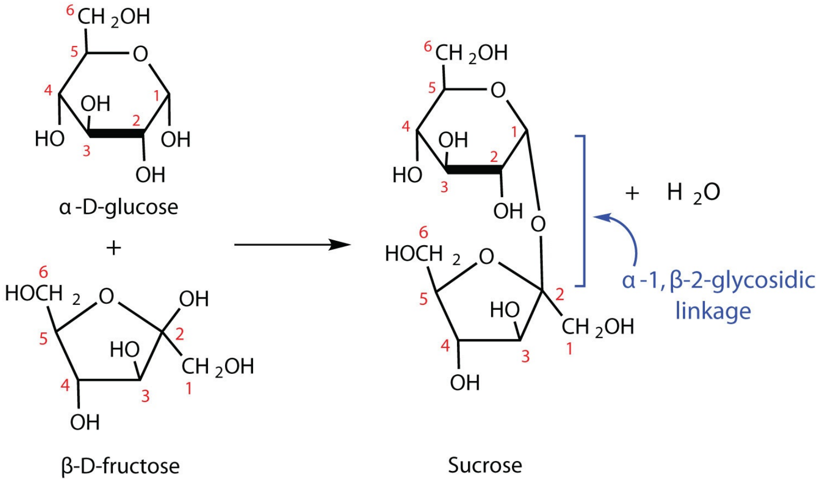
Galactosemia is a condition in which one of the enzymes needed to convert galactose to glucose is missing. Consequently, the blood galactose level is markedly elevated, and galactose is found in the urine. An infant with galactosemia experiences a lack of appetite, weight loss, diarrhea, and jaundice. The disease may result in impaired liver function, cataracts, mental retardation, and even death. If galactosemia is recognized in early infancy, its effects can be prevented by the exclusion of milk and all other sources of galactose from the diet. As a child with galactosemia grows older, he or she usually develops an alternate pathway for metabolizing galactose, so the need to restrict milk is not permanent. The incidence of galactosemia in the United States is 1 in every 65,000 newborn babies.

Sucrose

Sucrose, probably the largest-selling pure organic compound in the world, is known as *beet sugar*, *cane sugar*, *table sugar*, or simply *sugar*. Most of the sucrose sold commercially is obtained from sugar cane and sugar beets (whose juices are 14%–20%

sucrose) by evaporation of the water and recrystallization. The dark brown liquid that remains after the recrystallization of sugar is sold as molasses.

The sucrose molecule is unique among the common disaccharides in having an α-1,β-2-glycosidic (head-to-head) linkage. Because this glycosidic linkage is formed by the OH group on the anomeric carbon of α-D-glucose and the OH group on the anomeric carbon of β-D-fructose, it ties up the anomeric carbons of both glucose and fructose.



This linkage gives sucrose certain properties that are quite different from those of maltose and lactose. As long as the sucrose molecule remains intact, neither monosaccharide "uncyclizes" to form an open-chain structure. Thus, sucrose is incapable of mutarotation and exists in only one form both in the solid state and in solution. In addition, sucrose does not undergo reactions that are typical of aldehydes and ketones. Therefore, sucrose is a nonreducing sugar.

The hydrolysis of sucrose in dilute acid or through the action of the enzyme *sucrase* (also known as invertase) gives an equimolar mixture of glucose and fructose. This 1:1 mixture is referred to as *invert sugar* because it rotates plane-polarized light in the opposite direction than sucrose. The hydrolysis reaction has several practical applications. Sucrose readily recrystallizes from a solution, but invert sugar has a much greater tendency to remain in solution. In the manufacture of jelly and candy and in the canning of fruit, the recrystallization of sugar is undesirable. Therefore, conditions leading to the hydrolysis of sucrose are employed in these processes. Moreover, because fructose is sweeter than sucrose, the hydrolysis adds to the sweetening effect. Bees carry out this reaction when they make honey.

The average American consumes more than 100 lb of sucrose every year. About two-thirds of this amount is ingested in soft drinks, presweetened cereals, and other highly processed foods. The widespread use of sucrose is a contributing factor to obesity and tooth decay. Carbohydrates such as sucrose, are converted to fat when the caloric intake exceeds the body's requirements, and sucrose causes tooth decay by promoting the formation of plaque that sticks to teeth.

Summary

Maltose is composed of two molecules of glucose joined by an α-1,4-glycosidic linkage. It is a reducing sugar that is found in sprouting grain. Lactose is composed of a molecule of galactose joined to a molecule of glucose by a β-1,4-glycosidic linkage. It is a reducing sugar that is found in milk. Sucrose is composed of a molecule of glucose joined to a molecule of fructose by an α-1,β-2-glycosidic linkage. It is a nonreducing sugar that is found in sugar cane and sugar beets

16.7: Polysaccharides

Learning Objectives

- To compare and contrast the structures and uses of starch, glycogen, and cellulose.

The polysaccharides are the most abundant carbohydrates in nature and serve a variety of functions, such as energy storage or as components of plant cell walls. Polysaccharides are very large polymers composed of tens to thousands of monosaccharides joined together by glycosidic linkages. The three most abundant polysaccharides are starch, glycogen, and cellulose. These three are referred to as *homopolymers* because each yields only one type of monosaccharide (glucose) after complete hydrolysis. *Heteropolymers* may contain sugar acids, amino sugars, or noncarbohydrate substances in addition to monosaccharides. Heteropolymers are common in nature (gums, pectins, and other substances) but will not be discussed further in this textbook. The polysaccharides are nonreducing carbohydrates, are not sweet tasting, and do not undergo mutarotation.

Starch

Starch is the most important source of carbohydrates in the human diet and accounts for more than 50% of our carbohydrate intake. It occurs in plants in the form of granules, and these are particularly abundant in seeds (especially the cereal grains) and tubers, where they serve as a storage form of carbohydrates. The breakdown of starch to glucose nourishes the plant during periods of reduced photosynthetic activity. We often think of potatoes as a “starchy” food, yet other plants contain a much greater percentage of starch (potatoes 15%, wheat 55%, corn 65%, and rice 75%). Commercial starch is a white powder.

Starch is a mixture of two polymers: amylose and amylopectin. Natural starches consist of about 10%–30% amylose and 70%–90% amylopectin. Amylose is a linear polysaccharide composed entirely of D-glucose units joined by the α-1,4-glycosidic linkages we saw in maltose (part (a) of Figure 16.7.1). Experimental evidence indicates that amylose is not a straight chain of glucose units but instead is coiled like a spring, with six glucose monomers per turn (part (b) of Figure 16.7.1). When coiled in this fashion, amylose has just enough room in its core to accommodate an iodine molecule. The characteristic blue-violet color that appears when starch is treated with iodine is due to the formation of the amylose-iodine complex. This color test is sensitive enough to detect even minute amounts of starch in solution.

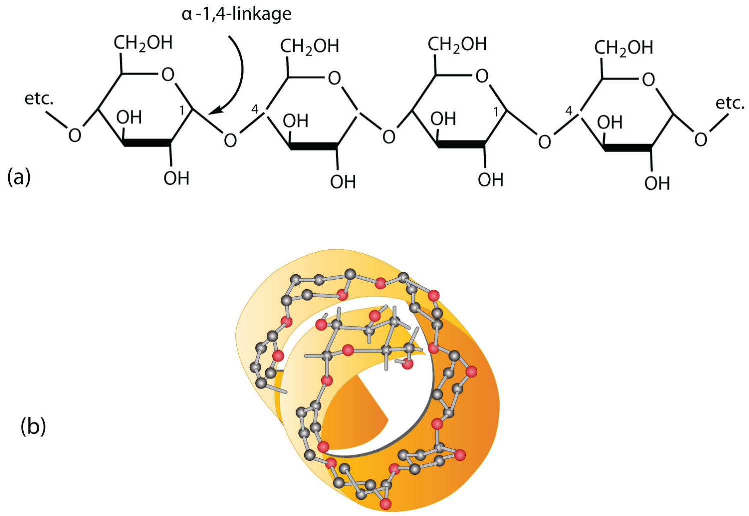


Figure 16.7.1: Amylose. (a) Amylose is a linear chain of α-D-glucose units joined together by α-1,4-glycosidic bonds. (b) Because of hydrogen bonding, amylose acquires a spiral structure that contains six glucose units per turn.

Amylopectin is a branched-chain polysaccharide composed of glucose units linked primarily by α-1,4-glycosidic bonds but with occasional α-1,6-glycosidic bonds, which are responsible for the branching. A molecule of amylopectin may contain many thousands of glucose units with branch points occurring about every 25–30 units (Figure 16.7.2). The helical structure of amylopectin is disrupted by the branching of the chain, so instead of the deep blue-violet color amylose gives with iodine, amylopectin produces a less intense reddish brown.

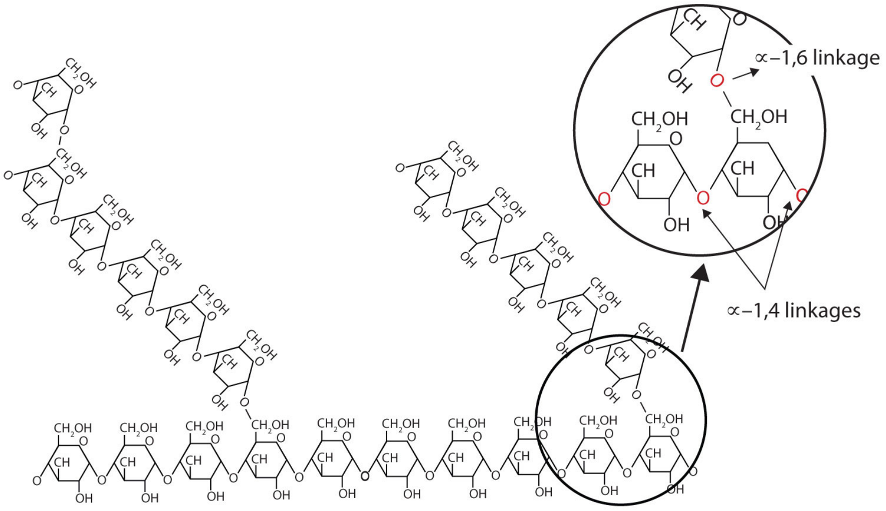


Figure 16.7.2: Representation of the Branching in Amylopectin and Glycogen. Both amylopectin and glycogen contain branch points that are linked through α-1,6-linkages. These branch points occur more often in glycogen.

Dextrins are glucose polysaccharides of intermediate size. The shine and stiffness imparted to clothing by starch are due to the presence of dextrins formed when clothing is ironed. Because of their characteristic stickiness with wetting, dextrins are used as adhesives on stamps, envelopes, and labels; as binders to hold pills and tablets together; and as pastes. Dextrins are more easily digested than starch and are therefore used extensively in the commercial preparation of infant foods.

The complete hydrolysis of starch yields, in successive stages, glucose:

$$\text{starch} \rightarrow \text{dextrins} \rightarrow \text{maltose} \rightarrow \text{glucose}$$

In the human body, several enzymes known collectively as amylases degrade starch sequentially into usable glucose units.

Glycogen

Glycogen is the energy reserve carbohydrate of animals. Practically all mammalian cells contain some stored carbohydrates in the form of glycogen, but it is especially abundant in the liver (4%–8% by weight of tissue) and in skeletal muscle cells (0.5%–1.0%). Like starch in plants, glycogen is found as granules in liver and muscle cells. When fasting, animals draw on these glycogen reserves during the first day without food to obtain the glucose needed to maintain metabolic balance.

Glycogen is structurally quite similar to amylopectin, although glycogen is more highly branched (8–12 glucose units between branches) and the branches are shorter. When treated with iodine, glycogen gives a reddish brown color. Glycogen can be broken down into its D-glucose subunits by acid hydrolysis or by the same enzymes that catalyze the breakdown of starch. In animals, the enzyme phosphorylase catalyzes the breakdown of glycogen to phosphate esters of glucose.

> *About 70% of the total glycogen in the body is stored in muscle cells. Although the percentage of glycogen (by weight) is higher in the liver, the much greater mass of skeletal muscle stores a greater total amount of glycogen.*

Cellulose

Cellulose, a fibrous carbohydrate found in all plants, is the structural component of plant cell walls. Because the earth is covered with vegetation, cellulose is the most abundant of all carbohydrates, accounting for over 50% of all the carbon found in the vegetable kingdom. Cotton fibrils and filter paper are almost entirely cellulose (about 95%), wood is about 50% cellulose, and the dry weight of leaves is about 10%–20% cellulose. The largest use of cellulose is in the manufacture of paper and paper products. Although the use of noncellulose synthetic fibers is increasing, rayon (made from cellulose) and cotton still account for over 70% of textile production.

Like amylose, cellulose is a linear polymer of glucose. It differs, however, in that the glucose units are joined by β-1,4-glycosidic linkages, producing a more extended structure than amylose (part (a) of Figure 16.7.3). This extreme linearity allows a great deal of hydrogen bonding between OH groups on adjacent chains, causing them to pack closely into fibers (part (b) of Figure 16.7.3).

As a result, cellulose exhibits little interaction with water or any other solvent. Cotton and wood, for example, are completely insoluble in water and have considerable mechanical strength. Because cellulose does not have a helical structure, it does not bind to iodine to form a colored product.

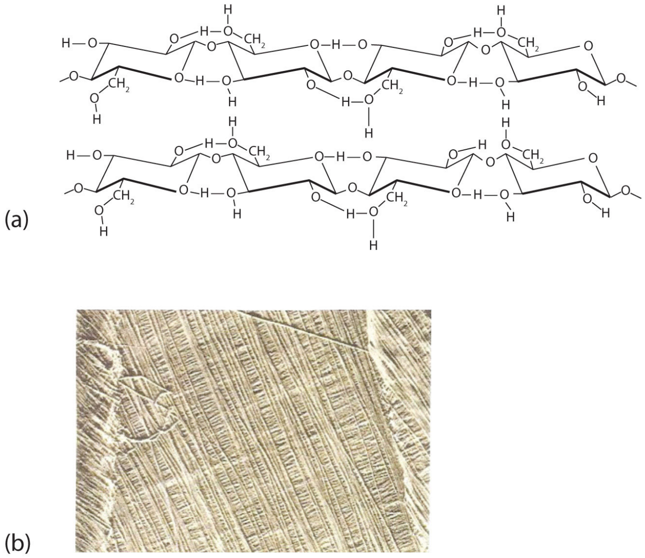


Figure 16.7.3: Cellulose. (a) There is extensive hydrogen bonding in the structure of cellulose. (b) In this electron micrograph of the cell wall of an alga, the wall consists of successive layers of cellulose fibers in parallel arrangement.

Cellulose yields D-glucose after complete acid hydrolysis, yet humans are unable to metabolize cellulose as a source of glucose. Our digestive juices lack enzymes that can hydrolyze the β-glycosidic linkages found in cellulose, so although we can eat potatoes, we cannot eat grass. However, certain microorganisms can digest cellulose because they make the enzyme cellulase, which catalyzes the hydrolysis of cellulose. The presence of these microorganisms in the digestive tracts of herbivorous animals (such as cows, horses, and sheep) allows these animals to degrade the cellulose from plant material into glucose for energy. Termites also contain cellulase-secreting microorganisms and thus can subsist on a wood diet. This example once again demonstrates the extreme stereospecificity of biochemical processes.

Career Focus: Certified Diabetes Educator

Certified diabetes educators come from a variety of health professions, such as nursing and dietetics, and specialize in the education and treatment of patients with diabetes. A diabetes educator will work with patients to manage their diabetes. This involves teaching the patient to monitor blood sugar levels, make good food choices, develop and maintain an exercise program, and take medication, if required.

A certified diabetes educator at Naval Medical Center Portsmouth (left) and a registered dietician at the medical center (center), provide nutritional information to a diabetes patient and her mother at the Diabetes Boot Camp.

Diabetes educators also work with hospital or nursing home staff to improve the care of diabetic patients. Educators must be willing to spend time attending meetings and reading the current literature to maintain their knowledge of diabetes medications, nutrition, and blood monitoring devices so that they can pass this information to their patients.

Summary

Starch is a storage form of energy in plants. It contains two polymers composed of glucose units: amylose (linear) and amylopectin (branched). Glycogen is a storage form of energy in animals. It is a branched polymer composed of glucose units. It is more highly branched than amylopectin. Cellulose is a structural polymer of glucose units found in plants. It is a linear polymer with the glucose units linked through β-1,4-glycosidic bonds.

16.S: Carbohydrates (Summary)

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

Carbohydrates, a large group of biological compounds containing carbon, hydrogen, and oxygen atoms, include sugars, starch, glycogen, and cellulose. All carbohydrates contain alcohol functional groups, and either an aldehyde or a ketone group (or a functional group that can be converted to an aldehyde or ketone). The simplest carbohydrates are **monosaccharides**. Those with two monosaccharide units are **disaccharides**, and those with many monosaccharide units are **polysaccharides**. Most sugars are either monosaccharides or disaccharides. Cellulose, glycogen, and starch are polysaccharides.

Many carbohydrates exist as **stereoisomers**, in which the three-dimensional spatial arrangement of the atoms in space is the only difference between the isomers. These particular stereoisomers contain at least one **chiral carbon**, a carbon atom that has four different groups bonded to it. A molecule containing a chiral carbon is nonsuperimposable on its mirror image, and two molecules that are nonsuperimposable mirror images of each other are a special type of stereoisomer called **enantiomers**. Enantiomers have the same physical properties, such as melting point, but differ in the direction they rotate polarized light.

A sugar is designated as being a D sugar or an L sugar according to how, in a Fischer projection of the molecule, the hydrogen atom and OH group are attached to the *penultimate* carbon atom, which is the carbon atom immediately before the terminal alcohol carbon atom. If the structure at this carbon atom is the same as that of D-glyceraldehyde (OH to the right), the sugar is a **D sugar**; if the configuration is the same as that of L-glyceraldehyde (OH to the left), the sugar is an **L sugar**.

Monosaccharides of five or more carbons atoms readily form cyclic structures when the carbonyl carbon atom reacts with an OH group on a carbon atom three or four carbon atoms distant. Consequently, glucose in solution exists as an equilibrium mixture of three forms, two of them cyclic (α- and β-) and one open chain. In Haworth projections, the *alpha* form is drawn with the OH group on the “former” carbonyl carbon atom (**anomeric carbon**) pointing downward; the *beta* form, with the OH group pointing upward; these two compounds are stereoisomers and are given the more specific term of **anomers**. Any solid sugar can be all alpha or all beta. Once the sample is dissolved in water, however, the ring opens up into the open-chain structure and then closes to form either the α- or the β-anomer. These interconversions occur back and forth until a dynamic equilibrium mixture is achieved in a process called **mutarotation**.

The carbonyl group present in monosaccharides is easily oxidized by Tollens’ or Benedict’s reagents (as well as others). Any mono- or disaccharide containing a free anomeric carbon is a **reducing sugar**. The disaccharide *maltose* contains two glucose units joined in an α-1,4-glycosidic linkage. The disaccharide *lactose* contains a galactose unit and a glucose unit joined by a β-1,4-glycosidic linkage. Both maltose and lactose contain a free anomeric carbon that can convert to an aldehyde functional group, so they are reducing sugars; they also undergo mutarotation. Many adults, and some children, have a deficiency of the enzyme lactase (which is needed to break down lactose) and are said to be **lactose intolerant**. A more serious problem is the genetic disease **galactosemia**, which results from the absence of an enzyme needed to convert galactose to glucose.

The disaccharide *sucrose* (table sugar) consists of a glucose unit and a fructose unit joined by a glycosidic linkage. The linkage is designated as an α-1,β-2-glycosidic linkage because it involves the OH group on the first carbon atom of glucose and the OH group on the second carbon atom of fructose. Sucrose is not a reducing sugar because it has no anomeric carbon that can reform a carbonyl group, and it cannot undergo mutarotation because of the restrictions imposed by this linkage.

Starch, the principal carbohydrate of plants, is composed of the polysaccharides **amylose** (10%–30%) and **amylopectin** (70%–90%). When ingested by humans and other animals, starch is hydrolyzed to glucose and becomes the body’s energy source. *Glycogen* is the polysaccharide animals use to store excess carbohydrates from their diets. Similar in structure to amylopectin, glycogen is hydrolyzed to glucose whenever an animal needs energy for a metabolic process. The polysaccharide *cellulose* provides structure for plant cells. It is a linear polymer of glucose units joined by β-1,4-glycosidic linkages. It is indigestible in the human body but digestible by many microorganisms, including microorganisms found in the digestive tracts of many herbivores.

CHAPTER OVERVIEW

17: Lipids

The lipids are a large and diverse group of naturally occurring organic compounds that are related by their solubility in nonpolar organic solvents (e.g., ether, chloroform, acetone and benzene) and general insolubility in water. There is great structural variety among the lipids, as will be demonstrated in the following sections.

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17.0: Prelude to Lipids

> On July 11, 2003, the Food and Drug Administration amended its food labeling regulations to require that manufacturers list the amount of *trans* fatty acids on Nutrition Facts labels of foods and dietary supplements, effective January 1, 2006. This amendment was a response to published studies demonstrating a link between the consumption of *trans* fatty acids and an increased risk of heart disease. *Trans* fatty acids are produced in the conversion of liquid oils to solid fats, as in the creation of many commercial margarines and shortenings. They have been shown to increase the levels of low-density lipoproteins (LDLs)—complexes that are often referred to as bad cholesterol—in the blood. In this chapter, you will learn about fatty acids and what is meant by a *trans* fatty acid, as well as the difference between fats and oils. You will also learn what cholesterol is and why it is an important molecule in the human body.

Fats and oils, found in many of the foods we eat, belong to a class of biomolecules known as lipids. Gram for gram, they pack more than twice the caloric content of carbohydrates: the oxidation of fats and oils supplies about 9 kcal of energy for every gram oxidized, whereas the oxidation of carbohydrates supplies only 4 kcal/g. Although the high caloric content of fats may be bad news for the dieter, it says something about the efficiency of nature’s designs. Our bodies use carbohydrates, primarily in the form of glucose, for our *immediate* energy needs. Our capacity for storing carbohydrates for later use is limited to tucking away a bit of glycogen in the liver or in muscle tissue. We store our *reserve* energy in lipid form, which requires far less space than the same amount of energy stored in carbohydrate form. Lipids have other biological functions besides energy storage. They are a major component of the membranes of the 10 trillion cells in our bodies. They serve as protective padding and insulation for vital organs. Furthermore, without lipids in our diets, we would be deficient in the fat-soluble vitamins A, D, E, and K.

Lipids are not defined by the presence of specific functional groups, as carbohydrates are, but by a physical property—solubility. Compounds isolated from body tissues are classified as lipids if they are more soluble in organic solvents, such as dichloromethane, than in water. By this criterion, the lipid category includes not only fats and oils, which are esters of the trihydroxy alcohol glycerol and fatty acids, but also compounds that incorporate functional groups derived from phosphoric acid, carbohydrates, or amino alcohols, as well as steroid compounds such as cholesterol (Figure 17.0.1 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.

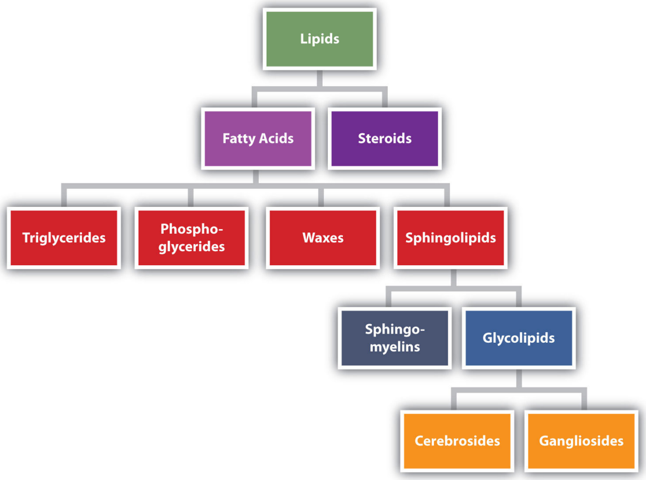


Figure 17.0.1: Lipid Organization Based on Structural Relationships

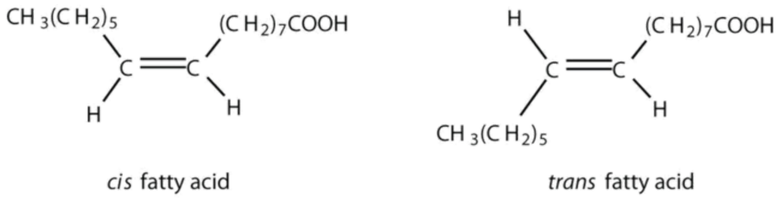
Lipid categorized into fatty acids and steroids. Fatty acids are further separated into triglycerides, phospho-glycerides, waxes, and sphingolipids. Sphingolipids are separated into sphingo-myelins and glycolipids. Glycolipids are separated into cerebrosides and gangliosides.

17.1: Fatty Acids

Learning Objectives

- To recognize the structures of common fatty acids and classify them as saturated, monounsaturated, or polyunsaturated.

Fatty acids are carboxylic acids that are structural components of fats, oils, and all other categories of lipids, except steroids. More than 70 have been identified in nature. They usually contain an even number of carbon atoms (typically 12–20), are generally unbranched, and can be classified by the presence and number of carbon-to-carbon double bonds. Thus, saturated fatty acids contain no carbon-to-carbon double bonds, monounsaturated fatty acids contain one carbon-to-carbon double bond, and polyunsaturated fatty acids contain two or more carbon-to-carbon double bonds.



Cis fatty acids have two H atoms on the same side of the plane of the fatty acid while trans has the two H atoms on opposite sides.

Table 17.1.1 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 17.1.1: Some Common Fatty Acids Found in Natural Fats

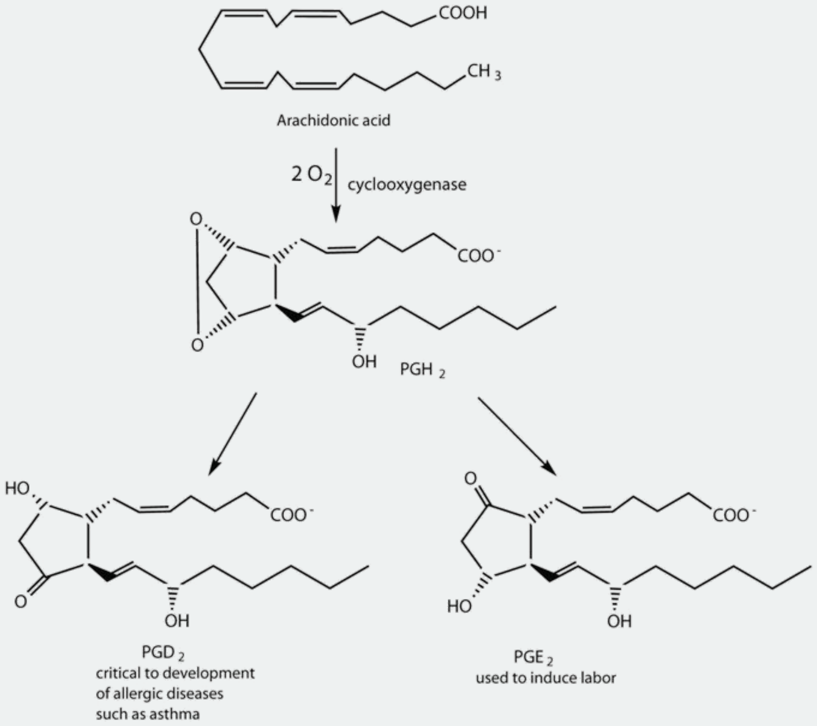
Name	Abbreviated Structural Formula	Condensed Structural Formula	Melting Point (°C)	Source
lauric acid	$C_{11}H_{23}COOH$	$CH_3(CH_2)_{10}COOH$	44	palm kernel oil
myristic acid	$C_{13}H_{27}COOH$	$CH_3(CH_2)_{12}COOH$	58	oil of nutmeg
palmitic acid	$C_{15}H_{31}COOH$	$CH_3(CH_2)_{14}COOH$	63	palm oil
palmitoleic acid	$C_{15}H_{29}COOH$	$CH_3(CH_2)_5CH=CH(CH_2)_7COOH$	0.5	macadamia oil
stearic acid	$C_{17}H_{35}COOH$	$CH_3(CH_2)_{16}COOH$	70	cocoa butter
oleic acid	$C_{17}H_{33}COOH$	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	16	olive oil
linoleic acid	$C_{17}H_{31}COOH$	$CH_3(CH_2)_3(CH_2CH=CH)_2(CH_2)_7COOH$	−5	canola oil
α-linolenic acid	$C_{17}H_{29}COOH$	$CH_3(CH_2CH=CH)_3(CH_2)_7COOH$	−11	flaxseed
arachidonic acid	$C_{19}H_{31}COOH$	$CH_3(CH_2)_4(CH_2CH=CH)_4(CH_2)_2COOH$	−50	liver

Two polyunsaturated fatty acids—linoleic and α-linolenic acids—are termed essential fatty acids because humans must obtain them from their diets. Both substances are required for normal growth and development, but the human body does not synthesize them. The body uses linoleic acid to synthesize many of the other unsaturated fatty acids, such as arachidonic acid, a precursor for the synthesis of prostaglandins. In addition, the essential fatty acids are necessary for the efficient transport and metabolism of cholesterol. The average daily diet should contain about 4–6 g of the essential fatty acids.

To Your Health: Prostaglandins

Prostaglandins are chemical messengers synthesized in the cells in which their physiological activity is expressed. They are unsaturated fatty acids containing 20 carbon atoms and are synthesized from arachidonic acid—a polyunsaturated fatty acid—when needed by a particular cell. They are called *prostaglandins* because they were originally isolated from semen found in the prostate gland. It is now known that they are synthesized in nearly all mammalian tissues and affect almost all organs in the body. The five major classes of prostaglandins are designated as PGA, PGB, PGE, PGF, and PGI. Subscripts are attached at the end of these abbreviations to denote the number of double bonds outside the five-carbon ring in a given prostaglandin.

The prostaglandins are among the most potent biological substances known. Slight structural differences give them highly distinct biological effects; however, all prostaglandins exhibit some ability to induce smooth muscle contraction, lower blood pressure, and contribute to the inflammatory response. Aspirin and other nonsteroidal anti-inflammatory agents, such as ibuprofen, obstruct the synthesis of prostaglandins by inhibiting cyclooxygenase, the enzyme needed for the initial step in the conversion of arachidonic acid to prostaglandins.



Their wide range of physiological activity has led to the synthesis of hundreds of prostaglandins and their analogs. Derivatives of PGE_2 are now used in the United States to induce labor. Other prostaglandins have been employed clinically to lower or increase blood pressure, inhibit stomach secretions, relieve nasal congestion, relieve asthma, and prevent the formation of blood clots, which are associated with heart attacks and strokes.

Although we often draw the carbon atoms in a straight line, they actually have more of a zigzag configuration (Figure $17.1.2a$). Viewed as a whole, however, the saturated fatty acid molecule is relatively straight (Figure $17.1.2b$). 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.

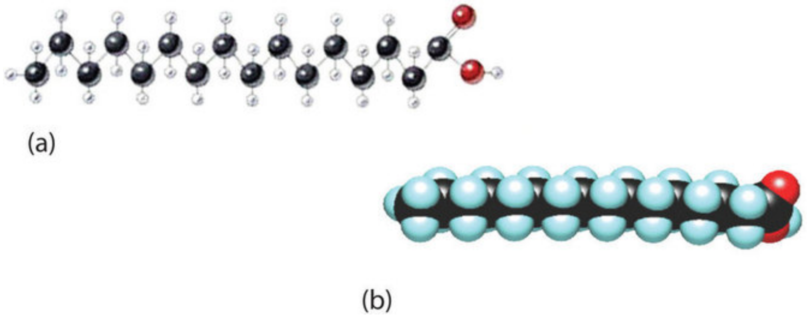
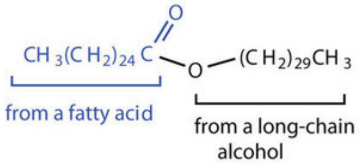


Figure 17.1.2: The Structure of Saturated Fatty Acids. (a) There is a zigzag pattern formed by the carbon-to-carbon single bonds in the ball-and-stick model of a palmitic acid molecule. (b) A space-filling model of palmitic acid shows the overall straightness of a saturated fatty acid molecule.

Waxes are esters formed from long-chain fatty acids and long-chain alcohols. Most natural waxes are mixtures of such esters. Plant waxes on the surfaces of leaves, stems, flowers, and fruits protect the plant from dehydration and invasion by harmful microorganisms. Carnauba wax, used extensively in floor waxes, automobile waxes, and furniture polish, is largely myricyl cerotate, obtained from the leaves of certain Brazilian palm trees. Animals also produce waxes that serve as protective coatings, keeping the surfaces of feathers, skin, and hair pliable and water repellent. In fact, if the waxy coating on the feathers of a water bird is dissolved as a result of the bird swimming in an oil slick, the feathers become wet and heavy, and the bird, unable to maintain its buoyancy, drowns.



$$\underbrace{CH_3(CH_2)_{24}\overset{O}{\overset{\|}{C}}}_{\text{from a fatty acid}}-O-\underbrace{(CH_2)_{29}CH_3}_{\text{from a long-chain alcohol}}$$

Myricyl cerotate
(found in carnauba wax)

Summary

Fatty acids are carboxylic acids that are the structural components of many lipids. They may be saturated or unsaturated. Most fatty acids are unbranched and contain an even number of carbon atoms. Unsaturated fatty acids have lower melting points than saturated fatty acids containing the same number of carbon atoms.

17.2: Fats and Oils

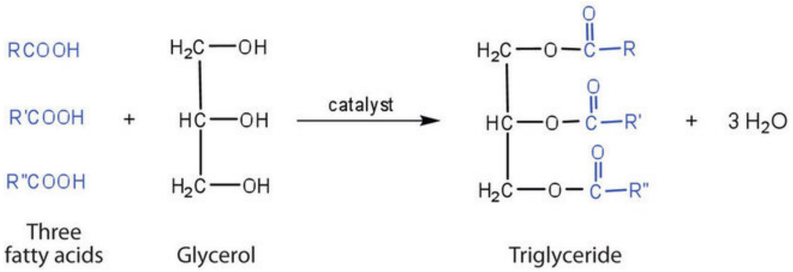
Learning Objectives

- Explain why fats and oils are referred to as triglycerides.
- Explain how the fatty acid composition of the triglycerides determines whether a substance is a fat or oil.
- Describe the importance of key reactions of triglycerides, such as hydrolysis, hydrogenation, and oxidation.

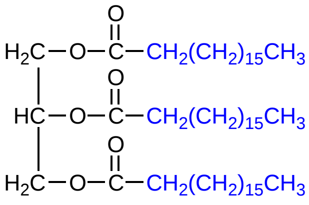
Fats and oils are the most abundant lipids in nature. They provide energy for living organisms, insulate body organs, and transport fat-soluble vitamins through the blood.

Structures of Fats and Oils

Fats and oils are called triglycerides (or *triacylcylgerols*) because they are esters composed of three fatty acid units joined to *glycerol*, a trihydroxy alcohol:

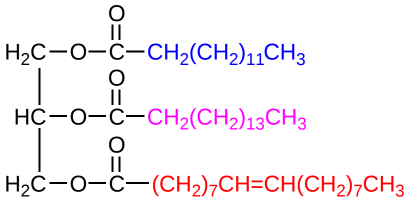


If all three OH groups on the glycerol molecule are esterified with the same fatty acid, the resulting ester is called a *simple triglyceride*. Although simple triglycerides have been synthesized in the laboratory, they rarely occur in nature. Instead, a typical triglyceride obtained from naturally occurring fats and oils contains two or three different fatty acid components and is thus termed a *mixed triglyceride*.



Tristearin

a simple triglyceride



a mixed triglyceride

A triglyceride is called a fat if it is a solid at 25°C; it is called an oil if it is a liquid at that temperature. These differences in melting points reflect differences in the degree of unsaturation and number of carbon atoms in the constituent fatty acids. Triglycerides obtained from animal sources are usually solids, while those of plant origin are generally oils. Therefore, we commonly speak of animal fats and vegetable oils.

No single formula can be written to represent the naturally occurring fats and oils because they are highly complex mixtures of triglycerides in which many different fatty acids are represented. Table 17.2.1 shows the fatty acid compositions of some common fats and oils. The composition of any given fat or oil can vary depending on the plant or animal species it comes from as well as on dietetic and climatic factors. To cite just one example, lard from corn-fed hogs is more highly saturated than lard from peanut-fed hogs. Palmitic acid is the most abundant of the saturated fatty acids, while oleic acid is the most abundant unsaturated fatty acid.

Table 17.2.1: Average Fatty Acid Composition of Some Common Fats and Oils (%)*

	Lauric	Myristic	Palmitic	Stearic	Oleic	Linoleic	Linolenic
Fats							
butter (cow)	3	11	27	12	29	2	1
tallow		3	24	19	43	3	1
lard		2	26	14	44	10	
Oils							
canola oil			4	2	62	22	10
coconut oil[†]	47	18	9	3	6	2	
corn oil			11	2	28	58	1
olive oil			13	3	71	10	1
peanut oil			11	2	48	32	
soybean oil			11	4	24	54	7

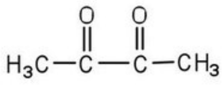
*Totals less than 100% indicate the presence of fatty acids with fewer than 12 carbon atoms or more than 18 carbon atoms.

[†] Coconut oil is highly saturated. It contains an unusually high percentage of the low-melting C_8, C_{10}, and C_{12} saturated fatty acids.

Terms such as *saturated fat* or *unsaturated oil* are often used to describe the fats or oils obtained from foods. Saturated fats contain a high proportion of saturated fatty acids, while unsaturated oils contain a high proportion of unsaturated fatty acids. The high consumption of saturated fats is a factor, along with the high consumption of cholesterol, in increased risks of heart disease.

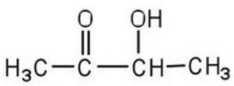
Physical Properties of Fats and Oils

Contrary to what you might expect, *pure* fats and oils are colorless, odorless, and tasteless. The characteristic colors, odors, and flavors that we associate with some of them are imparted by foreign substances that are lipid soluble and have been absorbed by these lipids. For example, the yellow color of butter is due to the presence of the pigment carotene; the taste of butter comes from two compounds—diacetyl and 3-hydroxy-2-butanone—produced by bacteria in the ripening cream from which the butter is made.



$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

Diacetyl



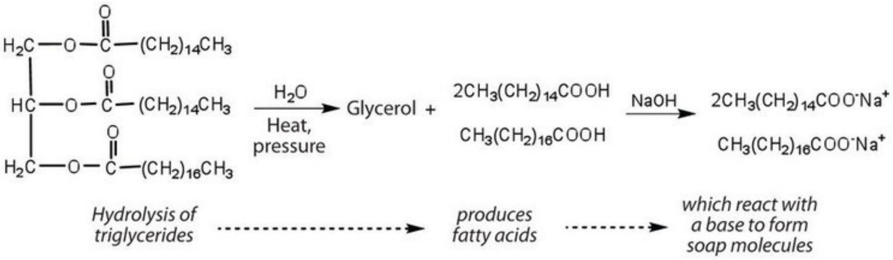
$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_3$

3-hydroxy-2-butanone

Fats and oils are lighter than water, having densities of about 0.8 g/cm^3. They are poor conductors of heat and electricity and therefore serve as excellent insulators for the body, slowing the loss of heat through the skin.

Chemical Reactions of Fats and Oils

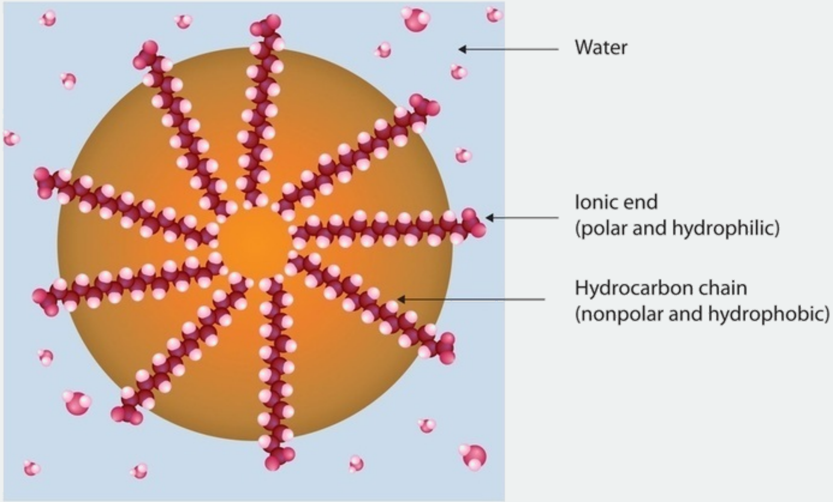
Fats and oils can participate in a variety of chemical reactions—for example, because triglycerides are esters, they can be hydrolyzed in the presence of an acid, a base, or specific enzymes known as lipases. The hydrolysis of fats and oils in the presence of a base is used to make soap and is called saponification. Today most soaps are prepared through the hydrolysis of triglycerides (often from tallow, coconut oil, or both) using water under high pressure and temperature [700 lb/in^2 (∼50 atm or 5,000 kPa) and 200°C]. Sodium carbonate or sodium hydroxide is then used to convert the fatty acids to their sodium salts (soap molecules):



Looking Closer: Soaps

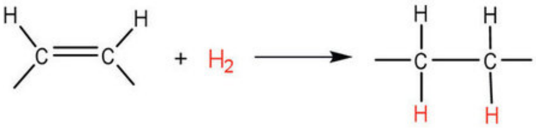
Ordinary soap is a mixture of the sodium salts of various fatty acids, produced in one of the oldest organic syntheses practiced by humans (second only to the fermentation of sugars to produce ethyl alcohol). Both the Phoenicians (600 BCE) and the Romans made soap from animal fat and wood ash. Even so, the widespread production of soap did not begin until the 1700s. Soap was traditionally made by treating molten lard or tallow with a slight excess of alkali in large open vats. The mixture was heated, and steam was bubbled through it. After saponification was completed, the soap was precipitated from the mixture by the addition of sodium chloride (NaCl), removed by filtration, and washed several times with water. It was then dissolved in water and reprecipitated by the addition of more NaCl. The glycerol produced in the reaction was also recovered from the aqueous wash solutions.

Pumice or sand is added to produce scouring soap, while ingredients such as perfumes or dyes are added to produce fragrant, colored soaps. Blowing air through molten soap produces a floating soap. Soft soaps, made with potassium salts, are more expensive but produce a finer lather and are more soluble. They are used in liquid soaps, shampoos, and shaving creams.



Dirt and grime usually adhere to skin, clothing, and other surfaces by combining with body oils, cooking fats, lubricating greases, and similar substances that act like glues. Because these substances are not miscible in water, washing with water alone does little to remove them. Soap removes them, however, because soap molecules have a dual nature. One end, called the *head*, carries an ionic charge (a carboxylate anion) and therefore dissolves in water; the other end, the *tail*, has a hydrocarbon structure and dissolves in oils. The hydrocarbon tails dissolve in the soil; the ionic heads remain in the aqueous phase, and the soap breaks the oil into tiny soap-enclosed droplets called *micelles*, which disperse throughout the solution. The droplets repel each other because of their charged surfaces and do not coalesce. With the oil no longer "gluing" the dirt to the soiled surface (skin, cloth, dish), the soap-enclosed dirt can easily be rinsed away.

The double bonds in fats and oils can undergo hydrogenation and also oxidation. The hydrogenation of vegetable oils to produce semisolid fats is an important process in the food industry. Chemically, it is essentially identical to the catalytic hydrogenation reaction described for alkenes.



In commercial processes, the number of double bonds that are hydrogenated is carefully controlled to produce fats with the desired consistency (soft and pliable). Inexpensive and abundant vegetable oils (canola, corn, soybean) are thus transformed into margarine and cooking fats. In the preparation of margarine, for example, partially hydrogenated oils are mixed with water, salt, and nonfat dry milk, along with flavoring agents, coloring agents, and vitamins A and D, which are added to approximate the look, taste, and nutrition of butter. (Preservatives and antioxidants are also added.) In most commercial peanut butter, the peanut oil has been partially hydrogenated to prevent it from separating out. Consumers could decrease the amount of saturated fat in their diet by using the original unprocessed oils on their foods, but most people would rather spread margarine on their toast than pour oil on it.

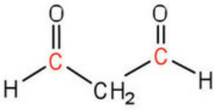
Many people have switched from butter to margarine or vegetable shortening because of concerns that saturated animal fats can raise blood cholesterol levels and result in clogged arteries. However, during the hydrogenation of vegetable oils, an isomerization reaction occurs that produces the *trans* fatty acids mentioned in the opening essay. However, studies have shown that *trans* fatty acids also raise cholesterol levels and increase the incidence of heart disease. *Trans* fatty acids do not have the bend in their structures, which occurs in *cis* fatty acids and thus pack closely together in the same way that the saturated fatty acids do. Consumers are now being advised to use polyunsaturated oils and soft or liquid margarine and reduce their total fat consumption to less than 30% of their total calorie intake each day.

Fats and oils that are in contact with moist air at room temperature eventually undergo oxidation and hydrolysis reactions that cause them to turn rancid, acquiring a characteristic disagreeable odor. One cause of the odor is the release of volatile fatty acids by hydrolysis of the ester bonds. Butter, for example, releases foul-smelling butyric, caprylic, and capric acids. Microorganisms present in the air furnish lipases that catalyze this process. Hydrolytic rancidity can easily be prevented by covering the fat or oil and keeping it in a refrigerator.

Another cause of volatile, odorous compounds is the oxidation of the unsaturated fatty acid components, particularly the readily oxidized structural unit

$$\sim CH{=}CH{-}CH_2{-}CH{=}CH\sim$$

in polyunsaturated fatty acids, such as linoleic and linolenic acids. One particularly offensive product, formed by the oxidative cleavage of both double bonds in this unit, is a compound called *malonaldehyde*.



Malonaldehyde

Rancidity is a major concern of the food industry, which is why food chemists are always seeking new and better antioxidants, substances added in very small amounts (0.001%–0.01%) to prevent oxidation and thus suppress rancidity. Antioxidants are compounds whose affinity for oxygen is greater than that of the lipids in the food; thus they function by preferentially depleting the supply of oxygen absorbed into the product. Because vitamin E has antioxidant properties, it helps reduce damage to lipids in the body, particularly to unsaturated fatty acids found in cell membrane lipids.

Summary

Fats and oils are composed of molecules known as triglycerides, which are esters composed of three fatty acid units linked to glycerol. An increase in the percentage of shorter-chain fatty acids and/or unsaturated fatty acids lowers the melting point of a fat or oil. The hydrolysis of fats and oils in the presence of a base makes soap and is known as saponification. Double bonds present in unsaturated triglycerides can be hydrogenated to convert oils (liquid) into margarine (solid). The oxidation of fatty acids can form compounds with disagreeable odors. This oxidation can be minimized by the addition of antioxidants.

17.3: Membranes and Membrane Lipids

Learning Objectives

- Identify the distinguishing characteristics of membrane lipids.
- Describe membrane components and how they are arranged.

All living cells are surrounded by a cell membrane. Plant cells (Figure $17.3.1A$) and animal cells (Figure $17.3.1B$) contain a cell nucleus that is also surrounded by a membrane and holds the genetic information for the cell. Everything between the cell membrane and the nuclear membrane—including intracellular fluids and various subcellular components such as the mitochondria and ribosomes—is called the cytoplasm. The membranes of all cells have a fundamentally similar structure, but membrane function varies tremendously from one organism to another and even from one cell to another within a single organism. This diversity arises mainly from the presence of different proteins and lipids in the membrane.

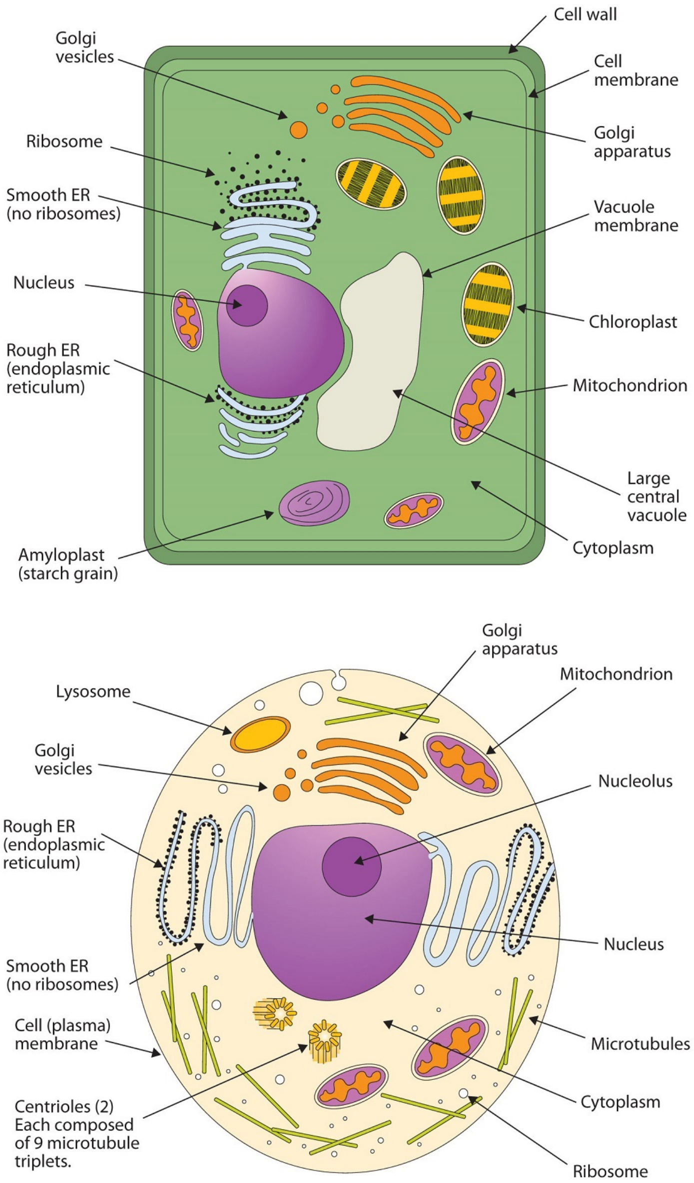


Figure 17.3.1: (A) An Idealized Plant Cell. Not all the structures shown here occur in every type of plant cell. (B) An Idealized Animal Cell. The structures shown here will seldom all be found in a single animal cell.

The lipids in cell membranes are highly polar but have dual characteristics: part of the lipid is ionic and therefore dissolves in water, whereas the rest has a hydrocarbon structure and therefore dissolves in nonpolar substances. Often, the ionic part is referred to as hydrophilic, meaning "water loving," and the nonpolar part as hydrophobic, meaning "water fearing" (repelled by water). When allowed to float freely in water, polar lipids spontaneously cluster together in any one of three arrangements: micelles, monolayers, and bilayers (Figure 17.3.2).

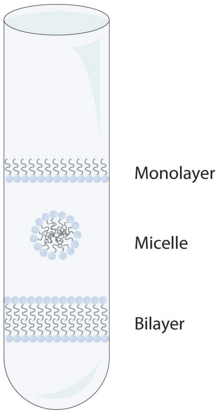


Figure 17.3.2: Spontaneously Formed Polar Lipid Structures in Water: Monolayer, Micelle, and Bilayer

Micelles are aggregations in which the lipids' hydrocarbon tails—being hydrophobic—are directed toward the center of the assemblage and away from the surrounding water while the hydrophilic heads are directed outward, in contact with the water. Each micelle may contain thousands of lipid molecules. Polar lipids may also form a monolayer, a layer one molecule thick on the surface of the water. The polar heads face into water, and the nonpolar tails stick up into the air. Bilayers are double layers of lipids arranged so that the hydrophobic tails are sandwiched between an inner surface and an outer surface consisting of hydrophilic heads. The hydrophilic heads are in contact with water on either side of the bilayer, whereas the tails, sequestered inside the bilayer, are prevented from having contact with the water. Bilayers like this make up every cell membrane (Figure 17.3.3).

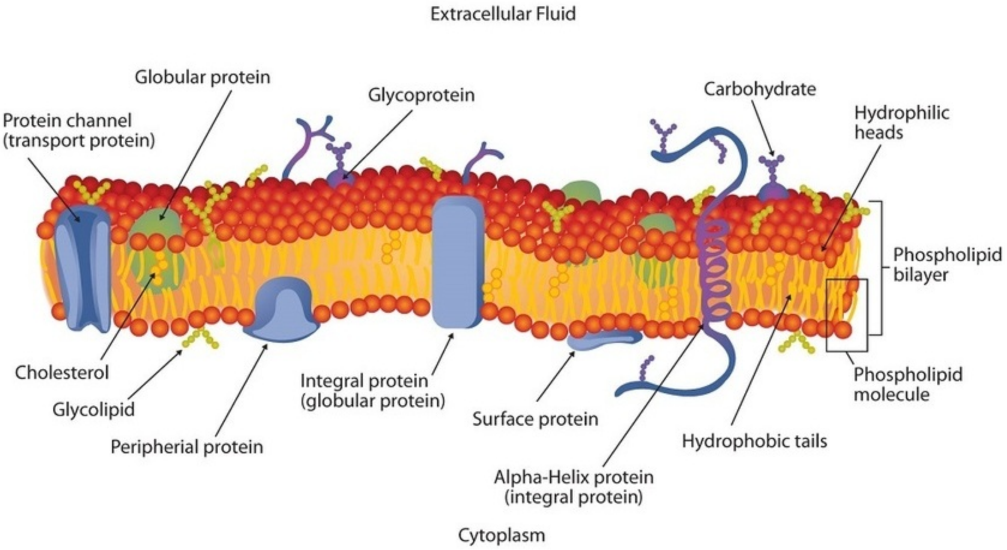


Figure 17.3.3: Schematic Diagram of a Cell Membrane. The membrane enclosing a typical animal cell is a phospholipid bilayer with embedded cholesterol and protein molecules. Short oligosaccharide chains are attached to the outer surface.

In the bilayer interior, the hydrophobic tails (that is, the fatty acid portions of lipid molecules) interact by means of dispersion forces. The interactions are weakened by the presence of unsaturated fatty acids. As a result, the membrane components are free to mill about to some extent, and the membrane is described as fluid.

The lipids found in cell membranes can be categorized in various ways. Phospholipids are lipids containing phosphorus. Glycolipids are sugar-containing lipids. The latter are found exclusively on the outer surface of the cell membrane, acting as distinguishing surface markers for the cell and thus serving in cellular recognition and cell-to-cell communication. Sphingolipids are phospholipids or glycolipids that contain the unsaturated amino alcohol sphingosine rather than glycerol. Diagrammatic structures of representative membrane lipids are presented in Figure 17.3.4.

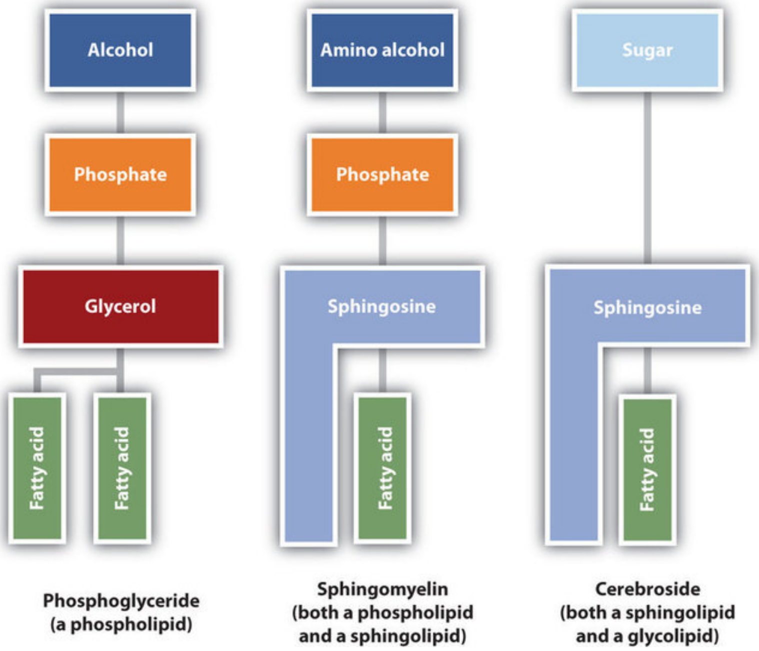


Figure 17.3.4: Component Structures of Some Important Membrane Lipids

Phosphoglyceride are composed of alcohol, phosphate, glycerol and 2 fatty acids. A sphingomyelin contains phosphate, sphingosine, and a fatty acid. A cerbroside contains sugar, sphingosine and a fatty acid.

Phosphoglycerides (also known as glycerophospholipids) are the most abundant phospholipids in cell membranes. They consist of a glycerol unit with fatty acids attached to the first two carbon atoms, while a phosphoric acid unit, esterified with an alcohol molecule (usually an amino alcohol, as in part (a) of Figure 17.3.5) is attached to the third carbon atom of glycerol (part (b) of Figure 17.3.5). Notice that the phosphoglyceride molecule is identical to a triglyceride up to the phosphoric acid unit (part (b) of Figure 17.3.5).

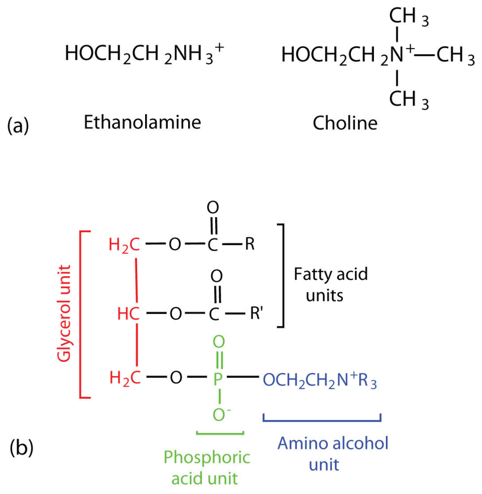
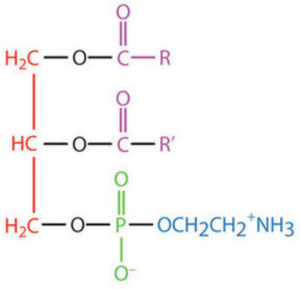


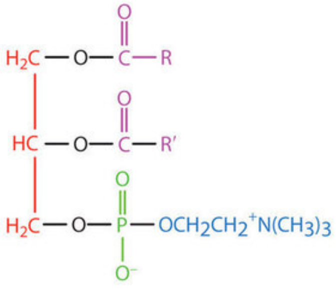
Figure 17.3.5: Phosphoglycerides. (a) Amino alcohols are commonly found in phosphoglycerides, which are evident in its structural formula (b).

Structural formula of ethanolamine and choline are shown. The structural formula of a phosphoglyceride is shown with the glycerol unit, phosphoric unit, and amino alcohol unit highlighted in different colors.

There are two common types of phosphoglycerides. Phosphoglycerides containing ethanolamine as the amino alcohol are called *phosphatidylethanolamines* or *cephalins*. Cephalins are found in brain tissue and nerves and also have a role in blood clotting. Phosphoglycerides containing choline as the amino alcohol unit are called *phosphatidylcholines* or *lecithins*. Lecithins occur in all living organisms. Like cephalins, they are important constituents of nerve and brain tissue. Egg yolks are especially rich in lecithins. Commercial-grade lecithins isolated from soybeans are widely used in foods as emulsifying agents. An emulsifying agent is used to stabilize an emulsion—a dispersion of two liquids that do not normally mix, such as oil and water. Many foods are emulsions. Milk is an emulsion of butterfat in water. The emulsifying agent in milk is a protein called *casein*. Mayonnaise is an emulsion of salad oil in water, stabilized by lecithins present in egg yolk.



Phosphatidylethanolamine
(cephalin)



Phosphatidycholine
(lecithin)

Sphingomyelins, the simplest sphingolipids, each contain a fatty acid, a phosphoric acid, sphingosine, and choline (Figure 17.3.6). Because they contain phosphoric acid, they are also classified as phospholipids. Sphingomyelins are important constituents of the myelin sheath surrounding the axon of a nerve cell. Multiple sclerosis is one of several diseases resulting from damage to the myelin sheath.

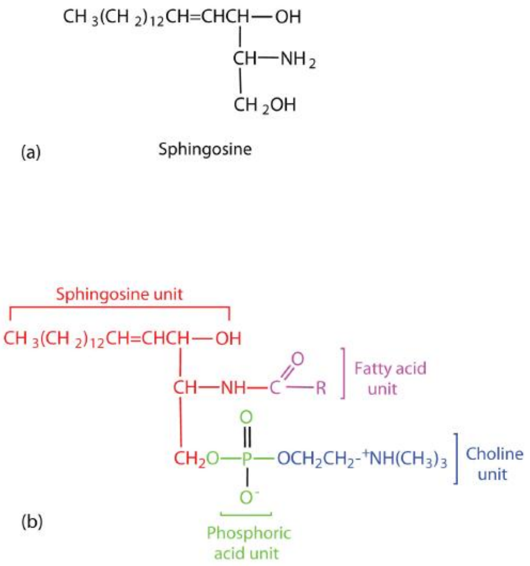


Figure 17.3.6: Sphingolipids. (a) Sphingosine, an amino alcohol, is found in all sphingolipids. (b) A sphingomyelin is also known as a phospholipid, as evidenced by the phosphoric acid unit in its structure.

Structural formula of sphingosine is shown. The general structure of a sphingolipid is shown with the sphingosine unit, fatty acid unit, phosphoric acid unit, and choline unit highlighted in different colors.

Most animal cells contain sphingolipids called cerebrosides (Figure 17.3.7). Cerebrosides are composed of sphingosine, a fatty acid, and galactose or glucose. They therefore resemble sphingomyelins but have a sugar unit in place of the choline phosphate group. Cerebrosides are important constituents of the membranes of nerve and brain cells.

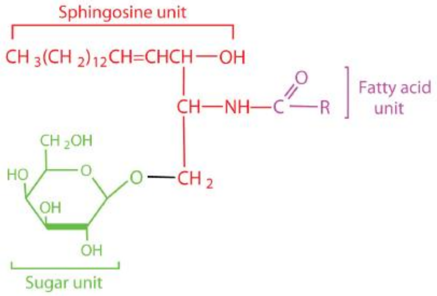


Figure 17.3.7: Cerebrosides. Cerebrosides are sphingolipids that contain a sugar unit.
General structure of a cerebroside with its sugar unit, sphingosine unit, and fatty acid unit highlighted in different colors.

The sphingolipids called gangliosides are more complex, usually containing a branched chain of three to eight monosaccharides and/or substituted sugars. Because of considerable variation in their sugar components, about 130 varieties of gangliosides have been identified. Most cell-to-cell recognition and communication processes (e.g., blood group antigens) depend on differences in the sequences of sugars in these compounds. Gangliosides are most prevalent in the outer membranes of nerve cells, although they also occur in smaller quantities in the outer membranes of most other cells. Because cerebrosides and gangliosides contain sugar groups, they are also classified as glycolipids.

Membrane Proteins

If membranes were composed only of lipids, very few ions or polar molecules could pass through their hydrophobic “sandwich filling” to enter or leave any cell. However, certain charged and polar species do cross the membrane, aided by proteins that move about in the lipid bilayer. The two major classes of proteins in the cell membrane are integral proteins, which span the hydrophobic interior of the bilayer, and peripheral proteins, which are more loosely associated with the surface of the lipid bilayer (Figure 17.3.3). Peripheral proteins may be attached to integral proteins, to the polar head groups of phospholipids, or to both by hydrogen bonding and electrostatic forces.

Small ions and molecules soluble in water enter and leave the cell by way of channels through the integral proteins. Some proteins, called *carrier proteins*, facilitate the passage of certain molecules, such as hormones and neurotransmitters, by specific interactions between the protein and the molecule being transported.

Summary

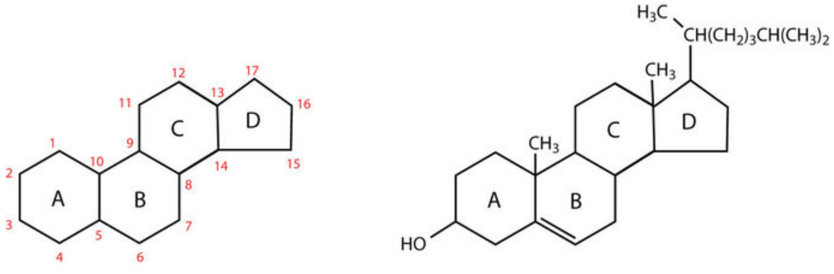
Lipids are important components of biological membranes. These lipids have dual characteristics: part of the molecule is hydrophilic, and part of the molecule is hydrophobic. Membrane lipids may be classified as phospholipids, glycolipids, and/or sphingolipids. Proteins are another important component of biological membranes. Integral proteins span the lipid bilayer, while peripheral proteins are more loosely associated with the surface of the membrane.

17.4: Steroids

Learning Objectives

- To identify the functions of steroids produced in mammals.

All the lipids discussed so far are *saponifiable*, reacting with aqueous alkali to yield simpler components, such as glycerol, fatty acids, amino alcohols, and sugars. Lipid samples extracted from cellular material, however, also contain a small but important fraction that does not react with alkali. The most important nonsaponifiable lipids are the steroids. These compounds include the *bile salts*, *cholesterol* and related compounds, and certain *hormones* (such as cortisone and the sex hormones).



(a) Steroid skeleton

(b) Cholesterol

Figure 17.4.1 Steroids. (a) The four-fused-ring steroid skeleton uses letter designations for each ring and the numbering of the carbon atoms. (b) The cholesterol molecule follows this pattern.

Steroids occur in plants, animals, yeasts, and molds but not in bacteria. They may exist in free form or combined with fatty acids or carbohydrates. All steroids have a characteristic structural component consisting of four fused rings. Chemists identify the rings by capital letters and number the carbon atoms as shown in Figure $17.4.1a$. Slight variations in this structure or in the atoms or groups attached to it produce profound differences in biological activity.

Cholesterol

Cholesterol (Figure $17.4.1b$) does not occur in plants, but it is the most abundant steroid in the human body (240 g is a typical amount). Excess cholesterol is believed to be a primary factor in the development of atherosclerosis and heart disease, which are major health problems in the United States today. About half of the body's cholesterol is interspersed in the lipid bilayer of cell membranes. Much of the rest is converted to cholic acid, which is used in the formation of bile salts. Cholesterol is also a precursor in the synthesis of sex hormones, adrenal hormones, and vitamin D.

Excess cholesterol not metabolized by the body is released from the liver and transported by the blood to the gallbladder. Normally, it stays in solution there until being secreted into the intestine (as a component of bile) to be eliminated. Sometimes, however, cholesterol in the gallbladder precipitates in the form of gallstones (Figure $17.4.2$). Indeed, the name *cholesterol* is derived from the Greek *chole*, meaning "bile," and *stereos*, meaning "solid."

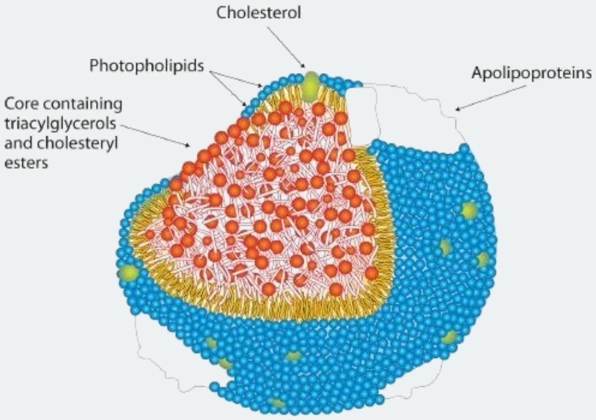
Figure 17.4.2: Numerous small gallstones made up largely of cholesterol, all removed in one patient. Grid scale 1 mm

To Your Health: Cholesterol and Heart Disease

Heart disease is the leading cause of death in the United States for both men and women. The Centers for Disease Control and Prevention reported that heart disease claimed 631,636 lives in the United States (26% of all reported deaths) in 2006.

Scientists agree that elevated cholesterol levels in the blood, as well as high blood pressure, obesity, diabetes, and cigarette smoking, are associated with an increased risk of heart disease. A long-term investigation by the National Institutes of Health showed that among men ages 30 to 49, the incidence of heart disease was five times greater for those whose cholesterol levels were above 260 mg/100 mL of serum than for those with cholesterol levels of 200 mg/100 mL or less. The cholesterol content of blood varies considerably with age, diet, and sex. Young adults average about 170 mg of cholesterol per 100 mL of blood, whereas males at age 55 may have cholesterol levels at 250 mg/100 mL or higher because the rate of cholesterol breakdown decreases with age. Females tend to have lower blood cholesterol levels than males.

To understand the link between heart disease and cholesterol levels, it is important to understand how cholesterol and other lipids are transported in the body. Lipids, such as cholesterol, are not soluble in water and therefore cannot be transported in the blood (an aqueous medium) unless they are complexed with proteins that are soluble in water, forming assemblages called *lipoproteins*. Lipoproteins are classified according to their density, which is dependent on the relative amounts of protein and lipid they contain. Lipids are less dense than proteins, so lipoproteins containing a greater proportion of lipid are less dense than those containing a greater proportion of protein.



Research on cholesterol and its role in heart disease has focused on serum levels of low-density lipoproteins (LDLs) and high-density lipoproteins (HDLs). One of the most fascinating discoveries is that high levels of HDLs reduce a person's risk of developing heart disease, whereas high levels of LDLs increase that risk. Thus the serum LDL:HDL ratio is a better predictor of heart disease risk than the overall level of serum cholesterol. Persons who, because of hereditary or dietary factors, have high LDL:HDL ratios in their blood have a higher incidence of heart disease.

How do HDLs reduce the risk of developing heart disease? No one knows for sure, but one role of HDLs appears to be the transport of excess cholesterol to the liver, where it can be metabolized. Therefore, HDLs aid in removing cholesterol from blood and from the smooth muscle cells of the arterial wall.

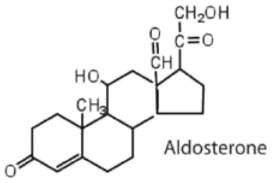
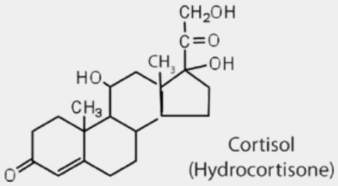
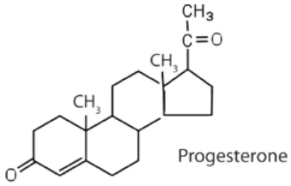
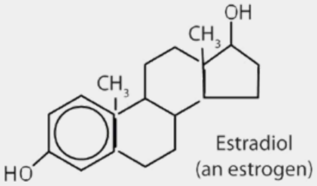
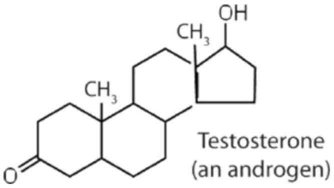
Dietary modifications and increased physical activity can help lower total cholesterol and improve the LDL:HDL ratio. The average American consumes about 600 mg of cholesterol from animal products each day and also synthesizes approximately 1 g of cholesterol each day, mostly in the liver. The amount of cholesterol synthesized is controlled by the cholesterol level in the blood; when the blood cholesterol level exceeds 150 mg/100 mL, the rate of cholesterol biosynthesis is halved. Hence, if cholesterol is present in the diet, a feedback mechanism suppresses its synthesis in the liver. However, the ratio of suppression is not a 1:1 ratio; the reduction in biosynthesis does not equal the amount of cholesterol ingested. Thus, dietary substitutions of unsaturated fat for saturated fat, as well as a reduction in consumption of *trans* fatty acids, is recommended to help lower serum cholesterol and the risk of heart disease.

Steroid Hormones

Hormones are chemical messengers that are released in one tissue and transported through the circulatory system to one or more other tissues. One group of hormones is known as steroid hormones because these hormones are synthesized from cholesterol, which is also a steroid. There are two main groups of steroid hormones: adrenocortical hormones and sex hormones.

The adrenocortical hormones, such as aldosterone and cortisol (Table $17.4.1$), are produced by the adrenal gland, which is located adjacent to each kidney. Aldosterone acts on most cells in the body, but it is particularly effective at enhancing the rate of reabsorption of sodium ions in the kidney tubules and increasing the secretion of potassium ions and/or hydrogen ions by the tubules. Because the concentration of sodium ions is the major factor influencing water retention in tissues, aldosterone promotes water retention and reduces urine output. Cortisol regulates several key metabolic reactions (for example, increasing glucose production and mobilizing fatty acids and amino acids). It also inhibits the inflammatory response of tissue to injury or stress. Cortisol and its analogs are therefore used pharmacologically as immunosuppressants after transplant operations and in the treatment of severe skin allergies and autoimmune diseases, such as rheumatoid arthritis.

Table 17.4.1: Representative Steroid Hormones and Their Physiological Effects

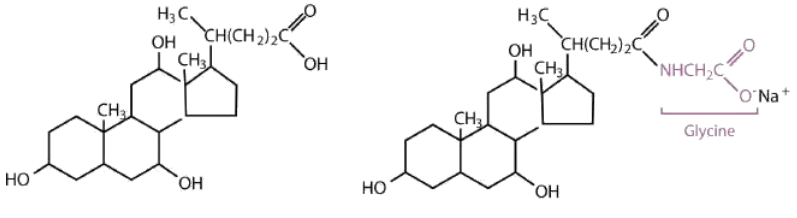
Hormone	Effect
	regulates salt metabolism; stimulates kidneys to retain sodium and excrete potassium
	stimulates the conversion of proteins to carbohydrates
	regulates the menstrual cycle; maintains pregnancy
	stimulates female sex characteristics; regulates changes during the menstrual cycle
	stimulates and maintains male sex characteristics

The sex hormones are a class of steroid hormones secreted by the gonads (ovaries or testes), the placenta, and the adrenal glands. Testosterone and androstenedione are the primary male sex hormones, or *androgens*, controlling the primary sexual characteristics of males, or the development of the male genital organs and the continuous production of sperm. Androgens are also responsible for the development of secondary male characteristics, such as facial hair, deep voice, and muscle strength. Two kinds of sex hormones are of particular importance in females: progesterone, which prepares the uterus for pregnancy and prevents the further release of eggs from the ovaries during pregnancy, and the estrogens, which are mainly responsible for the development of female secondary sexual characteristics, such as breast development and increased deposition of fat tissue in the breasts, the buttocks, and the thighs. Both males and females produce androgens and estrogens, differing in the amounts of secreted hormones rather than in the presence or absence of one or the other.

Sex hormones, both natural and synthetic, are sometimes used therapeutically. For example, a woman who has had her ovaries removed may be given female hormones to compensate. Some of the earliest chemical compounds employed in cancer chemotherapy were sex hormones. For example, estrogens are one treatment option for prostate cancer because they block the release and activity of testosterone. Testosterone enhances prostate cancer growth. Sex hormones are also administered in preparation for sex-change operations, to promote the development of the proper secondary sexual characteristics. Oral contraceptives are synthetic derivatives of the female sex hormones; they work by preventing ovulation.

Bile Salts

Bile is a yellowish green liquid (pH 7.8–8.6) produced in the liver. The most important constituents of bile are bile salts, which are sodium salts of amidelike combinations of bile acids, such as cholic acid (part (a) of Figure 17.4.3) and an amine such as the amino acid glycine (part (b) of Figure 17.4.3). They are synthesized from cholesterol in the liver, stored in the gallbladder, and then secreted in bile into the small intestine. In the gallbladder, the composition of bile gradually changes as water is absorbed and the other components become more concentrated.



(a) Cholic acid (a bile acid)

(b) Sodium glycocholate (a bile salt)

Figure 17.4.3 Bile Acids. (a) Cholic acid is an example of a bile acid. (b) Sodium glycocholate is a bile salt synthesized from cholic acid and glycine.

Because they contain both hydrophobic and hydrophilic groups, bile salts are highly effective detergents and emulsifying agents; they break down large fat globules into smaller ones and keep those smaller globules suspended in the aqueous digestive environment. Enzymes can then hydrolyze fat molecules more efficiently. Thus, the major function of bile salts is to aid in the digestion of dietary lipids.

> Surgical removal is often advised for a gallbladder that becomes infected, inflamed, or perforated. This surgery does not seriously affect digestion because bile is still produced by the liver, but the liver’s bile is more dilute and its secretion into the small intestine is not as closely tied to the arrival of food.

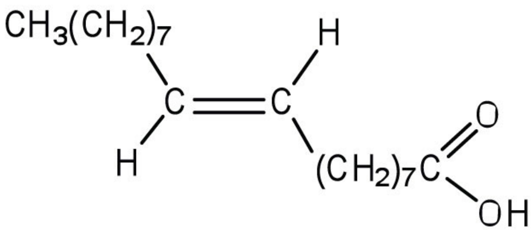
Summary

Steroids have a four-fused-ring structure and have a variety of functions. Cholesterol is a steroid found in mammals that is needed for the formation of cell membranes, bile acids, and several hormones. Bile salts are secreted into the small intestine to aid in the digestion of fats.

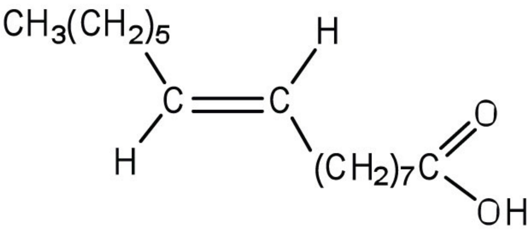
17.E: Exercises

Additional Exercises

1. The melting point of elaidic acid is 52°C.
   a. What trend is observed when comparing the melting points of elaidic acid, oleic acid, and stearic acid? Explain.
   b. Would you expect the melting point of palmitelaidic acid to be lower or higher than that of elaidic acid? Explain.

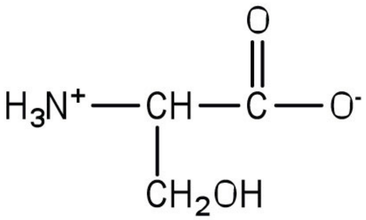


Elaidic acid



Palmitelaidic acid

2. Examine the labels on two brands of margarine and two brands of shortening and list the oils used in the various brands.
3. Draw a typical lecithin molecule that incorporates glycerol, palmitic acid, oleic acid, phosphoric acid, and choline. Circle all the ester bonds.
4. In cerebrosides, is the linkage between the fatty acid and sphingosine an amide bond or an ester bond? Justify your answer.
5. Serine is an amino acid that has the following structure. Draw the structure for a phosphatidylserine that contains a palmitic acid and a palmitoleic acid unit.

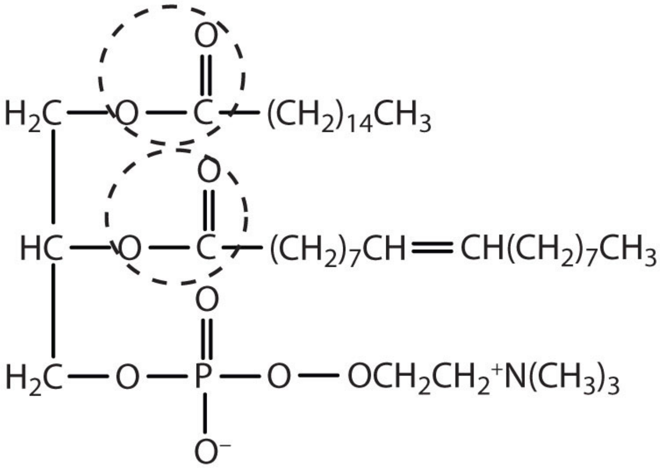


6. Explain whether each compound would be expected to diffuse through the lipid bilayer of a cell membrane.
   a. potassium chloride
   b. $CH_3CH_2CH_2CH_2CH_2CH_3$
   c. fructose
7. Identify the role of each steroid hormone in the body.
   a. progesterone
   b. aldosterone
   c. testosterone
   d. cortisol
8. How does the structure of cholic acid differ from that of cholesterol? Which compound would you expect to be more polar? Why?
9. a. What fatty acid is the precursor for the prostaglandins?
   b. Identify three biological effects of prostaglandins.
10. Why is it important to determine the ratio of LDLs to HDLs, rather than just the concentration of serum cholesterol?

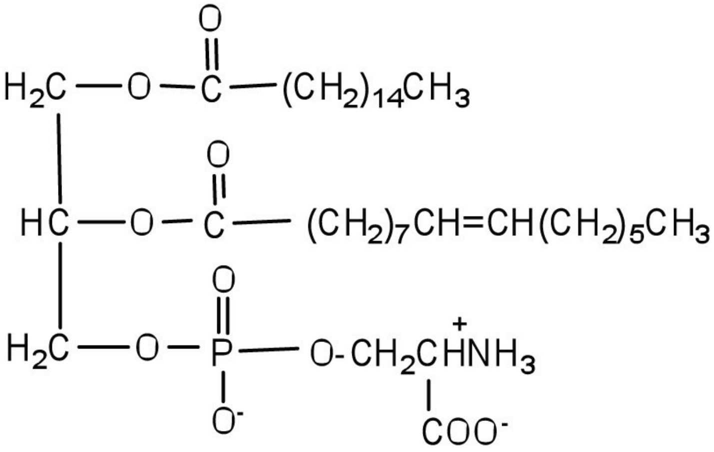
Answers

1. a. Stearic acid has the highest melting point, followed by elaidic acid, and then oleic acid with the lowest melting point. Elaidic acid is a *trans* fatty acid, and the carbon chains can pack together almost as tightly as those of the saturated stearic acid. Oleic acid is a *cis* fatty acid, and the bend in the hydrocarbon chain keeps these carbon chains from packing as closely together; fewer interactions lead to a much lower melting point.
    b. The melting point of palmitelaidic acid should be lower than that of elaidic acid because it has a shorter carbon chain (16, as compared to 18 for elaidic acid). The shorter the carbon chain, the lower the melting point due to a decrease in intermolecular interactions.

3.



5.



7. a. regulates the menstrual cycle and maintains pregnancy
    b. regulates salt metabolism by stimulating the kidneys to retain sodium and excrete potassium
    c. stimulates and maintains male sex characteristics
    d. stimulates the conversion of proteins to carbohydrates

9. a. arachidonic acid
    b. induce smooth muscle contraction, lower blood pressure, and contribute to the inflammatory response

17.S: Lipids (Summary)

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

Lipids, found in the body tissues of all organisms, are compounds that are more soluble in organic solvents than in water. Many of them contain **fatty acids**, which are carboxylic acids that generally contain an even number of 4–20 carbon atoms in an unbranched chain. **Saturated fatty acids** have no carbon-to-carbon double bonds. **Monounsaturated fatty acids** have a single carbon-to-carbon double bond, while **polyunsaturated fatty acids** have more than one carbon-to-carbon double bond. Linoleic and linolenic acid are known as **essential fatty acids** because the human body cannot synthesize these polyunsaturated fatty acids. The lipids known as **fats** and **oils** are triacylglycerols, more commonly called **triglycerides**—esters composed of three fatty acids joined to the trihydroxy alcohol glycerol. Fats are triglycerides that are solid at room temperature, and oils are triglycerides that are liquid at room temperature. Fats are found mainly in animals, and oils found mainly in plants. *Saturated triglycerides* are those containing a higher proportion of saturated fatty acid chains (fewer carbon-to-carbon double bonds); *unsaturated triglycerides* contain a higher proportion of unsaturated fatty acid chains.

Saponification is the hydrolysis of a triglyceride in a basic solution to form glycerol and three carboxylate anions or soap molecules. Other important reactions are the hydrogenation and oxidation of double bonds in unsaturated fats and oils.

Phospholipids are lipids containing phosphorus. In **phosphoglycerides**, the phosphorus is joined to an amino alcohol unit. Some phosphoglycerides, like lecithins, are used to stabilize an **emulsion**—a dispersion of two liquids that do not normally mix, such as oil and water. **Sphingolipids** are lipids for which the precursor is the amino alcohol sphingosine, rather than glycerol. A **glycolipid** has a sugar substituted at one of the OH groups of either glycerol or sphingosine. All are highly polar lipids found in cell membranes.

Polar lipids have dual characteristics: one part of the molecule is ionic and dissolves in water; the rest has a hydrocarbon structure and dissolves in nonpolar substances. Often, the ionic part is referred to as **hydrophilic** (literally, “water loving”) and the nonpolar part as **hydrophobic** (“water fearing”). When placed in water, polar lipids disperse into any one of three arrangements: *micelles*, *monolayers*, and *bilayers*. **Micelles** are aggregations of molecules in which the hydrocarbon tails of the lipids, being hydrophobic, are directed inward (away from the surrounding water), and the hydrophilic heads that are directed outward into the water. **Bilayers** are double layers arranged so that the hydrophobic tails are sandwiched between the two layers of hydrophilic heads, which remain in contact with the water.

Every living cell is enclosed by a *cell membrane* composed of a lipid bilayer. In animal cells, the bilayer consists mainly of phospholipids, glycolipids, and the steroid cholesterol. Embedded in the bilayer are **integral proteins**, and **peripheral proteins** are loosely associated with the surface of the bilayer. Everything between the cell membrane and the membrane of the cell nucleus is called the **cytoplasm**.

Most lipids can be saponified, but some, such as **steroids**, cannot be saponified. The steroid **cholesterol** is found in animal cells but never in plant cells. It is a main component of all cell membranes and a precursor for hormones, vitamin D, and bile salts. Bile salts are the most important constituents of **bile**, which is a yellowish-green liquid secreted by the gallbladder into the small intestine and is needed for the proper digestion of lipids.

CHAPTER OVERVIEW

18: Amino Acids, Proteins, and Enzymes

Proteins may be defined as compounds of high molar mass consisting largely or entirely of chains of amino acids. Their masses range from several thousand to several million daltons (Da). In addition to carbon, hydrogen, and oxygen atoms, all proteins contain nitrogen and sulfur atoms, and many also contain phosphorus atoms and traces of other elements. Proteins serve a variety of roles in living organisms and are often classified by these biological roles. Muscle tissue is largely protein, as are skin and hair. Proteins are present in the blood, in the brain, and even in tooth enamel. Each type of cell in our bodies makes its own specialized proteins, as well as proteins common to all or most cells. We begin our study of proteins by looking at the properties and reactions of amino acids, which is followed by a discussion of how amino acids link covalently to form peptides and proteins. We end the chapter with a discussion of enzymes—the proteins that act as catalysts in the body.

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18.0: Prelude to Amino Acids, Proteins, and Enzymes

The 1923 Nobel Prize in Medicine or Physiology was awarded to Frederick Grant Banting and John James Richard Macleod for their discovery of the protein *insulin*. In 1958, the Nobel Prize in Chemistry was awarded to Frederick Sanger for his discoveries concerning the structure of proteins and, in particular, the structure of insulin. What is so important about insulin that two Nobel Prizes have been awarded for work on this protein?

Insulin is a hormone that is synthesized in the pancreas. Insulin stimulates the transport of glucose into cells throughout the body and the storage of glucose as glycogen. People with diabetes do not produce insulin or use it properly. The isolation of insulin in 1921 led to the first effective treatment for these individuals.

Figure 18.0.1: Insulin pump, showing an infusion set loaded into spring-loaded insertion device. A reservoir is attached to the infusion set (shown here removed from the pump). (Public Domain; User:David-i98).

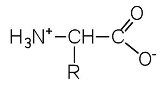
18.1: Properties of Amino Acids

Learning Objectives

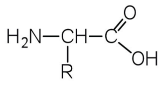
- To recognize amino acids and classify them based on the characteristics of their side chains.

The proteins in all living species, from bacteria to humans, are constructed from the same set of 20 amino acids, so called because each contains an amino group attached to a carboxylic acid. The amino acids in proteins are α-amino acids, which means the amino group is attached to the α-carbon of the carboxylic acid. Humans can synthesize only about half of the needed amino acids; the remainder must be obtained from the diet and are known as essential amino acids. However, two additional amino acids have been found in limited quantities in proteins: Selenocysteine was discovered in 1986, while pyrrolysine was discovered in 2002.

The amino acids are colorless, nonvolatile, crystalline solids, melting and decomposing at temperatures above 200°C. These melting temperatures are more like those of inorganic salts than those of amines or organic acids and indicate that the structures of the amino acids in the solid state and in neutral solution are best represented as having both a negatively charged group and a positively charged group. Such a species is known as a zwitterion.



α-Amino acid drawn as a zwitterion

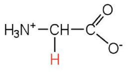
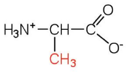
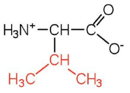
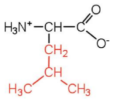


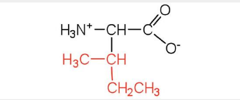
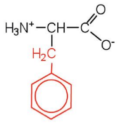
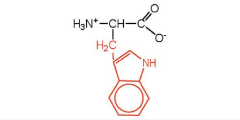
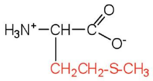
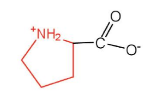
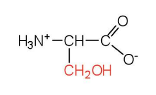
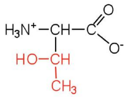
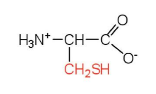
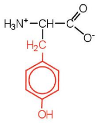
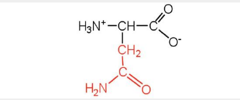
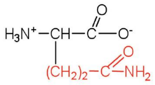
α-Amino acid drawn as an uncharged molecule; not an accurate respresentation of amino acid structure

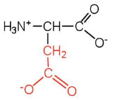
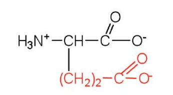
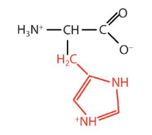
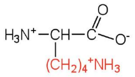
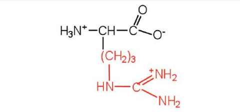
Classification

In addition to the amino and carboxyl groups, amino acids have a side chain or R group attached to the α-carbon. Each amino acid has unique characteristics arising from the size, shape, solubility, and ionization properties of its R group. As a result, the side chains of amino acids exert a profound effect on the structure and biological activity of proteins. Although amino acids can be classified in various ways, one common approach is to classify them according to whether the functional group on the side chain at neutral pH is nonpolar, polar but uncharged, negatively charged, or positively charged. The structures and names of the 20 amino acids, their one- and three-letter abbreviations, and some of their distinctive features are given in Table 18.1.1.

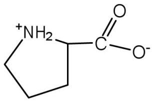
Table 18.1.1: Common Amino Acids Found in Proteins

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

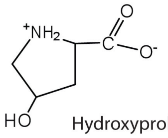
Common Name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
isoleucine	ile (I)		131	an essential amino acid because most animals cannot synthesize branched-chain amino acids
phenylalanine	phe (F)		165	also classified as an aromatic amino acid
tryptophan	trp (W)		204	also classified 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*
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				

Common Name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
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.



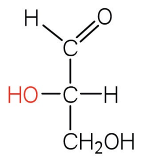
Proline



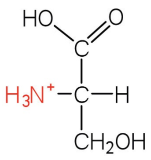
Hydroxyproline

Configuration

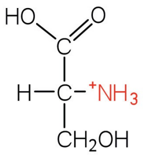
Notice in Table 18.1.1 that glycine is the only amino acid whose α-carbon is *not* chiral. Therefore, with the exception of glycine, the amino acids could theoretically exist in either the D- or the L-enantiomeric form and rotate plane-polarized light. As with sugars, chemists used L-glyceraldehyde as the reference compound for the assignment of absolute configuration to amino acids. Its structure closely resembles an amino acid structure except that in the latter, an amino group takes the place of the OH group on the chiral carbon of the L-glyceraldehyde and a carboxylic acid replaces the aldehyde. Modern stereochemistry assignments using the Cahn-Ingold-Prelog priority rules used ubiquitously in chemistry show that all of the naturally occurring chiral amino acids are S except Cys which is R.



L–(–)–Glyceraldehyde



L–Amino acid



D–Amino acid

We learned that all naturally occurring sugars belong to the D series. It is interesting, therefore, that nearly all known plant and animal proteins are composed entirely of L-amino acids. However, certain bacteria contain D-amino acids in their cell walls, and several antibiotics (e.g., actinomycin D and the gramicidins) contain varying amounts of D-leucine, D-phenylalanine, and D-valine.

Summary

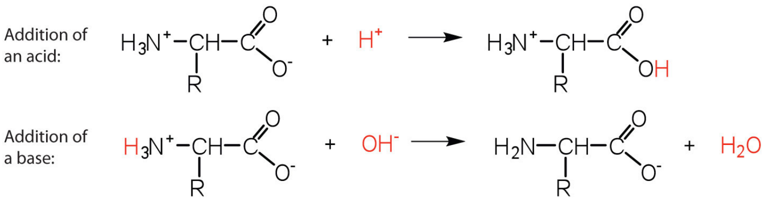
Amino acids can be classified based on the characteristics of their distinctive side chains as nonpolar, polar but uncharged, negatively charged, or positively charged. The amino acids found in proteins are L-amino acids.

18.2: Reactions of Amino Acids

Learning Objectives

- To explain how an amino acid can act as both an acid and a base.

The structure of an amino acid allows it to act as both an acid and a base. An amino acid has this ability because at a certain pH value (different for each amino acid) nearly all the amino acid molecules exist as zwitterions. If acid is added to a solution containing the zwitterion, the carboxylate group captures a hydrogen (H^+) ion, and the amino acid becomes positively charged. If base is added, ion removal of the H^+ ion from the amino group of the zwitterion produces a negatively charged amino acid. In both circumstances, the amino acid acts to maintain the pH of the system—that is, to remove the added acid (H^+) or base (OH^-) from solution.

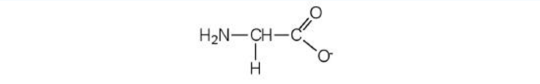


Example 18.2.1

a. Draw the structure for the anion formed when glycine (at neutral pH) reacts with a base.
b. Draw the structure for the cation formed when glycine (at neutral pH) reacts with an acid.

Solution

a. The base removes H^+ from the protonated amine group.



- The acid adds H^+ to the carboxylate group.

Exercise 18.2.1

a. Draw the structure for the cation formed when valine (at neutral pH) reacts with an acid.
b. Draw the structure for the anion formed when valine (at neutral pH) reacts with a base.

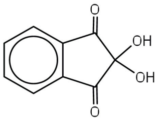
The particular pH at which a given amino acid exists in solution as a zwitterion is called the isoelectric point (pI). At its pI, the positive and negative charges on the amino acid balance, and the molecule as a whole is electrically neutral. The amino acids whose side chains are always neutral have isoelectric points ranging from 5.0 to 6.5. The basic amino acids (which have positively charged side chains at neutral pH) have relatively high examples. Acidic amino acids (which have negatively charged side chains at neutral pH) have quite low examples (Table 18.2.1).

Table 18.2.1: Examples of Some Representative Amino Acids

Amino Acid	Classification	pI
alanine	nonpolar	6.0
valine	nonpolar	6.0
serine	polar, uncharged	5.7

Amino Acid	Classification	pI
threonine	polar, uncharged	6.5
arginine	positively charged (basic)	10.8
histidine	positively charged (basic)	7.6
lysine	positively charged (basic)	9.8
aspartic acid	negatively charged (acidic)	3.0
glutamic acid	negatively charged (acidic)	3.2

Amino acids undergo reactions characteristic of carboxylic acids and amines. The reactivity of these functional groups is particularly important in linking amino acids together to form peptides and proteins, as you will see later in this chapter. Simple chemical tests that are used to detect amino acids take advantage of the reactivity of these functional groups. An example is the ninhydrin test in which the amine functional group of α-amino acids reacts with ninhydrin to form purple-colored compounds. Ninhydrin is used to detect fingerprints because it reacts with amino acids from the proteins in skin cells transferred to the surface by the individual leaving the fingerprint.



Ninhydrin

Summary

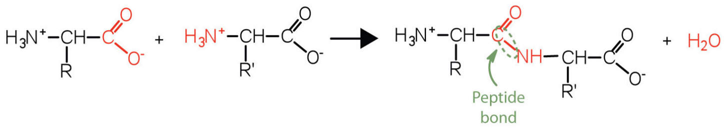
Amino acids can act as both an acid and a base due to the presence of the amino and carboxyl functional groups. The pH at which a given amino acid exists in solution as a zwitterion is called the *isoelectric point* (pI).

18.3: Peptides

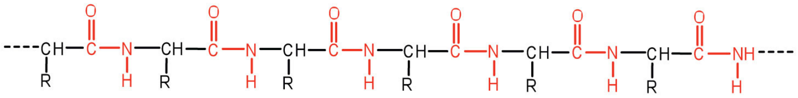
Learning Objectives

- Explain how a peptide is formed from individual amino acids.
- Explain why the sequence of amino acids in a protein is important.

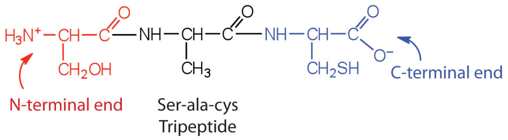
Two or more amino acids can join together into chains called peptides. Previously, we discussed the reaction between ammonia and a carboxylic acid to form an amide. In a similar reaction, the amino group on one amino acid molecule reacts with the carboxyl group on another, releasing a molecule of water and forming an amide linkage:



An amide bond joining two amino acid units is called a peptide bond. Note that the product molecule still has a reactive amino group on the left and a reactive carboxyl group on the right. These can react with additional amino acids to lengthen the peptide. The process can continue until thousands of units have joined, resulting in large proteins.



A chain consisting of only two amino acid units is called a *dipeptide*; a chain consisting of three is a *tripeptide*. By convention, peptide and protein structures are depicted with the amino acid whose amino group is free (the N-terminal end) on the left and the amino acid with a free carboxyl group (the C-terminal end) to the right.



The general term *peptide* refers to an amino acid chain of unspecified length. However, chains of about 50 amino acids or more are usually called proteins or polypeptides. In its physiologically active form, a protein may be composed of one or more polypeptide chains.

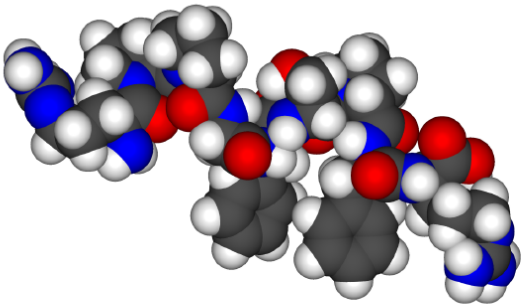


Figure 18.3.1: Space-filling model of bradykinin. (Public Domain; Fvasconcellos)

For peptides and proteins to be physiologically active, it is not enough that they incorporate certain amounts of specific amino acids. The order, or *sequence*, in which the amino acids are connected is also of critical importance. Bradykinin is a nine-amino acid peptide (Figure 18.3.1) produced in the blood that has the following amino acid sequence:

arg-pro-pro-gly-phe-ser-pro-phe-arg

This peptide lowers blood pressure, stimulates smooth muscle tissue, increases capillary permeability, and causes pain. When the order of amino acids in bradykinin is reversed,

arg-phe-pro-ser-phe-gly-pro-pro-arg

the peptide resulting from this synthesis shows none of the activity of bradykinin.

Just as millions of different words are spelled with our 26-letter English alphabet, millions of different proteins are made with the 20 common amino acids. However, just as the English alphabet can be used to write gibberish, amino acids can be put together in the *wrong sequence* to produce nonfunctional proteins. Although the correct sequence is ordinarily of utmost importance, it is not always absolutely required. Just as you can sometimes make sense of incorrectly spelled English words, a protein with a small percentage of “incorrect” amino acids may continue to function. However, it rarely functions as well as a protein having the correct sequence. There are also instances in which seemingly minor errors of sequence have disastrous effects. For example, in some people, every molecule of hemoglobin (a protein in the blood that transports oxygen) has a single incorrect amino acid unit out of about 300 (a single valine replaces a glutamic acid). That “minor” error is responsible for sickle cell anemia, an inherited condition that usually is fatal.

Summary

The amino group of one amino acid can react with the carboxyl group on another amino acid to form a peptide bond that links the two amino acids together. Additional amino acids can be added on through the formation of addition peptide (amide) bonds. A sequence of amino acids in a peptide or protein is written with the N-terminal amino acid first and the C-terminal amino acid at the end (writing left to right).

18.4: Proteins

Learning Objectives

- Describe the four levels of protein structure.
- Identify the types of attractive interactions that hold proteins in their most stable three-dimensional structure.
- Explain what happens when proteins are denatured.
- Identify how a protein can be denatured.

Each of the thousands of naturally occurring proteins has its own characteristic amino acid composition and sequence that result in a unique three-dimensional shape. Since the 1950s, scientists have determined the amino acid sequences and three-dimensional conformation of numerous proteins and thus obtained important clues on how each protein performs its specific function in the body.

Proteins are compounds of high molar mass consisting largely or entirely of chains of amino acids. Because of their great complexity, protein molecules cannot be classified on the basis of specific structural similarities, as carbohydrates and lipids are categorized. The two major structural classifications of proteins are based on far more general qualities: whether the protein is (1) fiberlike and insoluble or (2) globular and soluble. Some proteins, such as those that compose hair, skin, muscles, and connective tissue, are fiberlike. These fibrous proteins are insoluble in water and usually serve structural, connective, and protective functions. Examples of fibrous proteins are keratins, collagens, myosins, and elastins. Hair and the outer layer of skin are composed of keratin. Connective tissues contain collagen. Myosins are muscle proteins and are capable of contraction and extension. Elastins are found in ligaments and the elastic tissue of artery walls.

Globular proteins, the other major class, are soluble in aqueous media. In these proteins, the chains are folded so that the molecule as a whole is roughly spherical. Familiar examples include egg albumin from egg whites and serum albumin in blood. Serum albumin plays a major role in transporting fatty acids and maintaining a proper balance of osmotic pressures in the body. Hemoglobin and myoglobin, which are important for binding oxygen, are also globular proteins.

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 $18.4.1$.

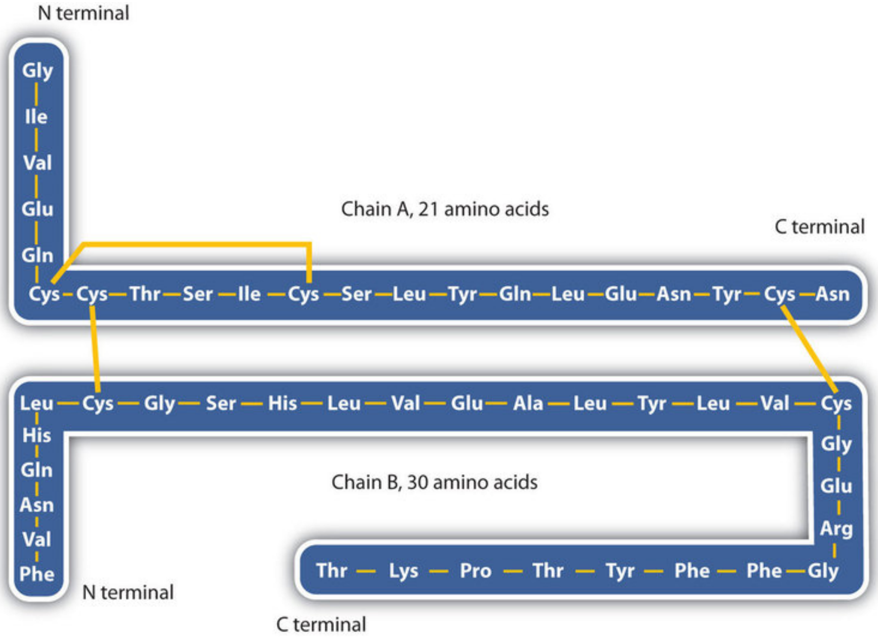


Figure 18.4.1: Primary Structure of Human Insulin. Human insulin, whose amino acid sequence is shown here, is a hormone that is required for the proper metabolism of glucose.

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 18.4.2). 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.

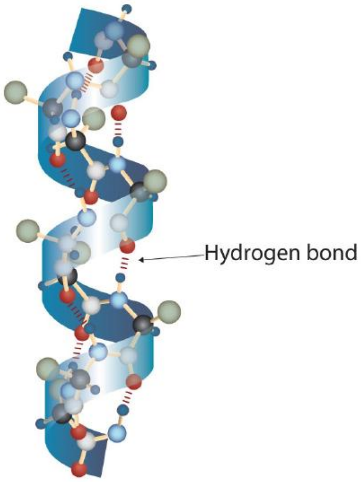


Figure 18.4.2 A Ball-and-Stick Model of an α-Helix. This ball-and-stick model shows the intrachain hydrogen bonding between carbonyl oxygen atoms and amide hydrogen atoms. Each turn of the helix spans 3.6 amino acids. Note that the side chains (represented as green spheres) point out from the helix.

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 18.4.3). 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.

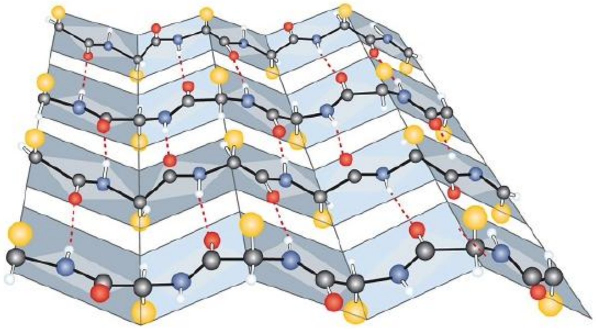


Figure 18.4.3: A Ball-and-Stick Model of the β-Pleated Sheet Structure in Proteins. The side chains extend above or below the sheet and alternate along the chain. The protein chains are held together by interchain hydrogen bonding.

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 18.4.4 shows a depiction of the three-dimensional structure of insulin.

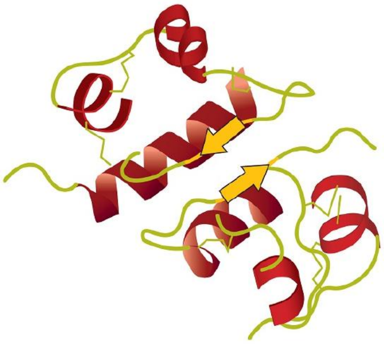
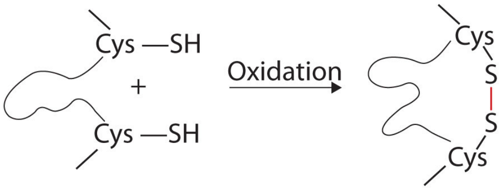


Figure 18.4.4: A Ribbon Model of the Three-Dimensional Structure of Insulin. The spiral regions represent sections of the polypeptide chain that have an α-helical structure, while the broad arrows represent β-pleated sheet structures.

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 18.4.5).
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 18.4.5).
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 18.4.5). Intrachain disulfide linkages are found in many proteins, including insulin (yellow bars in Figure 18.4.1) 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 18.4.5). 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.

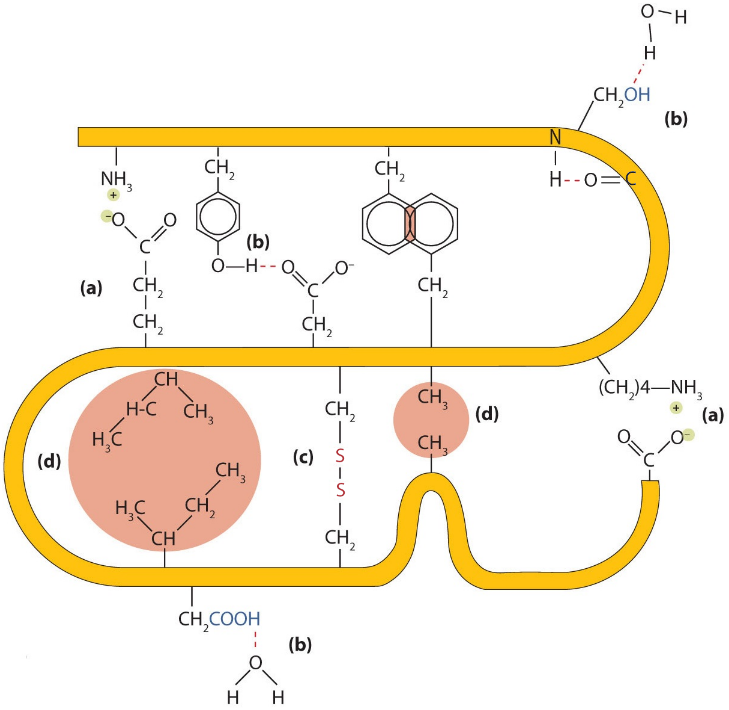


Figure 18.4.5: Tertiary Protein Structure Interactions. Four interactions stabilize the tertiary structure of a protein: (a) ionic bonding, (b) hydrogen bonding, (c) disulfide linkages, and (d) dispersion forces.

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 18.4.6). 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 18.4.7.

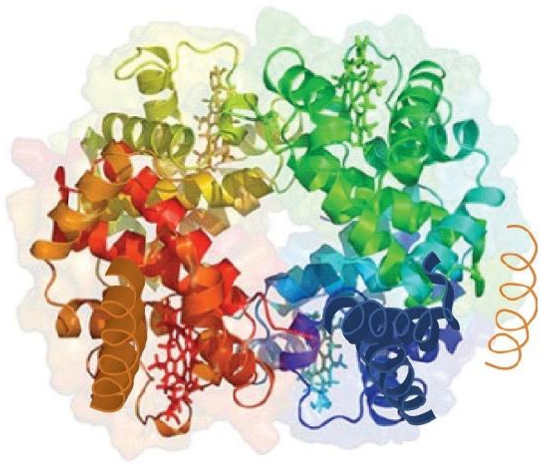


Figure 18.4.6 The Quaternary Structure of Hemoglobin. Hemoglobin is a protein that transports oxygen throughout the body.

Source: Image from the RCSB PDB (www.pdb.org(opens in new window)) of PDB ID 1I3D (R.D. Kidd, H.M. Baker, A.J. Mathews, T. Brittain, E.N. Baker (2001) Oligomerization and ligand binding in a homotetrameric hemoglobin: two high-resolution crystal structures of hemoglobin Bart's (gamma(4)), a marker for alpha-thalassemia. Protein Sci. 1739–1749).

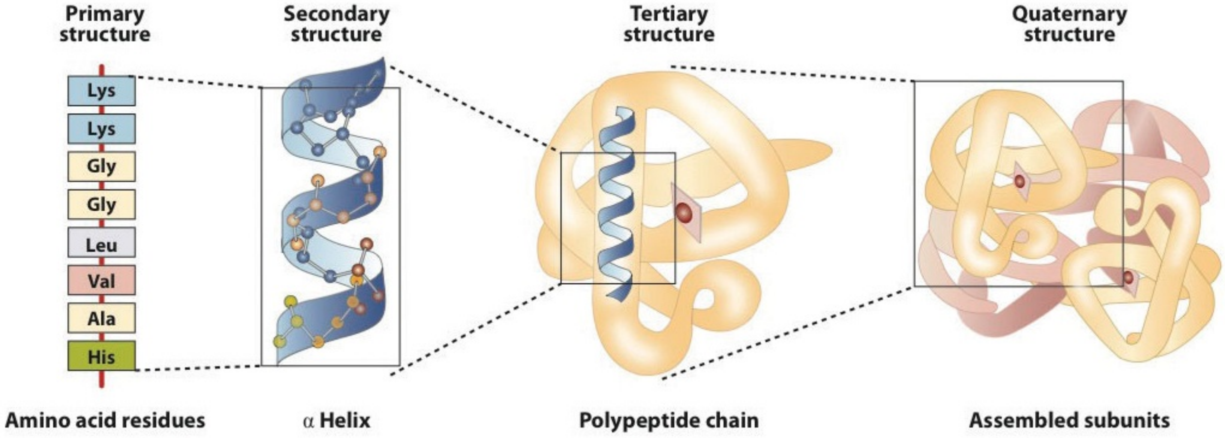


Figure 18.4.7: Levels of Structure in Proteins

The *primary structure* consists of the specific amino acid sequence. The resulting peptide chain can twist into an α-helix, which is one type of *secondary structure*. This helical segment is incorporated into the *tertiary structure* of the folded polypeptide chain. The single polypeptide chain is a subunit that constitutes the *quaternary structure* of a protein, such as hemoglobin that has four polypeptide chains.

Denaturation of Proteins

The highly organized structures of proteins are truly masterworks of chemical architecture. But highly organized structures tend to have a certain delicacy, and this is true of proteins. Denaturation is the term used for any change in the three-dimensional structure of a protein that renders it incapable of performing its assigned function. A denatured protein cannot do its job. (Sometimes denaturation is equated with the precipitation or coagulation of a protein; our definition is a bit broader.) A wide variety of reagents and conditions, such as heat, organic compounds, pH changes, and heavy metal ions can cause protein denaturation (Figure 18.4.1).

Figure 18.4.1: Protein Denaturation Methods

Method	Effect on Protein Structure
Heat above 50°C or ultraviolet (UV) radiation	Heat or UV radiation supplies kinetic energy to protein molecules, causing their atoms to vibrate more rapidly and disrupting relatively weak hydrogen bonding and dispersion forces.
Use of organic compounds, such as ethyl alcohol	These compounds are capable of engaging in intermolecular hydrogen bonding with protein molecules, disrupting intramolecular hydrogen bonding within the protein.
Salts of heavy metal ions, such as mercury, silver, and lead	These ions form strong bonds with the carboxylate anions of the acidic amino acids or SH groups of cysteine, disrupting ionic bonds and disulfide linkages.
Alkaloid reagents, such as tannic acid (used in tanning leather)	These reagents combine with positively charged amino groups in proteins to disrupt ionic bonds.

Anyone who has fried an egg has observed denaturation. The clear egg white turns opaque as the albumin denatures and coagulates. No one has yet reversed that process. However, given the proper circumstances and enough time, a protein that has unfolded under sufficiently gentle conditions can refold and may again exhibit biological activity (Figure 18.4.8). Such evidence suggests that, at least for these proteins, the primary structure determines the secondary and tertiary structure. A given sequence of amino acids seems to adopt its particular three-dimensional arrangement naturally if conditions are right.

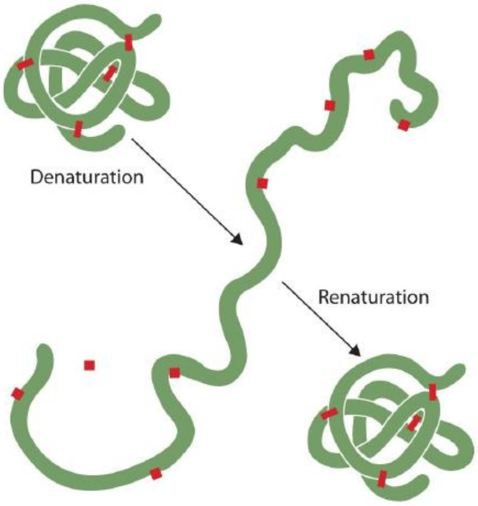


Figure 18.4.8: Denaturation and Renaturation of a Protein. The denaturation (unfolding) and renaturation (refolding) of a protein is depicted. The red boxes represent stabilizing interactions, such as disulfide linkages, hydrogen bonding, and/or ionic bonds.

The primary structures of proteins are quite sturdy. In general, fairly vigorous conditions are needed to hydrolyze peptide bonds. At the secondary through quaternary levels, however, proteins are quite vulnerable to attack, though they vary in their vulnerability to denaturation. The delicately folded globular proteins are much easier to denature than are the tough, fibrous proteins of hair and skin.

Summary

Proteins can be divided into two categories: fibrous, which tend to be insoluble in water, and globular, which are more soluble in water. A protein may have up to four levels of structure. The primary structure consists of the specific amino acid sequence. The resulting peptide chain can form an α-helix or β-pleated sheet (or local structures not as easily categorized), which is known as secondary structure. These segments of secondary structure are incorporated into the tertiary structure of the folded polypeptide chain. The quaternary structure describes the arrangements of subunits in a protein that contains more than one subunit. Four major types of attractive interactions determine the shape and stability of the folded protein: ionic bonding, hydrogen bonding, disulfide linkages, and dispersion forces. A wide variety of reagents and conditions can cause a protein to unfold or denature.

18.5: Enzymes

Learning Objectives

- Explain the functions of enzymes.
- Explain how enzymes are classified and named.

A catalyst is any substance that increases the *rate* or speed of a chemical reaction without being changed or consumed in the reaction. Enzymes are biological catalysts, and nearly all of them are proteins. The reaction rates attained by enzymes are truly amazing. In their presence, reactions occur at rates that are a million (10^6) or more times faster than would be attainable in their absence. What is even more amazing is that enzymes perform this function at body temperature (~37°C) and physiological pH (pH ~7), rather than at the conditions that are typically necessary to increase reaction rates (high temperature or pressure, the use of strong oxidizing or reducing agents or strong acids or bases, or a combination of any of these). In addition, enzymes are highly specific in their action; that is, each enzyme catalyzes only one type of reaction in only one compound or a group of structurally related compounds. The compound or compounds on which an enzyme acts are known as its substrates.

Hundreds of enzymes have been purified and studied in an effort to understand how they work so effectively and with such specificity. The resulting knowledge has been used to design drugs that inhibit or activate particular enzymes. An example is the intensive research to improve the treatment of or find a cure for acquired immunodeficiency syndrome (AIDS). AIDS is caused by the human immunodeficiency virus (HIV). Researchers are studying the enzymes produced by this virus and are developing drugs intended to block the action of those enzymes without interfering with enzymes produced by the human body. Several of these drugs have now been approved for use by AIDS patients.

Table 18.5.1: Classes of Enzymes

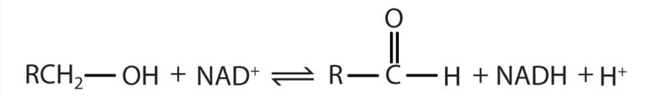
Class	Type of Reaction Catalyzed	Examples
oxidoreductases	oxidation-reduction reactions	Dehydrogenases catalyze oxidation-reduction reactions involving hydrogen and reductases catalyze reactions in which a substrate is reduced.
transferases	transfer reactions of groups, such as methyl, amino, and acetyl	Transaminases catalyze the transfer of amino group, and kinases catalyze the transfer of a phosphate group.
hydrolases	hydrolysis reactions	Lipases catalyze the hydrolysis of lipids, and proteases catalyze the hydrolysis of proteins
lyases	reactions in which groups are removed without hydrolysis or addition of groups to a double bond	Decarboxylases catalyze the removal of carboxyl groups.
isomerases	reactions in which a compound is converted to its isomer	Isomerases may catalyze the conversion of an aldose to a ketose, and mutases catalyze reactions in which a functional group is transferred from one atom in a substrate to another.
ligases	reactions in which new bonds are formed between carbon and another atom; energy is required	Synthetases catalyze reactions in which two smaller molecules are linked to form a larger one.

The first enzymes to be discovered were named according to their source or method of discovery. The enzyme *pepsin*, which aids in the hydrolysis of proteins, is found in the digestive juices of the stomach (Greek *pepsis*, meaning “digestion”). *Papain*, another enzyme that hydrolyzes protein (in fact, it is used in meat tenderizers), is isolated from papayas. As more enzymes were discovered, chemists recognized the need for a more systematic and chemically informative identification scheme. In the current numbering and naming scheme, under the oversight of the Nomenclature Commission of the International Union of Biochemistry, enzymes are arranged into six groups according to the general type of reaction they catalyze (Table 18.5.1), with subgroups and secondary subgroups that specify the reaction more precisely.

Figure* 18.5.1*: *Structure of the alcohol dehydrogenase protein (E.C.1.1.1.1) (EE ISOZYME) complexed wtih nicotinamide adenini dinulceotide (NAD) and zinc (PDB: 1CDO).*

Each enzyme is assigned a four-digit number, preceded by the prefix EC—for enzyme classification—that indicates its group, subgroup, and so forth. This is demonstrated in Table 18.5.2 for alcohol dehydrogenase. Each enzyme is also given a name consisting of the root of the name of its substrate or substrates and the *-ase* suffix. Thus urease is the enzyme that catalyzes the hydrolysis of urea.

Table 18.5.2: Assignment of an Enzyme Classification Number

Alcohol Dehydrogenase: EC 1.1.1.1	
The first digit indicates that this enzyme is an oxidoreductase; that is, an enzyme that catalyzes an oxidation-reduction reaction.	
The second digit indicates that this oxidoreductase catalyzes a reaction involving a primary or secondary alcohol.	
The third digit indicates that either the coenzyme NAD^+ or $NADP^+$ is required for this reaction.	
The fourth digit indicates that this was the first enzyme isolated, characterized, and named using this system of nomenclature.	
The systematic name for this enzyme is *alcohol:*NAD^+ *oxidoreductase*, while the recommended or common name is alcohol dehydrogenase.	
Reaction catalyzed:	 $\mathrm{RCH_2{-}OH + NAD^+ \rightleftharpoons R{-}\overset{O}{\overset{\Vert}{C}}{-}H + NADH + H^+}$

Summary

An enzyme is a biological catalyst, a substance that increases the rate of a chemical reaction without being changed or consumed in the reaction. A systematic process is used to name and classify enzymes.

18.6: Enzyme Action

Learning Objectives

- To describe the interaction between an enzyme and its substrate.

Enzyme-catalyzed reactions occur in at least two steps. In the first step, an enzyme molecule (E) and the substrate molecule or molecules (S) collide and react to form an intermediate compound called the *enzyme-substrate* (E–S) *complex*. (This step is reversible because the complex can break apart into the original substrate or substrates and the free enzyme.) Once the E–S complex forms, the enzyme is able to catalyze the formation of product (P), which is then released from the enzyme surface:

$$S + E \rightarrow E\text{–}S \tag{18.6.1}$$

$$E\text{–}S \rightarrow P + E \tag{18.6.2}$$

Hydrogen bonding and other electrostatic interactions hold the enzyme and substrate together in the complex. The structural features or functional groups on the enzyme that participate in these interactions are located in a cleft or pocket on the enzyme surface. This pocket, where the enzyme combines with the substrate and transforms the substrate to product is called the active site of the enzyme (Figure 18.6.1).

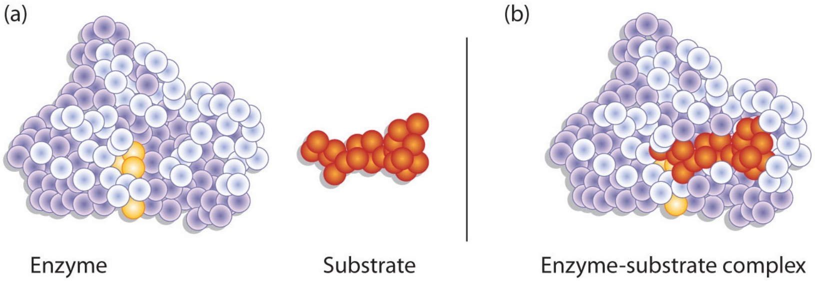


Figure 18.6.1: Substrate Binding to the Active Site of an Enzyme. The enzyme dihydrofolate reductase is shown with one of its substrates: NADP$^+$ (a) unbound and (b) bound. The NADP$^+$ (shown in red) binds to a pocket that is complementary to it in shape and ionic properties.

The active site of an enzyme possesses a unique conformation (including correctly positioned bonding groups) that is complementary to the structure of the substrate, so that the enzyme and substrate molecules fit together in much the same manner as a key fits into a tumbler lock. In fact, an early model describing the formation of the enzyme-substrate complex was called the lock-and-key model (Figure 18.6.2). This model portrayed the enzyme as conformationally rigid and able to bond only to substrates that exactly fit the active site.

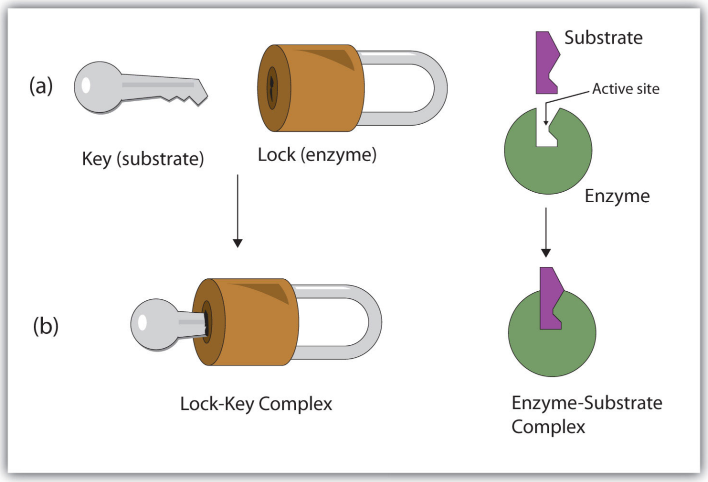


Figure 18.6.2: The Lock-and-Key Model of Enzyme Action. (a) Because the substrate and the active site of the enzyme have complementary structures and bonding groups, they fit together as a key fits a lock. (b) The catalytic reaction occurs while the two are bonded together in the enzyme-substrate complex.

Working out the precise three-dimensional structures of numerous enzymes has enabled chemists to refine the original lock-and-key model of enzyme actions. They discovered that the binding of a substrate often leads to a large conformational change in the enzyme, as well as to changes in the structure of the substrate or substrates. The current theory, known as the induced-fit model, says that enzymes can undergo a change in conformation when they bind substrate molecules, and the active site has a shape complementary to that of the substrate only *after* the substrate is bound, as shown for hexokinase in Figure 18.6.3. After catalysis, the enzyme resumes its original structure.

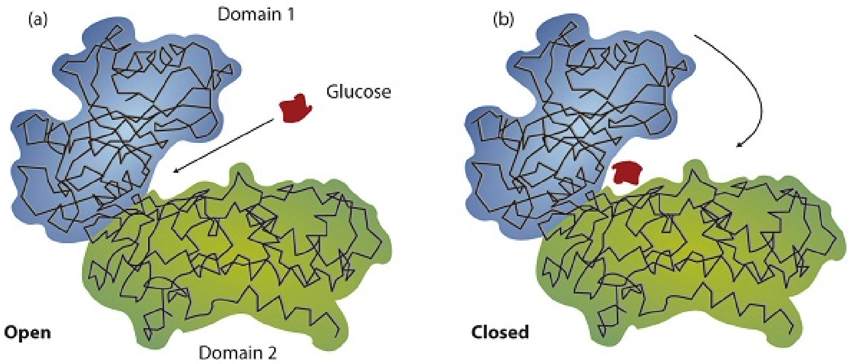


Figure 18.6.3: The Induced-Fit Model of Enzyme Action. (a) The enzyme hexokinase without its substrate (glucose, shown in red) is bound to the active site. (b) The enzyme conformation changes dramatically when the substrate binds to it, resulting in additional interactions between hexokinase and glucose.

The structural changes that occur when an enzyme and a substrate join together bring specific parts of a substrate into alignment with specific parts of the enzyme's active site. Amino acid side chains in or near the binding site can then act as acid or base catalysts, provide binding sites for the transfer of functional groups from one substrate to another or aid in the rearrangement of a substrate. The participating amino acids, which are usually widely separated in the primary sequence of the protein, are brought close together in the active site as a result of the folding and bending of the polypeptide chain or chains when the protein acquires its tertiary and quaternary structure. Binding to enzymes brings reactants close to each other and aligns them properly, which has the same effect as increasing the concentration of the reacting compounds.

✓ Example 18.6.1

a. What type of interaction would occur between an OH group present on a substrate molecule and a functional group in the active site of an enzyme?
b. Suggest an amino acid whose side chain might be in the active site of an enzyme and form the type of interaction you just identified.

Solution

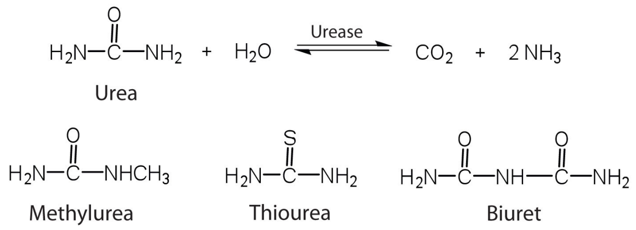
a. An OH group would most likely engage in hydrogen bonding with an appropriate functional group present in the active site of an enzyme.
b. Several amino acid side chains would be able to engage in hydrogen bonding with an OH group. One example would be asparagine, which has an amide functional group.

? Exercise 18.6.1

a. What type of interaction would occur between an COO^- group present on a substrate molecule and a functional group in the active site of an enzyme?
b. Suggest an amino acid whose side chain might be in the active site of an enzyme and form the type of interaction you just identified.

One characteristic that distinguishes an enzyme from all other types of catalysts is its *substrate specificity*. An inorganic acid such as sulfuric acid can be used to increase the reaction rates of many different reactions, such as the hydrolysis of disaccharides, polysaccharides, lipids, and proteins, with complete impartiality. In contrast, enzymes are much more specific. Some enzymes act on a single substrate, while other enzymes act on any of a group of related molecules containing a similar functional group or chemical bond. Some enzymes even distinguish between D- and L-stereoisomers, binding one stereoisomer but not the other.

Urease, for example, is an enzyme that catalyzes the hydrolysis of a single substrate—urea—but not the closely related compounds methyl urea, thiourea, or biuret. The enzyme carboxypeptidase, on the other hand, is far less specific. It catalyzes the removal of nearly any amino acid from the carboxyl end of any peptide or protein.



Enzyme specificity results from the uniqueness of the active site in each different enzyme because of the identity, charge, and spatial orientation of the functional groups located there. It regulates cell chemistry so that the proper reactions occur in the proper place at the proper time. Clearly, it is crucial to the proper functioning of the living cell.

Summary

A substrate binds to a specific region on an enzyme known as the active site, where the substrate can be converted to product. The substrate binds to the enzyme primarily through hydrogen bonding and other electrostatic interactions. The induced-fit model says that an enzyme can undergo a conformational change when binding a substrate. Enzymes exhibit varying degrees of substrate specificity.

18.7: Enzyme Activity

Learning Objectives

- To describe how pH, temperature, and the concentration of an enzyme and its substrate influence enzyme activity.

The single most important property of enzymes is the ability to increase the rates of reactions occurring in living organisms, a property known as *catalytic activity*. Because most enzymes are proteins, their activity is affected by factors that disrupt protein structure, as well as by factors that affect catalysts in general. Factors that disrupt protein structure include temperature and pH; factors that affect catalysts in general include reactant or substrate concentration and catalyst or enzyme concentration. The activity of an enzyme can be measured by monitoring either the rate at which a substrate disappears or the rate at which a product forms.

Concentration of Substrate

In the presence of a given amount of enzyme, the rate of an enzymatic reaction increases as the substrate concentration increases until a limiting rate is reached, after which further increase in the substrate concentration produces no significant change in the reaction rate (part (a) of Figure 18.7.1). At this point, so much substrate is present that essentially all of the enzyme active sites have substrate bound to them. In other words, the enzyme molecules are saturated with substrate. The excess substrate molecules cannot react until the substrate already bound to the enzymes has reacted and been released (or been released without reacting).

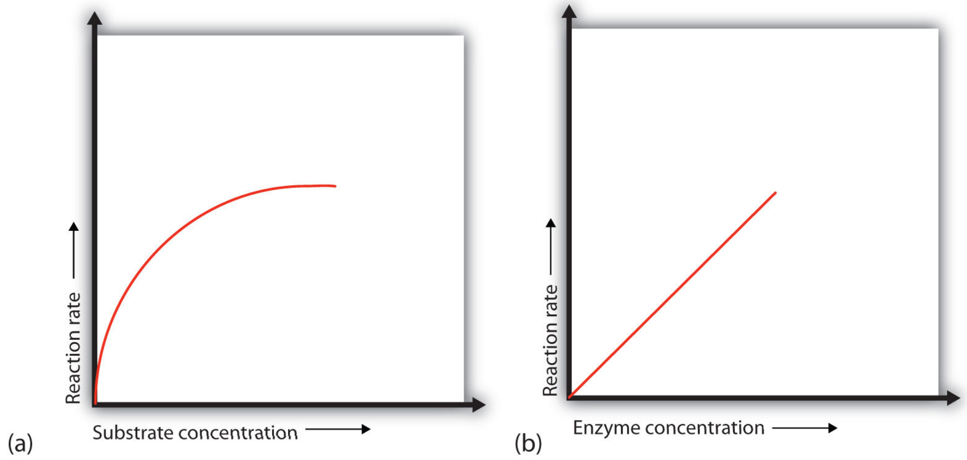


Figure 18.7.1: Concentration versus Reaction Rate. (a) This graph shows the effect of substrate concentration on the rate of a reaction that is catalyzed by a fixed amount of enzyme. (b) This graph shows the effect of enzyme concentration on the reaction rate at a constant level of substrate.

Let's consider an analogy. Ten taxis (enzyme molecules) are waiting at a taxi stand to take people (substrate) on a 10-minute trip to a concert hall, one passenger at a time. If only 5 people are present at the stand, the rate of their arrival at the concert hall is 5 people in 10 minutes. If the number of people at the stand is increased to 10, the rate increases to 10 arrivals in 10 minutes. With 20 people at the stand, the rate would still be 10 arrivals in 10 minutes. The taxis have been "saturated." If the taxis could carry 2 or 3 passengers each, the same principle would apply. The rate would simply be higher (20 or 30 people in 10 minutes) before it leveled off.

Concentration of Enzyme

When the concentration of the enzyme is significantly lower than the concentration of the substrate (as when the number of taxis is far lower than the number of waiting passengers), the rate of an enzyme-catalyzed reaction is directly dependent on the enzyme concentration (part (b) of Figure 18.7.1). This is true for any catalyst; the reaction rate increases as the concentration of the catalyst is increased.

Temperature

A general rule of thumb for most chemical reactions is that a temperature rise of 10°C approximately doubles the reaction rate. To some extent, this rule holds for all enzymatic reactions. After a certain point, however, an increase in temperature causes a decrease in the reaction rate, due to denaturation of the protein structure and disruption of the active site (part (a) of Figure 18.7.2). For many proteins, denaturation occurs between 45°C and 55°C. Furthermore, even though an enzyme may appear to have a maximum reaction rate between 40°C and 50°C, most biochemical reactions are carried out at lower temperatures because enzymes are not stable at these higher temperatures and will denature after a few minutes.

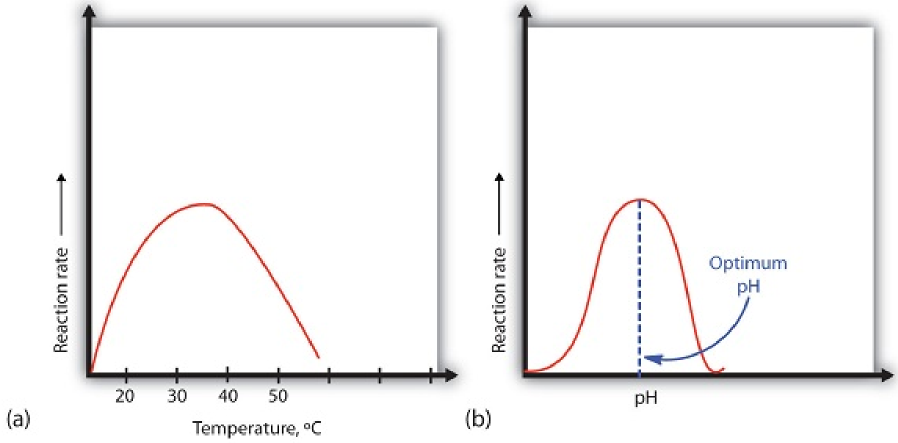


Figure 18.7.2: Temperature and pH versus Concentration. (a) This graph depicts the effect of temperature on the rate of a reaction that is catalyzed by a fixed amount of enzyme. (b) This graph depicts the effect of pH on the rate of a reaction that is catalyzed by a fixed amount of enzyme.

At 0°C and 100°C, the rate of enzyme-catalyzed reactions is nearly zero. This fact has several practical applications. We sterilize objects by placing them in boiling water, which denatures the enzymes of any bacteria that may be in or on them. We preserve our food by refrigerating or freezing it, which slows enzyme activity. When animals go into hibernation in winter, their body temperature drops, decreasing the rates of their metabolic processes to levels that can be maintained by the amount of energy stored in the fat reserves in the animals' tissues.

Hydrogen Ion Concentration (pH)

Because most enzymes are proteins, they are sensitive to changes in the hydrogen ion concentration or pH. Enzymes may be denatured by extreme levels of hydrogen ions (whether high or low); *any* change in pH, even a small one, alters the degree of ionization of an enzyme's acidic and basic side groups and the substrate components as well. Ionizable side groups located in the active site must have a certain charge for the enzyme to bind its substrate. Neutralization of even one of these charges alters an enzyme's catalytic activity.

An enzyme exhibits maximum activity over the narrow pH range in which a molecule exists in its properly charged form. The median value of this pH range is called the optimum pH of the enzyme (part (b) of Figure 18.7.2). With the notable exception of gastric juice (the fluids secreted in the stomach), most body fluids have pH values between 6 and 8. Not surprisingly, most enzymes exhibit optimal activity in this pH range. However, a few enzymes have optimum pH values outside this range. For example, the optimum pH for pepsin, an enzyme that is active in the stomach, is 2.0.

Summary

Initially, an increase in substrate concentration leads to an increase in the rate of an enzyme-catalyzed reaction. As the enzyme molecules become saturated with substrate, this increase in reaction rate levels off. The rate of an enzyme-catalyzed reaction increases with an increase in the concentration of an enzyme. At low temperatures, an increase in temperature increases the rate of an enzyme-catalyzed reaction. At higher temperatures, the protein is denatured, and the rate of the reaction dramatically decreases. An enzyme has an optimum pH range in which it exhibits maximum activity.

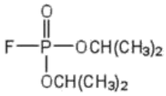
18.8: Enzyme Inhibition

Learning Objectives

- Explain what an enzyme inhibitor is.
- Distinguish between reversible and irreversible inhibitors.
- Distinguish between competitive and noncompetitive inhibitors.

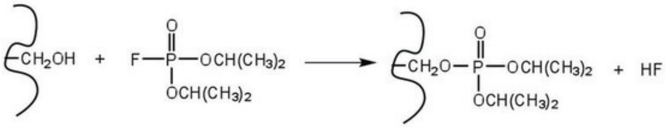
Previously, we noted that enzymes are inactivated at high temperatures and by changes in pH. These are nonspecific factors that would inactivate any enzyme. The activity of enzymes can also be regulated by more specific inhibitors. Many compounds are poisons because they bind covalently to particular enzymes or kinds of enzymes and inactivate them (Table 18.8.1).

Table 18.8.1: Poisons as Enzyme Inhibitors

Poison	Formula	Example of Enzyme Inhibited	Action
arsenate	AsO_4^{3-}	glyceraldehyde 3-phosphate dehydrogenase	substitutes for phosphate
iodoacetate	ICH_2COO^-	triose phosphate dehydrogenase	binds to cysteine SH group
diisopropylfluoro-phosphate (DIFP; a nerve poison)	 $\mathrm{F-\underset{\underset{OCH(CH_3)_2}{\vert}}{\overset{\overset{O}{\Vert}}{P}}-OCH(CH_3)_2}$	acetylcholinesterase	binds to serine OH group

Irreversible Inhibition: Poisons

An irreversible inhibitor inactivates an enzyme by bonding covalently to a particular group at the active site. The inhibitor-enzyme bond is so strong that the inhibition cannot be reversed by the addition of excess substrate. The nerve gases, especially Diisopropyl fluorophosphate (DIFP), irreversibly inhibit biological systems by forming an enzyme-inhibitor complex with a specific OH group of serine situated at the active sites of certain enzymes. The peptidases trypsin and chymotrypsin contain serine groups at the active site and are inhibited by DIFP.



Reversible Inhibition

A reversible inhibitor inactivates an enzyme through noncovalent, more easily reversed, interactions. Unlike an irreversible inhibitor, a reversible inhibitor can dissociate from the enzyme. Reversible inhibitors include competitive inhibitors and noncompetitive inhibitors. (There are additional types of reversible inhibitors.) A competitive inhibitor is any compound that bears a structural resemblance to a particular substrate and thus competes with that substrate for binding at the active site of an enzyme. The inhibitor is not acted on by the enzyme but does prevent the substrate from approaching the active site.

The degree to which a competitive inhibitor interferes with an enzyme's activity depends on the relative concentrations of the substrate and the inhibitor. If the inhibitor is present in relatively large quantities, it will initially block most of the active sites. But because the binding is reversible, some substrate molecules will eventually bind to the active site and be converted to product. Increasing the substrate concentration promotes displacement of the inhibitor from the active site. Competitive inhibition can be completely reversed by adding substrate so that it reaches a much higher concentration than that of the inhibitor.

Studies of competitive inhibition have provided helpful information about certain enzyme-substrate complexes and the interactions of specific groups at the active sites. As a result, pharmaceutical companies have synthesized drugs that competitively inhibit metabolic processes in bacteria and certain cancer cells. Many drugs are competitive inhibitors of specific enzymes.

A classic example of competitive inhibition is the effect of malonate on the enzyme activity of succinate dehydrogenase (Figure 18.8.1). Malonate and succinate are the anions of dicarboxylic acids and contain three and four carbon atoms, respectively. The malonate molecule binds to the active site because the spacing of its carboxyl groups is not greatly different from that of succinate.

However, no catalytic reaction occurs because malonate does not have a CH_2CH_2 group to convert to CH=CH. This reaction will also be discussed in connection with the Krebs cycle and energy production.

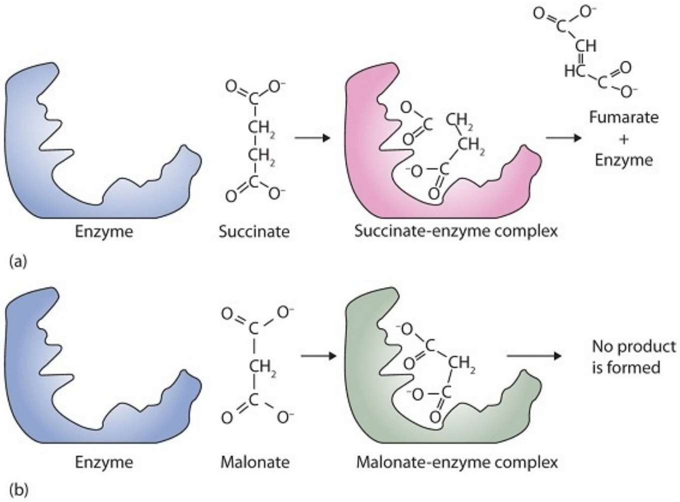


Figure 18.8.1: Competitive Inhibition. (a) Succinate binds to the enzyme succinate dehydrogenase. A dehydrogenation reaction occurs, and the product—fumarate—is released from the enzyme. (b) Malonate also binds to the active site of succinate dehydrogenase. In this case, however, no subsequent reaction occurs while malonate remains bound to the enzyme.

✓ To Your Health: Penicillin

Chemotherapy is the strategic use of chemicals (that is, drugs) to destroy infectious microorganisms or cancer cells without causing excessive damage to the other, healthy cells of the host. From bacteria to humans, the metabolic pathways of all living organisms are quite similar, so the search for safe and effective chemotherapeutic agents is a formidable task. Many well-established chemotherapeutic drugs function by inhibiting a critical enzyme in the cells of the invading organism.

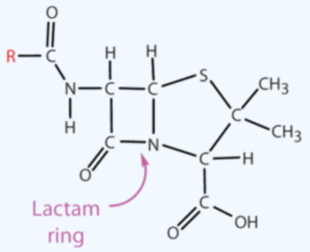
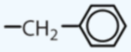
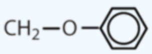
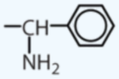
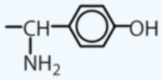
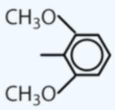
An *antibiotic* is a compound that kills bacteria; it may come from a natural source such as molds or be synthesized with a structure analogous to a naturally occurring antibacterial compound. Antibiotics constitute no well-defined class of chemically related substances, but many of them work by effectively inhibiting a variety of enzymes essential to bacterial growth.

Penicillin, one of the most widely used antibiotics in the world, was fortuitously discovered by Alexander Fleming in 1928, when he noticed antibacterial properties in a mold growing on a bacterial culture plate. In 1938, Ernst Chain and Howard Florey began an intensive effort to isolate penicillin from the mold and study its properties. The large quantities of penicillin needed for this research became available through development of a corn-based nutrient medium that the mold loved and through the discovery of a higher-yielding strain of mold at a United States Department of Agriculture research center near Peoria, Illinois. Even so, it was not until 1944 that large quantities of penicillin were being produced and made available for the treatment of bacterial infections.

Penicillin functions by interfering with the synthesis of cell walls of reproducing bacteria. It does so by inhibiting an enzyme—transpeptidase—that catalyzes the last step in bacterial cell-wall biosynthesis. The defective walls cause bacterial cells to burst. Human cells are not affected because they have cell membranes, not cell walls.

Several naturally occurring penicillins have been isolated. They are distinguished by different R groups connected to a common structure: a four-member cyclic amide (called a lactam ring) fused to a five-member ring. The addition of appropriate organic compounds to the culture medium leads to the production of the different kinds of penicillin.

The penicillins are effective against gram-positive bacteria (bacteria capable of being stained by Gram's stain) and a few gram-negative bacteria (including the intestinal bacterium *Escherichia coli*). They are effective in the treatment of diphtheria, gonorrhea, pneumonia, syphilis, many pus infections, and certain types of boils. Penicillin G was the earliest penicillin to be used on a wide scale. However, it cannot be administered orally because it is quite unstable; the acidic pH of the stomach converts it to an inactive derivative. The major oral penicillins—penicillin V, ampicillin, and amoxicillin—on the other hand, are acid stable.

Penicillin Structure	R Group	Drug Name
		penicillin G
		penicillin V
		ampicillin
		amoxicillin
		methicillin

Some strains of bacteria become resistant to penicillin through a mutation that allows them to synthesize an enzyme—penicillinase—that breaks the antibiotic down (by cleavage of the amide linkage in the lactam ring). To combat these strains, scientists have synthesized penicillin analogs (such as methicillin) that are not inactivated by penicillinase.

Some people (perhaps 5% of the population) are allergic to penicillin and therefore must be treated with other antibiotics. Their allergic reaction can be so severe that a fatal coma may occur if penicillin is inadvertently administered to them. Fortunately, several other antibiotics have been discovered. Most, including aureomycin and streptomycin, are the products of microbial synthesis. Others, such as the semisynthetic penicillins and tetracyclines, are made by chemical modifications of antibiotics; and some, like chloramphenicol, are manufactured entirely by chemical synthesis. They are as effective as penicillin in destroying infectious microorganisms. Many of these antibiotics exert their effects by blocking protein synthesis in microorganisms.

Initially, antibiotics were considered miracle drugs, substantially reducing the number of deaths from blood poisoning, pneumonia, and other infectious diseases. Some seven decades ago, a person with a major infection almost always died. Today, such deaths are rare. Seven decades ago, pneumonia was a dreaded killer of people of all ages. Today, it kills only the very old or those ill from other causes. Antibiotics have indeed worked miracles in our time, but even miracle drugs have limitations. Not long after the drugs were first used, disease organisms began to develop strains resistant to them. In a race to stay ahead of resistant bacterial strains, scientists continue to seek new antibiotics. The penicillins have now been partially displaced by related compounds, such as the cephalosporins and vancomycin. Unfortunately, some strains of bacteria have already shown resistance to these antibiotics.

Some reversible inhibitors are noncompetitive. A noncompetitive inhibitor can combine with either the free enzyme or the enzyme-substrate complex because its binding site on the enzyme is distinct from the active site. Binding of this kind of inhibitor alters the three-dimensional conformation of the enzyme, changing the configuration of the active site with one of two results. Either the enzyme-substrate complex does not form at its normal rate, or, once formed, it does not yield products at the normal rate. Because the inhibitor does not structurally resemble the substrate, the addition of excess substrate does *not* reverse the inhibitory effect.

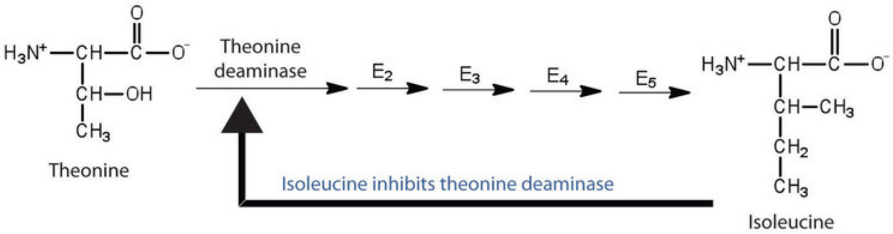


Figure 18.8.2: Feedback Inhibition of Threonine Deaminase by Isoleucine. Threonine deaminase is the first enzyme in the conversion of threonine to isoleucine. Isoleucine inhibits threonine deaminase through feedback inhibition.

Feedback inhibition is a normal biochemical process that makes use of noncompetitive inhibitors to control some enzymatic activity. In this process, the final product inhibits the enzyme that catalyzes the first step in a series of reactions. Feedback inhibition is used to regulate the synthesis of many amino acids. For example, bacteria synthesize isoleucine from threonine in a series of five enzyme-catalyzed steps. As the concentration of isoleucine increases, some of it binds as a noncompetitive inhibitor to the first enzyme of the series (threonine deaminase), thus bringing about a decrease in the amount of isoleucine being formed (Figure 18.8.2).

Summary

An irreversible inhibitor inactivates an enzyme by bonding covalently to a particular group at the active site. A reversible inhibitor inactivates an enzyme through noncovalent, reversible interactions. A competitive inhibitor competes with the substrate for binding at the active site of the enzyme. A noncompetitive inhibitor binds at a site distinct from the active site.

18.9: Enzyme Cofactors and Vitamins

Learning Objectives

- To explain why vitamins are necessary in the diet.

Many enzymes are simple proteins consisting entirely of one or more amino acid chains. Other enzymes contain a nonprotein component called a **cofactor** that is necessary for the enzyme's proper functioning. There are two types of cofactors: inorganic ions [e.g., zinc or Cu(I) ions] and organic molecules known as coenzymes. Most **coenzymes** are vitamins or are derived from vitamins.

Vitamins are organic compounds that are essential in very small (trace) amounts for the maintenance of normal metabolism. They generally cannot be synthesized at adequate levels by the body and must be obtained from the diet. The absence or shortage of a vitamin may result in a vitamin-deficiency disease. In the first half of the 20th century, a major focus of biochemistry was the identification, isolation, and characterization of vitamins. Despite accumulating evidence that people needed more than just carbohydrates, fats, and proteins in their diets for normal growth and health, it was not until the early 1900s that research established the need for trace nutrients in the diet.

Table 18.9.1: Fat-Soluble Vitamins and Physiological Functions

Vitamin	Physiological Function	Effect of Deficiency
vitamin A (retinol)	formation of vision pigments; differentiation of epithelial cells	night blindness; continued deficiency leads to total blindness
vitamin D (cholecalciferol)	increases the body's ability to absorb calcium and phosphorus	osteomalacia (softening of the bones); known as rickets in children
vitamin E (tocopherol)	fat-soluble antioxidant	damage to cell membranes
vitamin K (phylloquinone)	formation of prothrombin, a key enzyme in the blood-clotting process	increases the time required for blood to clot

Because organisms differ in their synthetic abilities, a substance that is a vitamin for one species may not be so for another. Over the past 100 years, scientists have identified and isolated 13 vitamins required in the human diet and have divided them into two broad categories: the *fat-soluble vitamins*, which include vitamins A, D, E, and K, and the *water-soluble vitamins*, which are the B complex vitamins and vitamin C. All fat-soluble vitamins contain a high proportion of hydrocarbon structural components. There are one or two oxygen atoms present, but the compounds as a whole are nonpolar. In contrast, water-soluble vitamins contain large numbers of electronegative oxygen and nitrogen atoms, which can engage in hydrogen bonding with water. Most water-soluble vitamins act as coenzymes or are required for the synthesis of coenzymes. The fat-soluble vitamins are important for a variety of physiological functions. The key vitamins and their functions are found in Tables $18.9.1$ and $18.9.2$

Table 18.9.2: Water-Soluble Vitamins and Physiological Functions

Vitamin	Coenzyme	Coenzyme Function	Deficiency Disease
vitamin B_1 (thiamine)	thiamine pyrophosphate	decarboxylation reactions	beri-beri
vitamin B_2 (riboflavin)	flavin mononucleotide or flavin adenine dinucleotide	oxidation-reduction reactions involving two hydrogen atoms	—
vitamin B_3 (niacin)	nicotinamide adenine dinucleotide or nicotinamide adenine dinucleotide phosphate	oxidation-reduction reactions involving the hydride ion (H^-)	pellagra
vitamin B_6 (pyridoxine)	pyridoxal phosphate	variety of reactions including the transfer of amino groups	—
vitamin B_{12} (cyanocobalamin)	methylcobalamin or deoxyadenoxylcobalamin	intramolecular rearrangement reactions	pernicious anemia

Vitamin	Coenzyme	Coenzyme Function	Deficiency Disease
biotin	biotin	carboxylation reactions	—
folic acid	tetrahydrofolate	carrier of one-carbon units such as the formyl group	anemia
pantothenic Acid	coenzyme A	carrier of acyl groups	—
vitamin C (ascorbic acid)	none	antioxidant; formation of collagen, a protein found in tendons, ligaments, and bone	scurvy

Vitamins C and E, as well as the provitamin β-carotene can act as antioxidants in the body. Antioxidants prevent damage from free radicals, which are molecules that are highly reactive because they have unpaired electrons. Free radicals are formed not only through metabolic reactions involving oxygen but also by such environmental factors as radiation and pollution.

> *β-carotene is known as a provitamin because it can be converted to vitamin A in the body.*

Free radicals react most commonly react with lipoproteins and unsaturated fatty acids in cell membranes, removing an electron from those molecules and thus generating a new free radical. The process becomes a chain reaction that finally leads to the oxidative degradation of the affected compounds. Antioxidants react with free radicals to stop these chain reactions by forming a more stable molecule or, in the case of vitamin E, a free radical that is much less reactive (vitamin E is converted back to its original form through interaction with vitamin C).

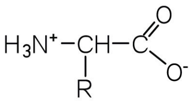
Summary

Vitamins are organic compounds that are essential in very small amounts for the maintenance of normal metabolism. Vitamins are divided into two broad categories: fat-soluble vitamins and water-soluble vitamins. Most water-soluble vitamins are needed for the formation of coenzymes, which are organic molecules needed by some enzymes for catalytic activity.

18.E: Amino Acids, Proteins, and Enzymes (Exercises)

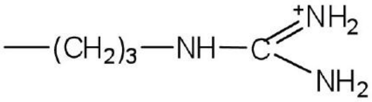
18.1: Properties of Amino Acids

Concept Review Exercises

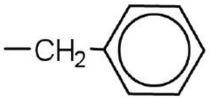
1. What is the general structure of an α-amino acid?
2. Identify the amino acid that fits each description.
   a. also known as aspartate
   b. almost as strong a base as sodium hydroxide
   c. does not have a chiral carbon
3. 
4. a. aspartic acid
   b. arginine
   c. glycine
5. Write the side chain of each amino acid.
   a. serine
   b. arginine
   c. phenylalanine
6. Write the side chain of each amino acid.
   a. aspartic acid
   b. methionine
   c. valine
7. Draw the structure for each amino acid.
   a. alanine
   b. cysteine
   c. histidine
8. Draw the structure for each amino acid.
   a. threonine
   b. glutamic acid
   c. leucine
9. Identify an amino acid whose side chain contains a(n)
   a. amide functional group.
   b. aromatic ring.
   c. carboxyl group.
10. Identify an amino acid whose side chain contains a(n)
   a. OH group
   b. branched chain
   c. amino group

1. a. CH_2OH^-

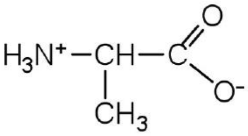
b.



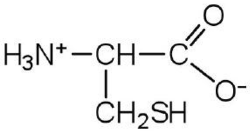
c.



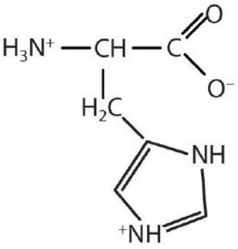
2.
3. a.



b.



c.



4.
5. a. asparagine or glutamine
   b. phenylalanine, tyrosine, or tryptophan
   c. aspartic acid or glutamic acid

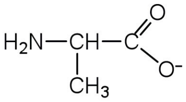
18.2: Reactions of Amino Acids

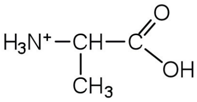
Concept Review Exercises

1. Define each term.
   a. zwitterion
   b. isoelectric point
2. Draw the structure for the anion formed when alanine (at neutral pH) reacts with a base.
3. Draw the structure for the cation formed when alanine (at neutral pH) reacts with an acid.

Answers

1. a. an electrically neutral compound that contains both negatively and positively charged groups
   b. the pH at which a given amino acid exists in solution as a zwitterion

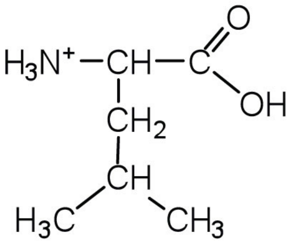
2. 

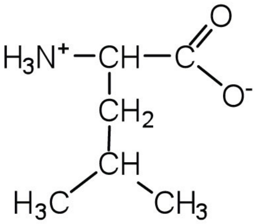
3. 

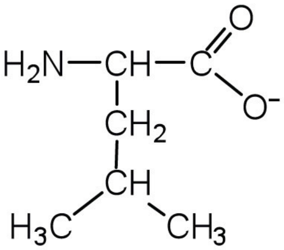
Exercises

1. Draw the structure of leucine and determine the charge on the molecule in a(n)
    1. acidic solution (pH = 1).
    2. neutral solution (pH = 7).
    3. a basic solution (pH = 11)
2. Draw the structure of isoleucine and determine the charge on the molecule in a(n)
    1. acidic solution (pH = 1).
    2. neutral solution (pH = 7).
    3. 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?

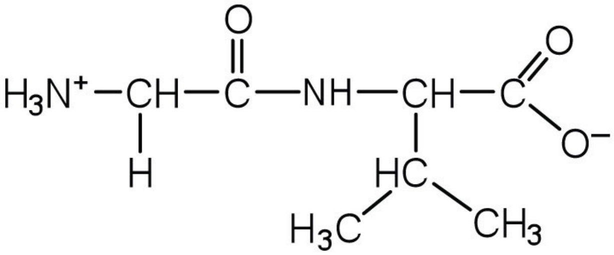
Answers

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

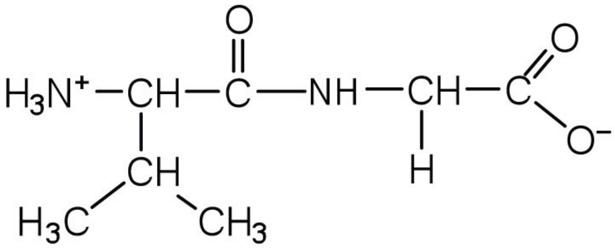
Exercises

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).

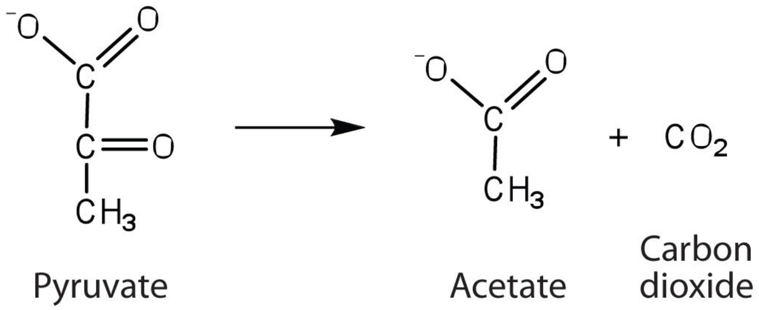
4. Write equations to show how isoleucine can act as a buffer (that is, how it can neutralize added acid or base).

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.

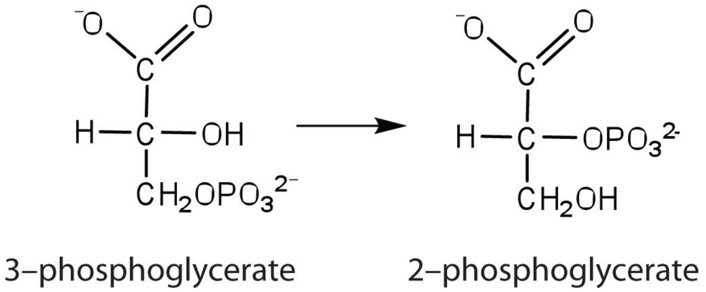
6. Draw the structure of the pentapeptide whose sequence is arg-his-gly-leu-asp. Identify which of the amino acids have R groups that can donate or gain hydrogen ions.

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



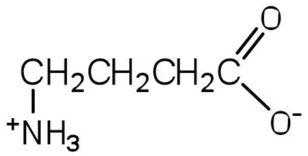
    b. the enzyme that catalyzes the rearrangement of 3-phosphoglycerate to form 2-phosphoglycerate



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.

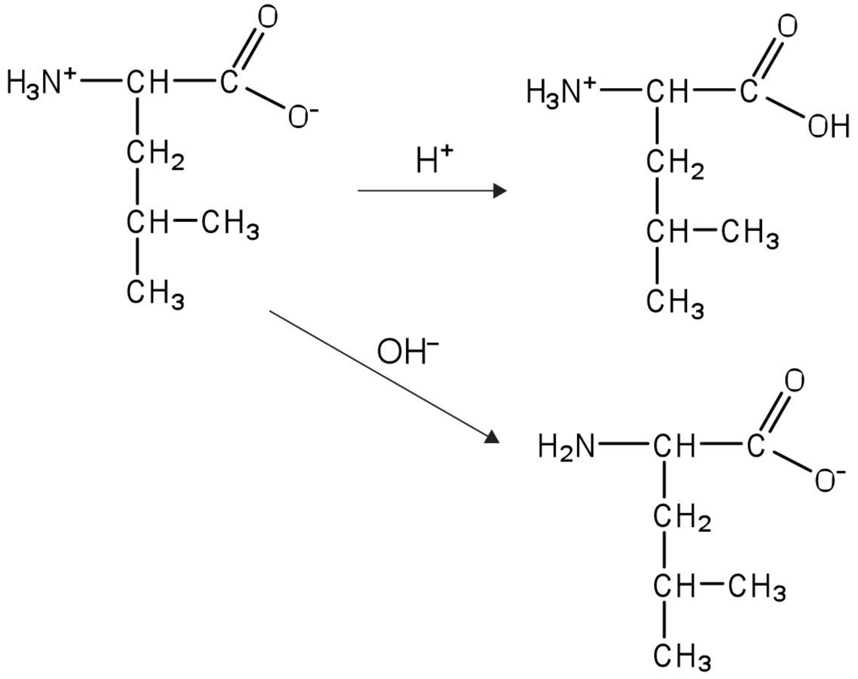
16. A patient has a fever of 39°C. Would you expect the activity of enzymes in the body to increase or decrease relative to their activity at normal body temperature (37°C)?
17. Using your knowledge of factors that influence enzyme activity, describe what happens when milk is pasteurized.

Answers

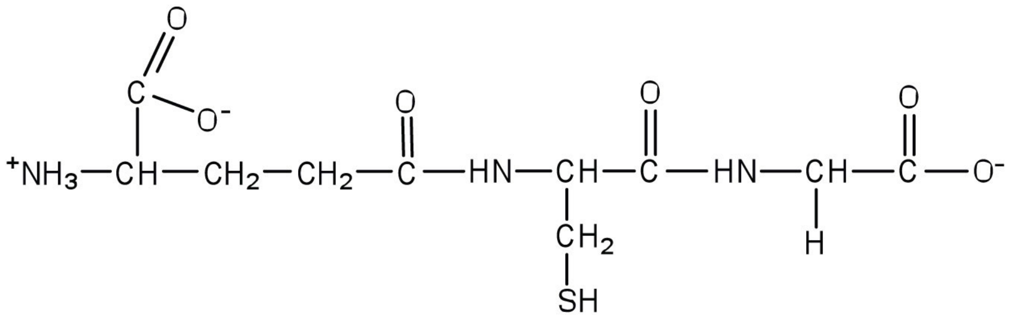


1.

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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18.S: Amino Acids, Proteins, and Enzymes (Summary)

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

A **protein** is a large biological polymer synthesized from **amino acids**, which are carboxylic acids containing an α-amino group. Proteins have a variety of important roles in living organisms, yet they are made from the same 20 L-amino acids. About half of these amino acids, the **essential amino acids**, cannot be synthesized by the human body and must be obtained from the diet. In the solid state and in neutral solutions, amino acids exist as **zwitterions**, species that are charged but electrically neutral. In this form, they behave much like inorganic salts. Each amino acid belongs to one of four classes depending on the characteristics of its R group or amino acid side chain: nonpolar, polar but neutral, positively charged, and negatively charged. Depending on the conditions, amino acids can act as either acids or bases, which means that proteins act as buffers. The pH at which an amino acid exists as the zwitterion is called the **isoelectric point (pI)**.

The amino acids in a protein are linked together by **peptide bonds**. Protein chains containing 10 or fewer amino acids are usually referred to as **peptides**, with a prefix such as di- or tri- indicating the number of amino acids. Chains containing more than 50 amino acid units are referred to as *proteins* or **polypeptides**. Proteins are classified globular or fibrous, depending on their structure and resulting solubility in water. **Globular proteins** are nearly spherical and are soluble in water; **fibrous proteins** have elongated or fibrous structures and are not soluble in water.

Protein molecules can have as many as four levels of structure. The **primary structure** is the sequence of amino acids in the chain. The **secondary structure** is the arrangement of adjacent atoms in the peptide chain; the most common arrangements are α-helices or β-pleated sheets. The **tertiary structure** is the overall three-dimensional shape of the molecule that results from the way the chain bends and folds in on itself. Proteins that consist of more than one chain have **quaternary structure**, which is the way the multiple chains are packed together.

Four types of intramolecular and intermolecular forces contribute to secondary, tertiary, and quaternary structure: (1) **hydrogen bonding** between an oxygen or a nitrogen atom and a hydrogen atom bound to an oxygen atom or a nitrogen atom, either on the same chain or on a neighboring chain; (2) **ionic bonding** between one positively charged side chain and one negatively charged side chain; (3) **disulfide linkages** between cysteine units; and (4) **dispersion forces** between nonpolar side chains.

Because of their complexity, protein molecules are delicate and easy to disrupt. A *denatured* protein is one whose conformation has been changed, in a process called **denaturation**, so that it can no longer do its physiological job. A variety of conditions, such as heat, ultraviolet radiation, the addition of organic compounds, or changes in pH can denature a protein.

An **enzyme** is an organic catalyst produced by a living cell. Enzymes are such powerful catalysts that the reactions they promote occur rapidly at body temperature. Without the help of enzymes, these reactions would require high temperatures and long reaction times.

The molecule or molecules on which an enzyme acts are called its **substrates**. An enzyme has an **active site** where its substrate or substrates bind to form an enzyme-substrate complex. The reaction occurs, and product is released:

$$E+S \rightarrow E\text{–}S \rightarrow E+P$$

The original **lock-and-key model** of enzyme and substrate binding pictured a rigid enzyme of unchanging configuration binding to the appropriate substrate. The newer **induced-fit model** describes the enzyme active site as changing its conformation after binding to the substrate.

Most enzymes have maximal activity in a narrow pH range centered on an **optimum pH**. In this pH range, the enzyme is correctly folded, and catalytic groups in the active site have the correct charge (positive, negative, or neutral). For most enzymes, the optimum pH is between 6 and 8.

Substances that interfere with enzyme function are called inhibitors. An **irreversible inhibitor** inactivates enzymes by forming covalent bonds to the enzyme, while a **reversible inhibitor** inactivates an enzyme by a weaker, noncovalent interaction that is easier to disrupt. A **competitive inhibitor** is a reversible inhibitor that is structurally similar to the substrate and binds to the active site. When the inhibitor is bound, the substrate is blocked from the active site and no reaction occurs. Because the binding of such an inhibitor is reversible, a high substrate concentration will overcome the inhibition because it increases the likelihood of the substrate binding. A **noncompetitive inhibitor** binds reversibly at a site distinct from the active site. Thus, it can bind to either the enzyme or the enzyme-substrate complex. The inhibitor changes the conformation of the active site so that the enzyme cannot function properly. Noncompetitive inhibitors are important in **feedback inhibition**, in which the amount of product produced by a series of reactions is carefully controlled. The final product in a series of reactions acts as a noncompetitive inhibitor of the initial enzyme.

Simple enzymes consist entirely of one or more amino acid chains. Complex enzymes are composed of one or more amino acid chains joined to **cofactors**—inorganic ions or organic **coenzymes**. **Vitamins** are organic compounds that are essential in very small amounts for the maintenance of normal metabolism and generally cannot be synthesized at adequate levels by the body. Vitamins are divided into two broad categories: *fat-soluble* vitamins and *water-soluble* vitamins. Many of the water-soluble vitamins are used for the synthesis of coenzymes.

CHAPTER OVERVIEW

19: Nucleic Acids

The blueprint for the reproduction and the maintenance of each organism is found in the nuclei of its cells, concentrated in elongated, threadlike structures called chromosomes. These complex structures, consisting of DNA and proteins, contain the basic units of heredity, called genes. The number of chromosomes (and genes) varies with each species. Human body cells have 23 pairs of chromosomes having 20,000–40,000 different genes.

Sperm and egg cells contain only a single copy of each chromosome; that is, they contain only one member of each chromosome pair. Thus, in sexual reproduction, the entire complement of chromosomes is achieved only when an egg and sperm combine. A new individual receives half its hereditary material from each parent. Calling the unit of heredity a “gene” merely gives it a name. But what really are genes and how is the information they contain expressed? One definition of a gene is that it is a segment of DNA that constitutes the code for a specific polypeptide. If genes are segments of DNA, we need to learn more about the structure and physiological function of DNA. We begin by looking at the small molecules needed to form DNA and RNA (ribonucleic acid)—the nucleotides.

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19.0: Prelude to Nucleic Acids

Following the initial isolation of insulin in 1921, diabetic patients could be treated with insulin obtained from the pancreases of cattle and pigs. Unfortunately, some patients developed an allergic reaction to this insulin because its amino acid sequence was not identical to that of human insulin. In the 1970s, an intense research effort began that eventually led to the production of genetically engineered human insulin—the first genetically engineered product to be approved for medical use. To accomplish this feat, researchers first had to determine how insulin is made in the body and then find a way of causing the same process to occur in nonhuman organisms, such as bacteria or yeast cells. Many aspects of these discoveries are presented in this chapter on nucleic acids.

Figure 19.0.1: A vial of insulin. It has been given a trade name, Actrapid, by the manufacturer. (Public Domain; Mr Hyde).

19.1: Nucleotides

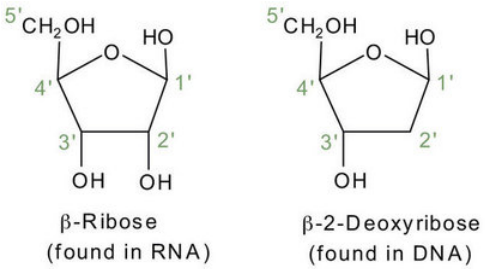
Learning Objectives

- To identify the different molecules that combine to form nucleotides.

The repeating, or monomer, units that are linked together to form nucleic acids are known as nucleotides. The deoxyribonucleic acid (DNA) of a typical mammalian cell contains about 3 × 10^9 nucleotides. Nucleotides can be further broken down to phosphoric acid (H_3PO_4), a pentose sugar (a sugar with five carbon atoms), and a nitrogenous base (a base containing nitrogen atoms).

$$\text{nucleic acids} \xrightarrow[\text{down into}]{\text{can be broken}} \text{nucleotides} \xrightarrow[\text{down into}]{\text{can be broken}} \mathrm{H_3PO_4} + \text{nitrogen base} + \text{pentose sugar}$$

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 19.1.1).

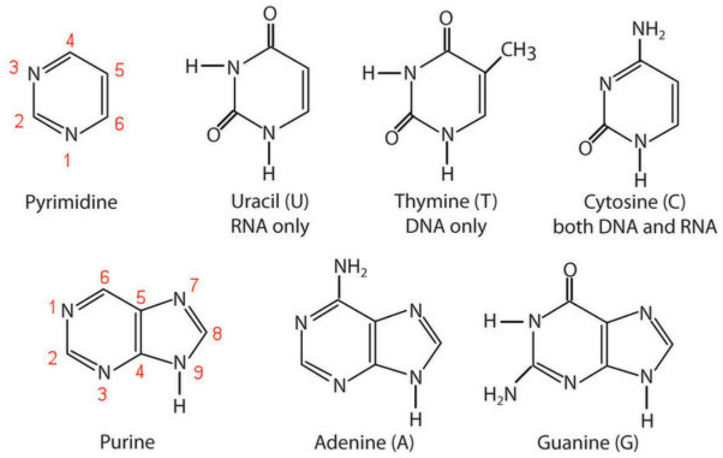


Figure 19.1.1: The Nitrogenous Bases Found in DNA and RNA

The formation of a bond between C1′ of the pentose sugar and N1 of the pyrimidine base or N9 of the purine base joins the pentose sugar to the nitrogenous base. In the formation of this bond, a molecule of water is removed. Table 19.1.1 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 19.1.1: Composition of Nucleotides in DNA and RNA

Composition	DNA	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 19.1.2.

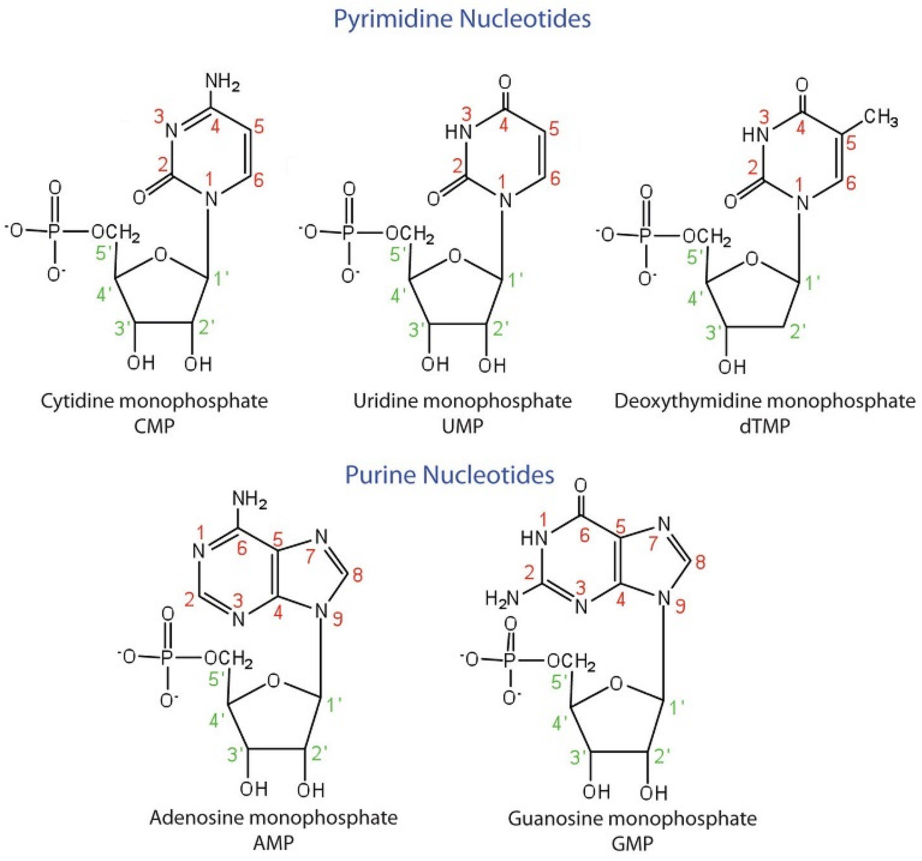


Figure 19.1.2: The Pyrimidine and Purine Nucleotides

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 19.1.3, 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.

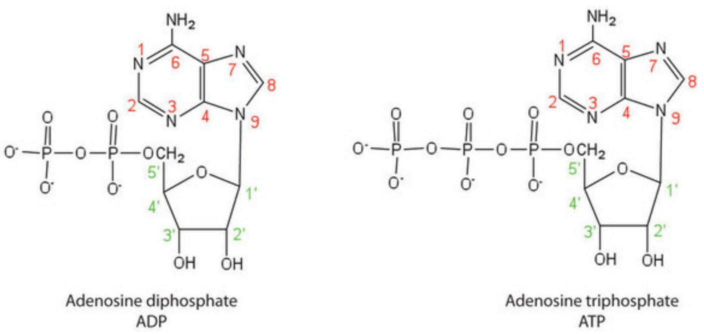


Figure 19.1.3: Structures of Two Important Adenine-Containing Nucleotides

Summary

Nucleotides are composed of phosphoric acid, a pentose sugar (ribose or deoxyribose), and a nitrogen-containing base (adenine, cytosine, guanine, thymine, or uracil). Ribonucleotides contain ribose, while deoxyribonucleotides contain deoxyribose.

19.2: Nucleic Acid Structure

Skills to Develop

- Identify the two types of nucleic acids and the function of each type.
- Describe how nucleotides are linked together to form nucleic acids.
- Describe the secondary structure of DNA and the importance of complementary base pairing.

Nucleic acids are large polymers formed by linking nucleotides together and are found in every cell. Deoxyribonucleic acid (DNA) is the nucleic acid that stores genetic information. If all the DNA in a typical mammalian cell were stretched out end to end, it would extend more than 2 m. Ribonucleic acid (RNA) is the nucleic acid responsible for using the genetic information encoded in DNA to produce the thousands of proteins found in living organisms.

Primary Structure of Nucleic Acids

Nucleotides are joined together through the phosphate group of one nucleotide connecting in an ester linkage to the OH group on the third carbon atom of the sugar unit of a second nucleotide. This unit joins to a third nucleotide, and the process is repeated to produce a long nucleic acid chain (Figure 19.2.1). The backbone of the chain consists of alternating phosphate and sugar units (2-deoxyribose in DNA and ribose in RNA). The purine and pyrimidine bases branch off this backbone.

> *Each phosphate group has one acidic hydrogen atom that is ionized at physiological pH. This is why these compounds are known as nucleic acids.*

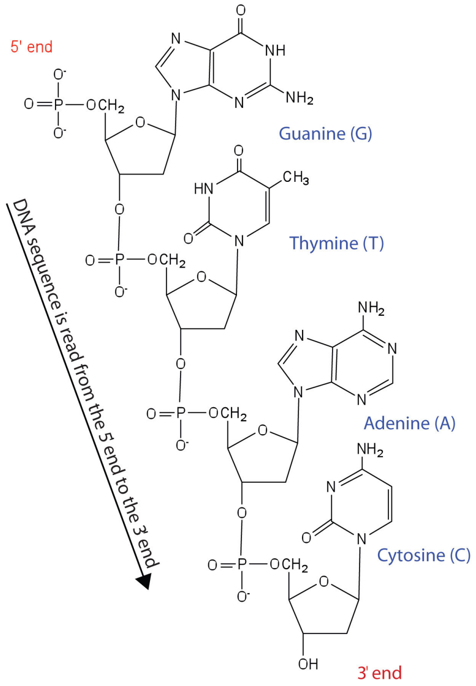


Figure 19.2.1 *Structure of a Segment of DNA. A similar segment of RNA would have OH groups on each C2', and uracil would replace thymine.*

Like proteins, nucleic acids have a primary structure that is defined as the sequence of their nucleotides. Unlike proteins, which have 20 different kinds of amino acids, there are only 4 different kinds of nucleotides in nucleic acids. For amino acid sequences in proteins, the convention is to write the amino acids in order starting with the N-terminal amino acid. In writing nucleotide sequences for nucleic acids, the convention is to write the nucleotides (usually using the one-letter abbreviations for the bases, shown in Figure 19.2.1) starting with the nucleotide having a free phosphate group, which is known as the 5′ end, and indicate the nucleotides in order. For DNA, a lowercase *d* is often written in front of the sequence to indicate that the monomers are deoxyribonucleotides. The final nucleotide has a free OH group on the 3′ carbon atom and is called the *3′ end*. The sequence of nucleotides in the DNA segment shown in Figure 19.2.1 would be written 5′-dG-dT-dA-dC-3′, which is often further abbreviated to dGTAC or just GTAC.

Secondary Structure of DNA

The three-dimensional structure of DNA was the subject of an intensive research effort in the late 1940s to early 1950s. Initial work revealed that the polymer had a regular repeating structure. In 1950, Erwin Chargaff of Columbia University showed that the molar amount of adenine (A) in DNA was always equal to that of thymine (T). Similarly, he showed that the molar amount of guanine (G) was the same as that of cytosine (C). Chargaff drew no conclusions from his work, but others soon did.

At Cambridge University in 1953, James D. Watson and Francis Crick announced that they had a model for the secondary structure of DNA. Using the information from Chargaff's experiments (as well as other experiments) and data from the X ray studies of Rosalind Franklin (which involved sophisticated chemistry, physics, and mathematics), Watson and Crick worked with models that were not unlike a child's construction set and finally concluded that DNA is composed of two nucleic acid chains running antiparallel to one another—that is, side-by-side with the 5′ end of one chain next to the 3′ end of the other. Moreover, as their model showed, the two chains are twisted to form a double helix—a structure that can be compared to a spiral staircase, with the phosphate and sugar groups (the backbone of the nucleic acid polymer) representing the outside edges of the staircase. The purine and pyrimidine bases face the inside of the helix, with guanine always opposite cytosine and adenine always opposite thymine. These specific base pairs, referred to as complementary bases, are the steps, or treads, in our staircase analogy (Figure 19.2.2).

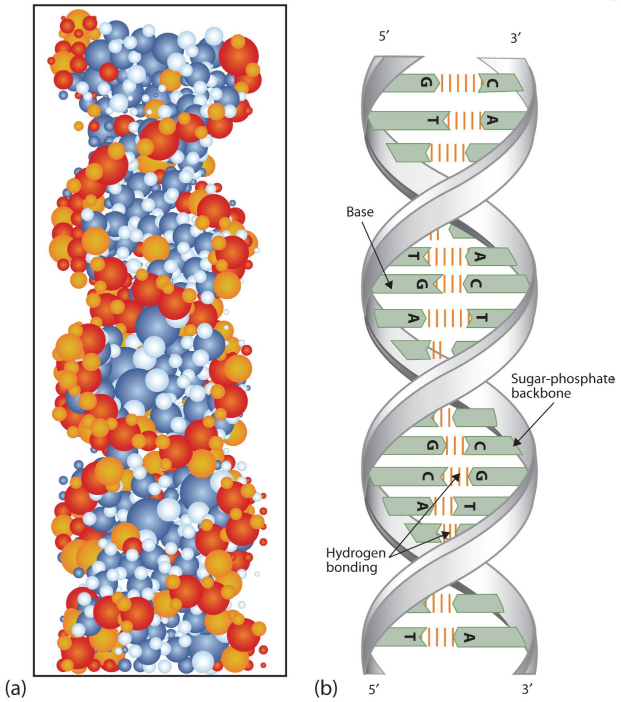


Figure 19.2.2 *DNA Double Helix. (a) This represents a computer-generated model of the DNA double helix. (b) This represents a schematic representation of the double helix, showing the complementary bases.*

The structure proposed by Watson and Crick provided clues to the mechanisms by which cells are able to divide into two identical, functioning daughter cells; how genetic data are passed to new generations; and even how proteins are built to required specifications. All these abilities depend on the pairing of complementary bases. Figure 19.2.3 shows the two sets of base pairs and illustrates two things. First, a pyrimidine is paired with a purine in each case, so that the long dimensions of both pairs are identical (1.08 nm).

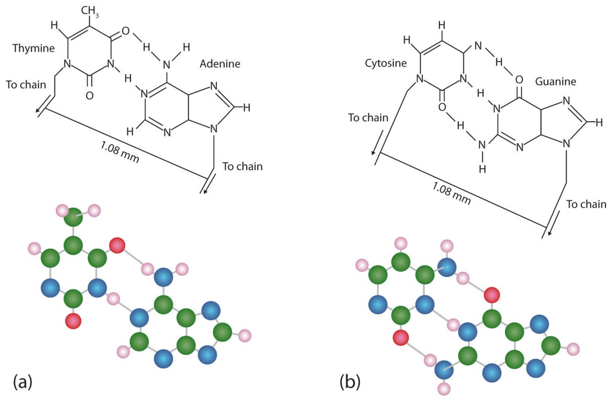


Figure **19.2.3** *Complementary Base Pairing. Complementary bases engage in hydrogen bonding with one another: (a) thymine and adenine; (b) cytosine and guanine.*

If two pyrimidines were paired or two purines were paired, the two pyrimidines would take up less space than a purine and a pyrimidine, and the two purines would take up more space, as illustrated in Figure 19.2.4 If these pairings were ever to occur, the structure of DNA would be like a staircase made with stairs of different widths. For the two strands of the double helix to fit neatly, a pyrimidine must always be paired with a purine. The second thing you should notice in Figure 19.2.3 is that the correct pairing enables formation of three instances of hydrogen bonding between guanine and cytosine and two between adenine and thymine. The additive contribution of this hydrogen bonding imparts great stability to the DNA double helix.

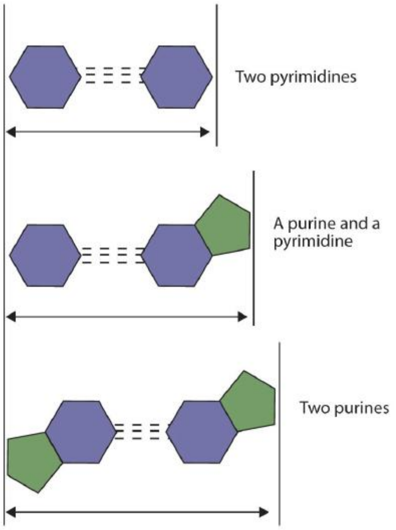


Figure **19.2.4** *Difference in Widths of Possible Base Pairs*

Summary

- DNA is the nucleic acid that stores genetic information. RNA is the nucleic acid responsible for using the genetic information in DNA to produce proteins.
- Nucleotides are joined together to form nucleic acids through the phosphate group of one nucleotide connecting in an ester linkage to the OH group on the third carbon atom of the sugar unit of a second nucleotide.
- Nucleic acid sequences are written starting with the nucleotide having a free phosphate group (the 5′ end).
- Two DNA strands link together in an antiparallel direction and are twisted to form a double helix. The nitrogenous bases face the inside of the helix. Guanine is always opposite cytosine, and adenine is always opposite thymine.

Concept Review Exercises

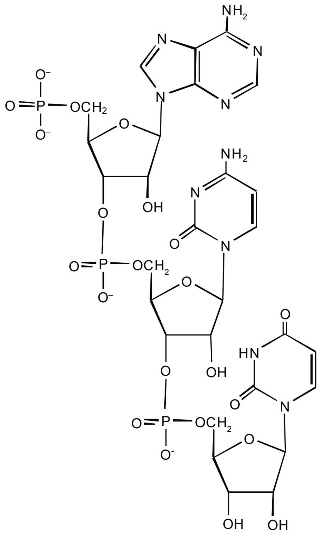
1.
   a. Name the two kinds of nucleic acids.
   b. Which type of nucleic acid stores genetic information in the cell?
2. What are complementary bases?
3. Why is it structurally important that a purine base always pair with a pyrimidine base in the DNA double helix?

Answers

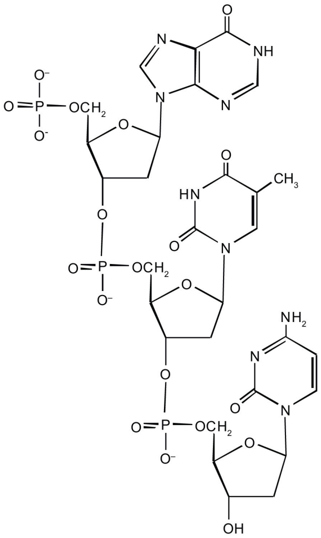
1.
   a. deoxyribonucleic acid (DNA) and ribonucleic acid (RNA)
   b. DNA
2. the specific base pairings in the DNA double helix in which guanine is paired with cytosine and adenine is paired with thymine
3. The width of the DNA double helix is kept at a constant width, rather than narrowing (if two pyrimidines were across from each other) or widening (if two purines were across from each other).

Exercises

1. For this short RNA segment,
   a. identify the 5′ end and the 3′ end of the molecule.
   b. circle the atoms that comprise the backbone of the nucleic acid chain.
   c. write the nucleotide sequence of this RNA segment.



2. For this short DNA segment,
   a. identify the 5′ end and the 3′ end of the molecule.
   b. circle the atoms that comprise the backbone of the nucleic acid chain.
   c. write the nucleotide sequence of this DNA segment.

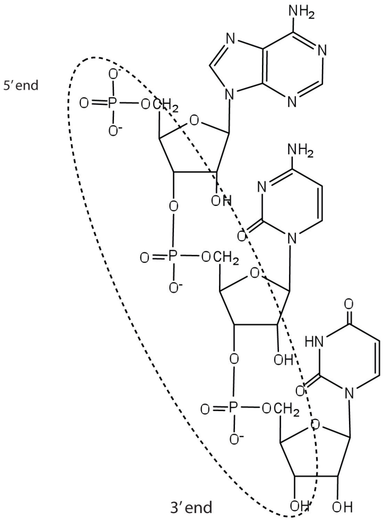


3. Which nitrogenous base in DNA pairs with each nitrogenous base?
    - a. cytosine
    - b. adenine
    - c. guanine
    - d. thymine
4. Which nitrogenous base in RNA pairs with each nitrogenous base?
    - a. cytosine
    - b. adenine
    - c. guanine
    - d. thymine
5. How many hydrogen bonds can form between the two strands in the short DNA segment shown below?

   5′ ATGCGACTA 3′ 3′ TACGCTGAT 5′
6. How many hydrogen bonds can form between the two strands in the short DNA segment shown below?

   5′ CGATGAGCC 3′ 3′ GCTACTCGG 5′

Answers



1. c. ACU

3.

   a. guanine
   b. thymine
   c. cytosine
   d. adenine

5. 22 (2 between each AT base pair and 3 between each GC base pair)

19.3: Replication and Expression of Genetic Information

Learning Objectives

- Describe how a new copy of DNA is synthesized.
- Describe how RNA is synthesized from DNA.
- Identify the different types of RNA and the function of each type of RNA.

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.

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 19.3.1). 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.

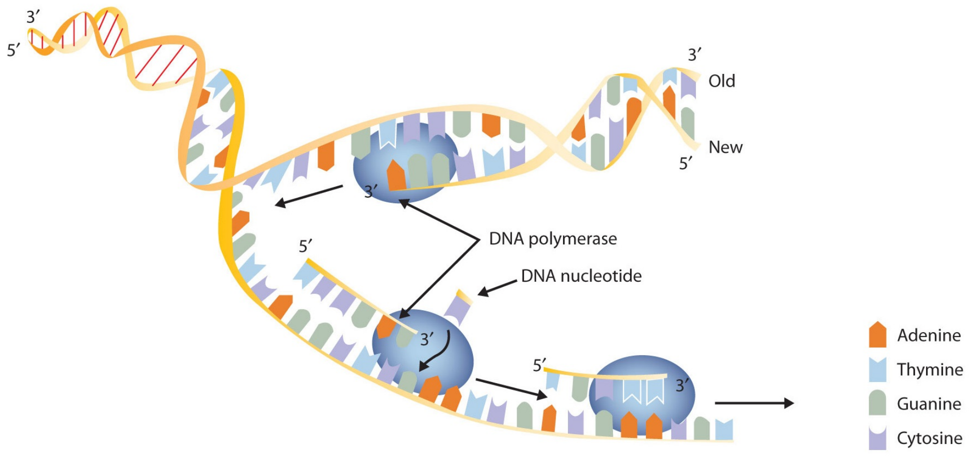


Figure 19.3.1: A Schematic Diagram of DNA Replication. DNA replication occurs by the sequential unzipping of segments of the double helix. Each new nucleotide is brought into position by DNA polymerase and is added to the growing strand by the formation of a phosphate ester bond. Thus, two double helixes 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 19.3.1

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′ (can also be written as TCAACTCATGGA).

? Exercise 19.3.1

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?

What do we mean when we say information is encoded in the DNA molecule? An organism's DNA can be compared to a book containing directions for assembling a model airplane or for knitting a sweater. Letters of the alphabet are arranged into words, and these words direct the individual to perform certain operations with specific materials. If all the directions are followed correctly, a model airplane or sweater is produced.

In DNA, the particular sequences of nucleotides along the chains encode the directions for building an organism. Just as *saw* means one thing in English and *was* means another, the sequence of bases CGT means one thing, and TGC means something different. Although there are only four letters—the four nucleotides—in the genetic code of DNA, their sequencing along the DNA strands can vary so widely that information storage is essentially unlimited.

Transcription

For the hereditary information in DNA to be useful, it must be "expressed," that is, used to direct the growth and functioning of an organism. The first step in the processes that constitute DNA expression is the synthesis of RNA, by a template mechanism that is in many ways analogous to DNA replication. Because the RNA that is synthesized is a complementary copy of information contained in DNA, RNA synthesis is referred to as transcription. There are three key differences between replication and transcription:

1. RNA molecules are much shorter than DNA molecules; only a portion of one DNA strand is copied or transcribed to make an RNA molecule.
2. RNA is built from ribonucleotides rather than deoxyribonucleotides.
3. The newly synthesized RNA strand does not remain associated with the DNA sequence it was transcribed from.

The DNA sequence that is transcribed to make RNA is called the *template strand*, while the complementary sequence on the other DNA strand is called the *coding* or *informational strand*. To initiate RNA synthesis, the two DNA strands unwind at specific sites along the DNA molecule. Ribonucleotides are attracted to the uncoiling region of the DNA molecule, beginning at the 3′ end of the template strand, according to the rules of base pairing. Thymine in DNA calls for adenine in RNA, cytosine specifies guanine, guanine calls for cytosine, and adenine requires uracil. RNA polymerase—an enzyme—binds the complementary ribonucleotide and catalyzes the formation of the ester linkage between ribonucleotides, a reaction very similar to that catalyzed by DNA polymerase (Figure $19.3.2$). Synthesis of the RNA strand takes place in the 5′ to 3′ direction, antiparallel to the template strand. Only a short segment of the RNA molecule is hydrogen-bonded to the template strand at any time during transcription. When transcription is completed, the RNA is released, and the DNA helix reforms. The nucleotide sequence of the RNA strand formed during transcription is identical to that of the corresponding coding strand of the DNA, except that U replaces T.

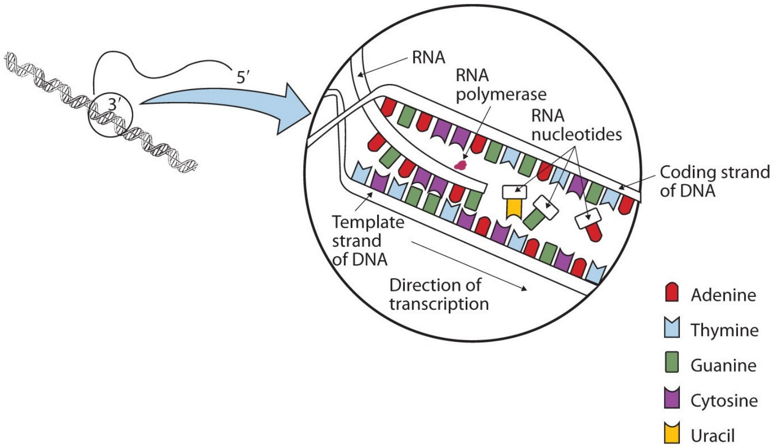


Figure 19.3.2: A Schematic Diagram of RNA Transcription from a DNA Template. The representation of RNA polymerase is proportionately much smaller than the actual molecule, which encompasses about 50 nucleotides at a time.

✓ Example 19.3.2

A portion of the template strand of a gene has the sequence 5′-TCCATGAGTTGA-3′. What is the sequence of nucleotides in the RNA that is formed from this template?

Solution

Four things must be remembered in answering this question: (1) the DNA strand and the RNA strand being synthesized are antiparallel; (2) RNA is synthesized in a 5′ to 3′ direction, so transcription begins at the 3′ end of the template strand; (3) ribonucleotides are used in place of deoxyribonucleotides; and (4) thymine (T) base pairs with adenine (A), A base pairs with uracil (U; in RNA), and cytosine (C) base pairs with guanine (G). The sequence is determined to be 3′-AGGUACUCAACU-5′ (can also be written as 5′-UCAACUCAUGGA-3′).

? Exercise 19.3.2

A portion of the template strand of a gene has the sequence 5′-CCAGTGAATTGCCTAT-3′. What is the sequence of nucleotides in the RNA that is formed from this template?

Three types of RNA are formed during transcription: *messenger RNA* (mRNA), *ribosomal RNA* (rRNA), and *transfer RNA* (tRNA). These three types of RNA differ in function, size, and percentage of the total cell RNA (Table 19.3.1). mRNA makes up only a small percent of the total amount of RNA within the cell, primarily because each molecule of mRNA exists for a relatively short time; it is continuously being degraded and resynthesized. The molecular dimensions of the mRNA molecule vary according to the amount of genetic information a given molecule contains. After transcription, which takes place in the nucleus, the mRNA passes into the cytoplasm, carrying the genetic message from DNA to the ribosomes, the sites of protein synthesis. Elsewhere, we shall see how mRNA directly determines the sequence of amino acids during protein synthesis.

Table 19.3.1: Properties of Cellular RNA in Escherichia coli

Type	Function	Approximate Number of Nucleotides	Percentage of Total Cell RNA
mRNA	codes for proteins	100–6,000	~3
rRNA	component of ribosomes	120–2900	83
tRNA	adapter molecule that brings the amino acid to the ribosome	75–90	14

Ribosomes are cellular substructures where proteins are synthesized. They contain about 65% rRNA and 35% protein, held together by numerous noncovalent interactions, such as hydrogen bonding, in an overall structure consisting of two globular particles of unequal size.

Molecules of tRNA, which bring amino acids (one at a time) to the ribosomes for the construction of proteins, differ from one another in the kinds of amino acid each is specifically designed to carry. A set of three nucleotides, known as a codon, on the mRNA determines which kind of tRNA will add its amino acid to the growing chain. Each of the 20 amino acids found in proteins has at least one corresponding kind of tRNA, and most amino acids have more than one.

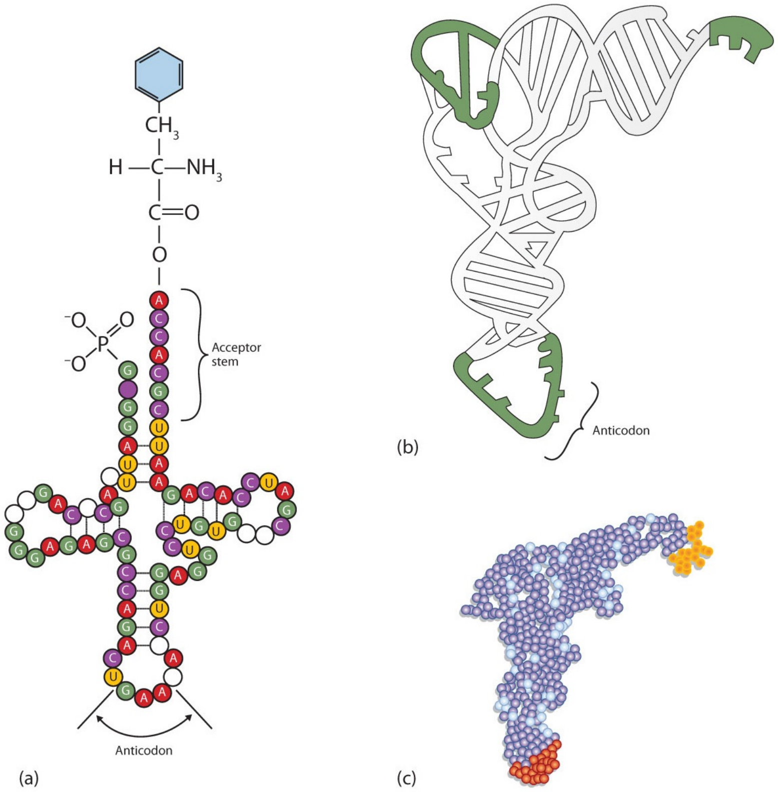


Figure 19.3.3: Transfer RNA. (a) In the two-dimensional structure of a yeast tRNA molecule for phenylalanine, the amino acid binds to the acceptor stem located at the 3′ end of the tRNA primary sequence. (The nucleotides that are not specifically identified here are slightly altered analogs of the four common ribonucleotides A, U, C, and G.) (b) In the three-dimensional structure of yeast phenylalanine tRNA, note that the anticodon loop is at the bottom and the acceptor stem is at the top right. (c) This shows a space-filling model of the tRNA.

The two-dimensional structure of a tRNA molecule has three distinctive loops, reminiscent of a cloverleaf (Figure 19.3.3). On one loop is a sequence of three nucleotides that varies for each kind of tRNA. This triplet, called the anticodon, is complementary to and pairs with the codon on the mRNA. At the opposite end of the molecule is the acceptor stem, where the amino acid is attached.

Summary

- 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.
- 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.
- Three types of RNA are formed during transcription: mRNA, rRNA, and tRNA.

19.4: 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 VCell, NDSU(opens in new window) [vcell.ndsu.nodak.edu]*

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.

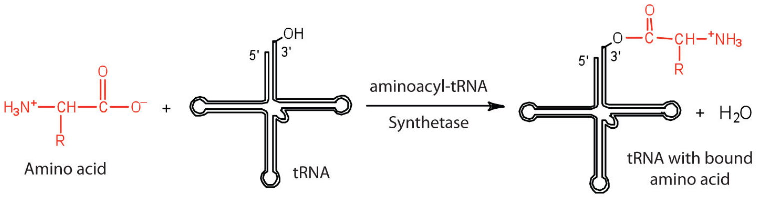


Figure 19.4.1: Binding of an Amino Acid to Its tRNA

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 19.4.1). 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 19.4.2 depicts a schematic stepwise representation of this all-important process.

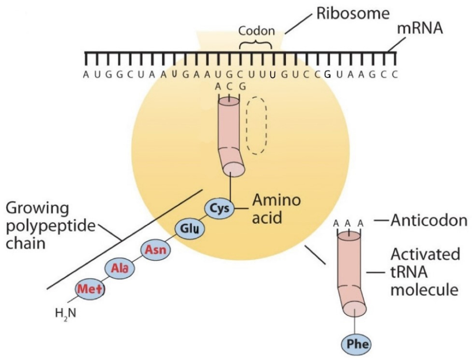


Figure 19.4.2*a*: The Elongation Steps in Protein Synthesis - Protein synthesis is already in progress at the ribosome. The growing polypeptide chain is attached to the tRNA that brought in the previous amino acid (in this illustration, cys.)

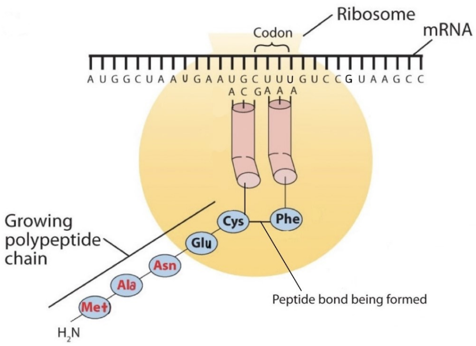


Figure 19.4.2*b*: The Elongation Steps in Protein Synthesis - An activated tRNA, which has the anticodon AAA, binds to the ribosome next to the previous bound tRNA and interacts with the mRNA molecule though basepairing of the codon and anticodon. The amino acid Phe is being incorporated into the polypeptide 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.

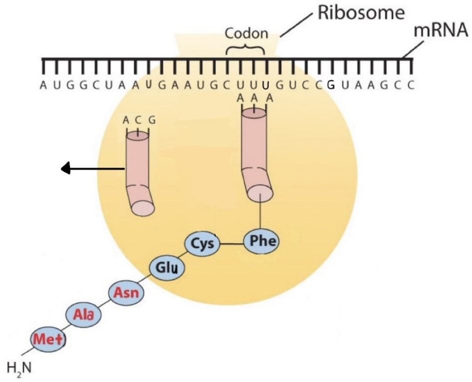


Figure 19.4.2*c*: The Elongation Steps in Protein Synthesis - The Cys-Phe linkage is now complete, and the growing polypeptide chain remains attached to the tRNA for Phe.

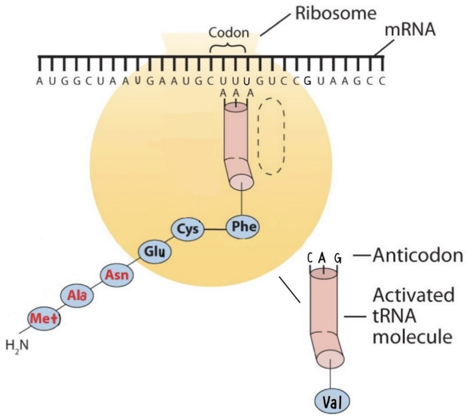
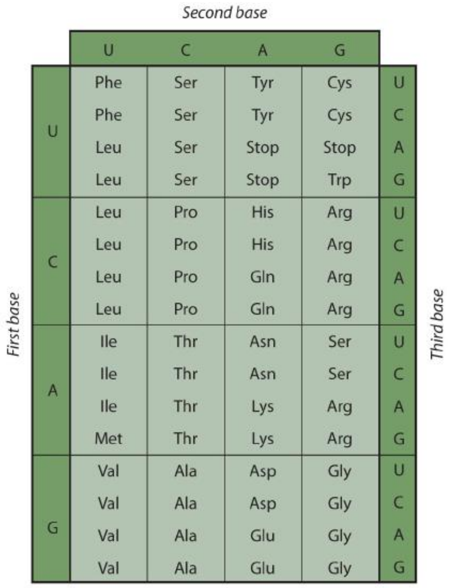


Figure 19.4.2*d*: The Elongation Steps in Protein Synthesis - The ribosome moves to the right along the mRNA strand. This shift brings the next codon, GUC, into its correct position on the surface of the ribosome. Note that an activated tRNA molecule, containing the next amino acid to be attached to the chain is moving to the ribosome. Steps (b)-(d) will be repeated until the ribosome reaches a stop codon.

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 19.4.3, 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.



	Second base				
First base	U	C	A	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 19.4.3: The Genetic Code

✓ Example 19.4.1: 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 19.4.3 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 19.4.4

A portion of an RNA molecule has the sequence 5′-AUGCUGAAUUGCGUAGGA-3′. What amino acid sequence does this code for?

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 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.

19.5: Mutations and Genetic Diseases

Learning Objectives

- To describe the causes of genetic mutations and how they lead to genetic diseases.

We have seen that the sequence of nucleotides in a cell's deoxyribonucleic acid (DNA) is what ultimately determines the sequence of amino acids in proteins made by the cell and thus is critical for the proper functioning of the cell. On rare occasions, however, the nucleotide sequence in DNA may be modified either spontaneously (by errors during replication, occurring approximately once for every 10 billion nucleotides) or from exposure to heat, radiation, or certain chemicals. Any chemical or physical change that alters the nucleotide sequence in DNA is called a mutation. When a mutation occurs in an egg or sperm cell that then produces a living organism, it will be inherited by all the offspring of that organism.

Common types of mutations include **substitution** (a different nucleotide is substituted), **insertion** (the addition of a new nucleotide), and **deletion** (the loss of a nucleotide). These changes within DNA are called point mutations because only one nucleotide is substituted, added, or deleted (Figure $19.5.1$). Because an insertion or deletion results in a frame-shift that changes the reading of subsequent codons and, therefore, alters the entire amino acid sequence that follows the mutation, insertions and deletions are usually more harmful than a substitution in which only a single amino acid is altered.

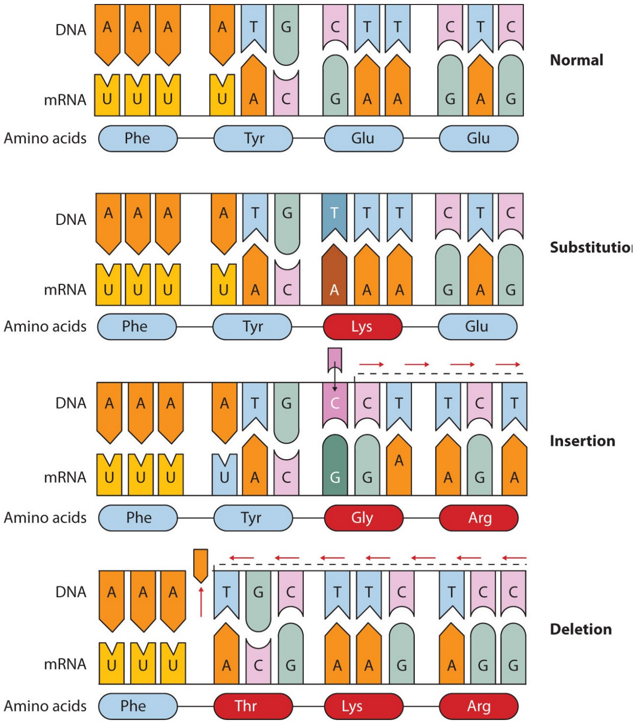


Figure $19.5.1$: Three Types of Point Mutations

The chemical or physical agents that cause mutations are called mutagens. Examples of physical mutagens are ultraviolet (UV) and gamma radiation. Radiation exerts its mutagenic effect either directly or by creating free radicals that in turn have mutagenic effects. Radiation and free radicals can lead to the formation of bonds between nitrogenous bases in DNA. For example, exposure to UV light can result in the formation of a covalent bond between two adjacent thymines on a DNA strand, producing a thymine dimer (Figure $19.5.2$). If not repaired, the dimer prevents the formation of the double helix at the point where it occurs. The genetic disease *xeroderma pigmentosum* is caused by a lack of the enzyme that cuts out the thymine dimers in damaged DNA. Individuals affected by this condition are abnormally sensitive to light and are more prone to skin cancer than normal individuals.

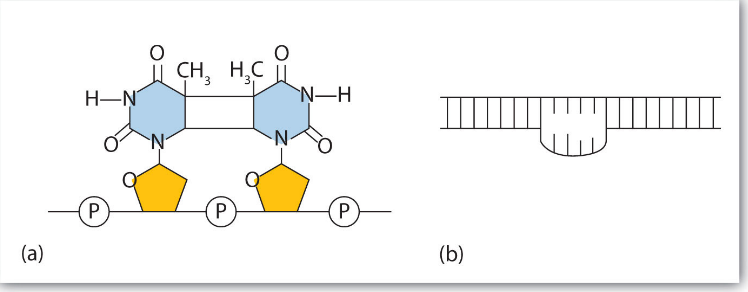


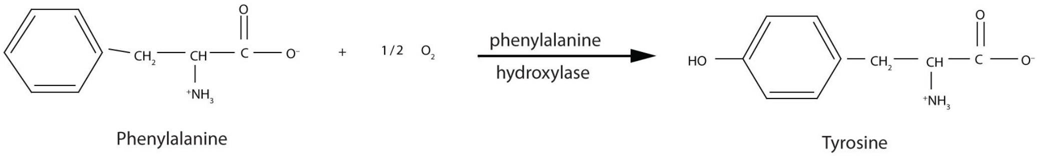
Figure 19.5.2: An Example of Radiation Damage to DNA. (a) The thymine dimer is formed by the action of UV light. (b) When a defect in the double strand is produced by the thymine dimer, this defect temporarily stops DNA replication, but the dimer can be removed, and the region can be repaired by an enzyme repair system.

Sometimes gene mutations are beneficial, but most of them are detrimental. For example, if a point mutation occurs at a crucial position in a DNA sequence, the affected protein will lack biological activity, perhaps resulting in the death of a cell. In such cases the altered DNA sequence is lost and will not be copied into daughter cells. Nonlethal mutations in an egg or sperm cell may lead to metabolic abnormalities or hereditary diseases. Such diseases are called *inborn errors of metabolism* or genetic diseases. A partial listing of genetic diseases is presented in Figure 19.5.1, and two specific diseases are discussed in the following sections. In most cases, the defective gene results in a failure to synthesize a particular enzyme.

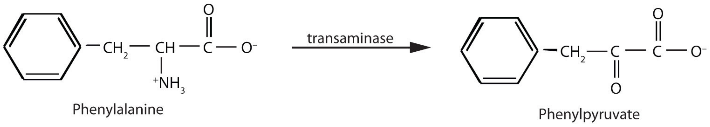
Figure 19.5.1: Some Representative Genetic Diseases in Humans and the Protein or Enzyme Responsible

Disease	Responsible Protein or Enzyme
alkaptonuria	homogentisic acid oxidase
galactosemia	galactose 1-phosphate uridyl transferase, galactokinase, or UDP galactose epimerase
Gaucher disease	glucocerebrosidase
gout and Lesch-Nyhan syndrome	hypoxanthine-guanine phosphoribosyl transferase
hemophilia	antihemophilic factor (factor VIII) or Christmas factor (factor IX)
homocystinuria	cystathionine synthetase
maple syrup urine disease	branched chain α-keto acid dehydrogenase complex
McArdle syndrome	muscle phosphorylase
Niemann-Pick disease	sphingomyelinase
phenylketonuria (PKU)	phenylalanine hydroxylase
sickle cell anemia	hemoglobin
Tay-Sachs disease	hexosaminidase A
tyrosinemia	fumarylacetoacetate hydrolase or tyrosine aminotransferase
von Gierke disease	glucose 6-phosphatase
Wilson disease	Wilson disease protein

PKU results from the absence of the enzyme phenylalanine hydroxylase. Without this enzyme, a person cannot convert phenylalanine to tyrosine, which is the precursor of the neurotransmitters dopamine and norepinephrine as well as the skin pigment melanin.



When this reaction cannot occur, phenylalanine accumulates and is then converted to higher than normal quantities of phenylpyruvate. The disease acquired its name from the high levels of phenylpyruvate (a phenyl ketone) in urine. Excessive amounts of phenylpyruvate impair normal brain development, which causes severe mental retardation.



PKU may be diagnosed by assaying a sample of blood or urine for phenylalanine or one of its metabolites. Medical authorities recommend testing every newborn's blood for phenylalanine within 24 h to 3 weeks after birth. If the condition is detected, mental retardation can be prevented by immediately placing the infant on a diet containing little or no phenylalanine. Because phenylalanine is plentiful in naturally produced proteins, the low-phenylalanine diet depends on a synthetic protein substitute plus very small measured amounts of naturally produced foods. Before dietary treatment was introduced in the early 1960s, severe mental retardation was a common outcome for children with PKU. Prior to the 1960s, 85% of patients with PKU had an intelligence quotient (IQ) less than 40, and 37% had IQ scores below 10. Since the introduction of dietary treatments, however, over 95% of children with PKU have developed normal or near-normal intelligence. The incidence of PKU in newborns is about 1 in 12,000 in North America.

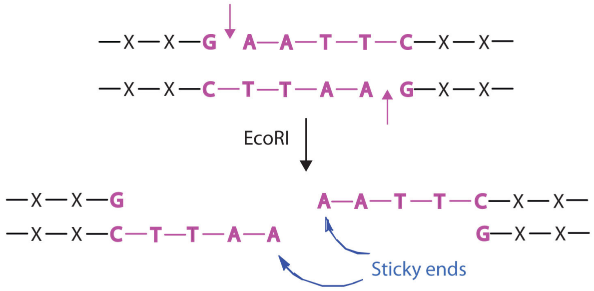
> *Every state in the United States has mandated that screening for PKU be provided to all newborns.*

Several genetic diseases are collectively categorized as *lipid-storage diseases*. Lipids are constantly being synthesized and broken down in the body, so if the enzymes that catalyze lipid degradation are missing, the lipids tend to accumulate and cause a variety of medical problems. When a genetic mutation occurs in the gene for the enzyme hexosaminidase A, for example, gangliosides cannot be degraded but accumulate in brain tissue, causing the ganglion cells of the brain to become greatly enlarged and nonfunctional. This genetic disease, known as *Tay-Sachs disease*, leads to a regression in development, dementia, paralysis, and blindness, with death usually occurring before the age of three. There is currently no treatment, but Tay-Sachs disease can be diagnosed in a fetus by assaying the amniotic fluid (amniocentesis) for hexosaminidase A. A blood test can identify Tay-Sachs carriers—people who inherit a defective gene from only one rather than both parents—because they produce only half the normal amount of hexosaminidase A, although they do not exhibit symptoms of the disease.

Looking Closer: Recombinant DNA Technology

More than 3,000 human diseases have been shown to have a genetic component, caused or in some way modulated by the person's genetic composition. Moreover, in the last decade or so, researchers have succeeded in identifying many of the genes and even mutations that are responsible for specific genetic diseases. Now scientists have found ways of identifying and isolating genes that have specific biological functions and placing those genes in another organism, such as a bacterium, which can be easily grown in culture. With these techniques, known as *recombinant DNA technology*, the ability to cure many serious genetic diseases appears to be within our grasp.

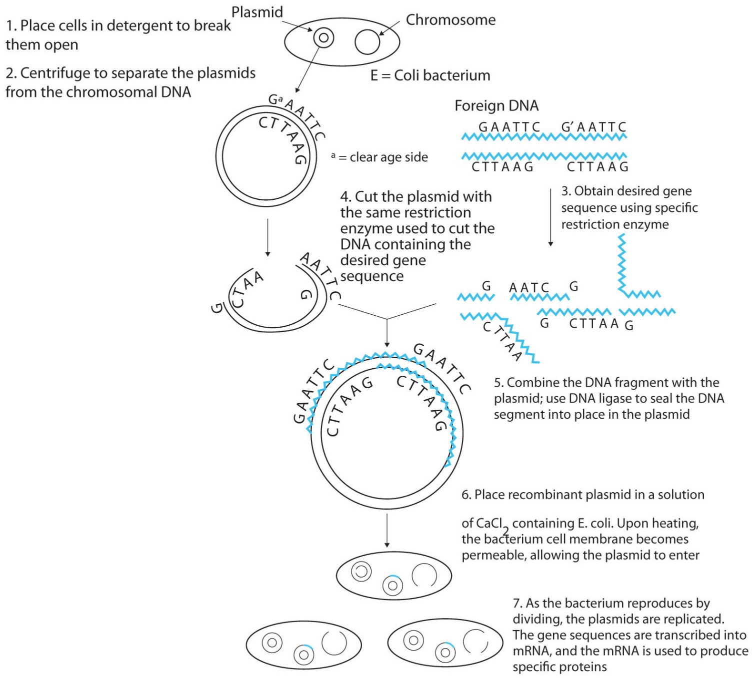
Isolating the specific gene or genes that cause a particular genetic disease is a monumental task. One reason for the difficulty is the enormous amount of a cell's DNA, only a minute portion of which contains the gene sequence. Thus, the first task is to obtain smaller pieces of DNA that can be more easily handled. Fortunately, researchers are able to use *restriction enzymes* (also known as restriction endonucleases), discovered in 1970, which are enzymes that cut DNA at specific, known nucleotide sequences, yielding DNA fragments of shorter length. For example, the restriction enzyme *EcoRI* recognizes the nucleotide sequence shown here and cuts both DNA strands as indicated:



Once a DNA strand has been fragmented, it must be cloned; that is, multiple identical copies of each DNA fragment are produced to make sure there are sufficient amounts of each to detect and manipulate in the laboratory. Cloning is accomplished by inserting the individual DNA fragments into phages (bacterial viruses) that can enter bacterial cells and be replicated. When a bacterial cell infected by the modified phage is placed in an appropriate culture medium, it forms a colony of cells, all containing copies of the original DNA fragment. This technique is used to produce many bacterial colonies, each containing a different DNA fragment. The result is a *DNA library*, a collection of bacterial colonies that together contain the entire genome of a particular organism.

The next task is to screen the DNA library to determine which bacterial colony (or colonies) has incorporated the DNA fragment containing the desired gene. A short piece of DNA, known as a *hybridization probe*, which has a nucleotide sequence complementary to a known sequence in the gene, is synthesized, and a radioactive phosphate group is added to it as a "tag." You might be wondering how researchers are able to prepare such a probe if the gene has not yet been isolated. One way is to use a segment of the desired gene isolated from another organism. An alternative method depends on knowing all or part of the amino acid sequence of the protein produced by the gene of interest: the amino acid sequence is used to produce an approximate genetic code for the gene, and this nucleotide sequence is then produced synthetically. (The amino acid sequence used is carefully chosen to include, if possible, many amino acids such as methionine and tryptophan, which have only a single codon each.)

After a probe identifies a colony containing the desired gene, the DNA fragment is clipped out, again using restriction enzymes, and spliced into another replicating entity, usually a plasmid. *Plasmids* are tiny mini-chromosomes found in many bacteria, such as *Escherichia coli* (*E. coli*). A recombined plasmid would then be inserted into the host organism (usually the bacterium *E. coli*), where it would go to work to produce the desired protein.



Proponents of recombinant DNA research are excited about its great potential benefits. An example is the production of human growth hormone, which is used to treat children who fail to grow properly. Formerly, human growth hormone was available only in tiny amounts obtained from cadavers. Now it is readily available through recombinant DNA technology. Another gene that has been cloned is the gene for epidermal growth factor, which stimulates the growth of skin cells and can be used to speed the healing of burns and other skin wounds. Recombinant techniques are also a powerful research tool, providing enormous aid to scientists as they map and sequence genes and determine the functions of different segments of an organism's DNA.

In addition to advancements in the ongoing treatment of genetic diseases, recombinant DNA technology may actually lead to cures. When appropriate genes are successfully inserted into *E. coli*, the bacteria can become miniature pharmaceutical factories, producing great quantities of insulin for people with diabetes, clotting factor for people with hemophilia, missing enzymes, hormones, vitamins, antibodies, vaccines, and so on. Recent accomplishments include the production in *E. coli* of recombinant DNA molecules containing synthetic genes for tissue plasminogen activator, a clot-dissolving enzyme that can rescue heart attack victims, as well as the production of vaccines against hepatitis B (humans) and hoof-and-mouth disease (cattle).

Scientists have used other bacteria besides *E. coli* in gene-splicing experiments and also yeast and fungi. Plant molecular biologists use a bacterial plasmid to introduce genes for several foreign proteins (including animal proteins) into plants. The bacterium is *Agrobacterium tumefaciens*, which can cause tumors in many plants, but which can be treated so that its tumor-causing ability is eliminated. One practical application of its plasmids would be to enhance a plant's nutritional value by transferring into it the gene necessary for the synthesis of an amino acid in which the plant is normally deficient (for example, transferring the gene for methionine synthesis into pinto beans, which normally do not synthesize high levels of methionine).

> Restriction enzymes have been isolated from a number of bacteria and are named after the bacterium of origin. *EcoRI* is a restriction enzyme obtained from the R strain of *E. coli*. The roman numeral I indicates that it was the first restriction enzyme obtained from this strain of bacteria.

Summary

- The nucleotide sequence in DNA may be modified either spontaneously or from exposure to heat, radiation, or certain chemicals and can lead to mutations.
- Mutagens are the chemical or physical agents that cause mutations.
- Genetic diseases are hereditary diseases that occur because of a mutation in a critical gene.

19.6: Viruses

Learning Objectives

- To explain how viruses reproduce in cells.

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 $19.6.1$).

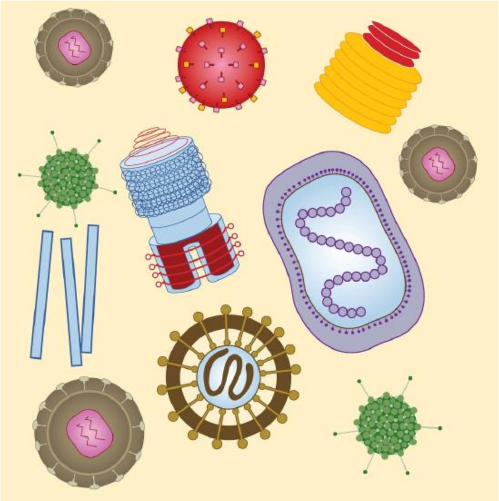


Figure 19.6.1: Viruses. Viruses come in a variety of shapes that are determined by their protein coats.

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 $19.6.2$), 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.

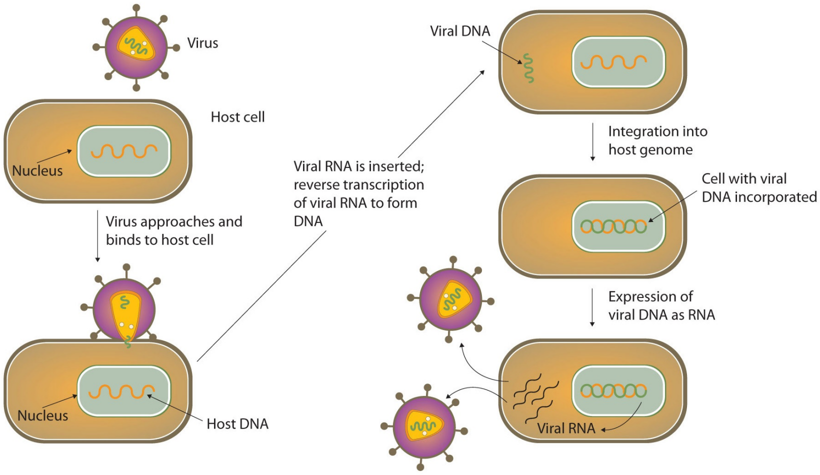
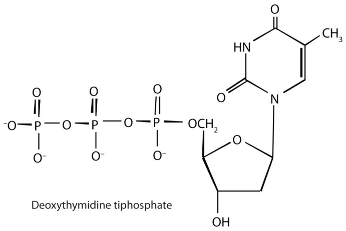
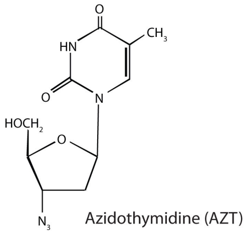


Figure 19.6.2: Life Cycle of a Retrovirus

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.

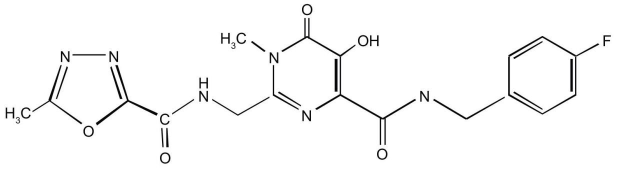


Deoxythymidine tiphosphate



Azidothymidine (AZT)

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.

✓ Career Focus: Genetics Counselor

A genetics counselor works with individuals and families who have birth defects or genetic disorders or a family history of a disease, such as cancer, with a genetic link. A genetics counselor may work in a variety of health-care settings (such as a hospital) to obtain family medical and reproductive histories; explain how genetic conditions are inherited; explain the causes, diagnosis, and care of these conditions; interpret the results of genetic tests; and aid the individual or family in making decisions regarding genetic diseases or conditions. A certified genetics counselor must obtain a master’s degree from an accredited program. Applicants to these graduate programs usually have an undergraduate degree in biology, psychology, or genetics.

Photo courtesy of the United States National Institutes for Health, commons.wikimedia.org/wiki/File:Geneticcounseling.jpg.

Summary

Viruses are very small infectious agents that contain either DNA or RNA as their genetic material. The human immunodeficiency virus (HIV) causes acquired immunodeficiency syndrome (AIDS).

19.E: Nucleic Acids (Exercises)

19.1: Nucleotides

Concept Review Exercises

1. Identify the three molecules needed to form the nucleotides in each nucleic acid.
   a. DNA
   b. RNA
2. Classify each compound as a pentose sugar, a purine, or a pyrimidine.
   a. adenine
   b. guanine
   c. deoxyribose
   d. thymine
   e. ribose
   f. cytosine

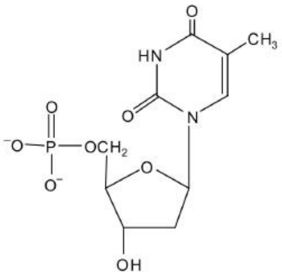
Answers

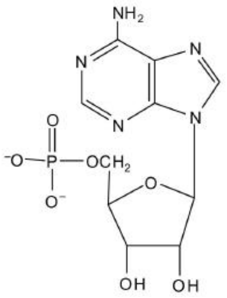
1. a. nitrogenous base (adenine, guanine, cytosine, and thymine), 2-deoxyribose, and H_3PO_4
   b. nitrogenous base (adenine, guanine, cytosine, and uracil), ribose, and H_3PO_4
2. a. purine
   b. purine
   c. pentose sugar
   d. pyrimidine
   e. pentose sugar
   f. pyrimidine

Exercises

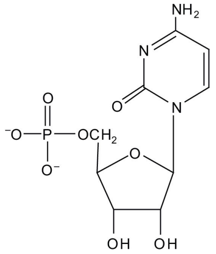
1. What is the sugar unit in each nucleic acid?
   a. RNA
   b. DNA
2. Identify the major nitrogenous bases in each nucleic acid.
   a. DNA
   b. RNA
3. For each structure, circle the sugar unit and identify the nucleotide as a ribonucleotide or a deoxyribonucleotide.

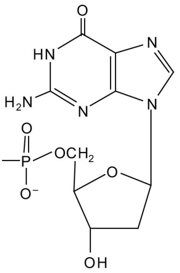
a.



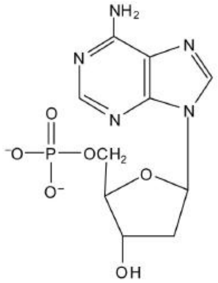
b. 

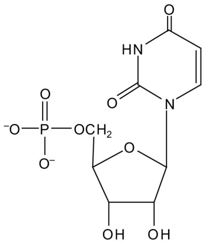
4. For each structure, circle the sugar unit and identify the nucleotide as a ribonucleotide or a deoxyribonucleotide.

a. 

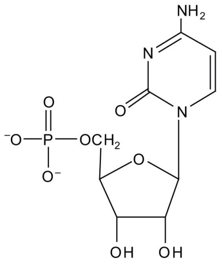
b. 

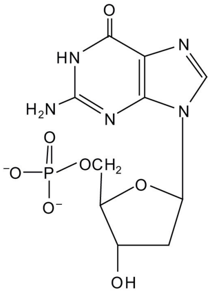
5. For each structure, circle the nitrogenous base and identify it as a purine or pyrimidine.

a. 

b. 

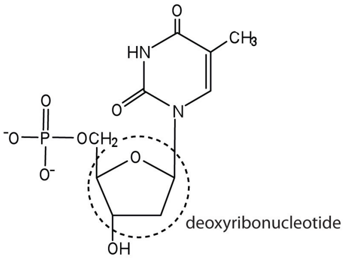
6. For each structure, circle the nitrogenous base and identify it as a purine or pyrimidine.

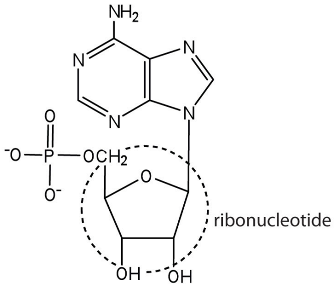
a. 

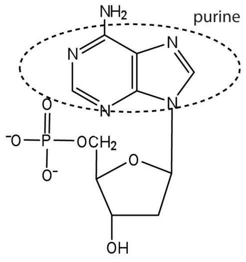
b. 

Answers

1. a. ribose
   b. deoxyribose

3. a. 

   b. 

a. 

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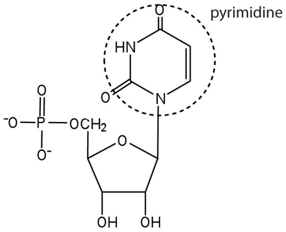


19.2: Nucleic Acid Structure

Concept Review Exercises

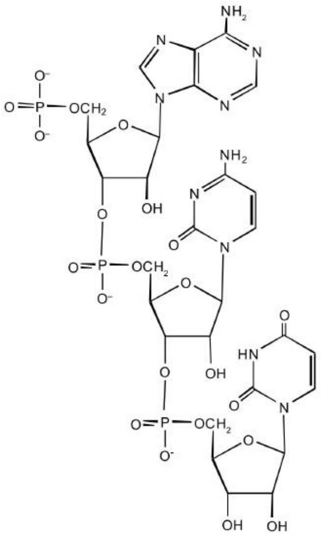
1. a. Name the two kinds of nucleic acids.
   b. Which type of nucleic acid stores genetic information in the cell?
2. What are complementary bases?
3. Why is it structurally important that a purine base always pair with a pyrimidine base in the DNA double helix?

Answers

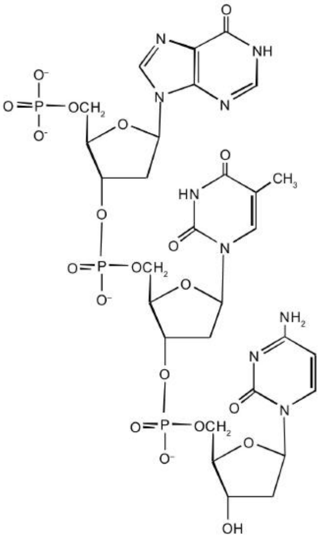
1. a. deoxyribonucleic acid (DNA) and ribonucleic acid (RNA)
   b. DNA
2. the specific base pairings in the DNA double helix in which guanine is paired with cytosine and adenine is paired with thymine
3. The width of the DNA double helix is kept at a constant width, rather than narrowing (if two pyrimidines 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.



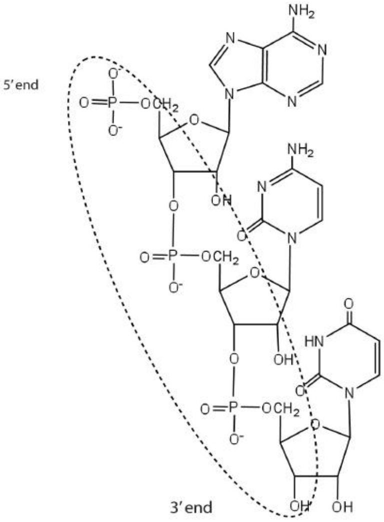
3. Which nitrogenous base in DNA pairs with each nitrogenous base?
   a. cytosine
   b. adenine
   c. guanine
   d. thymine
4. Which nitrogenous base in RNA pairs with each nitrogenous base?
   a. cytosine
   b. adenine
   c. guanine
   d. thymine
5. How many hydrogen bonds can form between the two strands 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 $19.E.3$ to identify the amino acids carried by each tRNA molecule in Exercise 1.
6. Use Figure $19.E.3$ to identify the amino acids carried by each tRNA molecule in Exercise 2.
7. Use Figure $19.E.3$ to determine the amino acid sequence produced from this mRNA sequence: 5′-AUGAGCGACUUUGCGGGAUUA-3′.
8. Use Figure $19.E.3$ to determine the amino acid sequence produced from this mRNA sequence: 5′-AUGGCAAUCCUCAAACGCUGU-3′

Answers

1. a. 3′-AAA-5′
   b. 3′-GUA-5′
   c. 3′-UCG-5′
   d. 3′-GGC-5′

3. 27 nucleotides (3 nucleotides/codon)

5. 1a: phenylalanine; 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

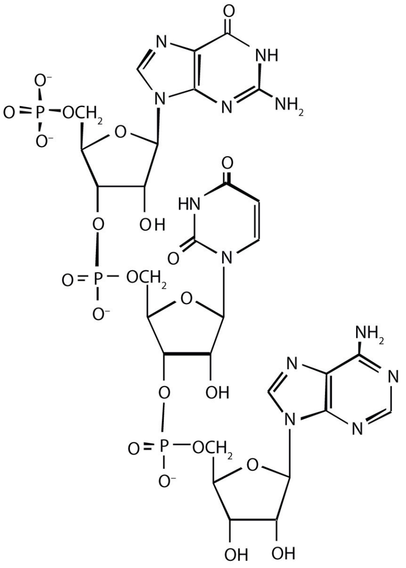
1. Describe the general structure of a virus.
2. How does a DNA virus differ from an RNA virus?
3. Why is HIV known as a retrovirus?
4. Describe how a DNA virus invades and destroys a cell.
5.
   a. Describe how an RNA virus invades and destroys a cell.
   b. How does this differ from a DNA virus?
6. 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. -

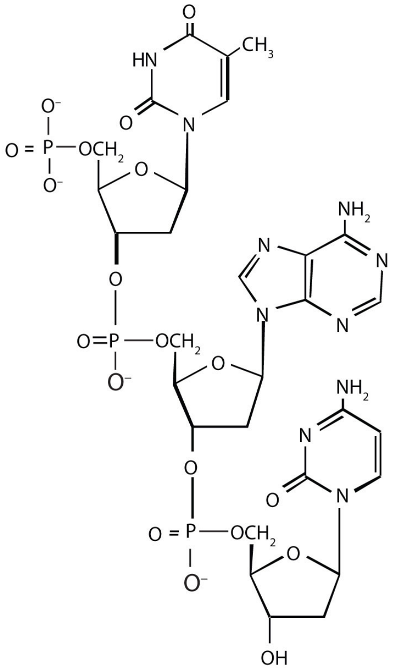
Additional Exercises

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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19.S: Nucleic Acids (Summary)

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

A cell's hereditary information is encoded in **chromosomes** in the cell's nucleus. Each chromosome is composed of proteins and **deoxyribonucleic acid (DNA)**. The chromosomes contain smaller hereditary units called **genes,** which are relatively short segments of DNA. The hereditary information is expressed or used through the synthesis of **ribonucleic acid (RNA)**. Both **nucleic acids**—DNA and RNA—are polymers composed of monomers known as **nucleotides**, which in turn consist of phosphoric acid (H_3PO_4), a nitrogenous base, and a pentose sugar.

The two types of *nitrogenous bases* most important in nucleic acids are **purines**—adenine (A) and guanine (G)—and **pyrimidines**—cytosine (C), thymine (T), and uracil (U). DNA contains the nitrogenous bases adenine, cytosine, guanine, and thymine, while the bases in RNA are adenine, cytosine, guanine, and uracil. The sugar in the nucleotides of RNA is ribose; the one in DNA is 2-deoxyribose. The sequence of nucleotides in a nucleic acid defines the primary structure of the molecule.

RNA is a single-chain nucleic acid, whereas DNA possesses two nucleic-acid chains intertwined in a secondary structure called a **double helix**. The sugar-phosphate backbone forms the outside the double helix, with the purine and pyrimidine bases tucked inside. Hydrogen bonding between **complementary bases** holds the two strands of the double helix together; A always pairs with T and C always pairs with G.

Cell growth requires **replication**, or reproduction of the cell's DNA. The double helix unwinds, and hydrogen bonding between complementary bases breaks so that there are two single strands of DNA, and each strand is a *template* for the synthesis of a new strand. For protein synthesis, three types of RNA are needed: *messenger RNA* (mRNA), *ribosomal RNA* (rRNA), and *transfer RNA* (tRNA). All are made from a DNA template by a process called **transcription**. The double helix uncoils, and ribonucleotides base-pair to the deoxyribonucleotides on one DNA strand; however, RNA is produced using *uracil* rather than thymine. Once the RNA is formed, it dissociates from the template and leaves the nucleus, and the DNA double helix reforms.

Translation is the process in which proteins are synthesized from the information in mRNA. It occurs at structures called **ribosomes**, which are located outside the nucleus and are composed of rRNA and protein. The 64 possible three-nucleotide combinations of the 4 nucleotides of DNA constitute the **genetic code** that dictates the sequence in which amino acids are joined to make proteins. Each three-nucleotide sequence on mRNA is a **codon**. Each kind of tRNA molecule binds a specific amino acid and has a site containing a three-nucleotide sequence called an **anticodon**.

The general term for any change in the genetic code in an organism's DNA is **mutation**. A change in which a single base is substituted, inserted, or deleted is a **point mutation**. The chemical and/or physical agents that cause mutations are called **mutagens**. Diseases that occur due to mutations in critical DNA sequences are referred to as **genetic diseases**.

Viruses are infectious agents composed of a tightly packed central core of nucleic acids enclosed by a protective shell of proteins. Viruses contain either DNA or RNA as their genetic material but not both. Some RNA viruses, called **retroviruses**, synthesize DNA in the host cell from their RNA genome. The human immunodeficiency virus (HIV) causes acquired immunodeficiency syndrome (AIDS).

CHAPTER OVERVIEW

20: Energy Metabolism

Metabolism is the set of life-sustaining chemical transformations within the cells of living organisms. The three main purposes of metabolism are the conversion of food/fuel to energy to run cellular processes, the conversion of food/fuel to building blocks for proteins, lipids, nucleic acids, and some carbohydrates, and the elimination of nitrogenous wastes. These enzyme-catalyzed reactions allow organisms to grow and reproduce, maintain their structures, and respond to their environments. Metabolism is usually divided into two categories: **catabolism**, the breaking down of organic matter, for example, by cellular respiration, and **anabolism**, the building up of components of cells such as proteins and nucleic acids. Usually, breaking down releases energy and building up consumes energy.

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20.0: Prelude to Energy Metabolism

The discovery of the link between insulin and diabetes led to a period of intense research aimed at understanding exactly how insulin works in the body to regulate glucose levels. Hormones in general act by binding to some protein, known as the hormone's receptor, thus initiating a series of events that lead to a desired outcome. In the early 1970s, the insulin receptor was purified, and researchers began to study what happens after insulin binds to its receptor and how those events are linked to the uptake and metabolism of glucose in cells.

The insulin receptor is located in the cell membrane and consists of four polypeptide chains: two identical chains called α chains and two identical chains called β chains. The α chains, positioned on the outer surface of the membrane, consist of 735 amino acids each and contain the binding site for insulin. The β chains are integral membrane proteins, each composed of 620 amino acids. The binding of insulin to its receptor stimulates the β chains to catalyze the addition of phosphate groups to the specific side chains of tyrosine (referred to as phosphorylation) in the β chains and other cell proteins, leading to the activation of reactions that metabolize glucose. In this chapter we will look at the pathway that breaks down glucose—in response to activation by insulin—for the purpose of providing energy for the cell.

GLmol

Figure 20.0.1: Model of the Structure of the Insulin Receptor (PDB code 4ZXB).

Life requires energy. Animals, for example, require heat energy to maintain body temperature, mechanical energy to move their limbs, and chemical energy to synthesize the compounds needed by their cells. Living cells remain organized and functioning properly only through a continual supply of energy. But only specific forms of energy can be used. Supplying a plant with energy by holding it in a flame will not prolong its life. On the other hand, a green plant is able to absorb radiant energy from the sun, the most abundant source of energy for life on the earth. Plants use this energy first to form glucose and then to make other carbohydrates, as well as lipids and proteins. Unlike plants, animals cannot directly use the sun's energy to synthesize new compounds. They must eat plants or other animals to get carbohydrates, fats, and proteins and the chemical energy stored in them. Once digested and transported to the cells, the nutrient molecules can be used in either of two ways: as building blocks for making new cell parts or repairing old ones or "burned" for energy.

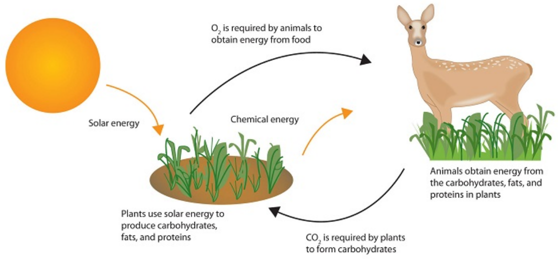


Figure 20.0.2: Some Energy Transformations in Living Systems. Plants and animals exist in a cycle; each requires products of the other.

The thousands of coordinated chemical reactions that keep cells alive are referred to collectively as **metabolism**. In general, metabolic reactions are divided into two classes: the breaking down of molecules to obtain energy is **catabolism**, and the building of new molecules needed by living systems is **anabolism**.

Definition: Metabolite

Any chemical compound that participates in a metabolic reaction is a *metabolite*.

Most of the energy required by animals is generated from lipids and carbohydrates. These fuels must be oxidized, or "burned," for the energy to be released. The oxidation process ultimately converts the lipid or carbohydrate to carbon dioxide (CO_2) and water (H_2O).

Carbohydrate:

$$C_6H_{12}O_6 + 6\,O_2 \rightarrow 6\,CO_2 + 6\,H_2O + 670\text{ kcal}$$

Lipid:

$$C_{16}H_{32}O_2 + 23\,O_2 \rightarrow 16\,CO_2 + 16\,H_2O + 2,385\text{ kcal}$$

These two equations summarize the biological combustion of a carbohydrate and a lipid by the cell through respiration. **Respiration** is the collective name for all metabolic processes in which gaseous oxygen is used to oxidize organic matter to carbon dioxide, water, and energy.

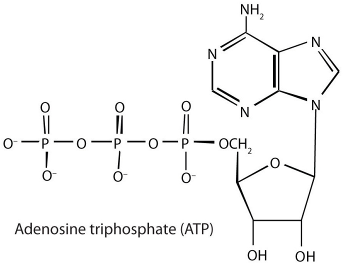
Like the combustion of the common fuels we burn in our homes and cars (wood, coal, gasoline), respiration uses oxygen from the air to break down complex organic substances to carbon dioxide and water. But the energy released in the burning of wood is manifested entirely in the form of heat, and excess heat energy is not only useless but also injurious to the living cell. Living organisms instead conserve much of the energy respiration releases by channeling it into a series of stepwise reactions that produce adenosine triphosphate (ATP) or other compounds that ultimately lead to the synthesis of ATP. The remainder of the energy is released as heat and manifested as body temperature.

20.1: ATP- the Universal Energy Currency

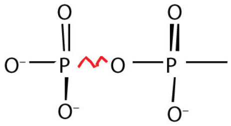
Learning Objectives

- To describe the importance of ATP as a source of energy in living organisms.

Adenosine triphosphate (ATP), a nucleotide composed of adenine, ribose, and three phosphate groups, is perhaps the most important of the so-called energy-rich compounds in a cell. Its concentration in the cell varies from 0.5 to 2.5 mg/mL of cell fluid.



Energy-rich compounds are substances having particular structural features that lead to a release of energy after hydrolysis. As a result, these compounds are able to supply energy for biochemical processes that require energy. The structural feature important in ATP is the phosphoric acid anhydride, or pyrophosphate, linkage:



The pyrophosphate bond, symbolized by a squiggle (~), is hydrolyzed when ATP is converted to adenosine diphosphate (ADP). In this hydrolysis reaction, the products contain less energy than the reactants; there is a release of energy (> 7 kcal/mol). One reason for the amount of energy released is that hydrolysis relieves the electron-electron repulsions experienced by the negatively charged phosphate groups when they are bonded to each other (Figure 20.1.1).

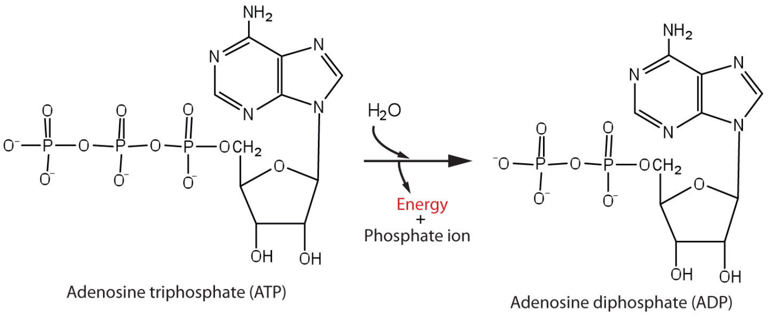


Figure 20.1.1: Hydrolysis of ATP to Form ADP

Energy is released because the products (ADP and phosphate ion) have less energy than the reactants [ATP and water (H_2O)].

The general equation for ATP hydrolysis is as follows:

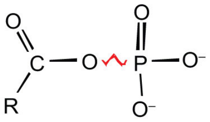
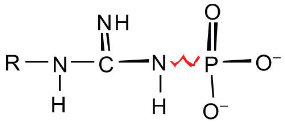
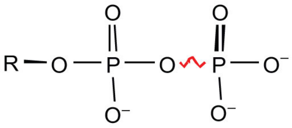
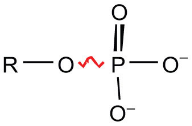
$$ATP + H_2O \rightarrow ADP + P_i + 7.4\ kcal/mol$$

If the hydrolysis of ATP releases energy, its synthesis (from ADP) requires energy. In the cell, ATP is produced by those processes that supply energy to the organism (absorption of radiant energy from the sun in green plants and breakdown of food in animals), and it is hydrolyzed by those processes that require energy (the syntheses of carbohydrates, lipids, proteins; the transmission of nerve impulses; muscle contractions). In fact, ATP is the principal medium of energy exchange in biological systems. Many scientists call it the energy currency of cells.

> P_i *is the symbol for the inorganic phosphate anions* $H_2PO_4^-$ *and* HPO_4^{2-}.

ATP is not the only high-energy compound needed for metabolism. Several others are listed in Table 20.1.1. Notice, however, that the energy released when ATP is hydrolyzed is approximately midway between those of the high-energy and the low-energy phosphate compounds. This means that the hydrolysis of ATP can provide energy for the phosphorylation of the compounds below it in the table. For example, the hydrolysis of ATP provides sufficient energy for the phosphorylation of glucose to form glucose 1-phosphate. By the same token, the hydrolysis of compounds, such as creatine phosphate, that appear *above* ATP in the table can provide the energy needed to resynthesize ATP from ADP.

Table 20.1.1: Energy Released by Hydrolysis of Some Phosphate Compounds

Type	Example	Energy Released (kcal/mol)
acyl phosphate 	1,3-bisphosphoglycerate (BPG)	−11.8
	acetyl phosphate	−11.3
guanidine phosphates 	creatine phosphate	−10.3
	arginine phosphate	−9.1
pyrophosphates 	$PP_{i*} \rightarrow 2P_i$	−7.8
	$ATP \rightarrow AMP + PP_i$	−7.7
	$ATP \rightarrow ADP + P_i$	−7.5
	$ADP \rightarrow AMP + P_i$	−7.5
sugar phosphates 	glucose 1-phosphate	−5.0
	fructose 6-phosphate	−3.8
	$AMP \rightarrow adenosine + P_i$	−3.4
	glucose 6-phosphate	−3.3
	glycerol 3-phosphate	−2.2

*PP_i is the pyrophosphate ion.

Summary

The hydrolysis of ATP releases energy that can be used for cellular processes that require energy.

20.2: Stage I of Catabolism

Learning Objectives

- To describe how carbohydrates, fats, and proteins are broken down during digestion.

We have said that animals obtain chemical energy from the food—carbohydrates, fats, and proteins—they eat through reactions defined collectively as *catabolism*. We can think of catabolism as occurring in three stages (Figure 20.2.1). In stage I, carbohydrates, fats, and proteins are broken down into their individual monomer units: carbohydrates into simple sugars, fats into fatty acids and glycerol, and proteins into amino acids. One part of stage I of catabolism is the breakdown of food molecules by hydrolysis reactions into the individual monomer units—which occurs in the mouth, stomach, and small intestine—and is referred to as digestion.

In stage II, these monomer units (or building blocks) are further broken down through different reaction pathways, one of which produces ATP, to form a common end product that can then be used in stage III to produce even more ATP. In this chapter, we will look at each stage of catabolism—as an overview and in detail.

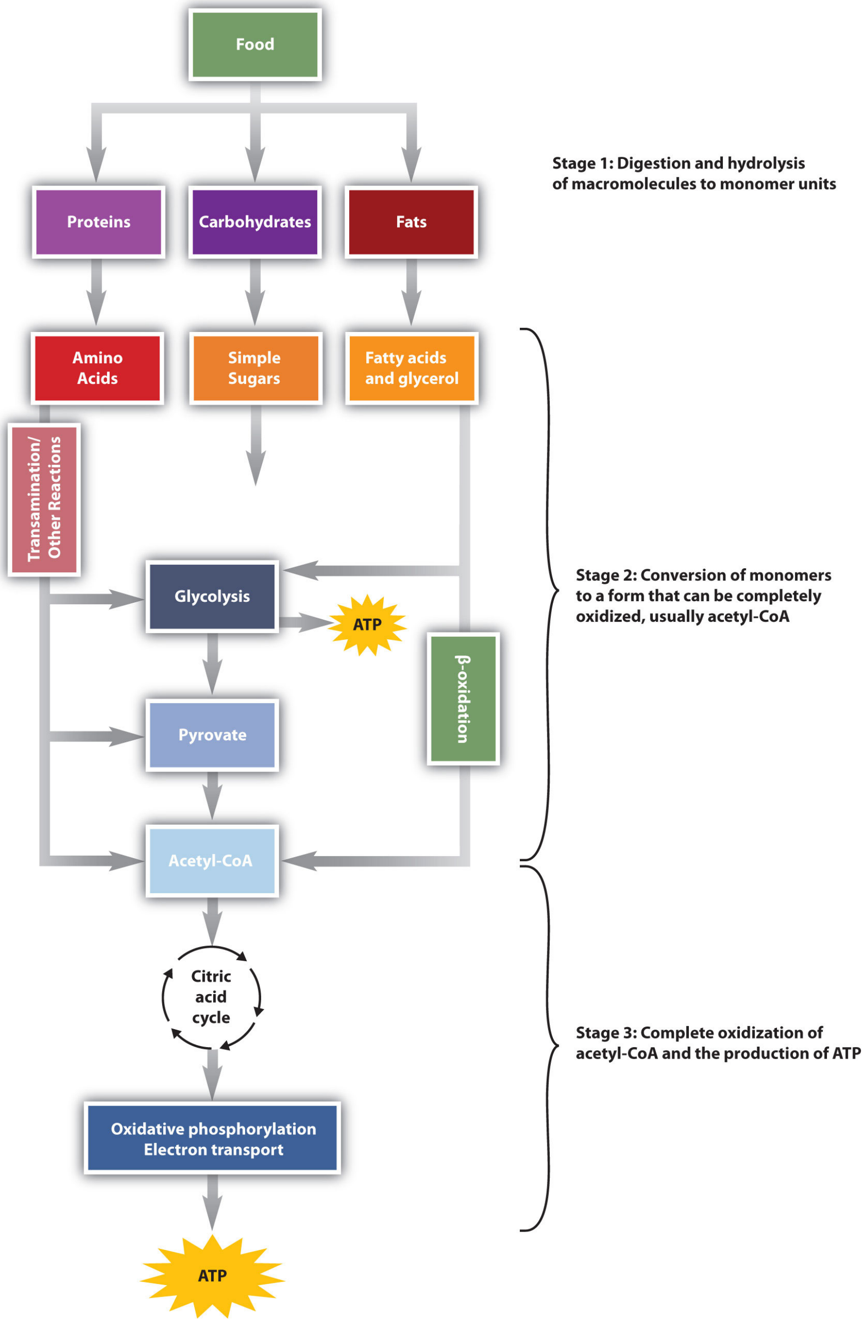


Figure 20.2.1: Energy Conversions

The conversion of food into cellular energy (as ATP) occurs in three stages.

Digestion of Carbohydrates

Carbohydrate digestion begins in the mouth (Figure 20.2.2) where salivary α-amylase attacks the α-glycosidic linkages in starch, the main carbohydrate ingested by humans. Cleavage of the glycosidic linkages produces a mixture of dextrins, maltose, and glucose. The α-amylase mixed into the food remains active as the food passes through the esophagus, but it is rapidly inactivated in the acidic environment of the stomach.

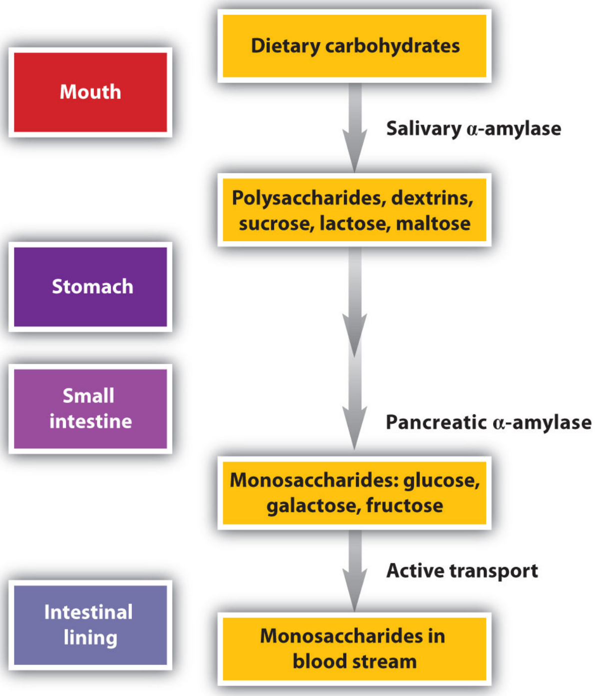


Figure 20.2.2: The Principal Events and Sites of Carbohydrate Digestion

The primary site of carbohydrate digestion is the small intestine. The secretion of α-amylase in the small intestine converts any remaining starch molecules, as well as the dextrins, to maltose. Maltose is then cleaved into two glucose molecules by maltase. Disaccharides such as sucrose and lactose are not digested until they reach the small intestine, where they are acted on by sucrase and lactase, respectively. The major products of the complete hydrolysis of disaccharides and polysaccharides are three monosaccharide units: glucose, fructose, and galactose. These are absorbed through the wall of the small intestine into the bloodstream.

Digestion of Proteins

Protein digestion begins in the stomach (Figure 20.2.3), where the action of gastric juice hydrolyzes about 10% of the peptide bonds. Gastric juice is a mixture of water (more than 99%), inorganic ions, hydrochloric acid, and various enzymes and other proteins.

> The pain of a gastric ulcer is at least partially due to irritation of the ulcerated tissue by acidic gastric juice.

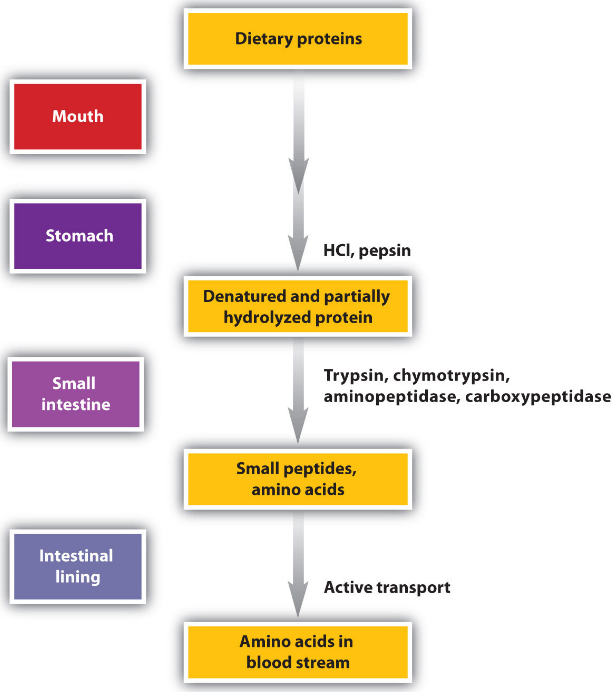


Figure 20.2.3: The Principal Events and Sites of Protein Digestion

The hydrochloric acid (HCl) in gastric juice is secreted by glands in the stomach lining. The pH of freshly secreted gastric juice is about 1.0, but the contents of the stomach may raise the pH to between 1.5 and 2.5. HCl helps to denature food proteins; that is, it unfolds the protein molecules to expose their chains to more efficient enzyme action. The principal digestive component of gastric juice is pepsinogen, an inactive enzyme produced in cells located in the stomach wall. When food enters the stomach after a period of fasting, pepsinogen is converted to its active form—pepsin—in a series of steps initiated by the drop in pH. Pepsin catalyzes the hydrolysis of peptide linkages within protein molecules. It has a fairly broad specificity but acts preferentially on linkages involving the aromatic amino acids tryptophan, tyrosine, and phenylalanine, as well as methionine and leucine.

Protein digestion is completed in the small intestine. Pancreatic juice, carried from the pancreas via the pancreatic duct, contains inactive enzymes such as trypsinogen and chymotrypsinogen. They are activated in the small intestine as follows (Figure 20.2.4): The intestinal mucosal cells secrete the proteolytic enzyme enteropeptidase, which converts trypsinogen to trypsin; trypsin then activates chymotrypsinogen to chymotrypsin (and also completes the activation of trypsinogen). Both of these active enzymes catalyze the hydrolysis of peptide bonds in protein chains. Chymotrypsin preferentially attacks peptide bonds involving the carboxyl groups of the aromatic amino acids (phenylalanine, tryptophan, and tyrosine). Trypsin attacks peptide bonds involving the carboxyl groups of the basic amino acids (lysine and arginine). Pancreatic juice also contains procarboxypeptidase, which is cleaved by trypsin to carboxypeptidase. The latter is an enzyme that catalyzes the hydrolysis of peptide linkages at the free carboxyl end of the peptide chain, resulting in the stepwise liberation of free amino acids from the carboxyl end of the polypeptide.

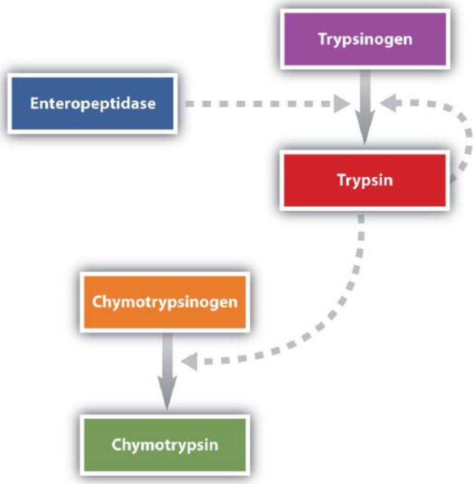


Figure 20.2.4: Activation of Some Pancreatic Enzymes in the Small Intestine

Aminopeptidases in the intestinal juice remove amino acids from the N-terminal end of peptides and proteins possessing a free amino group. Figure 20.2.5 illustrates the specificity of these protein-digesting enzymes. The amino acids that are released by protein digestion are absorbed across the intestinal wall into the circulatory system, where they can be used for protein synthesis.

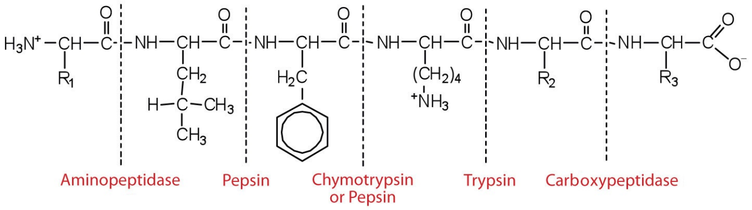


Figure 20.2.5: Hydrolysis of a Peptide by Several Peptidases

This diagram illustrates where in a peptide the different peptidases we have discussed would catalyze hydrolysis the peptide bonds.

Digestion of Lipids

Lipid digestion begins in the upper portion of the small intestine (Figure 20.2.6). A hormone secreted in this region stimulates the gallbladder to discharge bile into the duodenum. The principal constituents of bile are the bile salts, which emulsify large, water-insoluble lipid droplets, disrupting some of the hydrophobic interactions holding the lipid molecules together and suspending the resulting smaller globules (micelles) in the aqueous digestive medium. These changes greatly increase the surface area of the lipid particles, allowing for more intimate contact with the lipases and thus rapid digestion of the fats. Another hormone promotes the secretion of pancreatic juice, which contains these enzymes.

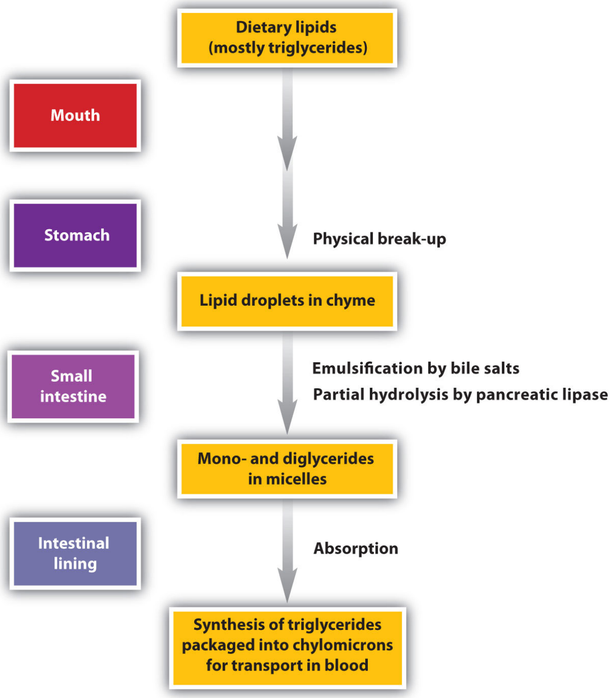
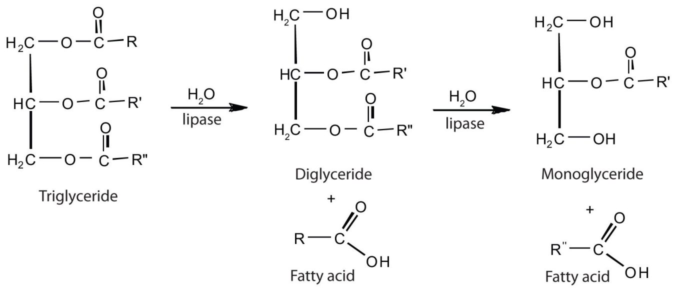


Figure 20.2.6: The Principal Events and Sites of Lipid (Primarily Triglyceride) Digestion

The lipases in pancreatic juice catalyze the digestion of triglycerides first to diglycerides and then to 2-monoglycerides and fatty acids:



The monoglycerides and fatty acids cross the intestinal lining into the bloodstream, where they are resynthesized into triglycerides and transported as lipoprotein complexes known as chylomicrons. Phospholipids and cholesteryl esters undergo similar hydrolysis in the small intestine, and their component molecules are also absorbed through the intestinal lining.

The further metabolism of monosaccharides, fatty acids, and amino acids released in stage I of catabolism occurs in stages II and III of catabolism.

Summary

During digestion, carbohydrates are broken down into monosaccharides, proteins are broken down into amino acids, and triglycerides are broken down into glycerol and fatty acids. Most of the digestion reactions occur in the small intestine.

20.3: Overview of Stage II of Catabolism

Learning Objectives

- To describe the role of acetyl-CoA in metabolism.

A metabolic pathway is a series of biochemical reactions by which an organism converts a given reactant to a specific end product. There are specific metabolic pathways—which are different for carbohydrates, triglycerides, and proteins—that break down the products of stage I of catabolism (monosaccharides, fatty acids, and amino acids) to produce a common end product, acetyl-coenzyme A (acetyl-CoA) in stage II of catabolism.

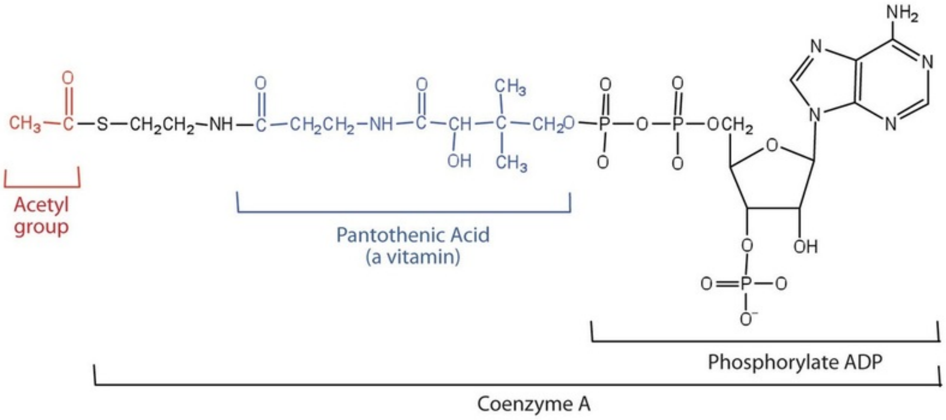


Figure 20.3.1: The Structure of Acetyl-Coenzyme A (Acetyl-CoA)

Acetyl-CoA is shown in Figure 20.3.1. The acetyl unit, derived (as we will see) from the breakdown of carbohydrates, lipids, and proteins, is attached to coenzyme A, making the acetyl unit more reactive. Acetyl-CoA is used in a myriad of biochemical pathways. For example, it may be used as the starting material for the biosynthesis of lipids (such as triglycerides, phospholipids, or cholesterol and other steroids). Most importantly for energy generation, it may enter the citric acid cycle and be oxidized to produce energy, if energy is needed and oxygen is available. The various fates or uses of acetyl-CoA are summarized in Figure 20.3.1.

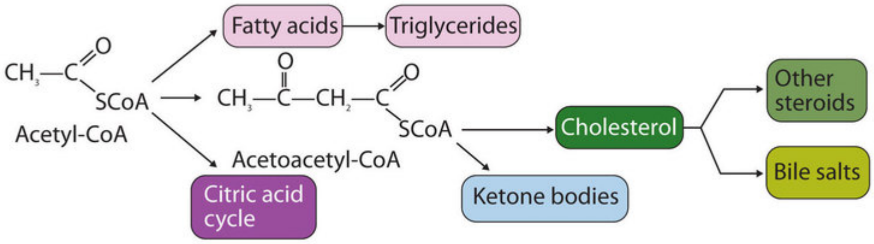


Figure 20.3.2: Cell Chemistry. Acetyl-CoA plays a variety of roles in cell chemistry.

Glycolysis

Glycolysis is the catabolic process in which glucose is converted into pyruvate via ten enzymatic steps. There are three regulatory steps, each of which is highly regulated that are separated into two phases:

1. the "priming phase" because it requires an input of energy in the form of 2 ATPs per glucose molecule and
2. the "pay off phase" because energy is released in the form of 4 ATPs, 2 per glyceraldehyde molecule.

The end result of Glycolysis is two new pyruvate molecules which can then be fed into the Citric Acid cycle (also known as the Kreb's Cycle) if oxygen is present, or can be reduced to lactate or ethanol in the absence of of oxygen using a process known as fermentation.

Video 20.3.1: Glycolysis: An Overview. Glycolysis is a series of 10 reactions that converts sugars, like glucose, into 3-carbon molecules called pyruvate. This animation provides an overview of the energy consumed and produced by the pathway. NDSU VCell Production's animation; for more information please see Vcell, NDSU(opens in new window) [vcell.ndsu.edu].

Glycolysis occurs within almost all living cells and is the primary source of Acetyl-CoA, which is the molecule responsible for the majority of energy output under aerobic conditions. The structures of Glycolysis intermediates can be found in Figure 20.3.3.

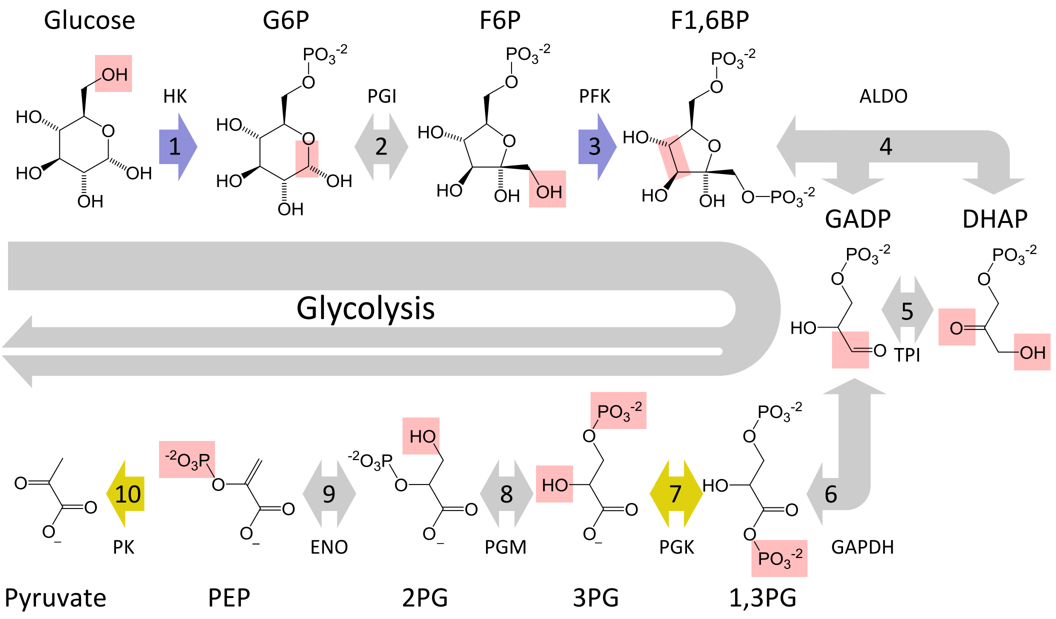


Figure 20.3.3: Glycolysis pathway. (CC BY-SA 4.0; International; Thomas Shafee via Wikipedia)

Phase 1: The "Priming Step"

The first phase of Glycolysis requires an input of energy in the form of ATP (adenosine triphosphate).

1. alpha-D-Glucose is phosphorolated at the 6 carbon by ATP via the enzyme Hexokinase (Class: Transferase) to yield alpha-D-Glucose-6-phosphate (G-6-P). This is a regulatory step which is negatively regulated by the presence of glucose-6-phosphate.
2. alpha-D-Glucose-6-phosphate is then converted into D-Fructose-6-phosphate (F-6-P) by Phosphoglucoisomerase (Class: Isomerase)
3. D-Fructose-6-phosphate is once again phosphorolated this time at the 1 carbon position by ATP via the enzyme Phosphofructokinase (Class: Transferase) to yield D-Fructose-1,6-bisphosphate (FBP). This is the committed step of glycolysis because of its large ΔG value.
4. D-Fructose-1,6-bisphosphate is then cleaved into two, three carbon molecules; Dihydroxyacetone phosphate (DHAP) and D-Glyceraldehyde-3-phosphate (G-3-P) by the enzyme Fructose bisphosphate aldolase (Class: Lyase)
5. Because the next portion of Glycolysis requires the molecule D-Glyceraldehyde-3-phosphate to continue Dihydroxyacetone phosphate is converted into D-Glyceraldehyde-3-phosphate by the enzyme Triose phosphate isomerase (Class: Isomerase)

Phase 2: The "Pay Off Step"

The second phase of Glycolysis where 4 molecules of ATP are produced per molecule of glucose. Enzymes appear in red:

1. D-Glyceraldehyde-3-phosphate is phosphorolated at the 1 carbon by the enzyme Glyceraldehyde-3-phosphate dehodrogenase to yield the high energy molecule 1,3-Bisphosphoglycerate (BPG)
2. ADP is then phosphorolated at the expense of 1,3-Bisphosphoglycerate by the enzyme Phosphoglycerate kinase (Class: Transferase) to yield ATP and 3-Phosphoglycerate (3-PG)
3. 3-Phosphoglycerate is then converted into 2-Phosphoglycerate by Phosphoglycerate mutase in preparation to yield another high energy molecule
4. 2-Phosphoglycerate is then converted to phosphoenolpyruvate (PEP) by Enolase. H_2O, potassium, and magnesium are all released as a result.
5. ADP is once again phosphorolated, this time at the expense of PEP by the enzyme pyruvate kinase to yield another molecule of ATP and and pyruvate. This step is regulated by the energy in the cell. The higher the energy of the cell the more inhibited pyruvate kinase becomes. Indicators of high energy levels within the cell are high concentrations of ATP, Acetyl-CoA, Alanine, and cAMP.

Because Glucose is split to yield two molecules of D-Glyceraldehyde-3-phosphate, each step in the "Pay Off" phase occurs twice per molecule of glucose.

Beta-Oxidation

The best source of energy for eukaryotic organisms are fats. Glucose offers a ratio 6.3 moles of ATP per carbon while saturated fatty acids offer 8.1 ATP per carbon. Also the complete oxidation of fats yields enormous amounts of water for those organisms that do not have adequate access to drinkable water. Camels and killer whales are good example of this, they obtain their water requirements from the complete oxidation of fats.

Video 20.3.2: Fatty acid metabolism / beta oxidation / β-Oxidation

There are four distinct stages in the oxidation of fatty acids. Fatty acid degradation takes place within the mitochondria and requires the help of several different enzymes. In order for fatty acids to enter the mitochondria the assistance of two carrier proteins is required, Carnitine acyltransferase I and II. It is also interesting to note the similarities between the four steps of beta-oxidation and the later four steps of the TCA cycle.

Entry into Beta-oxidation

Most fats stored in eukaryotic organisms are stored as triglycerides as seen below. In order to enter into beta-oxidation bonds must be broken usually with the use of a Lipase. The end result of these broken bonds are a glycerol molecule and three fatty acids in the case of triglycerides. Other lipids are capable of being degraded as well.

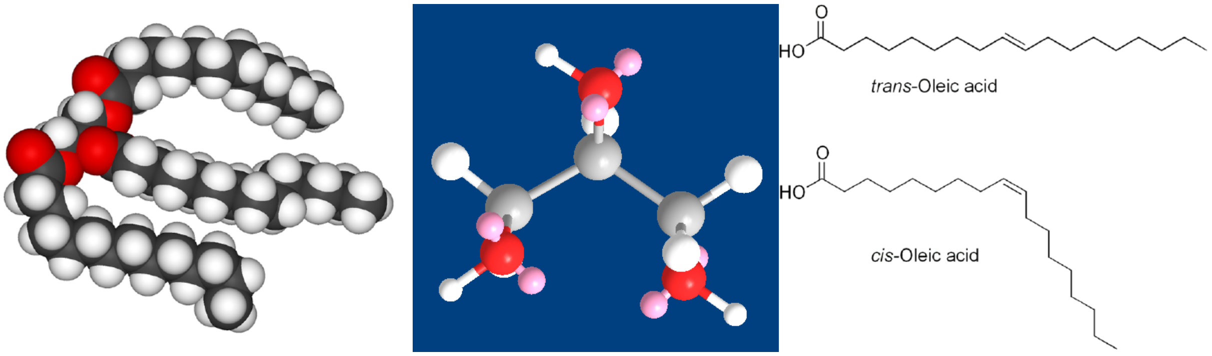


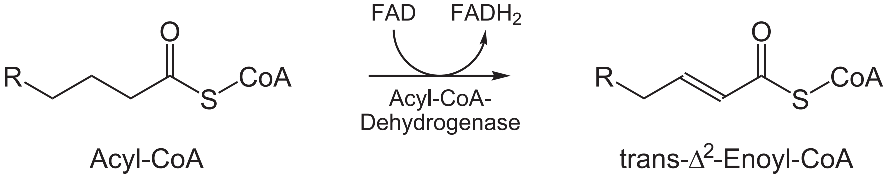
Figure 20.3.4: Key molecules in beta-oxidation: (left) A triglyceride molecule, (middle) Glycerol, (right) Fatty Acids (unsaturated)

Activation Step

- Once the triglycerides are broken down into glycerol and fatty acids they must be activated before they can enter into the mitochondria and proceed on with beta-oxidation. This is done by Acyl-CoA synthetase to yield fatty acyl-CoA.
- After the fatty acid has been acylated it is now ready to enter into the mitochondria.
- There are two carrier proteins (Carnitine acyltransferase I and II), one located on the outer membrane and one on the inner membrane of the mitochondria. Both are required for entry of the Acyl-CoA into the mitochondria.
- Once inside the mitochondria the fatty acyl-CoA can enter into beta-oxidation.

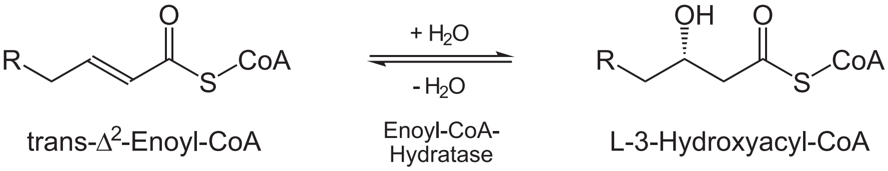
Oxidation Step

A fatty acyl-CoA is oxidized by Acyl-CoA dehydrogenase to yield a trans alkene. This is done with the aid of an [FAD] prosthetic group.



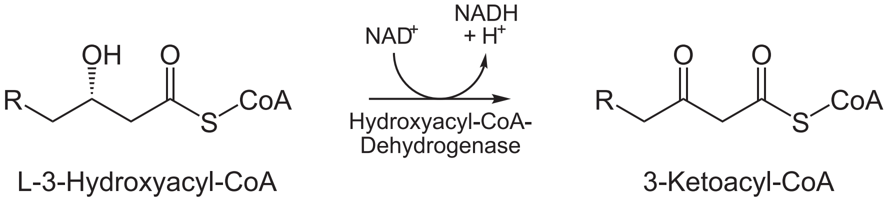
Hydration Step

The trans alkene is then hydrated with the help of Enoyl-CoA hydratase



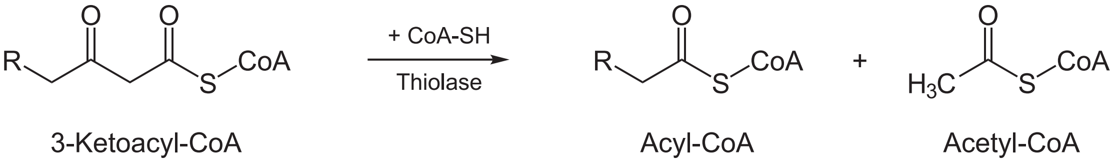
Oxidation Step

The alcohol of the hydroxyacly-CoA is then oxidized by NAD$^+$ to a carbonyl with the help of Hydroxyacyl-CoA dehydrogenase. NAD$^+$ is used to oxidize the alcohol rather then [FAD] because NAD$^+$ is capable of the alcohol while [FAD] is not.



Cleavage

Finally acetyl-CoA is cleaved off with the help of Thiolase to yield an Acyl-CoA that is two carbons shorter than before. The cleaved acetyl-CoA can then enter into the TCA and ETC because it is already within the mitochondria.



Summary

Acetyl-CoA is formed from the breakdown of carbohydrates, lipids, and proteins. It is used in many biochemical pathways.

References

1. Garrett, H., Reginald and Charles Grisham. Biochemistry. Boston: Twayne Publishers, 2008.
2. Raven, Peter. Biology. Boston: Twayne Publishers, 2005.

20.4: Stage III of Catabolism

Learning Objectives

- Describe the reactions of the citric acid cycle.
- Describe the function of the citric acid cycle and identify the products produced.
- Describe the role of the electron transport chain in energy metabolism.
- Describe the role of oxidative phosphorylation in energy metabolism.

The acetyl group enters a cyclic sequence of reactions known collectively as the citric acid cycle (or Krebs cycle or tricarboxylic acid [TCA] cycle). The cyclical design of this complex series of reactions, which bring about the oxidation of the acetyl group of acetyl-CoA to carbon dioxide and water, was first proposed by Hans Krebs in 1937. (He was awarded the 1953 Nobel Prize in Physiology or Medicine.) Acetyl-CoA's entrance into the citric acid cycle is the beginning of stage III of catabolism. The citric acid cycle produces adenosine triphosphate (ATP), reduced nicotinamide adenine dinucleotide (NADH), reduced flavin adenine dinucleotide ($FADH_2$), and metabolic intermediates for the synthesis of needed compounds.

Steps of the Citric Acid Cycle

At first glance, the citric acid cycle appears rather complex (Figure 20.4.1). All the reactions, however, are familiar types in organic chemistry: hydration, oxidation, decarboxylation, and hydrolysis. Each reaction of the citric acid cycle is numbered, and in Figure 20.4.1, the two acetyl carbon atoms are highlighted in red. Each intermediate in the cycle is a carboxylic acid, existing as an anion at physiological pH. All the reactions occur within the mitochondria, which are small organelles within the cells of plants and animals.

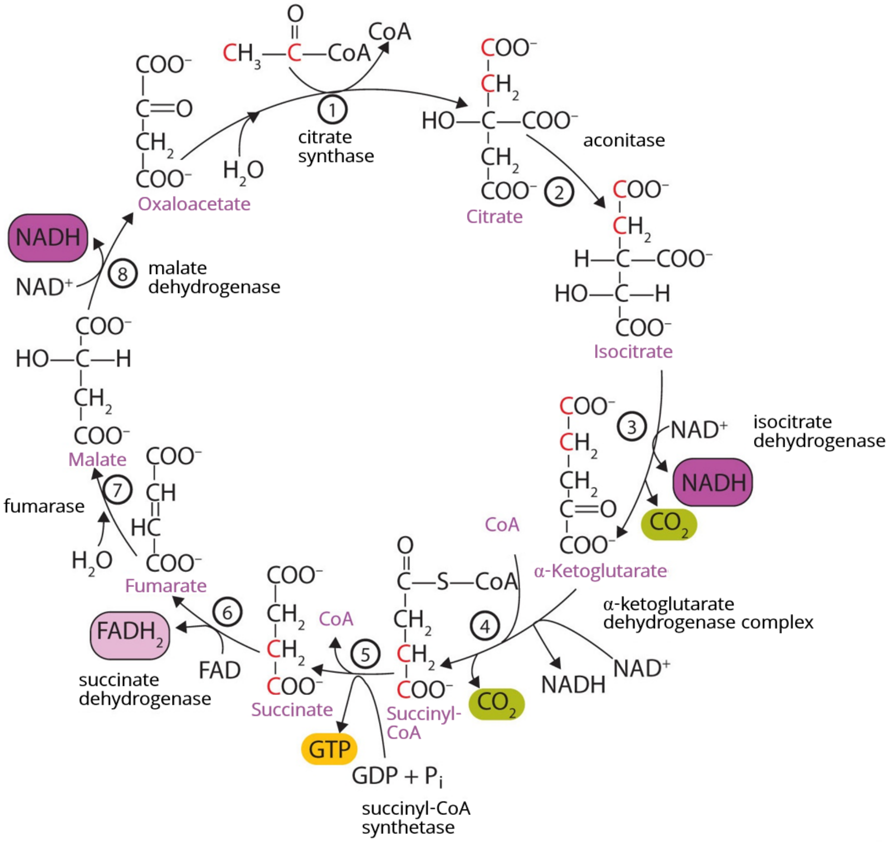


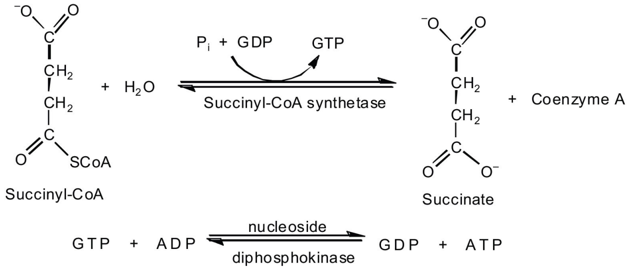
Figure 20.4.1: Reactions of the Citric Acid Cycle

1. In the first step, acetyl-CoA enters the citric acid cycle, and the acetyl group is transferred onto oxaloacetate, yielding citrate. Note that this step releases coenzyme A. The reaction is catalyzed by *citrate synthase*.

2. In the next step, *aconitase* catalyzes the isomerization of citrate to isocitrate. In this reaction, a tertiary alcohol, which cannot be oxidized, is converted to a secondary alcohol, which can be oxidized in the next step.
3. Isocitrate then undergoes a reaction known as oxidative decarboxylation because the alcohol is oxidized and the molecule is shortened by one carbon atom with the release of carbon dioxide (decarboxylation). The reaction is catalyzed by *isocitrate dehydrogenase*, and the product of the reaction is α-ketoglutarate. An important reaction linked to this is the reduction of the coenzyme nicotinamide adenine dinucleotide (NAD^+) to NADH. The NADH is ultimately reoxidized, and the energy released is used in the synthesis of ATP, as we shall see.
4. The fourth step is another oxidative decarboxylation. This time α-ketoglutarate is converted to succinyl-CoA, and another molecule of NAD^+ is reduced to NADH. The *α-ketoglutarate dehydrogenase complex* catalyzes this reaction. This is the only irreversible reaction in the citric acid cycle. As such, it prevents the cycle from operating in the reverse direction, in which acetyl-CoA would be synthesized from carbon dioxide.

> So far, in the first four steps, two carbon atoms have entered the cycle as an acetyl group, and two carbon atoms have been released as molecules of carbon dioxide. The remaining reactions of the citric acid cycle use the four carbon atoms of the succinyl group to resynthesize a molecule of oxaloacetate, which is the compound needed to combine with an incoming acetyl group and begin another round of the cycle.

In the fifth reaction, the energy released by the hydrolysis of the high-energy thioester bond of succinyl-CoA is used to form guanosine triphosphate (GTP) from guanosine diphosphate (GDP) and inorganic phosphate in a reaction catalyzed by *succinyl-CoA synthetase*. This step is the only reaction in the citric acid cycle that directly forms a high-energy phosphate compound. GTP can readily transfer its terminal phosphate group to adenosine diphosphate (ADP) to generate ATP in the presence of *nucleoside diphosphokinase*.



Succinate dehydrogenase then catalyzes the removal of two hydrogen atoms from succinate, forming fumarate. This oxidation-reduction reaction uses flavin adenine dinucleotide (FAD), rather than NAD^+, as the oxidizing agent. Succinate dehydrogenase is the only enzyme of the citric acid cycle located within the inner mitochondrial membrane. We will see soon the importance of this.

In the following step, a molecule of water is added to the double bond of fumarate to form L-malate in a reaction catalyzed by *fumarase*.

One revolution of the cycle is completed with the oxidation of L-malate to oxaloacetate, brought about by *malate dehydrogenase*. This is the third oxidation-reduction reaction that uses NAD^+ as the oxidizing agent. Oxaloacetate can accept an acetyl group from acetyl-CoA, allowing the cycle to begin again.

Video: "The Citric Acid Cycle: An Overview". In the matrix of the mitochondrion, the Citric Acid Cycle uses Acetyl CoA molecules to produce energy through eight chemical reactions. This animation provides an overview of the pathway and its products. NDSU VCell Production's animation; for more information please see Vcell, NDSU, Animations(opens in new window) [vcell.ndsu.edu].

Cellular Respiration

Respiration can be defined as the process by which cells oxidize organic molecules in the presence of gaseous oxygen to produce carbon dioxide, water, and energy in the form of ATP. We have seen that two carbon atoms enter the citric acid cycle from acetyl-CoA (step 1), and two different carbon atoms exit the cycle as carbon dioxide (steps 3 and 4). Yet nowhere in our discussion of the citric acid cycle have we indicated how oxygen is used. Recall, however, that in the four oxidation-reduction steps occurring in the citric acid cycle, the coenzyme NAD^+ or FAD is reduced to NADH or $FADH_2$, respectively. *Oxygen is needed to reoxidize these coenzymes*. Recall, too, that very little ATP is obtained directly from the citric acid cycle. Instead, oxygen participation and significant ATP production occur subsequent to the citric acid cycle, in two pathways that are closely linked: electron transport and oxidative phosphorylation.

All the enzymes and coenzymes for the citric acid cycle, the reoxidation of NADH and $FADH_{2,}$ and the production of ATP are located in the mitochondria, which are small, oval organelles with double membranes, often referred to as the “power plants” of the cell (Figure $20.4.2$). A cell may contain 100–5,000 mitochondria, depending on its function, and the mitochondria can reproduce themselves if the energy requirements of the cell increase.

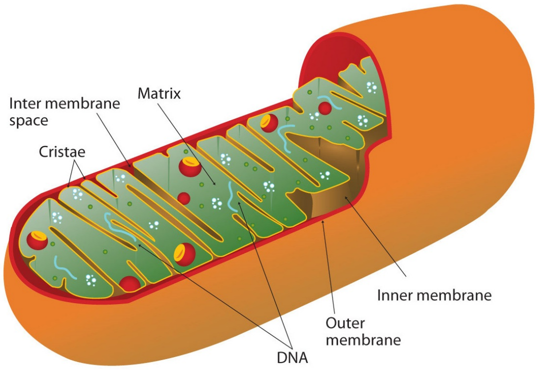


Figure $20.4.2$: Respiration

> ### *Cellular respiration occurs in the mitochondria*

Figure $20.4.2$ shows the mitochondrion’s two membranes: *outer* and *inner*. The inner membrane is extensively folded into a series of internal ridges called *cristae*. Thus there are two compartments in mitochondria: the *intermembrane space*, which lies between the membranes, and the *matrix*, which lies inside the inner membrane. The outer membrane is permeable, whereas the inner membrane is impermeable to most molecules and ions, although water, oxygen, and carbon dioxide can freely penetrate both membranes. The matrix contains all the enzymes of the citric acid cycle with the exception of succinate dehydrogenase, which is embedded in the inner membrane. The enzymes that are needed for the reoxidation of NADH and $FADH_2$ and ATP production are also located in the inner membrane. They are arranged in specific positions so that they function in a manner analogous to a bucket brigade. This highly organized sequence of oxidation-reduction enzymes is known as the electron transport chain (or respiratory chain).

Electron Transport

Figure $20.4.3$ illustrates the organization of the electron transport chain. The components of the chain are organized into four complexes designated I, II, III, and IV. Each complex contains several enzymes, other proteins, and metal ions. The metal ions can be reduced and then oxidized repeatedly as electrons are passed from one component to the next. Recall that a compound is reduced when it gains electrons or hydrogen atoms and is oxidized when it loses electrons or hydrogen atoms.

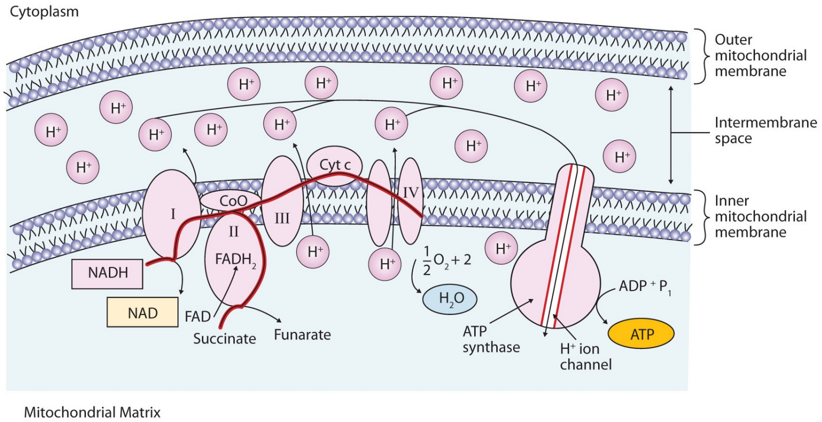
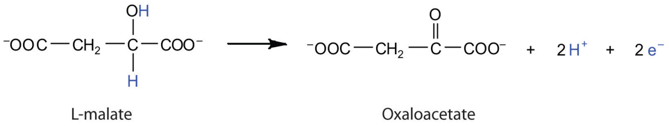


Figure $20.4.3$: The Mitochondrial Electron Transport Chain and ATP Synthase. The red line shows the path of electrons.

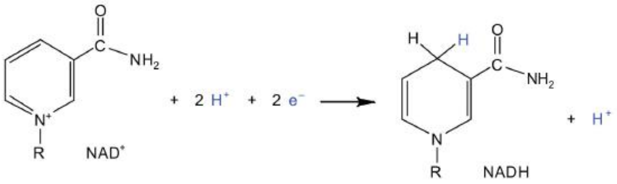
Electrons can enter the electron transport chain through either complex I or II. We will look first at electrons entering at complex I. These electrons come from NADH, which is formed in three reactions of the citric acid cycle. Let's use step 8 as an example, the reaction in which L-malate is oxidized to oxaloacetate and NAD$^+$ is reduced to NADH. This reaction can be divided into two half reactions:

- *Oxidation half-reaction*:



$$^{-}OOC-CH_2-\underset{H}{\overset{OH}{C}}-COO^{-} \longrightarrow {}^{-}OOC-CH_2-\overset{O}{\overset{\|}{C}}-COO^{-} + 2H^{+} + 2e^{-}$$

- *Reduction half-reaction*:

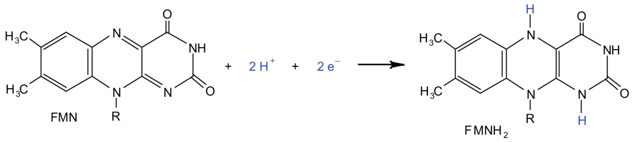


In the oxidation half-reaction, two hydrogen (H$^+$) ions and two electrons are removed from the substrate. In the reduction half-reaction, the NAD$^+$ molecule accepts both of those electrons and one of the H$^+$ ions. The other H$^+$ ion is transported from the matrix, across the inner mitochondrial membrane, and into the intermembrane space. The NADH diffuses through the matrix and is bound by complex I of the electron transport chain. In the complex, the coenzyme flavin mononucleotide (FMN) accepts both electrons from NADH. By passing the electrons along, NADH is oxidized back to NAD$^+$ and FMN is reduced to FMNH$_2$ (reduced form of flavin mononucleotide). Again, the reaction can be illustrated by dividing it into its respective half-reactions.

- *Oxidation half-reaction*:

$$NADH + H^{+} \longrightarrow NAD^{+} + 2H^{+} + 2e^{-}$$

- *Reduction half-reaction*:



Complex I contains several proteins that have iron-sulfur (Fe·S) centers. The electrons that reduced FMN to $FMNH_2$ are now transferred to these proteins. The iron ions in the Fe·S centers are in the Fe(III) form at first, but by accepting an electron, each ion is reduced to the Fe(II) form. Because each Fe·S center can transfer only one electron, two centers are needed to accept the two electrons that will regenerate FMN.

- *Oxidation half-reaction*:

$$\mathrm{FMNH_2} \longrightarrow \mathrm{FMN} + 2\,\mathrm{H^+} + 2\,\mathrm{e^-}$$

- *Reduction half-reaction*:

$$2\,\mathrm{Fe(III)} \cdot \mathrm{S} + 2\,\mathrm{e^-} \longrightarrow 2\,\mathrm{Fe(II)} \cdot \mathrm{S}$$

Electrons from $FADH_2$, formed in step 6 of the citric acid cycle, enter the electron transport chain through complex II. Succinate dehydrogenase, the enzyme in the citric acid cycle that catalyzes the formation of $FADH_2$ from FAD is part of complex II. The electrons from $FADH_2$ are then transferred to an Fe·S protein.

- *Oxidation half-reaction*:

$$\mathrm{FADH_2} \longrightarrow \mathrm{FAD} + 2\,\mathrm{H^+} + 2\,\mathrm{e^-}$$

- *Reduction half-reaction*:

$$2\,\mathrm{Fe(III)} \cdot \mathrm{S} + 2\,\mathrm{e^-} \rightarrow 2\,\mathrm{Fe(II)} \cdot \mathrm{S}$$

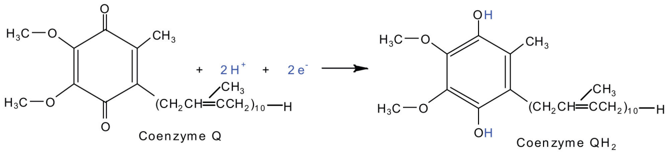
Electrons from complexes I and II are then transferred from the $\mathrm{Fe} \cdot \mathrm{S}$ protein to coenzyme Q (CoQ), a mobile electron carrier that acts as the electron shuttle between complexes I or II and complex III.

> *Coenzyme Q is also called ubiquinone because it is ubiquitous in living systems.*

- *Oxidation half-reaction*:

$$2\,\mathrm{Fe(II)} \cdot \mathrm{S} \longrightarrow 2\,\mathrm{Fe(III)} \cdot \mathrm{S} + 2\,\mathrm{e^-}$$

- *Reduction half-reaction*:



Complexes III and IV include several iron-containing proteins known as cytochromes. The iron in these enzymes is located in substructures known as iron porphyrins (Figure 20.4.4). Like the Fe·S centers, the characteristic feature of the cytochromes is the ability of their iron atoms to exist as either Fe(II) or Fe(III). Thus, each cytochrome in its oxidized form—Fe(III)—can accept one electron and be reduced to the Fe(II) form. This change in oxidation state is reversible, so the reduced form can donate its electron to the next cytochrome, and so on. Complex III contains cytochromes b and c, as well as Fe·S proteins, with cytochrome c acting as the electron shuttle between complex III and IV. Complex IV contains cytochromes a and a_3 in an enzyme known as *cytochrome oxidase*. This enzyme has the ability to transfer electrons to molecular oxygen, the last electron acceptor in the chain of electron transport reactions. In this final step, water (H_2O) is formed.

- *Oxidation half-reaction*:

$$4\,\mathrm{Cyt\,a_3}-\mathrm{Fe(II)} \longrightarrow 4\,\mathrm{Cyt\,a_3}-\mathrm{Fe(III)} + 4\,\mathrm{e^-}$$

- *Reduction half-reaction*:

$$\mathrm{O_2} + 4\,\mathrm{H^+} + 4\,\mathrm{e^-} \longrightarrow 2\,\mathrm{H_2O}$$

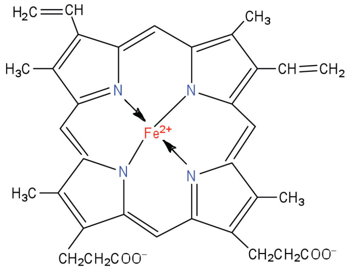


Figure 20.4.4: An Iron Porphyrin. Iron porphyrins are present in cytochromes as well as in myoglobin and hemoglobin.

Video: Cellular Respiration (Electron Transport Chain). Cellular respiration occurs in the mitochondria and provides both animals and plants with the energy needed to power other cellular processes. This section covers the electron transport chain.NDSU Virtual Cell Animations Project animation; ror more information please see Vcell, NDSU, Animations(opens in new window) [vcell.ndsu.edu]

Oxidative Phosphorylation

Each intermediate compound in the electron transport chain is reduced by the addition of one or two electrons in one reaction and then subsequently restored to its original form by delivering the electron(s) to the next compound along the chain. The successive electron transfers result in energy production. But how is this energy used for the synthesis of ATP? The process that links ATP synthesis to the operation of the electron transport chain is referred to as oxidative phosphorylation.

Electron transport is tightly coupled to oxidative phosphorylation. The coenzymes NADH and $FADH_2$ are oxidized by the respiratory chain *only* if ADP is simultaneously phosphorylated to ATP. The currently accepted model explaining how these two processes are linked is known as the *chemiosmotic hypothesis*, which was proposed by Peter Mitchell, resulting in Mitchell being awarded the 1978 Nobel Prize in Chemistry.

Looking again at Figure $20.4.3$, we see that as electrons are being transferred through the electron transport chain, hydrogen (H^+) ions are being transported across the inner mitochondrial membrane from the matrix to the intermembrane space. The concentration of H^+ is already higher in the intermembrane space than in the matrix, so energy is required to transport the additional H^+ there. This energy comes from the electron transfer reactions in the electron transport chain. But how does the extreme difference in H^+ concentration then lead to ATP synthesis? The buildup of H^+ ions in the intermembrane space results in an H^+ ion gradient that is a large energy source, like water behind a dam (because, given the opportunity, the protons will flow out of the intermembrane space and into the less concentrated matrix). Current research indicates that the flow of H^+ down this concentration gradient through a fifth enzyme complex, known as ATP synthase, leads to a change in the structure of the synthase, causing the synthesis and release of ATP.

In cells that are using energy, the turnover of ATP is very high, so these cells contain high levels of ADP. They must therefore consume large quantities of oxygen continuously, so as to have the energy necessary to phosphorylate ADP to form ATP. Consider, for example, that resting skeletal muscles use about 30% of a resting adult's oxygen consumption, but when the same muscles are working strenuously, they account for almost 90% of the total oxygen consumption of the organism.

Experiment has shown that 2.5–3 ATP molecules are formed for every molecule of NADH oxidized in the electron transport chain, and 1.5–2 ATP molecules are formed for every molecule of $FADH_2$ oxidized. Table 20.4.1 summarizes the theoretical maximum yield of ATP produced by the complete oxidation of 1 mol of acetyl-CoA through the sequential action of the citric acid cycle, the electron transport chain, and oxidative phosphorylation.

Table 20.4.1: Maximum Yield of ATP from the Complete Oxidation of 1 Mol of Acetyl-CoA

Reaction	Comments	Yield of ATP (moles)
Isocitrate → α-ketoglutarate + CO_2	produces 1 mol NADH	
α-ketoglutarate → succinyl-CoA + CO_2	produces 1 mol NADH	
Succinyl-CoA → succinate	produces 1 mol GTP	+1
Succinate → fumarate	produces 1 mol $FADH_2$	
Malate → oxaloacetate	produces 1 mol NADH	
1 $FADH_2$ from the citric acid cycle	yields 2 mol ATP	+2
3 NADH from the citric acid cycle	yields 3 mol ATP/NADH	+9
Net yield of ATP:		+12

Key Takeaways

- The acetyl group of acetyl-CoA enters the citric acid cycle. For each acetyl-CoA that enters the citric acid cycle, 2 molecules of carbon dioxide, 3 molecules of NADH, 1 molecule of ATP, and 1 molecule of $FADH_2$ are produced.
- The reduced coenzymes (NADH and $FADH_2$) produced by the citric acid cycle are reoxidized by the reactions of the electron transport chain. This series of reactions also produces a pH gradient across the inner mitochondrial membrane.
- The pH gradient produced by the electron transport chain drives the synthesis of ATP from ADP. For each NADH reoxidized, 2.5–3 molecules of ATP are produced; for each $FADH_2$ reoxidized, 1.5–2 molecules of ATP are produced.

20.5: Stage II of Carbohydrate Catabolism

Learning Objectives

- Describe the function of glycolysis and identify its major products.
- Describe how the presence or absence of oxygen determines what happens to the pyruvate and the NADH that are produced in glycolysis.
- Determine the amount of ATP produced by the oxidation of glucose in the presence and absence of oxygen.

In stage II of catabolism, the metabolic pathway known as glycolysis converts glucose into two molecules of pyruvate (a three-carbon compound with three carbon atoms) with the corresponding production of adenosine triphosphate (ATP). The individual reactions in glycolysis were determined during the first part of the 20th century. It was the first metabolic pathway to be elucidated, in part because the participating enzymes are found in soluble form in the cell and are readily isolated and purified. The pathway is structured so that the product of one enzyme-catalyzed reaction becomes the substrate of the next. The transfer of intermediates from one enzyme to the next occurs by diffusion.

Steps in Glycolysis

The 10 reactions of glycolysis, summarized in Figures $20.5.1$ and $20.5.2$, can be divided into two phases. In the first 5 reactions—phase I—glucose is broken down into two molecules of glyceraldehyde 3-phosphate. In the last five reactions—phase II—each glyceraldehyde 3-phosphate is converted into pyruvate, and ATP is generated. Notice that all the intermediates in glycolysis are phosphorylated and contain either six or three carbon atoms.

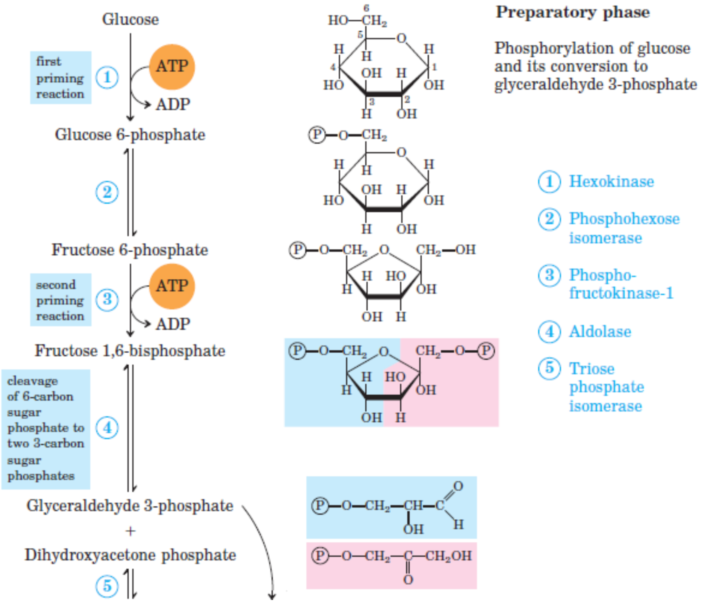


Figure 20.5.1: Phase 1 (preparatory phase) of Glycolysis

- When glucose enters a cell, it is immediately phosphorylated to form glucose 6-phosphate, in the first reaction of phase I. The phosphate donor in this reaction is ATP, and the enzyme—which requires magnesium ions for its activity—is *hexokinase*. In this reaction, ATP is being used rather than being synthesized. The presence of such a reaction in a catabolic pathway that is supposed to *generate* energy may surprise you. However, in addition to activating the glucose molecule, this initial reaction is essentially irreversible, an added benefit that keeps the overall process moving in the right direction. Furthermore, the addition of the negatively charged phosphate group prevents the intermediates formed in glycolysis from diffusing through the cell membrane, as neutral molecules such as glucose can do.
- In the next reaction, *phosphoglucose isomerase* catalyzes the isomerization of glucose 6-phosphate to fructose 6-phosphate. This reaction is important because it creates a primary alcohol, which can be readily phosphorylated.
- The subsequent phosphorylation of fructose 6-phosphate to form fructose 1,6-bisphosphate is catalyzed by *phosphofructokinase*, which requires magnesium ions for activity. ATP is again the phosphate donor.

- Fructose 1,6-bisphosphate is enzymatically cleaved by *aldolase* to form two triose phosphates: dihydroxyacetone phosphate and glyceraldehyde 3-phosphate.
- Isomerization of dihydroxyacetone phosphate into a second molecule of glyceraldehyde 3-phosphate is the final step in phase I. The enzyme catalyzing this reaction is *triose phosphate isomerase*.

> When a molecule contains two phosphate groups on different carbon atoms, the convention is to use the prefix *bis*. When the two phosphate groups are bonded to each other on the same carbon atom (for example, adenosine diphosphate [ADP]), the prefix is *di*.

> In steps 4 and 5, aldolase and triose phosphate isomerase effectively convert one molecule of fructose 1,6-bisphosphate into *two* molecules of glyceraldehyde 3-phosphate. Thus, phase I of glycolysis requires energy in the form of two molecules of ATP and releases none of the energy stored in glucose.

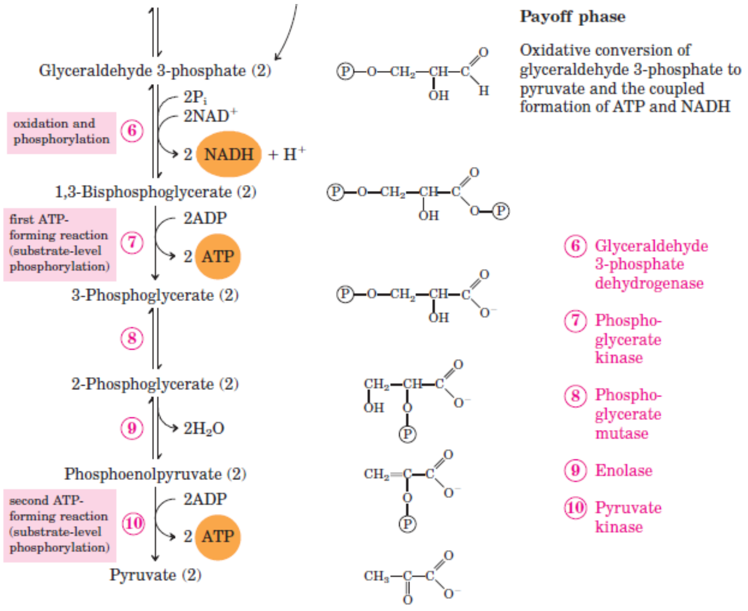


Figure 20.5.2: Phase 2 (payoff phase) of Glycolysis

In the initial step of phase II (Figure 20.5.2), glyceraldehyde 3-phosphate is both oxidized and phosphorylated in a reaction catalyzed by *glyceraldehyde-3-phosphate dehydrogenase*, an enzyme that requires nicotinamide adenine dinucleotide (NAD^+) as the oxidizing agent and inorganic phosphate as the phosphate donor. In the reaction, NAD^+ is reduced to reduced nicotinamide adenine dinucleotide (NADH), and 1,3-bisphosphoglycerate (BPG) is formed.

- BPG has a high-energy phosphate bond (Table 20.5.1) joining a phosphate group to C1. This phosphate group is now transferred directly to a molecule of ADP, thus forming ATP and 3-phosphoglycerate. The enzyme that catalyzes the reaction is **phosphoglycerate kinase**, which, like all other kinases, requires magnesium ions to function. This is the first reaction to produce ATP in the pathway. Because the ATP is formed by a direct transfer of a phosphate group from a metabolite to ADP—that is, from one substrate to another—the process is referred to as substrate-level phosphorylation, to distinguish it from the *oxidative phosphorylation* discussed in Section 20.4.
- In the next reaction, the phosphate group on 3-phosphoglycerate is transferred from the OH group of C3 to the OH group of C2, forming 2-phosphoglycerate in a reaction catalyzed by *phosphoglyceromutase*.
- A dehydration reaction, catalyzed by *enolase*, forms phosphoenolpyruvate (PEP), another compound possessing a high-energy phosphate group.
- The final step is irreversible and is the second reaction in which substrate-level phosphorylation occurs. The phosphate group of PEP is transferred to ADP, with one molecule of ATP being produced per molecule of PEP. The reaction is catalyzed by *pyruvate kinase*, which requires both magnesium and potassium ions to be active.

Table 20.5.1: Maximum Yield of ATP from the Complete Oxidation of 1 Mol of Glucose

Reaction	Comments	Yield of ATP (moles)
glucose → glucose 6-phosphate	consumes 1 mol ATP	−1
fructose 6-phosphate → fructose 1,6-bisphosphate	consumes 1 mol ATP	−1
glyceraldehyde 3-phosphate → BPG	produces 2 mol of cytoplasmic NADH	
BPG → 3-phosphoglycerate	produces 2 mol ATP	+2
phosphoenolpyruvate → pyruvate	produces 2 mol ATP	+2
pyruvate → acetyl-CoA + CO_2	produces 2 mol NADH	
isocitrate → α-ketoglutarate + CO_2	produces 2 mol NADH	
α-ketoglutarate → succinyl-CoA + CO_2	produces 2 mol NADH	
succinyl-CoA → succinate	produces 2 mol GTP	+2
succinate → fumarate	produces 2 mol $FADH_2$	
malate → oxaloacetate	produces 2 mol NADH	
2 cytoplasmic NADH from glycolysis	yields 2–3 mol ATP per NADH (depending on tissue)	+4 to +6
2 NADH from the oxidation of pyruvate	yields 3 mol ATP per NADH	+6
2 $FADH_2$ from the citric acid cycle	yields 2 ATP per $FADH_2$	+4
3 NADH from the citric acid cycle	yields 3 ATP per NADH	+18
Net yield of ATP:		+36 to +38

> In phase II, two molecules of glyceraldehyde 3-phosphate are converted to two molecules of pyruvate, along with the production of four molecules of ATP and two molecules of NADH.

✓ To Your Health: Diabetes

Although medical science has made significant progress against diabetes , it continues to be a major health threat. Some of the serious complications of diabetes are as follows:

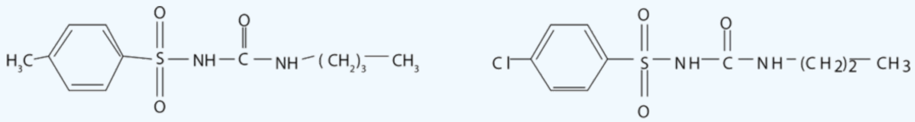
- It is the leading cause of lower limb amputations in the United States.
- It is the leading cause of blindness in adults over age 20.
- It is the leading cause of kidney failure.
- It increases the risk of having a heart attack or stroke by two to four times.

Because a person with diabetes is unable to use glucose properly, excessive quantities accumulate in the blood and the urine. Other characteristic symptoms are constant hunger, weight loss, extreme thirst, and frequent urination because the kidneys excrete large amounts of water in an attempt to remove excess sugar from the blood.

There are two types of diabetes. In immune-mediated diabetes, insufficient amounts of insulin are produced. This type of diabetes develops early in life and is also known as *Type 1 diabetes*, as well as insulin-dependent or juvenile-onset diabetes. Symptoms are rapidly reversed by the administration of insulin, and Type 1 diabetics can lead active lives provided they receive insulin as needed. Because insulin is a protein that is readily digested in the small intestine, it cannot be taken orally and must be injected at least once a day.

In Type 1 diabetes, insulin-producing cells of the pancreas are destroyed by the body's immune system. Researchers are still trying to find out why. Meanwhile, they have developed a simple blood test capable of predicting who will develop Type 1 diabetes several years before the disease becomes apparent. The blood test reveals the presence of antibodies that destroy the body's insulin-producing cells.

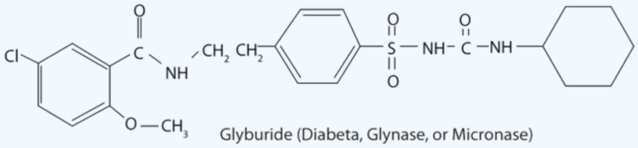
Type 2 diabetes, also known as noninsulin-dependent or adult-onset diabetes, is by far the more common, representing about 95% of diagnosed diabetic cases. (This translates to about 16 million Americans.) Type 2 diabetics usually produce sufficient amounts of insulin, but either the insulin-producing cells in the pancreas do not release enough of it, or it is not used properly because of defective insulin receptors or a lack of insulin receptors on the target cells. In many of these people, the disease can be controlled with a combination of diet and exercise alone. For some people who are overweight, losing weight is sufficient to bring their blood sugar level into the normal range, after which medication is not required if they exercise regularly and eat wisely.



Tolbutamide (Orinase)

Chlorpropamide (Diabinese)

First-Generation Antidiabetic Drugs



Glyburide (Diabeta, Glynase, or Micronase)

Second-Generation Antidiabetic Drugs

Those who require medication may use oral antidiabetic drugs that stimulate the islet cells to secrete insulin. First-generation antidiabetic drugs stimulated the release of insulin. Newer second-generation drugs, such as glyburide, do as well, but they also increase the sensitivity of cell receptors to insulin. Some individuals with Type 2 diabetes do not produce enough insulin and thus do not respond to these oral medications; they must use insulin. In both Type 1 and Type 2 diabetes, the blood sugar level must be carefully monitored and adjustments made in diet or medication to keep the level as normal as possible (70–120 mg/dL).

Metabolism of Pyruvate

The presence or absence of oxygen determines the fates of the pyruvate and the NADH produced in glycolysis. When plenty of oxygen is available, pyruvate is completely oxidized to carbon dioxide, with the release of much greater amounts of ATP through the combined actions of the citric acid cycle, the electron transport chain, and oxidative phosphorylation. However, in the absence of oxygen (that is, under anaerobic conditions), the fate of pyruvate is different in different organisms. In vertebrates, pyruvate is converted to lactate, while other organisms, such as yeast, convert pyruvate to ethanol and carbon dioxide. These possible fates of pyruvate are summarized in Figure $20.5.2$ The conversion to lactate or ethanol under anaerobic conditions allows for the reoxidation of NADH to NAD^+ in the absence of oxygen.

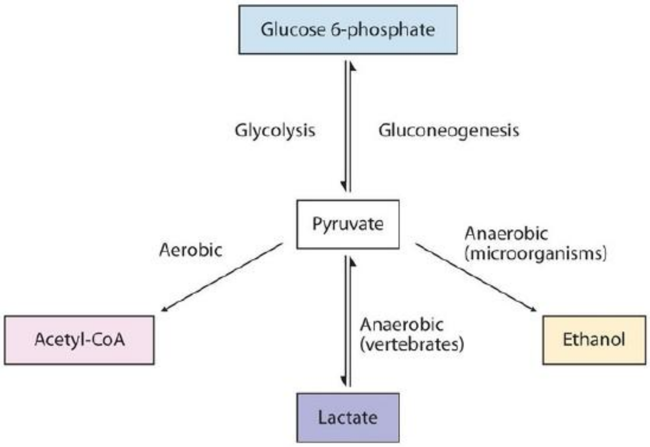


Figure 20.5.2: Metabolic Fates of Pyruvate

ATP Yield from Glycolysis

The net energy yield from anaerobic glucose metabolism can readily be calculated in moles of ATP. In the initial phosphorylation of glucose (step 1), 1 mol of ATP is expended, along with another in the phosphorylation of fructose 6-phosphate (step 3). In step 7, 2 mol of BPG (recall that 2 mol of 1,3-BPG are formed for each mole of glucose) are converted to 2 mol of 3-phosphoglycerate, and 2 mol of ATP are produced. In step 10, 2 mol of pyruvate and 2 mol of ATP are formed per mole of glucose.

For every mole of glucose degraded, 2 mol of ATP are initially consumed and 4 mol of ATP are ultimately produced. The net production of ATP is thus 2 mol for each mole of glucose converted to lactate or ethanol. If 7.4 kcal of energy is conserved per mole of ATP produced, and the total amount of energy that can theoretically be obtained from the complete oxidation of 1 mol of glucose is 670 kcal (as stated in the chapter introduction), the energy conserved in the anaerobic catabolism of glucose to two molecules of lactate (or ethanol) is as follows:

$$\frac{2 \times 7.4 \text{ kcal}}{670 \text{ kcal}} \times 100 = 2.2\%$$

Thus anaerobic cells extract only a very small fraction of the total energy of the glucose molecule.

Contrast this result with the amount of energy obtained when glucose is completely oxidized to carbon dioxide and water through glycolysis, the citric acid cycle, the electron transport chain, and oxidative phosphorylation as summarized in Table $20.5.1$. Note the indication in the table that a variable amount of ATP is synthesized, depending on the tissue, from the NADH formed in the cytoplasm during glycolysis. This is because NADH is not transported into the inner mitochondrial membrane where the enzymes for the electron transport chain are located. Instead, brain and muscle cells use a transport mechanism that passes electrons from the cytoplasmic NADH through the membrane to flavin adenine dinucleotide (FAD) molecules inside the mitochondria, forming reduced flavin adenine dinucleotide ($FADH_2$), which then feeds the electrons into the electron transport chain. This route lowers the yield of ATP to 1.5–2 molecules of ATP, rather than the usual 2.5–3 molecules. A more efficient transport system is found in liver, heart, and kidney cells where the formation of one cytoplasmic NADH molecule results in the formation of one mitochondrial NADH molecule, which leads to the formation of 2.5–3 molecules of ATP.The total amount of energy conserved in the aerobic catabolism of glucose in the liver is as follows:

$$\frac{38 \times 7.4 \text{ kcal}}{670 \text{ kcal}} \times 100 = 42\%$$

Conservation of 42% of the total energy released compares favorably with the efficiency of any machine. In comparison, automobiles are only about 20%–25% efficient in using the energy released by the combustion of gasoline.

As indicated earlier, the 58% of released energy that is not conserved enters the surroundings (that is, the cell) as heat that helps to maintain body temperature. If we are exercising strenuously and our metabolism speeds up to provide the energy needed for muscle contraction, more heat is produced. We begin to perspire to dissipate some of that heat. As the perspiration evaporates, the excess heat is carried away from the body by the departing water vapor.

Summary

- The monosaccharide glucose is broken down through a series of enzyme-catalyzed reactions known as glycolysis.
- For each molecule of glucose that is broken down, two molecules of pyruvate, two molecules of ATP, and two molecules of NADH are produced.
- In the absence of oxygen, pyruvate is converted to lactate, and NADH is reoxidized to NAD+. In the presence of oxygen, pyruvate is converted to acetyl-CoA and then enters the citric acid cycle.
- More ATP can be formed from the breakdown of glucose when oxygen is present.

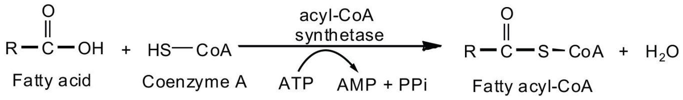
20.6: Stage II of Lipid Catabolism

Learning Objectives

- To describe the reactions needed to completely oxidize a fatty acid to carbon dioxide and water.

Like glucose, the fatty acids released in the digestion of triglycerides and other lipids are broken down in a series of sequential reactions accompanied by the gradual release of usable energy. Some of these reactions are oxidative and require nicotinamide adenine dinucleotide (NAD^+) and flavin adenine dinucleotide (FAD). The enzymes that participate in fatty acid catabolism are located in the mitochondria, along with the enzymes of the citric acid cycle, the electron transport chain, and oxidative phosphorylation. This localization of enzymes in the mitochondria is of the utmost importance because it facilitates efficient utilization of energy stored in fatty acids and other molecules.

Fatty acid oxidation is initiated on the outer mitochondrial membrane. There the fatty acids, which like carbohydrates are relatively inert, must first be activated by conversion to an energy-rich fatty acid derivative of coenzyme A called *fatty acyl-coenzyme A* (CoA). The activation is catalyzed by *acyl-CoA synthetase*. For each molecule of fatty acid activated, one molecule of coenzyme A and one molecule of adenosine triphosphate (ATP) are used, equaling a net utilization of the two high-energy bonds in one ATP molecule (which is therefore converted to adenosine monophosphate [AMP] rather than adenosine diphosphate [ADP]):



The fatty acyl-CoA diffuses to the inner mitochondrial membrane, where it combines with a carrier molecule known as carnitine in a reaction catalyzed by *carnitine acyltransferase*. The acyl-carnitine derivative is transported into the mitochondrial matrix and converted back to the fatty acyl-CoA.

Steps in the β-Oxidation of Fatty Acids

Further oxidation of the fatty acyl-CoA occurs in the mitochondrial matrix via a sequence of four reactions known collectively as β-oxidation because the β-carbon undergoes successive oxidations in the progressive removal of two carbon atoms from the carboxyl end of the fatty acyl-CoA (Figure 20.6.1).

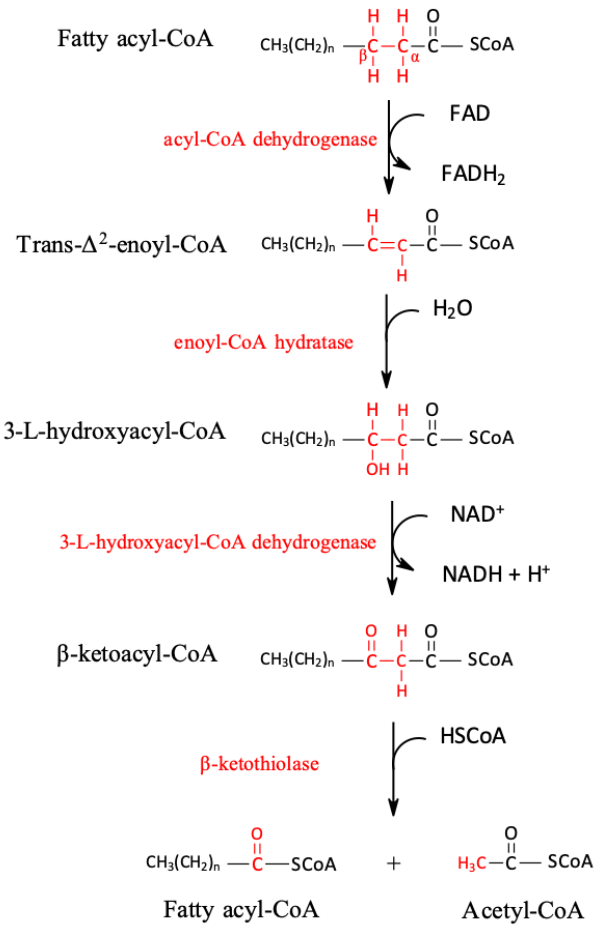


Figure 20.6.1: Fatty Acid Oxidation. The fatty acyl-CoA formed in the final step becomes the substrate for the first step in the next round of β-oxidation. β-oxidation continues until two acetyl-CoA molecules are produced in the final step.

The first step in the catabolism of fatty acids is the formation of an alkene in an oxidation reaction catalyzed by *acyl-CoA dehydrogenase*. In this reaction, the coenzyme FAD accepts two hydrogen atoms from the acyl-CoA, one from the α-carbon and one from the β-carbon, forming reduced flavin adenine dinucleotide ($FADH_2$).

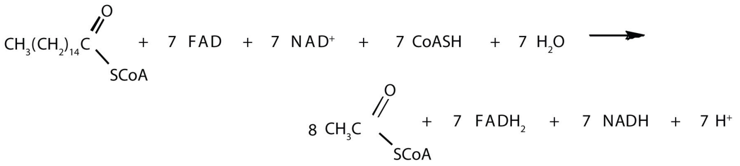
> The $FADH_2$ is reoxidized back to FAD via the electron transport chain that supplies energy to form 1.5–2 molecules of ATP.

Next, the *trans*-alkene is hydrated to form a secondary alcohol in a reaction catalyzed by *enoyl-CoA hydratase*. The enzyme forms only the L-isomer.

The secondary alcohol is then oxidized to a ketone by *β-hydroxyacyl-CoA dehydrogenase*, with NAD^+ acting as the oxidizing agent. The reoxidation of each molecule of NADH to NAD^+ by the electron transport chain furnishes 2.5–3 molecules of ATP.

The final reaction is cleavage of the β-ketoacyl-CoA by a molecule of coenzyme A. The products are acetyl-CoA and a fatty acyl-CoA that has been shortened by two carbon atoms. The reaction is catalyzed by *thiolase*.

The shortened fatty acyl-CoA is then degraded by repetitions of these four steps, each time releasing a molecule of acetyl-CoA. The overall equation for the β-oxidation of palmitoyl-CoA (16 carbon atoms) is as follows:



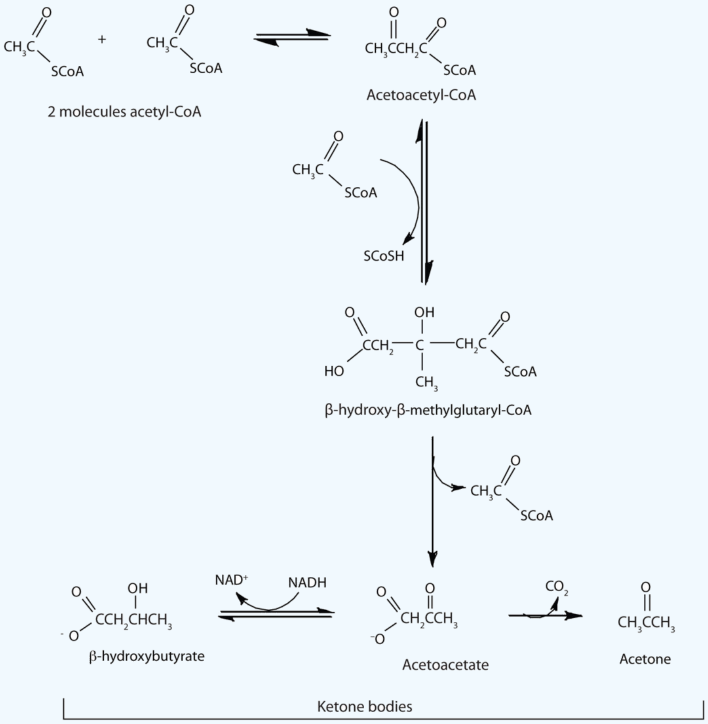
$$CH_3(CH_2)_{14}C(=O)SCoA + 7\ FAD + 7\ NAD^+ + 7\ CoASH + 7\ H_2O \longrightarrow 8\ CH_3C(=O)SCoA + 7\ FADH_2 + 7\ NADH + 7\ H^+$$

> *Because each shortened fatty acyl-CoA cycles back to the beginning of the pathway, β-oxidation is sometimes referred to as the fatty acid spiral.*

The fate of the acetyl-CoA obtained from fatty acid oxidation depends on the needs of an organism. It may enter the citric acid cycle and be oxidized to produce energy, it may be used for the formation of water-soluble derivatives known as ketone bodies, or it may serve as the starting material for the synthesis of fatty acids. For more information about the citric acid cycle, see Section 20.4.

✓ Looking Closer: Ketone Bodies

In the liver, most of the acetyl-CoA obtained from fatty acid oxidation is oxidized by the citric acid cycle. However, some of the acetyl-CoA is used to synthesize a group of compounds known as *ketone bodies*: acetoacetate, β-hydroxybutyrate, and acetone. Two acetyl-CoA molecules combine, in a reversal of the final step of β-oxidation, to produce acetoacetyl-CoA. The acetoacetyl-CoA reacts with another molecule of acetyl-CoA and water to form β-hydroxy-β-methylglutaryl-CoA, which is then cleaved to acetoacetate and acetyl-CoA. Most of the acetoacetate is reduced to β-hydroxybutyrate, while a small amount is decarboxylated to carbon dioxide and acetone.



The acetoacetate and β-hydroxybutyrate synthesized by the liver are released into the blood for use as a metabolic fuel (to be converted back to acetyl-CoA) by other tissues, particularly the kidney and the heart. Thus, during prolonged starvation, ketone bodies provide about 70% of the energy requirements of the brain. Under normal conditions, the kidneys excrete about 20 mg of ketone bodies each day, and the blood levels are maintained at about 1 mg of ketone bodies per 100 mL of blood.

In starvation, diabetes mellitus, and certain other physiological conditions in which cells do not receive sufficient amounts of carbohydrate, the rate of fatty acid oxidation increases to provide energy. This leads to an increase in the concentration of acetyl-CoA. The increased acetyl-CoA cannot be oxidized by the citric acid cycle because of a decrease in the concentration of oxaloacetate, which is diverted to glucose synthesis. In response, the rate of ketone body formation in the liver increases further, to a level much higher than can be used by other tissues. The excess ketone bodies accumulate in the blood and the urine, a condition referred to as *ketosis*. When the acetone in the blood reaches the lungs, its volatility causes it to be expelled in the breath. The sweet smell of acetone, a characteristic of ketosis, is frequently noticed on the breath of severely diabetic patients.

Because two of the three kinds of ketone bodies are weak acids, their presence in the blood in excessive amounts overwhelms the blood buffers and causes a marked decrease in blood pH (to 6.9 from a normal value of 7.4). This decrease in pH leads to a serious condition known as *acidosis*. One of the effects of acidosis is a decrease in the ability of hemoglobin to transport oxygen in the blood. In moderate to severe acidosis, breathing becomes labored and very painful. The body also loses fluids and becomes dehydrated as the kidneys attempt to get rid of the acids by eliminating large quantities of water. The lowered oxygen supply and dehydration lead to depression; even mild acidosis leads to lethargy, loss of appetite, and a generally run-down feeling. Untreated patients may go into a coma. At that point, prompt treatment is necessary if the person's life is to be saved.

ATP Yield from Fatty Acid Oxidation

The amount of ATP obtained from fatty acid oxidation depends on the size of the fatty acid being oxidized. For our purposes here. we'll study palmitic acid, a saturated fatty acid with 16 carbon atoms, as a typical fatty acid in the human diet. Calculating its energy yield provides a model for determining the ATP yield of all other fatty acids.

The breakdown by an organism of 1 mol of palmitic acid requires 1 mol of ATP (for activation) and forms 8 mol of acetyl-CoA. Recall from Table 20.4.1 that each mole of acetyl-CoA metabolized by the citric acid cycle yields 10 mol of ATP. The complete degradation of 1 mol of palmitic acid requires the β-oxidation reactions to be repeated seven times. Thus, 7 mol of NADH and 7 mol of $FADH_2$ are produced. Reoxidation of these compounds through respiration yields 2.5–3 and 1.5–2 mol of ATP, respectively. The energy calculations can be summarized as follows:

ATP Yield from Fatty Acid Oxidation

1 mol of ATP is split to AMP and $2P_i$	−2 ATP
8 mol of acetyl-CoA formed (8 × 12)	96 ATP
7 mol of $FADH_2$ formed (7 × 2)	14 ATP
7 mol of NADH formed (7 × 3)	21 ATP
Total	129 ATP

> *The number of times β-oxidation is repeated for a fatty acid containing n carbon atoms is n/2 – 1 because the final turn yields two acetyl-CoA molecules.*

The combustion of 1 mol of palmitic acid releases a considerable amount of energy:

$$C_{16}H_{32}O_2 + 23O_2 \rightarrow 16CO_2 + 16H_2O + 2,340\ kcal$$

The percentage of this energy that is conserved by the cell in the form of ATP is as follows:

$$\frac{\text{energy conserved}}{\text{total energy available}} \times 100 = \frac{(129\text{ ATP})(7.4\text{ kcal/ATP})}{2,340\text{ kcal}} \times 100 = 41\%$$

The efficiency of fatty acid metabolism is comparable to that of carbohydrate metabolism, which we calculated to be 42%. For more information about the efficiency of fatty acid metabolism, see II of Carbohydrate Catabolism" data-cke-saved-href="/Bookshelves/Introductory_Chemistry/Basics_of_General_Organic_and_Biological_Chemistry_(Ball_et_al.)/20:_Energy_Metabolism/20.05:_Stage_II_of_Carbohydrate_Catabolism" href="/Bookshelves/Introductory_Chemistry/Basics_of_General_Organic_and_Biological_Chemistry_(Ball_et_al.)/20:_Energy_Metabolism/20.05:_Stage_II_of_Carbohydrate_Catabolism" data-quail-id="91">Section 20.5.

> *The oxidation of fatty acids produces large quantities of water. This water, which sustains migratory birds and animals (such as the camel) for long periods of time.*

Summary

- Fatty acids, obtained from the breakdown of triglycerides and other lipids, are oxidized through a series of reactions known as β-oxidation.
- In each round of β-oxidation, 1 molecule of acetyl-CoA, 1 molecule of NADH, and 1 molecule of $FADH_2$ are produced.
- The acetyl-CoA, NADH, and $FADH_2$ are used in the citric acid cycle, the electron transport chain, and oxidative phosphorylation to produce ATP.

20.7: Stage II of Protein Catabolism

Learning Objectives

- To describe how excess amino acids are degraded.

The liver is the principal site of amino acid metabolism, but other tissues, such as the kidney, the small intestine, muscles, and adipose tissue, take part. Generally, the first step in the breakdown of amino acids is the separation of the amino group from the carbon skeleton, usually by a transamination reaction. The carbon skeletons resulting from the deaminated amino acids are used to form either glucose or fats, or they are converted to a metabolic intermediate that can be oxidized by the citric acid cycle. The latter alternative, amino acid catabolism, is more likely to occur when glucose levels are low—for example, when a person is fasting or starving.

Transamination

Transamination is an exchange of functional groups between any amino acid (except lysine, proline, and threonine) and an α-keto acid. The amino group is usually transferred to the keto carbon atom of pyruvate, oxaloacetate, or α-ketoglutarate, converting the α-keto acid to alanine, aspartate, or glutamate, respectively. Transamination reactions are catalyzed by specific transaminases (also called aminotransferases), which require pyridoxal phosphate as a coenzyme.

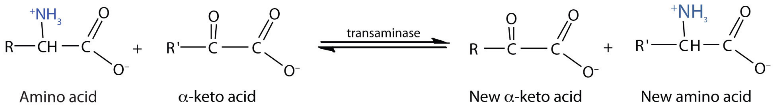


Figure 20.7.1).

> *In an α-keto acid, the carbonyl or keto group is located on the carbon atom adjacent to the carboxyl group of the acid.*

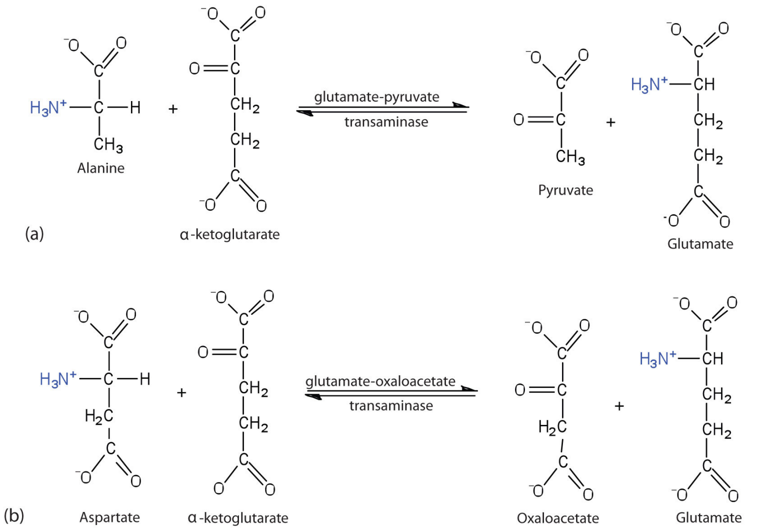
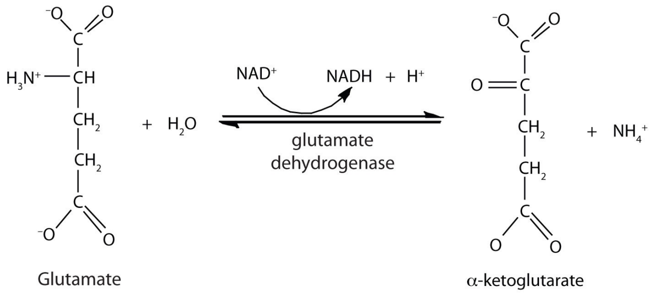


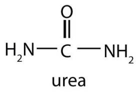
Figure 20.7.1: Two Transamination Reactions. In both reactions, the final acceptor of the amino group is α-ketoglutarate, and the final product is glutamate.

Oxidative Deamination

In the breakdown of amino acids for energy, the final acceptor of the α-amino group is α-ketoglutarate, forming glutamate. Glutamate can then undergooxidative deamination, in which it loses its amino group as an ammonium (NH_4^+) ion and is oxidized back to α-ketoglutarate (ready to accept another amino group):



This reaction occurs primarily in liver mitochondria. Most of the NH_4^+ ion formed by oxidative deamination of glutamate is converted to urea and excreted in the urine in a series of reactions known as the **urea cycle**.



The synthesis of glutamate occurs in animal cells by reversing the reaction catalyzed by glutamate dehydrogenase. For this reaction nicotinamide adenine dinucleotide phosphate (NADPH) acts as the reducing agent. The synthesis of glutamate is significant because it is one of the few reactions in animals that can incorporate inorganic nitrogen (NH_4^+) into an α-keto acid to form an amino acid. The amino group can then be passed on through transamination reactions, to produce other amino acids from the appropriate α-keto acids.

The Fate of the Carbon Skeleton

Any amino acid can be converted into an intermediate of the citric acid cycle. Once the amino group is removed, usually by transamination, the α-keto acid that remains is catabolized by a pathway unique to that acid and consisting of one or more reactions. For example, phenylalanine undergoes a series of six reactions before it splits into fumarate and acetoacetate. Fumarate is an intermediate in the citric acid cycle, while acetoacetate must be converted to acetoacetyl-coenzyme A (CoA) and then to acetyl-CoA before it enters the citric acid cycle.

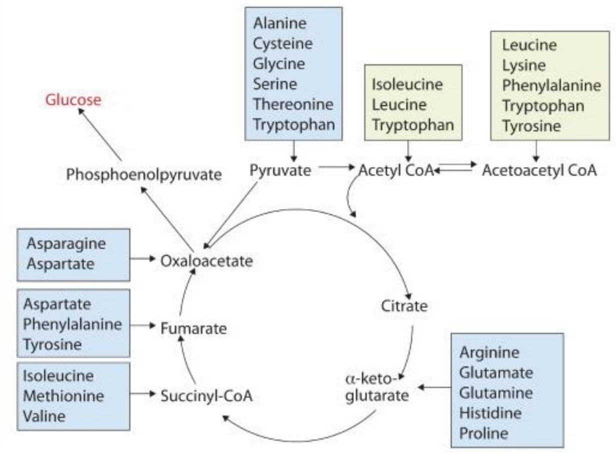


Figure 20.7.2: Fates of the Carbon Skeletons of Amino Acids

Those amino acids that can form any of the intermediates of carbohydrate metabolism can subsequently be converted to glucose via a metabolic pathway known as gluconeogenesis. These amino acids are called glucogenic amino acids. Amino acids that are converted to acetoacetyl-CoA or acetyl-CoA, which can be used for the synthesis of ketone bodies but not glucose, are called ketogenic amino acids. Some amino acids fall into both categories. Leucine and lysine are the only amino acids that are exclusively ketogenic. Figure 20.7.2 summarizes the ultimate fates of the carbon skeletons of the 20 amino acids.

✓ Career Focus: Exercise Physiologist

An exercise physiologist works with individuals who have or wish to prevent developing a wide variety of chronic diseases, such as diabetes, in which exercise has been shown to be beneficial. Each individual must be referred by a licensed physician. An exercise physiologist works in a variety of settings, such as a hospital or in a wellness program at a commercial business, to design and monitor individual exercise plans. A registered clinical exercise physiologist must have an undergraduate degree in exercise physiology or a related degree. Some job opportunities require a master's degree in exercise physiology or a related degree.

Ergospirometry laboratory for the measurement of metabolic changes during a graded exercise test on a treadmill. from Wikipedia.

Summary

Generally the first step in the breakdown of amino acids is the removal of the amino group, usually through a reaction known as transamination. The carbon skeletons of the amino acids undergo further reactions to form compounds that can either be used for the synthesis of glucose or the synthesis of ketone bodies.

20.E: Energy Metabolism (Exercises)

20.1: ATP- the Universal Energy Currency

Concept Review Exercise

1. Why is ATP referred to as the energy currency of the cell?

Answer

1. ATP is the principal molecule involved in energy exchange reactions in biological systems.

Exercises

1. How do ATP and ADP differ in structure?
2. Why does the hydrolysis of ATP to ADP involve the release of energy?
3. Identify whether each compound would be classified as a high-energy phosphate compound.
    a. ATP
    b. glucose 6-phosphate
    c. creatine phosphate
4. Identify whether each compound would be classified as a high-energy phosphate compound.
    a. ADP
    b. AMP
    c. glucose 1-phosphate

Answers

1. ATP has a triphosphate group attached, while ADP has only a diphosphate group attached.

3. a. yes
    b. no
    c. yes

20.2: Stage I of Catabolism

Concept Review Exercises

1. Distinguish between each pair of compounds.
    a. pepsin and pepsinogen
    b. chymotrypsin and trypsin
    c. aminopeptidase and carboxypeptidase
2. What are the primary end products of each form of digestion?
    a. carbohydrate digestion
    b. lipid digestion
    c. protein digestion
3. In what section of the digestive tract does most of the carbohydrate, lipid, and protein digestion take place?

Answers

1. a. Pepsinogen is an inactive form of pepsin; pepsin is the active form of the enzyme.
    b. Both enzymes catalyze the hydrolysis of peptide bonds. Chymotrypsin catalyzes the hydrolysis of peptide bonds following aromatic amino acids, while trypsin catalyzes the hydrolysis of peptide bonds following lysine and arginine.
    c. Aminopeptidase catalyzes the hydrolysis of amino acids from the N-terminal end of a protein, while carboxypeptidase catalyzes the hydrolysis of amino acids from the C-terminal end of a protein.
2. a. glucose, fructose, and galactose
    b. monoglycerides and fatty acids

   c. amino acids

3. the small intestine

Exercises

1. What are the products of digestion (or stage I of catabolism)?
2. What is the general type of reaction used in digestion?
3. Give the site of action and the function of each enzyme.
   a. chymotrypsin
   b. lactase
   c. pepsin
   d. maltase
4. Give the site of action and the function of each enzyme.
   a. α-amylase
   b. trypsin
   c. sucrase
   d. aminopeptidase
5. a. What is the meaning of the following statement? “Bile salts act to emulsify lipids in the small intestine.”
   b. Why is emulsification important?
6. Using chemical equations, describe the chemical changes that triglycerides undergo during digestion.
7. What are the expected products from the enzymatic action of chymotrypsin on each amino acid segment?
   a. gly-ala-phe-thr-leu
   b. ala-ile-tyr-ser-arg
   c. val-trp-arg-leu-cys
8. What are the expected products from the enzymatic action of trypsin on each amino acid segment?
   a. leu-thr-glu-lys-ala
   b. phe-arg-ala-leu-val
   c. ala-arg-glu-trp-lys

Answers

1. proteins: amino acids; carbohydrates: monosaccharides; fats: fatty acids and glycerol

3. a. Chymotrypsin is found in the small intestine and catalyzes the hydrolysis of peptide bonds following aromatic amino acids.
   b. Lactase is found in the small intestine and catalyzes the hydrolysis of lactose.
   c. Pepsin is found in the stomach and catalyzes the hydrolysis of peptide bonds, primarily those that occur after aromatic amino acids.
   d. Maltase is found in the small intestine and catalyzes the hydrolysis of maltose.

5. a. Bile salts aid in digestion by dispersing lipids throughout the aqueous solution in the small intestine.
   b. Emulsification is important because lipids are not soluble in water; it breaks lipids up into smaller particles that can be more readily hydrolyzed by lipases.

7. a. gly-ala-phe and thr-leu
   b. ala-ile-tyr and ser-arg
   c. val-trp and arg-leu-cys

20.3: Overview of Stage II of Catabolism

Concept Review Exercises

1. What is a metabolic pathway?
2. What vitamin is required to make coenzyme A?
3. What is the net yield of Glycolysis as far as ATP?
4. Name the enzymes that are key regulatory sites in Glycolysis.
5. Why are the enzymes in the previous question targets for regulation?
6. Why is the priming phase necessary?
7. Draw the entire pathway for glycolysis including enzymes, reactants and products for each step.
8. Where does beta-oxidation occur?
9. What is the average net yield of ATP per carbon?
10. Where exactly is water formed during the process of fatty acid degradation? (Hint: H_2O is formed when when the one of the products of beta-oxidation is passed through another of the metabolic pathways)
11. During the process of beta-oxidation, why is it that [FAD] is used to oxidize an alkane to an alkene while NAD^+ is used to oxidize an alchol to a carbonyl
12. Draw out the entire process of the degradation of a triglyceride, include enzymes and products and reactants for each step.

Answers

1. A metabolic pathway is a series of biochemical reactions by which an organism converts a given reactant to a specific end product.
2. pantothenic acid

20.4: Stage III of Catabolism

Concept Review Exercises

1. What is the main function of the citric acid cycle?
2. Two carbon atoms are fed into the citric acid cycle as acetyl-CoA. In what form are two carbon atoms removed from the cycle?
3. What are mitochondria and what is their function in the cell?

Answers

1. the complete oxidation of carbon atoms to carbon dioxide and the formation of a high-energy phosphate compound, energy rich reduced coenzymes (NADH and $FADH_2$), and metabolic intermediates for the synthesis of other compounds
2. as carbon dioxide
3. Mitochondria are small organelles with a double membrane that contain the enzymes and other molecules needed for the production of most of the ATP needed by the body.

Exercises

1. Replace each question mark with the correct compound.
   a. $? \xrightarrow{\text{aconitase}} \text{isocitrate}$
   b. $? + ? \xrightarrow{\text{citrate synthase}} \text{citrate} + \text{coenzyme A}$
   c. $\text{fumarate} \xrightarrow{\text{fumarase}} ?$
   d. $\text{isocitrate} + \text{NAD}^+ \xrightarrow{?} \alpha\text{-ketoglurate} + \text{NADH} + \text{CO}_2$
2. Replace each question mark with the correct compound.
   a. $\text{malate} + \text{NAD}^+ \xrightarrow{?} \text{oxaloacetate} + \text{NADH}$
   b. $? + ? \xrightarrow{\text{nucleoside diphosphokinase}} \text{GDP} + \text{ATP}$

c. $\text{succinyl-CoA} \xrightarrow{\text{succinyl-CoA synthetase}} ? + ?$

d. $\text{succinate} + \text{FAD} \xrightarrow{\text{succinate dehydrogenase}} ? + \text{FADH}_2$

3. From the reactions in Exercises 1 and 2, select the equation(s) by number and letter in which each type of reaction occurs.
   a. isomerization
   b. hydration
   c. synthesis
4. From the reactions in Exercises 1 and 2, select the equation(s) by number and letter in which each type of reaction occurs.
   a. oxidation
   b. decarboxylation
   c. phosphorylation
5. What similar role do coenzyme Q and cytochrome c serve in the electron transport chain?
6. What is the electron acceptor at the end of the electron transport chain? To what product is this compound reduced?
7. What is the function of the cytochromes in the electron transport chain?
8. a. What is meant by this statement? “Electron transport is tightly coupled to oxidative phosphorylation.”
   b. How are electron transport and oxidative phosphorylation coupled or linked?

Answers

1. a. citrate
   b. oxaloacetate + acetyl-CoA
   c. malate
   d. α-ketoglutarate hydrogenase complex

3. a. reaction in 1a
   b. reaction in 1c
   c. reaction in 1b

5. Both molecules serve as electron shuttles between the complexes of the electron transport chain.

7. Cytochromes are proteins in the electron transport chain and serve as one-electron carriers.

20.5: Stage II of Carbohydrate Catabolism

- ### Concept Review Exercises

1. In glycolysis, how many molecules of pyruvate are produced from one molecule of glucose?
2. In vertebrates, what happens to pyruvate when
   a. plenty of oxygen is available?
   b. oxygen supplies are limited?
3. In anaerobic glycolysis, how many molecules of ATP are produced from one molecule of glucose?

Answers

1. two
2. a. Pyruvate is completely oxidized to carbon dioxide.
   b. Pyruvate is reduced to lactate, allowing for the reoxidation of NADH to NAD^+.
3. There is a net production of two molecules of ATP.

Exercises

1. Replace each question mark with the correct compound.

   a. $\text{fructose } 1,6\text{-bisphosphate} \xrightarrow{\text{aldolase}} ? + ?$

   b. $? + \mathrm{ADP} \xrightarrow{\text{pyruvate kinase}} \text{pyruvate} + \mathrm{ATP}$
   c. $\text{dihydroxyacetone phosphate} \xrightarrow{?} \text{glyceraldehyde 3-phosphate}$
   d. $\text{glucose} + \mathrm{ATP} \xrightarrow{\text{hexokinase}} ? + \mathrm{ADP}$

2. Replace each question mark with the correct compound.
   a. $\text{fructose 6-phosphate} + \mathrm{ATP} \xrightarrow{?} \text{fructose } 1,6\text{-bisphosphate} + \mathrm{ADP}$
   b. $? \xrightarrow{\text{phosphoglucose isomerase}} \text{fructose 6-phosphate}$
   c. $\text{glyceraldehyde 3-phosphate} + \mathrm{NAD}^+ + \mathrm{P_i} \xrightarrow{?} 1,3\text{-bisphosphoglycerate} + \mathrm{NADH}$
   d. $\text{3-phosphoglycerate} \xrightarrow{\text{phosphoglyceromutase}} ?$
3. From the reactions in Exercises 1 and 2, select the equation(s) by number and letter in which each type of reaction occurs.
   a. hydrolysis of a high-energy phosphate compound
   b. synthesis of ATP
4. From the reactions in Exercises 1 and 2, select the equation(s) by number and letter in which each type of reaction occurs.
   a. isomerization
   b. oxidation
5. What coenzyme is needed as an oxidizing agent in glycolysis?
6. Calculate
   a. the *total* number of molecules of ATP produced for each molecule of glucose converted to pyruvate in glycolysis.
   b. the number of molecules of ATP hydrolyzed in phase I of glycolysis.
   c. the *net* ATP production from glycolysis alone.
7. How is the NADH produced in glycolysis reoxidized when oxygen supplies are limited in
   a. muscle cells?
   b. yeast?
8. a. Calculate the number of moles of ATP produced by the aerobic oxidation of 1 mol of glucose in a liver cell.
   b. Of the total calculated in Exercise 9a, determine the number of moles of ATP produced in each process.
      a. glycolysis alone
      b. the citric acid cycle
      c. the electron transport chain and oxidative phosphorylation

Answers

1. a. glyceraldehyde 3-phosphate + dihydroxyacetone phosphate
   b. phosphoenolpyruvate
   c. triose phosphate isomerase
   d. glucose 6-phosphate
3. a. reactions 1b, 1d, and 2a
   b. reaction 1b
5. NAD^+
7. a. Pyruvate is reduced to lactate, and NADH is reoxidized to NAD^+.
   b. Pyruvate is converted to ethanol and carbon dioxide, and NADH is reoxidized to NAD^+.

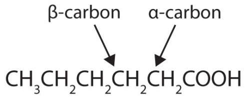
20.6: Stage II of Lipid Catabolism

-

Concept Review Exercises

1. How are fatty acids activated prior to being transported into the mitochondria and oxidized?
2. Draw the structure of hexanoic (caproic) acid and identify the α-carbon and the β-carbon.

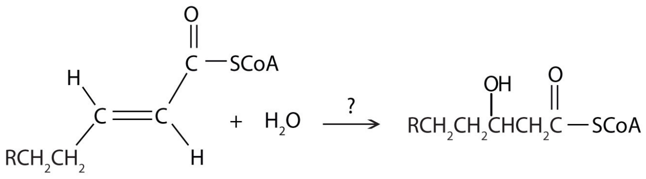
Answers

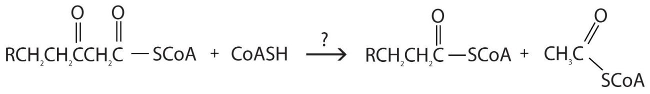
1. They react with CoA to form fatty acyl-CoA molecules.
2. 

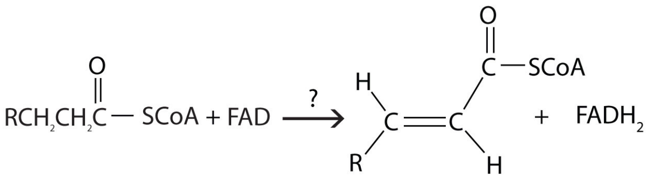
Key Takeaways

- Fatty acids, obtained from the breakdown of triglycerides and other lipids, are oxidized through a series of reactions known as β-oxidation.
- In each round of β-oxidation, 1 molecule of acetyl-CoA, 1 molecule of NADH, and 1 molecule of $FADH_2$ are produced.
- The acetyl-CoA, NADH, and $FADH_2$ are used in the citric acid cycle, the electron transport chain, and oxidative phosphorylation to produce ATP.

Exercises

1. For each reaction found in β-oxidation, identify the enzyme that catalyzes the reaction and classify the reaction as oxidation-reduction, hydration, or cleavage.
   a. 

   b. 

   c. 

2. What are the products of β-oxidation?
3. How many rounds of β-oxidation are necessary to metabolize lauric acid (a saturated fatty acid with 12 carbon atoms)?
4. How many rounds of β-oxidation are necessary to metabolize arachidic acid (a saturated fatty acid with 20 carbon atoms)?
5. When myristic acid (a saturated fatty acid with 14 carbon atoms) is completely oxidized by β-oxidation, how many molecules of each are formed?
   a. acetyl-CoA
   b. $FADH_2$
   c. NADH
6. When stearic acid (a saturated fatty acid with 18 carbon atoms) is completely oxidized by β-oxidation, how many molecules of each are formed?
   a. acetyl-CoA
   b. $FADH_2$
   c. NADH
7. What is the net yield of ATP from the complete oxidation, in a liver cell, of one molecule of myristic acid?
8. What is the net yield of ATP from the complete oxidation, in a liver cell, of one molecule of stearic acid?

Answers

1. a. enoyl-CoA hydratase; hydration
   b. thiolase; cleavage
   c. acyl-CoA dehydrogenase; oxidation-reduction
3. five rounds
5. a. 7 molecules
   b. 6 molecules
   c. 6 molecules
7. 112 molecules

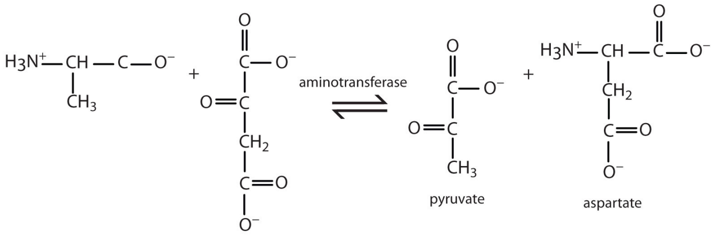
20.7: Stage II of Protein Catabolism

Concept Review Exercises

1. a. Write the equation for the transamination reaction between alanine and oxaloacetate.
   b. Name the two products that are formed.
2. What is the purpose of oxidative deamination?

Answers

1. a.



   b. pyruvate and aspartate
2. Oxidative deamination provides a reaction in which the amino group [as the ammonium (NH_4^+) ion] is removed from a molecule, not simply transferred from one molecule to another. Most of the NH_4^+ ion is converted to urea and excreted from the body.

Exercises

1. Write the equation for the transamination reaction between valine and pyruvate.
2. Write the equation for the transamination reaction between phenylalanine and oxaloacetate.
3. What products are formed in the oxidative deamination of glutamate?
4. Determine if each amino acid is glucogenic, ketogenic, or both.
   a. phenylalanine
   b. leucine
   c. serine
5. Determine if each amino acid is glucogenic, ketogenic, or both.
   a. asparagine
   b. tyrosine
   c. valine

Answers

1.

3. α-ketoglutarate, NADH, and NH_4^+
5.
   a. glucogenic
   b. both
   c. glucogenic

Additional Exercises

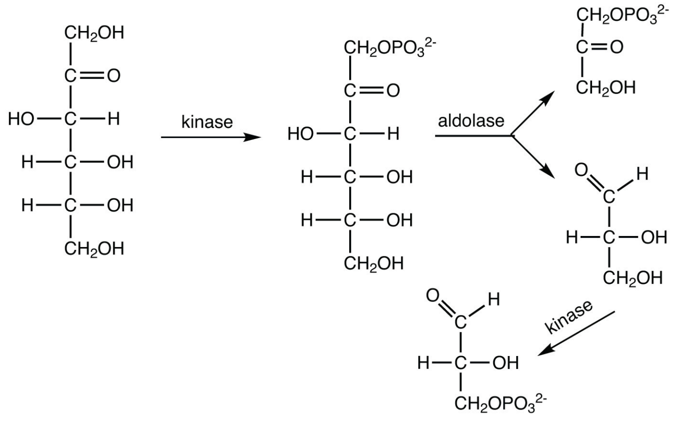
1. Hydrolysis of which compound—arginine phosphate or glucose 6-phosphate—would provide enough energy for the phosphorylation of ATP? Why?
2. If a cracker, which is rich in starch, is chewed for a long time, it begins to develop a sweet, sugary taste. Why?
3. Indicate where each enzymes would cleave the short peptide ala-ser-met-val-phe-gly-cys-lys-asp-leu.
   a. aminopeptidase
   b. chymotrypsin
4. Indicate where each enzymes would cleave the short peptide ala-ser-met-val-phe-gly-cys-lys-asp-leu.
   a. trypsin
   b. carboxypeptidase
5. If the methyl carbon atom of acetyl-CoA is labeled, where does the label appear after the acetyl-CoA goes through one round of the citric acid cycle?
6. If the carbonyl carbon atom of acetyl-CoA is labeled, where does the label appear after the acetyl-CoA goes through one round of the citric acid cycle?
7. The average adult consumes about 65 g of fructose daily (either as the free sugar or from the breakdown of sucrose). In the liver, fructose is first phosphorylated to fructose 1-phosphate, which is then split into dihydroxyacetone phosphate and glyceraldehyde. Glyceraldehyde is then phosphorylated to glyceraldehyde 3-phosphate, with ATP as the phosphate group donor. Write the equations (using structural formulas) for these three steps. Indicate the type of enzyme that catalyzes each step.
8. What critical role is played by both BPG and PEP in glycolysis?
9. How is the NADH produced in glycolysis reoxidized when oxygen supplies are abundant?
10. When a triglyceride is hydrolyzed to form three fatty acids and glycerol, the glycerol can be converted to glycerol 3-phosphate and then oxidized to form dihydroxyacetone phosphate, an intermediate of glycolysis. (In this reaction, NAD^+ is reduced to NADH.) If you assume that there is sufficient oxygen to completely oxidize the pyruvate formed from dihydroxyacetone phosphate, what is the maximum amount of ATP formed from the complete oxidation of 1 mol of glycerol?
11. How is the $FADH_2$ from β-oxidation converted back to FAD?
12. If 1 mol of alanine is converted to pyruvate in a muscle cell (through transamination) and the pyruvate is then metabolized via the citric acid cycle, the electron transport chain, and oxidative phosphorylation, how many moles of ATP are produced?
13. If the essential amino acid leucine (2-amino-4-methylpentanoic acid) is lacking in the diet, an α-keto acid can substitute for it. Give the structure of the α-keto acid and the probable reaction used to form leucine from this α-keto acid.

Answers

1. The hydrolysis of arginine phosphate releases more energy than is needed for the synthesis of ATP, while hydrolysis of glucose 6-phosphate does not.

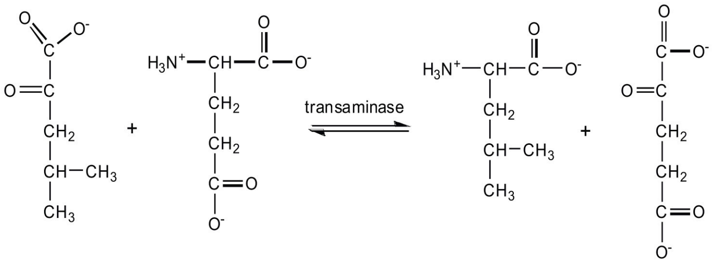
3.
   a. The enzyme will cleave off amino acids one at a time beginning with alanine (the N-terminal end).
   b. following phenylalanine

5. Half of the label will be on the second carbon atom of oxaloacetate, while the other half will be on the third carbon atom.

7. 

9. When oxygen is abundant, NADH is reoxidized through the reactions of the electron transport chain.

11. $FADH_2$ is reoxidized back to FAD via the electron transport chain.

13. 

20.S: Energy Metabolism (Summary)

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

Metabolism is the general term for all chemical reactions in living organisms. The two types of metabolism are **catabolism**—those reactions in which complex molecules (carbohydrates, lipids, and proteins) are broken down to simpler ones with the concomitant release of energy—and **anabolism**—those reactions that consume energy to build complex molecules. Metabolism is studied by looking at individual **metabolic pathways**, which are a series of biochemical reactions in which a given reactant is converted to a desired end product.

The oxidation of fuel molecules (primarily carbohydrates and lipids), a process called **respiration**, is the source of energy used by cells. Catabolic reactions release energy from food molecules and use some of that energy for the synthesis of *adenosine triphosphate* (ATP); anabolic reactions use the energy in ATP to create new compounds. Catabolism can be divided into three stages. In stage I, carbohydrates, lipids, and proteins are broken down into their individual monomer units—simple sugars, fatty acids, and amino acids, respectively. In stage II, these monomer units are broken down by specific metabolic pathways to form a common end product *acetyl-coenzyme A* (CoA). In stage III, acetyl-CoA is completely oxidized to form carbon dioxide and water, and ATP is produced.

The **digestion** of carbohydrates begins in the mouth as α-amylase breaks glycosidic linkages in carbohydrate molecules. Essentially no carbohydrate digestion occurs in the stomach, and food particles pass through to the small intestine, where α-amylase and intestinal enzymes convert complex carbohydrate molecules (starches) to monosaccharides. The monosaccharides then pass through the lining of the small intestine and into the bloodstream for transport to all body cells.

Protein digestion begins in the stomach as pepsinogen in **gastric juice** is converted to pepsin, the enzyme that hydrolyzes peptide bonds. The partially digested protein then passes to the small intestine, where the remainder of protein digestion takes place through the action of several enzymes. The resulting amino acids cross the intestinal wall into the blood and are carried to the liver.

Lipid digestion begins in the small intestine. Bile salts emulsify the lipid molecules, and then lipases hydrolyze them to fatty acids and monoglycerides. The hydrolysis products pass through the intestine and are repackaged for transport in the bloodstream.

In cells that are operating aerobically, acetyl-CoA produced in stage II of catabolism is oxidized to carbon dioxide. The **citric acid cycle** describes this oxidation, which takes place with the formation of the coenzymes reduced nicotinamide adenine dinucleotide (NADH) and reduced flavin adenine dinucleotide ($FADH_2$). The sequence of reactions needed to oxidize these coenzymes and transfer the resulting electrons to oxygen is called the **electron transport chain**, or the **respiratory chain**. The compounds responsible for this series of oxidation-reduction reactions include proteins known as **cytochromes**, Fe·S proteins, and other molecules that ultimately result in the reduction of molecular oxygen to water. Every time a compound with two carbon atoms is oxidized in the citric acid cycle, a respiratory chain compound accepts the electrons lost in the oxidation (and so is reduced) and then passes them on to the next metabolite in the chain. The energy released by the electron transport chain is used to transport hydrogen (H^+) ions from the mitochondrial matrix to the intermembrane space. The flow of H^+ back through ATP synthase leads to the synthesis and release of ATP from adenosine diphosphate (ADP) and inorganic phosphate ions (P_i) in a process known as **oxidative phosphorylation**. Electron transport and oxidative phosphorylation are tightly coupled to each other. The enzymes and intermediates of the citric acid cycle, the electron transport chain, and oxidative phosphorylation are located in organelles called **mitochondria**.

The oxidation of carbohydrates is the source of over 50% of the energy used by cells. Glucose is oxidized to two molecules of pyruvate through a series of reactions known as **glycolysis**. Some of the energy released in these reactions is conserved by the formation of ATP from ADP. Glycolysis can be divided into two phases: phase I consists of the first five reactions and requires energy to “prime” the glucose molecule for phase II, the last five reactions in which ATP is produced through **substrate-level phosphorylation**.

The pyruvate produced by glycolysis has several possible fates, depending on the organism and whether or not oxygen is present. In animal cells, pyruvate can be further oxidized to acetyl-CoA and then to carbon dioxide (through the citric acid cycle) if oxygen supplies are sufficient. When oxygen supplies are insufficient, pyruvate is reduced to lactate. In yeast and other microorganisms, pyruvate is not converted to lactate in the absence of oxygen but instead is converted to ethanol and carbon dioxide.

The amount of ATP formed by the oxidation of glucose depends on whether or not oxygen is present. If oxygen is present, glucose is oxidized to carbon dioxide, and 36–38 ATP molecules are produced for each glucose molecule oxidized, using the combined pathways of glycolysis, the citric acid cycle, the electron transport chain, and oxidative phosphorylation. Thus, approximately 42% of the energy released by the complete oxidation of glucose is conserved by the synthesis of ATP. In the absence of oxygen, only 2 molecules of ATP are formed for each molecule of glucose converted to lactate (2 molecules), and the amount of energy conserved is much less (2%).

Fatty acids, released by the degradation of triglycerides and other lipids, are converted to fatty acyl-CoA, transported into the mitochondria, and oxidized by repeated cycling through a sequence of four reactions known as **β-oxidation**. In each round of β-oxidation, the fatty acyl-CoA is shortened by two carbon atoms as one molecule of acetyl-CoA is formed. The final round of β-oxidation, once the chain has been shortened to four carbon atoms, forms two molecules of acetyl-CoA. β-oxidation also forms the reduced coenzymes $FADH_2$ and NADH, whose reoxidation through the electron transport chain and oxidative phosphorylation leads to the synthesis of ATP. The efficiency of fatty acid oxidation in the human body is approximately 41%.

Amino acids from the breakdown of proteins can be catabolized to provide energy. Amino acids whose carbon skeletons are converted to intermediates that can be converted to glucose through gluconeogenesis are known as **glucogenic amino acids**. Amino acids whose carbon skeletons are broken down to compounds used to form ketone bodies are known as **ketogenic amino acids**.

The first step in amino acid catabolism is separation of the amino group from the carbon skeleton. In a **transamination**, the amino acid gives its NH_2 to pyruvate, α-ketoglutarate, or oxaloacetate. The products of this reaction are a new amino acid and an α-keto acid containing the carbon skeleton of the original amino acid. Pyruvate is transaminated to alanine, α-ketoglutarate to glutamate, and oxaloacetate to aspartate. The amino groups used to form alanine and aspartate are ultimately transferred to α-ketoglutarate, forming glutamate. The glutamate then undergoes **oxidative deamination** to yield α-ketoglutarate and ammonia.

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Index

Glossary

Acetyl-CoA | A molecule that participates in many biochemical reactions in protein, carbohydrate and lipid metabolism. Its main function is to deliver the acetyl group to the citric acid cycle (Krebs cycle) to be oxidized for energy production.

addition polymerization | A reaction in which monomers add to one another to produce a polymeric product that contains all the atoms of the starting monomers.

addition reactions | A reaction in which substituent groups join to hydrocarbon molecules at points of unsaturation—the double or triple bonds.

alcohol | An organic compound with an OH functional group on an aliphatic carbon atom.

aldehyde | An organic compound with a carbonyl functional group that has an hydrogen atom attached and either a hydrocarbon group or a second hydrogen atom.

alkaloid | A nitrogen-containing organic compound obtained from plants that has physiological properties.

alkanes (or saturated hydrocarbons) | A hydrocarbon with only carbon-to-carbon single bonds and existing as a continuous chain of carbon atoms also bonded to hydrogen atoms

alkenes | A hydrocarbon with one or more carbon–carbon double bonds.

alkyl group | A hydrocarbon group derived from an alkane by removal of a hydrogen atom.

alkyl halide (or haloalkane) | A compound resulting from the replacement of a hydrogen atom of an alkane with a halogen atom.

Alkynes | A hydrocarbon with a carbon–carbon triple bond.

alloy | A solid solution of a metal with other substances dissolved in it.

alpha particle | A type of radioactive emission that is equivalent to a helium atom nucleus.

amide | An organic compound with a carbonyl group joined to a nitrogen atom from ammonia or an amine.

amine | An organic compound derived from ammonia by the replacement of one, two, or three of the hydrogens atoms by alkyl or aryl groups.

amino group | An NH_2 unit.

amorphous | A solid with no regular structure.

amphiprotic | A substance that can either donate or accept a proton, depending on the circumstances.

amylopectin | A branched polymer of glucose units found in starch.

anabolism | Metabolic reactions in which molecules are synthesized.

anaerobic metabolism | A biochemical process that takes place in the absence of oxygen.

anions | A negatively charged ion.

anomeric carbon | The carbon atom that was the carbonyl carbon atom in the straight-chain form of a monosaccharide.

anticodon | A set of three nucleotides on the tRNA that is complementary to, and pairs with, the codon on the mRNA.

antioxidants | A substance in foods that acts as a reducing agent.

aromatic compound | Any compound that contains a benzene ring or has certain benzene-like properties.

aromatic hydrocarbons | A hydrocarbon with a benzene-like structure.

aryl group | A group derived from an aromatic hydrocarbon by the removal of a hydrogen atom.

atomic bomb | A weapon that depends on a nuclear chain reaction to generate immense forces.

atomic mass | A weighted average of the masses of all the element's naturally occurring isotopes.

atomic mass unit | One-twelfth the mass of a ^{12}C atom.

atomic radius | The approximate size of an atom.

autoionization of water | The process by which water ionizes into hydronium ions and hydroxide ions as it acts as an acid and a base.

Avogadro's number | The value 6.022×10^{23}.

balanced | A property of a chemical equation when there are the same number of atoms of each element in the reactants and products.

base | A compound that increases the concentration of hydroxide ion (OH^-) in aqueous solution.

Base (or basic) units | A fundamental unit of SI.

beta particle | A type of radioactive emission that is equivalent to an electron.

Bilayers | A double layer of lipids arranged so that nonpolar tails are found between an inner surface and outer surface consisting of hydrophilic heads.

Bile | The yellowish green liquid produced in the liver.

biochemistry | The chemistry of molecules found in living organisms.

boiling point | The temperature at which a substance goes from a liquid to a gas (or from a gas to a liquid).

boiling point elevation | The raising of the boiling point of a solution versus the pure solvent.

bond length | The distance between two nuclei in a covalent bond.

Boyle's law | The gas law that relates pressure and volume.

Brønsted-Lowry base | A compound that accepts a hydrogen ion (H^+) in a reaction; a proton acceptor.

buffer | A solution that resists dramatic changes in pH.

calorie | A unit of energy widely used in the health professions and everyday life.

capacity | The amount of strong acid or base a buffer can counteract.

carbohydrates | A compound composed of carbon, hydrogen, and oxygen atoms that is a polyhydroxy aldehyde or ketone or a compound that can be broken down to form such a compound. It is one of the three main components of the human diet.

carboxyl group | A functional group that contains a carbon–oxygen bond and an OH group also attached to the same carbon atom.

carboxylic acids | An organic compound that has a carboxyl functional group.

cations | A positively charged ion.

cerebrosides | A sphingolipid that contains a fatty acid unit, a sphingosine unit, and galactose or glucose.

chain reaction | An exponential growth in a process.

Charles's law | The gas law that relates volume and absolute temperature.

chemical bond | A very strong attraction between two atoms.

chemical equilibrium (or equilibrium) | The condition in which the extent of a chemical reaction does not change any further.

chemical formula | A concise list of the elements in a compound and the ratios of these elements.

Chemical properties | A characteristic that describes how matter changes its chemical structure or composition.

chemical reaction | A representation of a chemical change.

chemical symbol | A one- or two-letter abbreviation for an element.

chiral carbon | A carbon atom that has four different groups attached to it.

Cholesterol | A steroid that is found in mammals.

cis-trans isomers (or geometric isomers) | Isomers that have different configurations because of the presence of a rigid structure such as a double bond or ring.

citric acid cycle | A cyclic sequence of reactions that brings about the oxidation of a two-C unit to carbon dioxide and water.

codon | A set of three nucleotides on the mRNA that specifies a particular amino acid.

coefficient | A number that gives the number of molecules of a substance in a balanced chemical equation.

coenzymes | A cofactor that is an organic molecule.

colligative properties | A characteristic of solutions that depends only on the number of dissolved particles.

combination (composition) reaction | A chemical reaction that makes a single substance from two or more reactants.

combined gas law | The gas law that relates pressure, volume, and absolute temperature.

combustion reaction | A chemical reaction in which a substance combines with molecular oxygen to make oxygen-containing compounds of other elements in the reaction.

competitive inhibitor | A compound that resembles a particular substrate and competes with the substrate for binding at the active site of an enzyme to slow the rate of the reaction.

complementary bases | Specific base pairings in the DNA double helix.

compound | A substance that can be broken down into chemically simpler components.

concentration | How much solute is dissolved in a certain amount of solvent.

condensed structural formulas | An organic chemical formula that shows the hydrogen atoms (or other atoms or groups) right next to the carbon atoms to which they are attached.

conversion factor | A fraction that has equivalent quantities in the numerator and the denominator but expressed in different units.

core electrons | An electron in a lower-numbered shell of an atom.

covalent network bonding | A type of interaction in which all the atoms in a sample are covalently bonded to other atoms.

curie (Ci) | A unit of radioactivity equal to 3.7×10^{10} decays per second.

cyclic hydrocarbons | A hydrocarbon with a ring of carbon atoms.

cycloalkanes | A cyclic hydrocarbon with only single bonds.

cytochromes | A protein that contains an iron porphyrin in which iron can alternate between Fe(II) and Fe(III).

cytoplasm | Everything between the cell membrane and the nuclear membrane.

decomposition reaction | A chemical reaction in which a single substance is converted into two or more products.

Denaturation | Any change in the three-dimensional structure of a macromolecule that renders it incapable of performing its assigned function.

Density | The mass of an object divided by its volume.

Derived units | A combinations of the SI base units.

diatomic molecules | A two-atom grouping that behaves as a single chemical entity.

digestion | The breakdown of food molecules by hydrolysis reactions into the individual monomer units in the mouth, stomach, and small intestine.

dipole-dipole interaction | An attraction between polar molecules.

Dispersion forces | A force caused by the instantaneous imbalance of electrons about a molecule.

dispersion forces (or London forces) | A force caused by the instantaneous imbalance of electrons about a molecule.

dissociation | The process of cations and anions of an ionic solute separating when the solute dissolves.

Disulfide linkages | A covalent bond that forms by the oxidation and linkage of two sulfur atoms from the side chains of two cysteine residues.

double bond | Two pairs of electrons being shared by two atoms in a molecule.

electron | A subatomic particle with a negative electric charge.

electron configuration | A shorthand description of the arrangement of electrons in an atom.

electron transport chain (or respiratory chain) | An organized sequence of oxidation-reduction reactions that ultimately transports electrons to oxygen, reducing it to water.

electronegativity | A relative measure of how strongly an atom attracts electrons when it forms a covalent bond.

emulsion | A dispersion of two liquids that do not normally mix.

enantiomers | Stereoisomers that are nonsuperimposable mirror images of each other.

endothermic | A process that absorbs energy.

Energy | The ability to do work.

equivalents (Eq) | One mole of charge (either positive or negative).

essential fatty acids | A fatty acid that must be obtained from the diet because it cannot be synthesized by the human body.

ester | An organic compound derived from a carboxylic acid and an alcohol in which the OH of the acid is replaced by an OR group.

esterification | The formation of an ester from a carboxylic acid and an alcohol.

ether | An organic compound that has an oxygen atom between two hydrocarbon groups.

Exact numbers | A number that is defined or counted.

exothermic | A process that gives off energy.

fats | A compound, composed largely of hydrocarbon chains, that supplies energy for the body.

Feedback inhibition | A normal biochemical process that makes use of noncompetitive inhibitors to control some enzymatic activity.

fibrous proteins | A protein that is elongated or fiberlike and insoluble in water.

formula mass | The sum of the masses of the elements in the formula of an ionic compound.

formula unit | A set of oppositely charged ions that compose an ionic compound.

freezing point depression | The lowering of the freezing point of a solution versus the pure solvent.

functional group | A structural arrangement of atoms and/or bonds that imparts a wide range of important properties to organic compounds.

Fusion | A nuclear process in which small nuclei are combined into larger nuclei, releasing energy.

galactosemia | A genetic disease caused by the absence of one of the enzymes needed to convert galactose to glucose.

gamma rays | A type of radioactive emission that is a very energetic form of electromagnetic radiation.

gangliosides | A sphingolipid that contains a fatty acid unit, a sphingosine unit, and a complex oligosaccharide.

gas law | A simple mathematical formula that relates two or more properties of a gas.

Gastric juice | A mixture of water, inorganic ions, hydrochloric acid, and various enzymes and proteins found in the stomach.

Geiger counter | An electrical device that detects radioactivity.

genes | The basic unit of heredity.

genetic code | The identification of each group of three nucleotides and its particular amino acid.

genetic diseases | A hereditary condition caused by an altered DNA sequence.

Globular proteins | A protein that is generally spherical in structure and soluble in water.

glycols | An alcohol with two OH functional groups.

glycolysis | The metabolic pathway in which glucose is broken down to two molecules of pyruvate with the corresponding production of ATP.

glycosidic linkage | The carbon–oxygen-carbon linkage between monosaccharide units in more complex carbohydrates, such as disaccharides or polysaccharides.

groups (or families) | A column of elements on the periodic table.

half reactions | A chemical reaction that shows only oxidation or reduction.

half-life | The amount of time it takes for one-half of a radioactive isotope to decay.

halogenated hydrocarbons | A hydrocarbon in which one or more hydrogen atoms has been replaced by a halogen atom.

halogenation | A reaction in which a halogen reacts at a carbon-to-carbon double or triple bond to add halogen atoms to carbon atoms.

heat | The transfer of energy from one part of the universe to another due to temperature differences.

heat of vaporization | The amount of heat per gram or per mole required for a phase change that occurs at the boiling point.

heterocyclic compounds | A cyclic compound in which one or more atoms in the ring is an element other than a carbon atom.

homogeneous mixtures | A mixture that acts as a single substance so that it is not obvious that two or more substances are present.

homologous series | Any family of compounds in which adjacent members differ from each other by a definite factor.

hydration | Solvation by water molecules.

Hydrogen bonding | Bonding between a highly electronegative oxygen atom or nitrogen atom and a hydrogen atom attached to another oxygen atom or nitrogen atom.

hydrogenation | A reaction in which hydrogen gas reacts at a carbon-to-carbon double or triple bond or a carbon-to-oxygen double bond to add hydrogen atoms to carbon atoms.

hydrolysis | The reaction of a substance with water.

ideal gas law | The gas law that relates volume, pressure, temperature, and amount of a gas.

ideal gas law constant | The constant the appears in the ideal gas law.

immiscible | Liquids that do not dissolve in each other.

induced-fit model | A model that says an enzyme can undergo a conformational change when it binds substrate molecules.

inner transition metals | An element in the two rows beneath the main body on the periodic table. Such metals are also called the lanthanide and actinide elements.

inorganic chemistry | The study of the chemistry of all other elements.

intermolecular interactions | A force of attraction between different molecules.

Ionic bonding | Bonding that results from electrostatic attractions between positively and negatively charged groups.

ionic compounds | A compound formed with an ionic bond.

ionic interactions | An attraction due to ions of opposite charges.

irreversible inhibitor | A substance that inactivates an enzyme by bonding covalently to a specific group at the active site.

isoelectric point | The pH at which a given amino acid exists in solution as a zwitterion.

isomers | Compounds having the same molecular formula but different structural formulas and properties.

isothermal | A process that occurs at constant temperature.

isotopes | Atoms of the same element that have different numbers of neutrons.

IUPAC System of Nomenclature | A systematic way of naming chemical substances so that each has a unique name.

joule | The SI unit of energy, work, and heat.

ketogenic amino acids | An amino acid that is converted to acetoacetyl-CoA or acetyl-CoA, which can be used for the synthesis of ketone bodies but not glucose.

ketone | An organic compound whose molecules have a carbonyl functional group between two hydrocarbon groups.

ketoses | A monosaccharide that contains a ketone functional group on the second carbon atom.

kinetic theory of gases | The fundamental theory of the behavior of gases.

L sugars | A sugar whose Fischer projection terminates in the same configuration as L-glyceraldehyde.

lattice energy | The strength of interactions between atoms that make ionic bonds.

law | A general statement that explains a large number of observations.

law of conservation of matter | In any given system that is closed to the transfer of matter (in and out), the amount of matter in the system stays constant.

Lewis diagrams | A representation that shows valence electrons as dots around the chemical symbol of an atom (also called Lewis electron dot diagrams).

line-angle formula | An organic chemical formula in which carbon atoms are implied at the corners and ends of lines. Each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds.

lipids | A compound isolated from body tissues that is more soluble in organic solvents than in water.

lock-and-key model | A model that portrays an enzyme as conformationally rigid and able to bond only to a substrate or substrates that exactly fit the active site.

mass number | The sum of the numbers of protons and neutrons in a nucleus of an atom.

mass-mass calculations | A stoichiometry calculation converting between the mass of one substance and the mass of a different substance in a chemical reaction.

mass/mass percent | A concentration unit that relates the mass of the solute to the mass of the solution.

mass/volume percent | A concentration unit that relates the mass of the solute to the volume of the solution.

Matter | Anything that has mass and takes up space.

metabolic pathway | A series of biochemical reactions by which an organism converts a given reactant to a specific end product.

microscopic | A view of the universe in which one is working with a few atoms or molecules at a time.

mitochondria | Small, oval organelles with double membranes; the “power plants” of a cell.

modern atomic theory | The fundamental concept that all elements are composed of atoms.

molar mass | The mass of 1 mol of atoms or molecules.

Molarity | Number of moles of solute per liter of solution.

mole-mass calculations | A stoichiometry calculation converting between masses and moles of different substances in a chemical reaction.

mole-mass conversion | The conversion from moles of material to the mass of that same material.

molecular formulas | A chemical formula for a covalent compound.

molecular mass | The mass of a molecule, which is the sum of the masses of its atoms.

molecule | A discrete group of atoms connected by covalent bonds.

mutagens | A chemical or physical agent that cause mutations.

mutarotation | The ongoing interconversion between anomeric forms of a monosaccharide to form an equilibrium mixture.

mutation | Any chemical or physical change that alters the nucleotide sequence in DNA.

neutralization | The reaction of acid and base to make water and a salt.

neutron | A subatomic particle with no electric charge.

nomenclature | The systematic naming of chemical compounds.

nonbonding pairs (or lone pairs) | Electron pair that does not participate in covalent bonds.

noncompetitive inhibitor | A compound that can combine with either the free enzyme or the enzyme-substrate complex at a site distinct from the active site to slow the rate of the reaction.

nonelectrolytes | A compound that does not ionize at all when it dissolves.

nonpolar covalent bond | A covalent bond with a balanced electron distribution across the bond.

Nuclear energy | The controlled harvesting of energy from fission reactions.

nuclear reactor | An apparatus designed to carefully control the progress of a nuclear reaction and extract the resulting energy for useful purposes.

nucleotides | A monomer unit that is linked together to form nucleic acids.

nucleus | The central part of an atom that contains protons and neutrons.

octet rule | The idea that atoms tend to have eight electrons in their valence shell.

oil | A triglyceride that is a liquid at room temperature.

optimum pH | The pH at which a particular enzyme exhibits maximum activity.

Organic chemistry | The study of the chemistry of carbon compounds.

organic compound | A compound containing carbon atoms.

Osmolarity | A way of reporting the total number of particles in a solution to determine the osmotic pressure.

osmotic pressure | The 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.

oxidative deamination | A reaction in which glutamate loses its amino group as an ammonium ion and is oxidized back to α-ketoglutarate.

oxidative phosphorylation | The process that links ATP synthesis to the operation of the electron transport chain.

oxidizing agent | A species that causes oxidation, which is itself reduced.

parts per billion (ppb) | The mass of a solute compared to the mass of a solution times 1,000,000,000.

peptide bond | The amide bond joining two amino acid units in a peptide or protein.

period | A row of elements on the periodic table.

periodic table | A chart of elements that groups the elements by some of their properties.

peripheral proteins | A protein that is more loosely associated with the membrane surface.

pH scale | A logarithmic scale that relates the concentration of the hydrogen ion in solution.

phase | A form of matter that has the same physical properties throughout.

phase change | A physical process in which a substance goes from one phase to another.

phases | A certain form of matter that includes a specific set of physical properties.

phenols | An aromatic compound with an OH group attached directly to a benzene ring.

photosynthesis | The process by which plants use solar energy to convert carbon dioxide and water to glucose.

point mutations | A change in which one nucleotide is substituted, added, or deleted.

polar | A molecule with a net unequal distribution of electrons in its covalent bonds.

polyamide | A condensation polymer in which the monomer units are joined by an amide linkage.

polyatomic ions | An ion with more than one atom.

polycyclic aromatic hydrocarbons (PAHs) | An aromatic hydrocarbon consisting of fused benzene rings sharing a common side.

polymers | A giant molecule formed by the combination of monomers in a repeating manner.

polypeptides | A chain of about 50 or more amino acids.

polysaccharides | A carbohydrate containing many monosaccharide units.

polyunsaturated fatty acids | A fatty acid that has two or more carbon-to-carbon double bonds.

power | The exponent in a number expressed in scientific notation.

pressure | Force divided by area.

primary (1°) alcohol | A compound with an OH group on a carbonatom that is attached to only one other carbon atom.

primary structure | The sequence of amino acids in a polypeptide chain or protein.

products | A substance on the right side of the arrow in a chemical equation.

Proteins | A compound of high molar mass consisting largely or entirely of amino acids linked together.

proton | A subatomic particle with a positive charge.

purines | A heterocyclic amine consisting of a pyrimidine ring fused to a five-member ring with two nitrogen atoms.

quantized | Having a fixed value.

quantum mechanics | The modern theory of electron behavior.

quaternary structure | The arrangement of multiple subunits in a protein.

rad | A unit of radioactive exposure equal to 0.01 J/g of tissue.

radioactivity | Emanations of particles and radiation from atomic nuclei.

reducing sugar | Any carbohydrate capable of reducing a mild oxidizing agent, such as Tollens' or Benedict's reagents, without first undergoing hydrolysis.

rem | A unit of radioactive exposure that includes a factor to account for the type of radioactivity.

replication | The process in which the DNA in a dividing cell is copied.

respiration | The process by which cells oxidize organic molecules in the presence of gaseous oxygen to produce carbon dioxide, water, and energy in the form of ATP.

retroviruses | An RNA virus that directs the synthesis of a DNA copy in the host cell.

ribonucleic acid | The nucleic acid responsible for using the genetic information encoded in DNA.

ribosomes | A cellular substructure where proteins are synthesized.

round | The process of assessing the final significant figure of a quantity to determine if it should be kept or moved higher.

saponification | The hydrolysis of fats and oils in the presence of a base to make soap.

science | The process by which we learn about the natural universe by observing, testing, and then generating models that explain our observations.

scientific method | An organized procedure for learning answers to questions.

secondary (2°) alcohol | A compound with an OH group on a carbon atom that is attached to two other carbon atoms.

secondary structure | The fixed arrangement of the polypeptide backbone.

semimetals | An element whose properties are intermediate between metals and nonmetals.

shells | A grouping of electrons within an atom.

significant figures | All the digits of a measured quantity known with certainty and the first uncertain, or estimated, digit.

single bond | A covalent bond formed by a single pair of electrons.

solubility | The limit of how much solute can be dissolved in a given amount of solvent.

solute | The minor component of a solution.

solution | Another name for a homogeneous mixture.

specific heat | A proportionality constant that relates heat to a temperature change.

Sphingolipids | A lipid that contains the unsaturated amino alcohol sphingosine.

Sphingomyelins | A sphingolipid that contains a fatty acid unit, a phosphoric acid unit, a sphingosine unit, and a choline unit.

spontaneous fission | The breaking apart of an atomic nucleus into smaller nuclei.

standard temperature and pressure | 273 K (0°C) and 1.00 atm pressure.

steroids | A lipid with a four-fused-ring structure.

Stock system | The system of indicating a cation's charge with roman numerals.

stoichiometry | The study of the numerical relationships between the reactants and the products in a balanced chemical equation.

strong acid | An acid that is 100% ionized in aqueous solution.

strong base | A base that is 100% ionized in aqueous solution.

structural formula | A chemical formula that shows how the atoms of a molecule are attached to one another.

subshells | A grouping of electrons within a shell.

substrate-level phosphorylation | The synthesis of ATP by the direct transfer of a phosphate group from a metabolite to ADP.

substrates | A compound on which an enzyme acts.

tertiary (3°) alcohol | A compound with an OH group on a carbon atom that is attached to three other carbon atoms.

tertiary (3°) amine | A compound that has three alkyl or aryl groups on the nitrogen atom.

tertiary structure | The unique three-dimensional shape of a polypeptide chain as a whole.

theory | A general statement that describes a large set of observations and data.

Thiols | A compound with an SH functional group.

torr | Another name for millimeters of mercury.

tracer | A substance that can be used to follow the pathway of that substance through some structure.

transamination | An exchange of functional groups between any amino acid and an α-keto acid.

transcription | The process in which RNA is synthesized from a DNA template.

translation | The process in which the information encoded in mRNA is used to direct the sequencing of amino acids to synthesize a protein.

triglycerides | An ester composed of three fatty acid units linked to glycerol and found in fats and oils.

triple bonds | Three pairs of electrons being shared by two atoms in a molecule.

unit | The scale of measurement for a quantity.

unsaturated | A solution whose solute is less than its solubility limit.

unsaturated hydrocarbons | An alkene or alkyne having one or more multiple (double or triple) bonds between carbon atoms.

valence shell electron pair repulsion | The general concept that estimates the shape of a simple molecule.

vapor pressure | The pressure of a vapor that is in equilibrium with its liquid phase.

vapor pressure depression | The lowering of the vapor pressure of a solution versus the pure solvent.

Viruses | An infectious agent that is much smaller and simpler than bacteria.

vitamins | An organic compound that is essential in very small amounts for the maintenance of normal metabolism.

volume | The amount of space that a given substance occupies.

volume/volume percent | A concentration unit that relates the volume of the solute to the volume of the solution.

weak base | A base that is less than 100% ionized in aqueous solution.

zwitterion | An electrically neutral compound that contains both negatively and positively charged groups.

β-oxidation | A sequence of four reactions in which fatty acyl-CoA molecules are oxidized, leading to the removal of acetyl-CoA molecules.

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  - 1: Chemistry, Matter, and Measurement - *CC BY-NC-SA 3.0*
    - 1.0: Prelude to Chemistry, Matter, and Measurement - *CC BY-NC-SA 3.0*
    - 1.1: What is Chemistry? - *CC BY-NC-SA 3.0*
    - 1.2: The Classification of Matter - *CC BY-NC-SA 3.0*
    - 1.3: Measurements - *CC BY-NC-SA 3.0*
    - 1.4: Expressing Numbers - Scientific Notation - *CC BY-NC-SA 3.0*
    - 1.5: Expressing Numbers - Significant Figures - *CC BY-NC-SA 3.0*
    - 1.6: The International System of Units - *CC BY-NC-SA 3.0*
    - 1.7: Converting Units - *CC BY-NC-SA 3.0*
    - 1.8: Dosage Calculations - *CC BY-NC-SA 3.0*
    - 1.E: Chemistry, Matter, and Measurement (Exercises) - *CC BY-NC-SA 3.0*
    - 1.S: Chemistry, Matter, and Measurement (Summary) - *CC BY-NC-SA 3.0*
  - 2: Elements, Atoms, and the Periodic Table - *CC BY-NC-SA 3.0*
    - 2.0: Prelude to Elements, Atoms, and the Periodic Table - *CC BY-NC-SA 3.0*
    - 2.1: The Elements - *CC BY-NC-SA 3.0*
    - 2.2: Atomic Theory - *CC BY-NC-SA 3.0*
    - 2.3: The Structure of Atoms - *CC BY-NC-SA 3.0*
    - 2.4: Nuclei of Atoms - *CC BY-NC-SA 3.0*
    - 2.5: Atomic Masses - *CC BY-NC-SA 3.0*
    - 2.6: Arrangements of Electrons - *CC BY-NC-SA 3.0*
    - 2.7: The Periodic Table - *CC BY-NC-SA 3.0*
    - 2.E: Elements, Atoms, and the Periodic Table (Exercises) - *CC BY-NC-SA 3.0*
    - 2.S: Elements, Atoms, and the Periodic Table (Summary) - *CC BY-NC-SA 3.0*
  - 3: Ionic Bonding and Simple Ionic Compounds - *CC BY-NC-SA 3.0*
    - 3.0: Prelude to Ionic Bonding and Simple Ionic Compounds - *CC BY-NC-SA 3.0*
    - 3.1: Two Types of Bonding - *CC BY-NC-SA 3.0*
    - 3.2: Ions - *CC BY-NC-SA 3.0*
    - 3.3: Formulas for Ionic Compounds - *CC BY-NC-SA 3.0*
    - 3.4: Ionic Nomenclature - *CC BY-NC-SA 3.0*
    - 3.5: Formula Mass - *CC BY-NC-SA 3.0*
    - 3.6: Characteristics of Ionic Compounds - *CC BY-NC-SA 3.0*
    - 3.E: Ionic Bonding and Simple Ionic Compounds (Exercises) - *CC BY-NC-SA 3.0*
    - 3.S: Ionic Bonding and Simple Ionic Compounds (Summary) - *CC BY-NC-SA 3.0*
  - 4: Covalent Bonding and Simple Molecular Compounds - *CC BY-NC-SA 3.0*
    - 4.0: Prelude to Covalent Bonding and Simple Molecular Compounds - *CC BY-NC-SA 3.0*
    - 4.1: Covalent Bonds - *CC BY-NC-SA 3.0*
    - 4.2: Covalent Compounds - Formulas and Names - *CC BY-NC-SA 3.0*
    - 4.3: Drawing Lewis Structures - *CC BY-NC-SA 3.0*
    - 4.4: Characteristics of Covalent Bonds - *CC BY-NC-SA 3.0*
    - 4.5: Characteristics of Molecules - *CC BY-NC-SA 3.0*
    - 4.6: Organic Chemistry - *CC BY-NC-SA 3.0*
    - 4.E: Covalent Bonding and Simple Molecular Compounds (Exercises) - *CC BY-NC-SA 3.0*
    - 4.S: Covalent Bonding and Simple Molecular Compounds (Summary) - *CC BY-NC-SA 3.0*

    - 12.2: Structures and Names of Alkanes - *CC BY-NC-SA 3.0*
    - 12.3: Branched-Chain Alkanes - *CC BY-NC-SA 3.0*
    - 12.4: Condensed Structural and Line-Angle Formulas - *CC BY-NC-SA 3.0*
    - 12.5: IUPAC Nomenclature - *CC BY-NC-SA 3.0*
    - 12.6: Physical Properties of Alkanes - *CC BY-NC-SA 3.0*
    - 12.7: Chemical Properties of Alkanes - *CC BY-NC-SA 3.0*
    - 12.8: Halogenated Hydrocarbons - *CC BY-NC-SA 3.0*
    - 12.9: Cycloalkanes - *CC BY-NC-SA 3.0*
    - 12.E: Organic Chemistry- Alkanes and Halogenated Hydrocarbons (Exercises) - *CC BY-NC-SA 3.0*
    - 12.S: Organic Chemistry- Alkanes and Halogenated Hydrocarbons (Summary) - *CC BY-NC-SA 3.0*
- 13: Unsaturated and Aromatic Hydrocarbons - *CC BY-NC-SA 3.0*
    - 13.0: Prelude to Unsaturated and Aromatic Hydrocarbons - *CC BY-NC-SA 3.0*
    - 13.1: Alkenes- Structures and Names - *CC BY-NC-SA 3.0*
    - 13.2: Cis-Trans Isomers (Geometric Isomers) - *CC BY-NC-SA 3.0*
    - 13.3: Physical Properties of Alkenes - *CC BY-NC-SA 3.0*
    - 13.4: Chemical Properties of Alkenes - *CC BY-NC-SA 3.0*
    - 13.5: Polymers - *CC BY-NC-SA 3.0*
    - 13.6: Alkynes - *CC BY-NC-SA 3.0*
    - 13.7: Aromatic Compounds- Benzene - *CC BY-NC-SA 3.0*
    - 13.8: Structure and Nomenclature of Aromatic Compounds - *CC BY-NC-SA 3.0*
    - 13.E: Unsaturated and Aromatic Hydrocarbons (Exercises) - *CC BY-NC-SA 3.0*
    - 13.S: Unsaturated and Aromatic Hydrocarbons (Summary) - *CC BY-NC-SA 3.0*
- 14: Organic Compounds of Oxygen - *CC BY-NC-SA 3.0*
    - 14.0: Prelude to Organic Compounds of Oxygen - *CC BY-NC-SA 3.0*
    - 14.1: Organic Compounds with Functional Groups - *CC BY-NC-SA 3.0*
    - 14.2: Alcohols - Nomenclature and Classification - *CC BY-NC-SA 3.0*
    - 14.3: Physical Properties of Alcohols - *CC BY-NC-SA 3.0*
    - 14.4: Reactions that Form Alcohols - *CC BY-NC-SA 3.0*
    - 14.5: Reactions of Alcohols - *CC BY-NC-SA 3.0*
    - 14.6: Glycols and Glycerol - *CC BY-NC-SA 3.0*
    - 14.7: Phenols - *CC BY-NC-SA 3.0*
    - 14.8: Ethers - *CC BY-NC-SA 3.0*
    - 14.9: Aldehydes and Ketones- Structure and Names - *CC BY-NC-SA 3.0*
    - 14.10: Properties of Aldehydes and Ketones - *CC BY-NC-SA 3.0*
    - 14.11: Organic Sulfur Compounds - *CC BY-NC-SA 3.0*
    - 14.E: Organic Compounds of Oxygen (Exercises) - *CC BY-NC-SA 3.0*
    - 14.S: Organic Compounds of Oxygen (Summary) - *CC BY-NC-SA 3.0*
- 15: Organic Acids and Bases and Some of Their Derivatives - *CC BY-NC-SA 3.0*
    - 15.0: Prelude to Organic Acids and Bases and Some of Their Derivatives - *CC BY-NC-SA 3.0*
    - 15.1: Carboxylic Acids - Structures and Names - *CC BY-NC-SA 3.0*
    - 15.2: The Formation of Carboxylic Acids - *CC BY-NC-SA 3.0*
    - 15.3: Physical Properties of Carboxylic Acids - *CC BY-NC-SA 3.0*
    - 15.4: Chemical Properties of Carboxylic Acids- Ionization and Neutralization - *CC BY-NC-SA 3.0*
    - 15.5: Esters - Structures and Names - *CC BY-NC-SA 3.0*
    - 15.6: Physical Properties of Esters - *CC BY-NC-SA 3.0*
    - 15.7: Preparation of Esters - *CC BY-NC-SA 3.0*
    - 15.8: Hydrolysis of Esters - *CC BY-NC-SA 3.0*
    - 15.9: Esters of Phosphoric Acid - *CC BY-NC-SA 3.0*
    - 15.10: Amines - Structures and Names - *CC BY-NC-SA 3.0*
    - 15.11: Physical Properties of Amines - *CC BY-NC-SA 3.0*
    - 15.12: Amines as Bases - *CC BY-NC-SA 3.0*
    - 15.13: Amides- Structures and Names - *CC BY-NC-SA 3.0*
    - 15.14: Physical Properties of Amides - *CC BY-NC-SA 3.0*
    - 15.15: Formation of Amides - *CC BY-NC-SA 3.0*
    - 15.16: Chemical Properties of Amides- Hydrolysis - *CC BY-NC-SA 3.0*
    - 15.S: Organic Acids and Bases and Some of Their Derivatives (Summary) - *CC BY-NC-SA 3.0*
- 16: Carbohydrates - *CC BY-NC-SA 3.0*
    - 16.0: Prelude to Carbohydrates - *CC BY-NC-SA 3.0*
    - 16.1: Carbohydrates - *CC BY-NC-SA 3.0*
    - 16.2: Classes of Monosaccharides - *CC BY-NC-SA 3.0*
    - 16.3: Important Hexoses - *CC BY-NC-SA 3.0*
    - 16.4: Cyclic Structures of Monosaccharides - *CC BY-NC-SA 3.0*

  - 16.5: Properties of Monosaccharides - *CC BY-NC-SA 3.0*
  - 16.6: Disaccharides - *CC BY-NC-SA 3.0*
  - 16.7: Polysaccharides - *CC BY-NC-SA 3.0*
  - 16.S: Carbohydrates (Summary) - *CC BY-NC-SA 3.0*
- 17: Lipids - *CC BY-NC-SA 3.0*
  - 17.0: Prelude to Lipids - *CC BY-NC-SA 3.0*
  - 17.1: Fatty Acids - *CC BY-NC-SA 3.0*
  - 17.2: Fats and Oils - *CC BY-NC-SA 3.0*
  - 17.3: Membranes and Membrane Lipids - *CC BY-NC-SA 3.0*
  - 17.4: Steroids - *CC BY-NC-SA 3.0*
  - 17.E: Exercises - *CC BY-NC-SA 3.0*
  - 17.S: Lipids (Summary) - *CC BY-NC-SA 3.0*
- 18: Amino Acids, Proteins, and Enzymes - *CC BY-NC-SA 3.0*
  - 18.0: Prelude to Amino Acids, Proteins, and Enzymes - *CC BY-NC-SA 3.0*
  - 18.1: Properties of Amino Acids - *CC BY-NC-SA 3.0*
  - 18.2: Reactions of Amino Acids - *CC BY-NC-SA 3.0*
  - 18.3: Peptides - *CC BY-NC-SA 3.0*
  - 18.4: Proteins - *CC BY-NC-SA 3.0*
  - 18.5: Enzymes - *CC BY-NC-SA 3.0*
  - 18.6: Enzyme Action - *CC BY-NC-SA 3.0*
  - 18.7: Enzyme Activity - *CC BY-NC-SA 3.0*
  - 18.8: Enzyme Inhibition - *CC BY-NC-SA 3.0*
  - 18.9: Enzyme Cofactors and Vitamins - *CC BY-NC-SA 3.0*
  - 18.E: Amino Acids, Proteins, and Enzymes (Exercises) - *CC BY-NC-SA 3.0*
  - 18.S: Amino Acids, Proteins, and Enzymes (Summary) - *CC BY-NC-SA 3.0*
- 19: Nucleic Acids - *CC BY-NC-SA 3.0*
  - 19.0: Prelude to Nucleic Acids - *CC BY-NC-SA 3.0*
  - 19.1: Nucleotides - *CC BY-NC-SA 3.0*
  - 19.2: Nucleic Acid Structure - *CC BY-NC-SA 3.0*
  - 19.3: Replication and Expression of Genetic Information - *CC BY-NC-SA 3.0*
  - 19.4: Protein Synthesis and the Genetic Code - *CC BY-NC-SA 3.0*
  - 19.5: Mutations and Genetic Diseases - *CC BY-NC-SA 3.0*
  - 19.6: Viruses - *CC BY-NC-SA 3.0*
  - 19.E: Nucleic Acids (Exercises) - *CC BY-NC-SA 3.0*
  - 19.S: Nucleic Acids (Summary) - *CC BY-NC-SA 3.0*
- 20: Energy Metabolism - *CC BY-NC-SA 3.0*
  - 20.0: Prelude to Energy Metabolism - *CC BY-NC-SA 3.0*
  - 20.1: ATP- the Universal Energy Currency - *CC BY-NC-SA 3.0*
  - 20.2: Stage I of Catabolism - *CC BY-NC-SA 3.0*
  - 20.3: Overview of Stage II of Catabolism - *CC BY-NC-SA 3.0*
  - 20.4: Stage III of Catabolism - *CC BY-NC-SA 3.0*
  - 20.5: Stage II of Carbohydrate Catabolism - *CC BY-NC-SA 3.0*
  - 20.6: Stage II of Lipid Catabolism - *CC BY-NC-SA 3.0*
  - 20.7: Stage II of Protein Catabolism - *CC BY-NC-SA 3.0*
  - 20.E: Energy Metabolism (Exercises) - *CC BY-NC-SA 3.0*
  - 20.S: Energy Metabolism (Summary) - *CC BY-NC-SA 3.0*
- Back Matter - *CC BY-NC-SA 3.0*
  - Index - *Undeclared*
  - Glossary - *CC BY-NC-SA 3.0*
  - Detailed Licensing - *Undeclared*