CHEM U109 CHEMISTRY OF LIVING THINGS



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CHEM U109 Chemistry of Living Things

Chad Mueller

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TABLE OF CONTENTS

InfoTitle

Licensing

1: Chemistry, Matter, and Measurement

1.1: What Is Chemistry?

1.2: The Classification of Matter

1.3: Measurements

1.4: Expressing Numbers: Scientific Notation

1.5: Expressing Numbers: Significant Figures

1.6: The International System of Units

1.7: Converting Units

1.8: Chapter Summary

1.E: Exercises

2: Elements, Atoms, and the Periodic Table

2.1: The Elements

2.2: Atomic Theory

2.3: The Structure of Atoms

2.4: Nuclei of Atoms

2.5: Atomic Masses

2.6: Arrangements of Electrons

2.7: The Periodic Table

2.8: Chapter Summary

2.E: Exercises

3: Ionic Bonding and Simple Ionic Compounds

3.1: Two Types of Bonding

3.2: Ions

3.3: Formulas for Ionic Compounds

3.4: Ionic Nomenclature

3.5: Formula Mass

3.6: Chapter Summary

3.E: Exercises

4: Covalent Bonding and Simple Molecular Compounds

4.1: Covalent Bonds

4.2: Multiple Covalent Bonds

4.3: Covalent Compounds: Formulas and Names

4.4: Characteristics of Covalent Bonds

4.5: Characteristics of Molecules

4.6: Organic Chemistry
4.7: Chapter Summary
4.E: Exercise

5: Introduction to Chemical Reactions

5.1: The Law of Conservation of Matter
5.2: Chemical Equations
5.3: Quantitative Relationships Based on Chemical Equations
5.4: Some Types of Chemical Reactions
5.5: Oxidation-Reduction (Redox) Reactions
5.6: Redox Reactions in Organic Chemistry and Biochemistry
5.7: Chapter Summary
5.E: Exercises

6: Quantities in Chemical Reactions

6.1: The Mole
6.2: Atomic and Molar Masses
6.3: Mole-Mass Conversions
6.4: Mole-Mole Relationships in Chemical Reactions
6.5: Mole-Mass and Mass-Mass Problems
6.6: Chapter Summary
6.E: Exercise

7: Energy and Chemical Processes

7.1: Energy and Its Units
7.2: Heat
7.3: Phase Changes
7.4: Bond Energies and Chemical Reactions
7.5: The Energy of Biochemical Reactions
7.6: Energetics and Kinetics
7.7: Equilibrium
7.8: Chapter Summary
7.E: Exercises

8: Solids, Liquids, and Gases

8.1: Intermolecular Interactions
8.2: Solids and Liquids
8.3 Gases and Pressure
8.4: Gas Laws
8.5: Chapter Summary
8.E: Exercises

9: Solutions

9.1: Solutions

9.2: Concentration
9.3: The Dissolution Process
9.4: Properties of Solutions
9.5: Chapter Summary
9.E: Exercises

10: Acids and Bases

10.1: Arrhenius Definition of Acids and Bases
10.2 Brønsted-Lowry Definition of Acids and Bases
10.3: Water - Both an Acid and a Base
10.4: The Strengths of Acids and Bases
10.5: Buffers
10.6: Chapter Summary
10.E: Exercises

11: Organic Chemistry

11.1: Organic Chemistry
11.2: Alkanes
11.3: Condensed Structural and Line-Angle Formulas
11.4: Cycloalkanes
11.5: Alkenes
11.6: IUPAC Nomenclature
11.7: Organic Compounds with Functional Groups
11.8: Physical Properties of Organic Compounds
11.9: Chemical Properties: Carboxylic Acids
11.10: Chemical Properties: Amines as Bases
11.E: Organic Chemistry (Exercises)
11.S: Organic Chemistry (Summary)

12: Carbohydrates

12.1: Carbohydrates
12.2: Classes of Monosaccharides
12.3: Important Hexoses
12.4: Cyclic Structures of Monosaccharides
12.5 Properties of Monosaccharides
12.6 Disaccharides
12.7 Polysaccharides
12.8: Chapter Summary

13: Lipids

13.0: Introduction to Lipids
13.1: Fatty Acids
13.2: Fats and Oils

13.3: Membranes and Membrane Lipids
13.4: Steroids
13.5: Chapter Summary
13.E: Exercises

14: Amino Acids, Proteins, and Enzymes

14.1: Properties of Amino Acids
14.2: Reactions of Amino Acids
14.3: Peptides
14.4: Proteins
14.5: Enzymes
14.6 Enzyme Action
14.7: Enzyme Activity
14.8: Enzyme Inhibition
14.9: Enzyme Cofactors and Vitamins
14.10: Chapter Summary
14.E: Exercises

15: Nucleic Acids

15.1: Nucleotides
15.2: Nucleic Acid Structure
15.3: Replication and Expression of Genetic Information
15.4: Protein Synthesis and the Genetic Code
15.5: Mutations and Genetic Diseases
15.6: Viruses
15.7: Chapter Summary
15.E: Exercises

16: Energy Metabolism

16.0: Introduction to Metabolism
16.1: ATP: the Universal Energy Currency
16.2: Stage I of Catabolism
16.3: Overview of Stage II of Catabolism
16.4: Stage III of Catabolism
16.5: Stage II of Carbohydrate Catabolism
16.6: Stage II of Lipid Catabolism
16.7: Stage II of Protein Catabolism
16.8: Chapter Summary
16.E: Exercises

17: Nuclear Chemistry

17.1: Radioactivity
17.2: Half-Life

17.3: Units of Radioactivity
17.4: Uses of Radioactive Isotopes
17.5: Nuclear Energy
17.6: Chapter Summary
17.E: Exercises

11: Organic Chemistry - Functional Groups and Properties

Index

Glossary

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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.

As you read each section in this and later chapters, work all of the examples and exercises. Practicing lots of problems is the best way to ensure that you have command of the subject material.

1.1: What Is Chemistry?

1.2: The Classification of Matter

1.3: Measurements

1.4: Expressing Numbers: Scientific Notation

1.5: Expressing Numbers: Significant Figures

1.6: The International System of Units

1.7: Converting Units

1.8: Chapter Summary

1.E: Exercises

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1.1: What Is Chemistry?

Skills to Develop

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.

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.

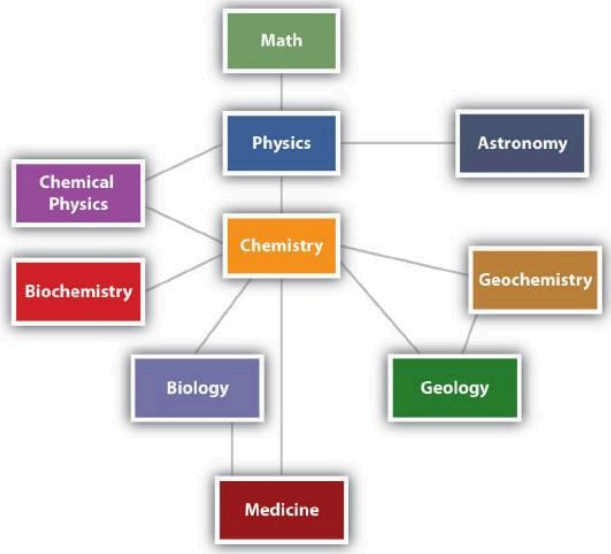


Figure 1.1.1*: The Relationships between Some of the Major Branches of Science. Chemistry lies more or less in the middle, which emphasizes its importance to many branches of science.*

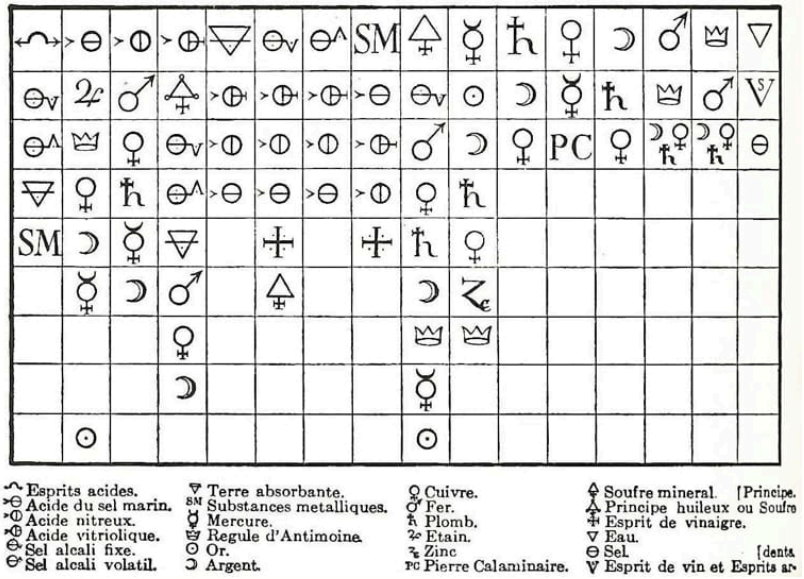
There are many other fields of science, in addition to the ones (biology, medicine, etc.) listed here.

Looking Closer: 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.

Example 1.1.1

Which fields of study are branches of science? Explain.

a. sculpture
b. astronomy

SOLUTION

a. Sculpture is not considered a science because it is not a study of some aspect of the natural universe.
b. Astronomy is the study of stars and planets, which are part of the natural universe. Astronomy is therefore a field of science.

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. 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:

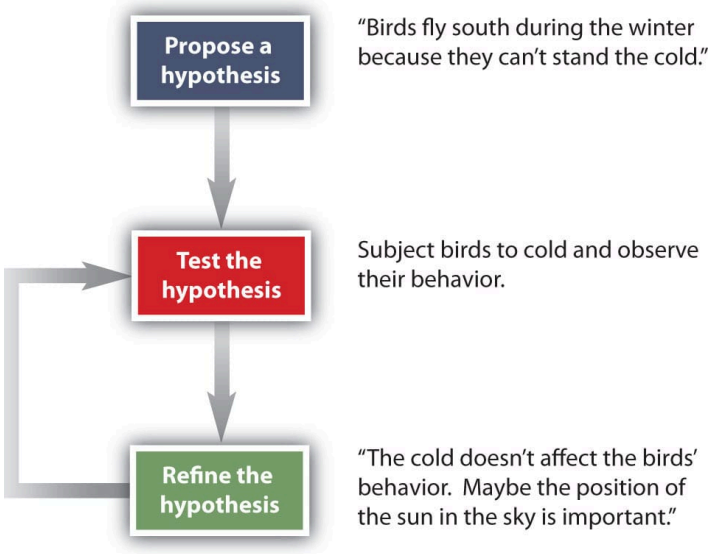


Figure 1.1.2***:*** *The General Steps of the Scientific Method*

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 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.

In science, we often use words in a slightly different way than in every-day language. In these discussions, it is helpful to understand the scientific meanings. The terms and definitions below were adapted from "Teaching About Evolution and the Nature of Science" by the National Academy of Sciences (Washington, D.C.: National Academy Press, 1998).

TERMS USED IN DESCRIBING THE NATURE OF SCIENCE*

FACT: In science, an observation that has been repeatedly confirmed and for all practical purposes is accepted as "true." Truth in science, however, is never final, and what is accepted as a fact today may be modified or even discarded tomorrow.

(e.g. The statement that water takes up space and has mass is considered a fact.)

HYPOTHESIS: A tentative statement about the natural world leading to deductions that can be tested. If the deductions are verified, it becomes more probable that the hypothesis is correct. If the deductions are incorrect, the original hypothesis can be abandoned or modified. Hypotheses can be used to build more complex inferences and explanations.

(e.g. The hypothesis that everything is made of earth, air, fire, and water has been abandoned by science because experimental tests did not support it.)

LAW: A descriptive generalization about how some aspect of the natural world behaves under stated circumstances.

(e.g. We will study the Law of Conservation of Matter, which states that matter is neither created nor destroyed, but only

changes form. So if liquid water evaporates and we can no longer see it, it was not destroyed; it changed to gas that we cannot see.)

THEORY: In science, a well-substantiated explanation of some aspect of the natural world that can incorporate facts, laws, inferences, and tested hypotheses.

The contention that evolution should be taught as a "theory, not as a fact" confuses the common use of these words with the scientific use. In science, theories do not turn into facts through the accumulation of evidence. Rather, theories are the end points of science. They are understandings that develop from extensive observation, experimentation, and creative reflection. They incorporate a large body of scientific facts, laws, tested hypotheses, and logical inferences.

(e.g. In Chapter 2, you will read about Atomic Theory. It is not a simple observation that we would call a “fact,” nor do we say it is “proven.” It has been supported by so much experimental evidence for such a long time, that it is generally accepted by the scientific community.)

Concept Review Exercises

1. Define science and chemistry.
2. Name the steps of the scientific method.

Answers

1. 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.

2. 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.

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1.2: The Classification of Matter

Skills to Develop

- 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. 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.

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 an element. Aluminum, which is used in soda cans, is an element. A substance that can be broken down into chemically simpler components (because it has more than one element) is a compound (Figure 1.2). Water is a compound composed of the elements hydrogen and oxygen. 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 added to substance, but this is not absolutely necessary. By definition, any single substance 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 1 inch long, you would need 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 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 view 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 1.2.1).

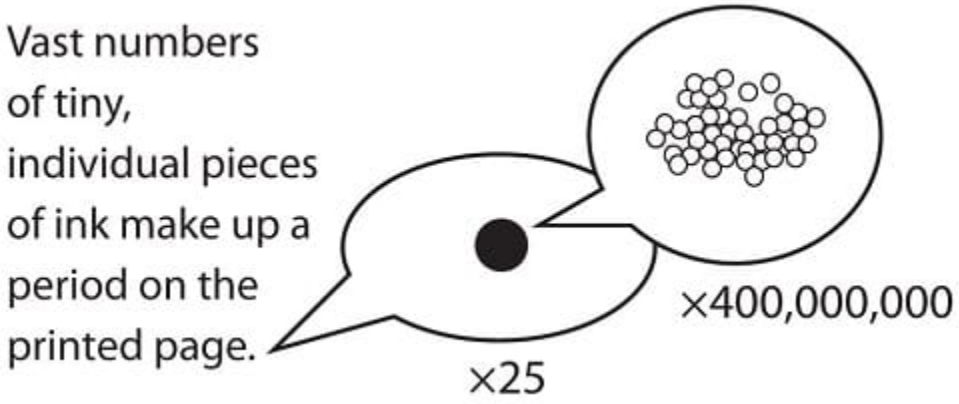


Figure 1.2.1***:*** *How Many Particles Are Needed for a Period in a Sentence?*

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 composition throughout are called homogeneous mixtures (or solutions). Sugar dissolved in water is an example of a solution. A metal alloy, such as steel, is an example of a solid solution. Air, a mixture of mainly nitrogen and oxygen, is a gaseous solution.

Example 1.2.1

How would a chemist categorize each example of matter?

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

SOLUTION

a. Sea water has salts dissolved in the water and acts as if it were a single substance even though it contains multiple substances—salts and water. Saltwater is a homogeneous mixture, or a solution. (This assumes you did not take a sample that included a fish or chunk of kelp, which would make it heterogeneous.)
b. Soil is composed of small pieces of a variety of materials (e.g. sand, plant matter, clay, etc.) so it is a heterogeneous mixture.
c. Water is a substance; more specifically, because water is composed of hydrogen and oxygen in a fixed ratio (H_2O), it is a compound.
d. Oxygen, a substance, is an element.

Phases

Another way to classify matter is to describe it as a solid, a liquid, or a gas, which was done in the examples of solutions. These three descriptions, each implying that the matter has certain physical properties, represent the three phases of matter. A solid has a definite shape and a definite volume. Liquids ordinarily have a definite volume but not a definite shape; they take the shape of their containers. Gases have neither a definite shape nor a definite volume, and they expand to fill their containers. We encounter matter in each phase every day; in fact, we regularly encounter water in all three phases: ice (solid), water (liquid), and steam (gas).



Figure 1.2.2***:*** *Boiling Water. When liquid water boils to make gaseous water, it undergoes a phase change. Figure used with permission from 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 goes from one phase to another (Figure 1.2.2). Phase changes have particular names depending on what phases are involved, as summarized in Table 1.2.1.

Table 1.2.1***:*** *Phase Changes*

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

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

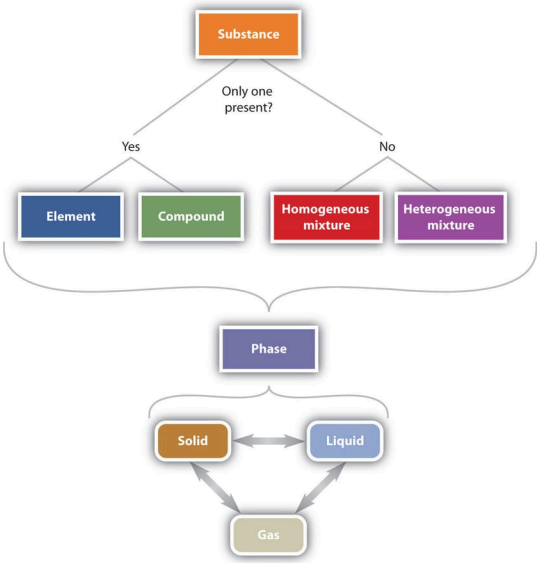


Figure 1.2.3***:*** *The Classification of Matter. Matter can be classified in a variety of ways, depending on its properties.*

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 --- you can see the different components if you look closely. A homogeneous mixture behaves like a single substance, such as saltwater --- you cannot distinguish the salt and water in the solution.
3. solid to liquid (melting) and liquid to gas (boiling) (answers will vary)

Key Takeaways

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

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1.3: Measurements

Skills to Develop

- To 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. Figure used with permission from Wikipedia.*

Chemists measure the properties of matter and express these measurements 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 kilometers," we know that the quantity has been expressed in units of kilometers and that the number of kilometers is 5. 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. *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.

Example 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

SOLUTION

a. The number is one, and the unit is dozen eggs.
b. The number is 2.54, and the unit is centimeter.
c. The number 1 is implied because the quantity is only *a* box. The unit is box of pencils.
d. The number is 88, and the unit is meters per second. Note that in this case the unit is actually a combination of two units: meters and seconds.

Concept Review Exercise

1. What are the two necessary parts of a quantity?

Answer

1. The two necessary parts are the number and the unit.

Key Takeaway

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

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1.4: Expressing Numbers: Scientific Notation

Skills to Develop

- To express a large number or a small number in scientific notation.

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. Note that sometimes commas or spaces are used every three digits (i.e. 12,000 or 12 000) and sometimes not (i.e. 12000).

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 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.

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

The 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. This figure 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. × 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 make it follow the first digit, so that the number being multiplied is between 1 and 10:

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

Example 1.4.1: Scientific Notation

Express each number in scientific notation.

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

SOLUTION

a. Moving the decimal point 10 places to the left gives 6.7×10^{10}.
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}.
c. In this case, we need to move the decimal point only one place to the left, which yields 1.26×10^{1}.

Example 1.4.2

Express each number in standard, or nonscientific, notation.

a. 5.27×10^{4}
b. 1.0008×10^{6}

SOLUTION

a. Rather than moving the decimal to the left, we move it four places to the right and add zeros to give 52,700.
b. Moving the decimal six places to the right gives 1,000,800.

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

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

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

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 follow the first nonzero digit. This is illustrated as follows:

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

In scientific notation, numbers with a magnitude greater than one have a positive power, while numbers with a magnitude less than one have a negative power.

Example 1.4.3

Express each number in scientific notation.

1. 0.000006567
2. −0.0004004
3. 0.000000000000123

SOUTION

1. Move the decimal point six places to the right to get 6.567×10^{-6}.
2. 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.
3. Move the decimal point 13 places to the right to get 1.23×10^{-13}.

Example 1.4.4

Express each number in standard, or nonscientific, notation.

a. 6.98×10^{8}
b. 1.005×10^{2}

SOLUTION

1. 698 000 000
2. 100.5

Example 1.4.5

Express each number in standard notation.

1. 6.22×10^{-2}
2. 9.9×10^{-9}

SOLUTION

1. 0.0622
2. 0.0000000099

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—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.

Contributors

- Anonymous

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1.5: Expressing Numbers: Significant Figures

Skills to Develop

- 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. Imagine, for example, that you are using a meterstick to measure the width of a table. The centimeters (cm) are marked off, telling you how many centimeters wide the table is. Many metersticks also have millimeters (mm) marked off, so we can measure the table to the nearest millimeter. But most metersticks do not have any finer measurements indicated, so you cannot report the table's width any more exactly than to the nearest millimeter. All you can do is estimate the next decimal place in the measurement (Figure 1.5.1).

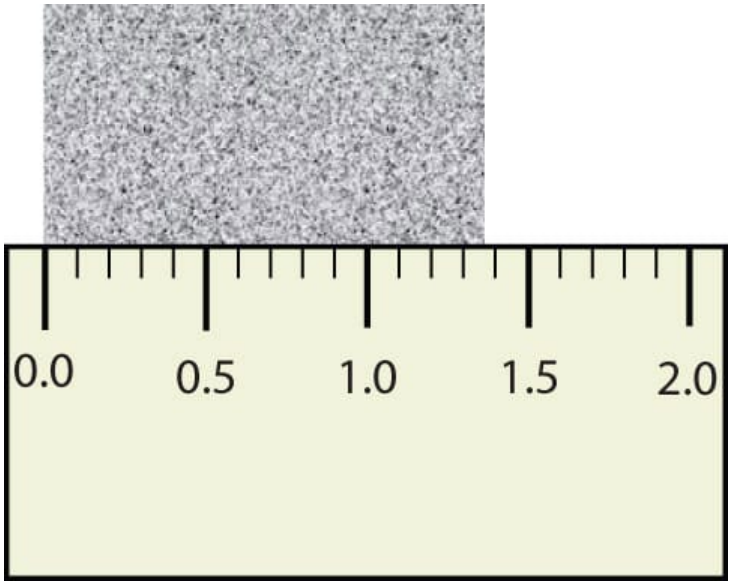


Figure 1.5.1*: Measuring an Object to the Correct Number of Digits. How many digits should be reported for the length of this object?*

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 and the first uncertain, or estimated, digit. 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 may not be significant figures.

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

Your instructor might even write " s f " on a graded assignment as a reminder about significant figures.

For example, if a table is measured and reported as being 1,357 mm wide, the number 1,357 has four significant figures. The 1 (thousands), the 3 (hundreds), and the 5 (tens) are certain; the 7 (units) is assumed to have been estimated. It would make no sense to report such a measurement as 1,357.0 or 1,357.00 because that would suggest the measuring instrument 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 the units have to be 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 instrument could have had marks indicating every 10 mm or marks indicating every 1 mm. Is the zero an estimate, or is the 5 an estimate and the zero a placeholder?

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

1. All nonzero digits are significant. In 1,357, all the digits are significant.
2. *Captive (or embedded) zeros*, which are zeros between significant digits, are significant. In 405, all the digits are significant.
3. *Leading zeros*, which are zeros at the beginning of a decimal number less than 1, are not significant. In 0.000458, 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 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, 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, all six digits are significant because the number has a decimal point.

Example 1.5.1

How many significant digits does each number have?

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

SOLUTION

a. four (by rules 1 and 4)
b. seven (by rules 1 and 2)
c. nine (by rules 1, 2, and 4)
d. four (by rules 1 and 3)

Combining Numbers

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.

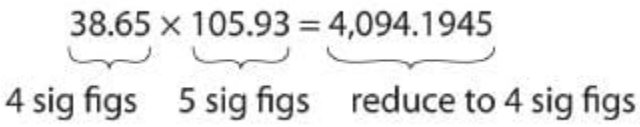
For addition or subtraction, the rule is to stack all the numbers with their decimal points aligned and then limit the answer's significant figures to the rightmost column for which all the numbers have significant figures. Consider the following:

$$\begin{array}{r} 56.789 \\ +\quad 102.2 \\ +\,1{,}300.099 \\ \hline =\,1{,}459.088 \end{array}$$

↑ Limit to this column

The arrow points to the rightmost column in which all the numbers have significant figures—in this case, the tenths place. Therefore, we will limit our final answer to the tenths place. Is our final answer therefore 1,459.0? No, because when we drop digits from the end of a number, we also have to round the number. Notice that the second 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 rules in rounding 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:



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

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

Example 1.5.2

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 + 363.06
d. (100.1 - 102.22)/7.333
e. 14.84 x 0.55 – 8.02

SOLUTION

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.
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. (1130 is also technically three significant figures also, but scientific notation is more clear.)
c. The calculator gives 2,000.06 as the answer, but because 610 has its farthest-right significant figure in the tens column, our answer must be limited to the tens position: 2.00×10^3. (In 2000.06 the underlined one's, tenth's, and hundredth's places are not significant.)
d. This involves two different rules, one for the multiplication and one for the subtraction, so the sig. fig.s must be evaluated after each step. Here the digits that are not significant will be underlined, then the answer will be rounded at the end.

Algebra rules dictate that we do the calculation inside the parentheses first (subtraction). Subtraction limits the answers by fewest decimal places.

The 100.1 is known to one decimal place and 102.22 is known to two decimal places, so the answer is limited to one decimal place.

(100.1 - 102.22) = - 2.12

When subtracting we limit by total significant figures in the original numbers.

The result of the subtraction, - 2.12 , only has two significant figures (not the underlined digit), whereas 7.333 has four significant figures.

(100.1 - 102.22) / 7.333 = (- 2.12) / 7.333 = = - 0.28910405 ≈ **- 0.29**

The final answer, - 0.28910405, should be rounded to two significant figures, -0.29. Since the first digit dropped off is 9, we round up.

The approximately equal to symbol "≈" is used here to indicate where digits were rounded off.

If we rounded after the subtraction, we get the same final answer here.

(100.1 - 102.22) / 7.333 ≈ (- 2.1) / 7.333 = - 0.286376653 ≈ **- 0.29**

e. This involves two different rules, one for the multiplication and one for the subtraction, so the sig. fig.s must be evaluated after each step.

Algebra rules dictate that the multiplication be done before subtraction.

There are four significant figures in 14.84 and two significant figures in 0.55, so the answer is limited to two significant figures.

Here the digits that are not significant will be underlined, then the answer will be rounded at the end.

14.84 x 0.55 = 8.162

When subtracting we limit by decimal places, not total significant figures.

The result of the multiplication, 8.162, is only known to one spot to the right of the decimal place.

14.84 x 0.55 – 8.02 = 8.162 – 8.02 = 0.142 ≈ **0.1**

NOTE ON ROUNDING. It is most accurate to round your answer at the very end (while still keeping track of the significant figures at each step), like done above by underlining the digits that are not significant.

While slightly less accurate, it is acceptable in Mueller's class to round at each step if it helps you keep track of significant figures as you go. Notice that the answer to Part e changes slightly here:

e. 14.84 x 0.55 – 8.02 = 8.162 – 8.02 ≈ 8.2 – 8.02 = 0.18 ≈ **0.2**

Concept Review Exercises

1. Explain why the concept of significant figures is important in numerical calculations.
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.
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.
- There are rules for applying significant figures in calculations.

Contributors

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1.6: The International System of Units

Skills to Develop

- To recognize the SI base units and explain the system of prefixes used with them.

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'Unité*s), 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:

$$K = °C + 273.15 \tag{1.6.1}$$

***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. 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 even 1.2×10^{-4} m, 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.

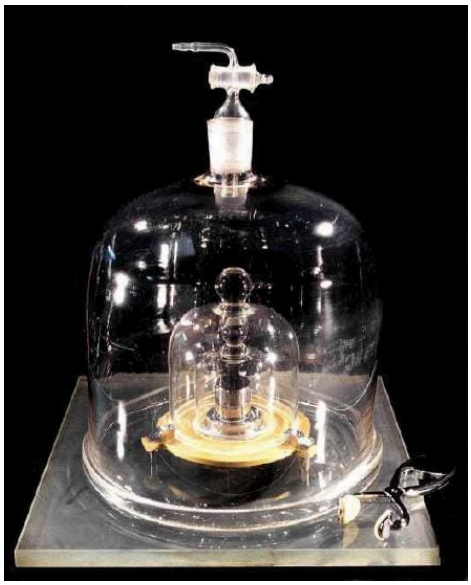


Figure 1.6.1***:*** *The Kilogram. The standard for the kilogram is a platinum-iridium cylinder kept in a special vault in France. Source: Photo reproduced by permission of the Bureau International des Poids et Mesures, who retain full internationally protected copyright.*

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.

What is 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. (Table 1.6.3 gives approximate equivalents for some of the units used in chemistry.)

Table 1.6.3***:*** *Approximate Equivalents to Some SI Units*

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

As shown in Figure 1.6.2, 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.

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

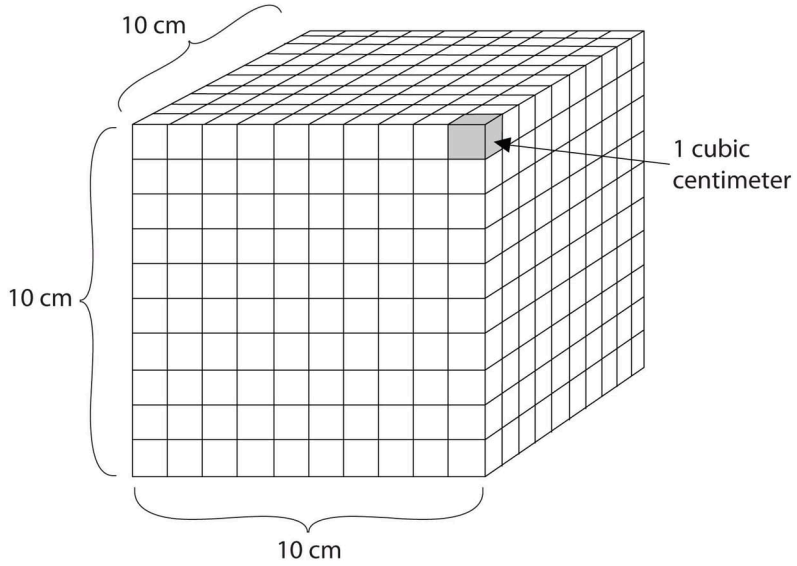


Figure 1.6.2***:*** *The Liter. A liter is defined as a cube 10 cm (1/10th of a meter) on a side. A milliliter, 1/1,000th of a liter, is equal to 1 cubic centimeter.*

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

SOLUTION

a. The abbreviation for a kiloliter is kL. Because kilo means "1,000 ×," 1 kL equals 1,000 L.
b. The abbreviation for microsecond is μs. Micro implies 10^{-6}, or 1/1,000,000th of a unit, so 1 μs equals 0.000001 s.
c. The abbreviation for decimeter is dm. Deci means 10^{-1}, or 1/10th, so 1 dm equals 0.1 m.
d. The abbreviation for nanogram is ng. Nano means 10^{-9}th of a unit, so 1 ng equals 0.000000001 g.

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, the calorie (cal), is also widely used. There are 4.184 J in 1 cal. All chemical processes occur with a simultaneous change in energy.

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.

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:

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

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

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.

Answers

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

Key Takeaways

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

Contributors

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1.7: Converting Units

Skills to Develop

- To 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 review the SI units described earlier, you can find that one kilogram (kg) is about equal to 2.20 pounds (lbs).

$$1\ \text{kg} = 2.20\ \text{lbs} \tag{1.7.1}$$

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

$$\frac{1\ \text{kg}}{1\ \text{kg}} = \frac{2.20\ \text{lbs}}{1\ \text{kg}} \tag{1.7.2}$$

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

$$\frac{1\ \text{kg}}{1\ \text{kg}} = 1 \quad \text{and} \quad \frac{2.20\ \text{lbs}}{1\ \text{kg}} = 1 \tag{1.7.3}$$

We know that one kilogram is equal to 2.20 pounds, 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***.

Instead of dividing both sides by 1 kg, as above, we could have obtained a conversion factor if we divided both sides by 2.20 kg.

$$1\ \text{kg} = 2.20\ \text{lbs} \tag{1.7.4}$$

will become

$$\frac{1\ \text{kg}}{2.20\ \text{lbs}} = \frac{2.20\ \text{lbs}}{2.20\ \text{lbs}} \tag{1.7.5}$$

Again, because we performed the same operation on both sides of the equals sign, the expression remains an equality (=1).

$$\frac{1\ \text{kg}}{2.20\ \text{lbs}} = 1 \quad \text{and} \quad \frac{2.20\ \text{lbs}}{2.20\ \text{lbs}} = 1 \tag{1.7.6}$$

This means that every conversion factor will have two forms, both equal to one, but reciprocated (flipped). For 1 kg = 2.20 lbs, the two conversion factors would be:

$$\frac{1\ \text{kg}}{2.20\ \text{lbs}} \text{ or } \frac{2.20\ \text{lbs}}{1\ \text{kg}} \tag{1.7.7}$$

Here is a simple example of how the conversion factor might be used. You are about to return from a European vacation with a suitcase full of gifts. The airline does not allow bags heavier than 55 pounds, but the scale in your hotel only reads in kilograms. How many kg are equal to 55 lbs? To solve the problem with the conversion factor used earlier, we first write the quantity we are given, 55 lbs. Then we multiply this quantity by a conversion factor, which is the same as multiplying it by 1. We can write 1 as either version of the conversion factor, $\frac{1\ \text{kg}}{2.20\ \text{lbs}}$ or $\frac{2.20\ \text{lbs}}{1\ \text{kg}}$. Here we will use $\frac{1\ \text{kg}}{2.20\ \text{lbs}}$ and multiply so that the units we started with (kg)

cancel and we end with the units we want (lbs).

$$55 \text{ lbs} \times \frac{1 \text{ kg}}{2.20 \text{ lbs}} \tag{1.7.8}$$

The 55 kg can be thought of as a fraction with a 1 in the denominator (though it is often not shown). Because kg, the abbreviation for kilograms, occurs in both the numerator (top) *and* the denominator (bottom) of our expression, they cancel out. The 55 on top is divided by 2.20 on bottom and the only units that did not cancel are kg.

$$\frac{55 \cancel{\text{ lbs}}}{1} \times \frac{1 \text{ kg}}{2.20 \cancel{\text{ lbs}}} = 25 \text{ kg} \tag{1.7.9}$$

In the final answer, we omit the 1 in the denominator. We find that 55 lbs equals 25 kg. A generalized description of this process is as follows:

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

This involved conversion only involved one step. We will see that the same basic principle applies for conversions with multiple steps. 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, if we had used the other possible reciprocated conversion factor, $\frac{2.20 \text{ lbs}}{1 \text{ kg}}$, the original unit would not have canceled, and the result would have been meaningless. Here is the incorrect we would have gotten:

$$55 \text{ lbs} \times \frac{2.20 \text{ lbs}}{1 \text{ kg}} = 0.0355 \frac{\text{lbs}^2}{\text{kg}} \tag{1.7.10}$$

For the answer to be meaningful, we have to *construct the conversion factor in a form that causes the original unit to cancel out*.

Conversion Factors With Prefix Multipliers (Exponents)

If you learned the prefixes described earlier in this chapter, then you know that the prefix centi (c) is 10^{-2}. The prefixes come in front of some other base unit, like meters (m). The base units must be included on both sides of the equality, so if c = 10^{-2}, then cm = 10^{-2} m. As before, this can be made into these two different reciprocal conversion factors:

$$\frac{1 \text{ cm}}{10^{-2} \text{ m}} \text{ or } \frac{10^{-2} \text{ m}}{1 \text{ cm}} \tag{1.7.11}$$

If you wanted to find out how many centimeters in 3.55 meters, we again follow the process:

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

$$\frac{3.55 \cancel{\text{ m}}}{1} \times \frac{1 \text{ cm}}{10^{-2} \cancel{\text{ m}}} = 355 \text{ cm} \tag{1.7.12}$$

Pull out your calculator and ensure that you get 355 as your answer when you divide 3.55 by 10^{-2}. If not, get help with how to properly use your calculator. (For example, in the Casio fx-260, 10^{-2} might be entered as [1], then [EXP], [+/-], and [2].)

To avoid using exponents, some instead use that 1 cm is 1/100th of a meter (because centi = 10^{-2} = 1/10^{2} = 1/100).

$$1 \text{ cm} = \frac{1}{100} \text{ m} \tag{1.7.13}$$

Since fractions of a unit can make conversions difficult later, both sides can be multiplied by 100 to cancel the 1/100 and get this version.

$$100 \text{ cm} = 1 \text{ m} \tag{1.7.14}$$

The two versions of the conversion factor are therefore:

$$\frac{100\text{ cm}}{1\text{ m}}\text{ or }\frac{1\text{ m}}{100\text{ cm}} \tag{1.7.15}$$

To convert 3.55 meters into centimeters this way, 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:

$$\frac{3.55\ \cancel{\text{m}}}{1}\times\frac{100\text{ cm}}{1\ \cancel{\text{m}}}=355\text{ cm} \tag{1.7.16}$$

Notice that we get the same answer, 355 cm, either way. Using the exponent is most direct and makes things easier with large exponents, like micro = 10^{-6} or giga = 10^{9}. But for those who have trouble with exponential notation, using micro = 1/1,000,000 or giga = 1,000,000,000 is also an option.

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, conversions that do not involve just a prefix change, like those between different systems of units, are usually not exact. For example, kilograms are S.I. units, but pounds come from an older system. If given 1 kg = 2.20 lbs, you sould assume three significant figures (but can be found to six or more figures, 1 kg = 2.20462 lbs). 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. The prefix milli is 10^{-3}. If m = 10^{-3}, adding the liters to both sides, makes it 1 mL = 10^{-3} L. From this relationship, we can construct two conversion factors:

$$\frac{10^{-3}\text{ L}}{1\text{ mL}}\text{ or }\frac{1\text{ mL}}{10^{-3}\text{ L}} \tag{1.7.17}$$

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.

$$4.7\cancel{\text{L}}\times\frac{1\text{ mL}}{10^{-3}\ \cancel{\text{L}}}=4,700\text{ mL} \tag{1.7.18}$$

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, 1 ms = 10^{-3} s:

$$\frac{1\text{ ms}}{10^{-3}\text{ s}}\text{ or }\frac{10^{-3}\text{ s}}{1\text{ ms}} \tag{1.7.19}$$

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:

$$18 \cancel{\text{ ms}} \times \frac{10^{-3} \text{ s}}{1 \cancel{\text{ ms}}} = 0.018 \text{ s} \tag{1.7.20}$$

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

(If you prefer the method without exponents, you could instead use that milli is 1/1,000. If you do it that way, ensure that you get the same answers.)

Example 1.7.2

Perform each conversion.

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

SOLUTION

a. The prefix nano is 10^{-9}. If n = 10^{-9}, adding the seconds to both sides, makes it 1 ns = 10^{-9} s. From this relationship, we can construct two conversion factors:

$$\frac{10^{-9} \text{ s}}{1 \text{ ns}} \text{ or } \frac{1 \text{ ns}}{10^{-9} \text{ s}} \tag{1.7.21}$$

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

$$101,000 \cancel{\text{ ns}} \times \frac{10^{-9} \text{ s}}{1 \cancel{\text{ ns}}} = 0.000101 \text{ s} \tag{1.7.22}$$

b. We can construct two conversion factors from the relationships between kilograms and grams, 1 kg = 10^3 g:

$$\frac{1 \text{ kg}}{10^3 \text{ g}} \text{ or } \frac{10^3 \text{ g}}{1 \text{ kg}} \tag{1.7.23}$$

To convert 32.08 kg to grams, we choose the conversion factor that will cancel out kilograms and introduce grams. The conversion factor on the left is the appropriate one. We set up the conversion as follows:

$$32.08 \cancel{\text{ kg}} \times \frac{10^3 \text{ g}}{1 \cancel{\text{ kg}}} = 32080 \text{ g} \tag{1.7.24}$$

To more clearly show that the answer has four significant figures, it can be written in scientific notation as 3.208x10^4 g.

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:

$$\frac{13.6 \text{ g}}{1 \text{ mL}} \text{ and } \frac{1 \text{ mL}}{13.6 \text{ g}} \tag{1.7.25}$$

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

$$16 \cancel{\text{mL}} \times \frac{13.6 \text{ g}}{1 \cancel{\text{mL}}} = 217.6 \text{ g} = 220 \text{ g} \tag{1.7.26}$$

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 1.7.3: 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 (bottom). The gram unit will cancel algebraically, and milliliters will be introduced in the numerator.

$$0.750 \cancel{\text{g}} \times \frac{1 \text{ mL}}{13.6 \cancel{\text{g}}} = 0.055147... \text{ mL} \approx 0.0551 \text{ mL} \tag{1.7.27}$$

We have limited the final answer to three significant figures.

You could instead rearrange the density formula, d = m/V, to solve for volume, V = m/d = (0.750g) / (13.6 g/mL) = 0.0551 mL, to arrive at the same answer.

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

$$\frac{\text{density of some material}}{\text{density of water}} \tag{1.7.28}$$

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.)

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 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 10^3 m in 1 km:

$$54.7 \cancel{\text{ km}} \times \frac{10^3 \text{ m}}{1 \cancel{\text{ km}}} = 54,700 \text{ m} \tag{1.7.29}$$

Then we take the result (54,700 m) and convert it to millimeters, remembering that there are 1 mm for every 10^{-3} m:

$$54,700 \cancel{\text{ m}} \times \frac{1 \text{ mm}}{10^{-3} \cancel{\text{ m}}} = 54,700,000 \text{ mm} = 5.47 \times 10^7 \text{ mm} \tag{1.7.30}$$

Expressing the final answer in scientific notation more clearly shows the three significant figures.

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

$$54.7 \cancel{\text{ km}} \times \frac{10^3 \cancel{\text{ m}}}{1 \cancel{\text{ km}}} \times \frac{1 \text{ mm}}{10^{-3} \cancel{\text{ m}}} = 54,700,000 \text{ mm} = 5.47 \times 10^7 \text{ mm} \tag{1.7.31}$$

NOTE: When using the prefixes and exponents, the prefix should always be on one side and the exponent that it equals should be on the other side. (In the first step here, since kilo is on bottom, the 10^3 must be on top. Then in the other step, because milli is on the top, the 10^{-3} should be on bottom.)

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 1.7.4

Convert 58.2 ms to megaseconds in one multistep calculation.

SOLUTION

The milli prefix abbreviatioin is lower case, m = 10^{-3}, so with base units of seconds it would be, ms = 10^{-3} s. The mega abbreviation is upper case, M = 10^6, so Ms = 10^6 s.

First, convert the given unit to the base unit—in this case, seconds—and then convert seconds to the final unit, megaseconds.

$$58.2 \cancel{\text{ ms}} \times \frac{10^{-3} \cancel{\text{s}}}{1 \cancel{\text{ ms}}} \times \frac{1 \text{ Ms}}{10^6 \cancel{\text{ s}}} = 0.0000000582 \text{ Ms} = 5.82 \times 10^{-8} \text{ Ms} \tag{1.7.32}$$

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

Example 1.7.5

Convert 43.00 ng to kilograms in one multistep calculation.

SOLUTION

For nano, n = 10^{-9}, so with base units of grams it would be, ng = 10^{-9} g. For kilo, k = 10^{3}, so kg = 10^{3} g.

First, cancel ng and convert the given unit to the base unit (g), and then convert grams to the final unit, kilograms.

$$43.00 \cancel{\text{ng}} \times \frac{10^{-9} \cancel{\text{g}}}{1 \cancel{\text{ng}}} \times \frac{1 \text{ kg}}{10^{3} \cancel{\text{g}}} = 0.00000000004300 \text{ kg} = 4.300 \times 10^{-11} \text{ kg} \tag{1.7.33}$$

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

Squared or Cubed Units

Area is often found by multiplying two lengths, and thus has squared units. For example length in feet, times width in feet, gives area in square feet, ft^2. Volume is often found by multiplying three lengths, and thus has cubed units. For a box, length in centimeters, times width in centimeters, times depth in centimeters, gives volume in cubic centimeters, cm^3. A length conversion factor must be used twice for squared area and three times for cubed volume.

Assume we find that the area of notebook page is 93.5 square inches and we want to convert that to square centimeters. Most often, you will only be able to find the relationship between inches and centimeters, 1 in = 2.54 cm. The conversion factor will need to be used twice here (so that both inches in in^2 cancel and so that the two centimeters on top leave you with cm^2).

$$93.5 \cancel{\text{in}^2} \times \frac{2.54 \text{ cm}}{1 \cancel{\text{in}}} \times \frac{2.54 \text{ cm}}{1 \cancel{\text{in}}} = 603 \text{ cm}^2 \tag{1.7.34}$$

Example 1.7.6

Tire pressure is often measured in pounds per square inch, abbreviated psi or lbs/in^2. Convert 32.0 psi to units of kilograms per square centimeter.

SOLUTION

The pressures have weight units (lbs or kg) on top and area units (in^2 or cm^2) on bottom. We will use 1 kg = 2.20 lbs and 1 in = 2.54 cm to create our conversion factors.

$$\frac{\cancel{32.0 \text{ lbs}}}{\cancel{\text{in}^2}} \times \frac{1\text{kg}}{2.20 \cancel{\text{lbs}}} \times \frac{\cancel{1 \text{ in}}}{2.54 \text{ cm}} \times \frac{\cancel{1 \text{ in}}}{2.54 \text{ cm}} = \frac{2.25 \text{ kg}}{\text{cm}^2} \tag{1.7.35}$$

Since 32.0 lbs/in^2 had inches twice on the bottom, $\frac{1 \text{ in}}{2.54 \text{ cm}}$ was used twice. The final answer is rounded to three significant figures.

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.

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.

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.

Key Takeaway

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

There are plenty more conversion exercises to practice in Section 1.E at the end of this chapter.

Contributors

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1.8: Chapter 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.

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1.E: Exercises

These are practice exercises to accompany Chapter 1. They are organized by section. For example, the exercises on the material for Section 1, "What is Chemistry" are first. Scroll down to see exercises for other sections. Try your best to work out them out on your own before looking at te answers (listed at the end of each section).

1.1: What Is Chemistry?

Exercises for Section 1.1

1. Which of the following are examples of matter?

    A. a baby

    B. an idea

    C. an emotion

    D. the air

    E. Alpha Centauri, the closest known star (excluding the sun) to our solar system

    F. the light emitted by a star

2. When someone says, “I have a theory that people behave more violently during a full moon,” does that person really have a theory? If it is not a theory, what is it?

Answers (Section 1.1)

1. Which of the following are examples of matter?

    A. a baby - MATTER

    B. an idea - NOT MATTER

    C. an emotion - NOT MATTER

    D. the air - MATTER

    E. Alpha Centauri, the closest known star (excluding the sun) to our solar system - MATTER

    F. the light emitted by a star - NOT MATTER

2. No, that prediction for behavior would be called a hypothesis in science. The next step in the scientific method would be to test the hypothesis. If the hypothesis is supported with extensive data over a long period of time, it might be incorporated into an explanation that could become a theory.

1.2: The Classification of Matter

Exercises for Section 1.2

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

A. Balsa is a very light wood. - PHYSICAL

B. If held in a flame, magnesium metal burns in air. - CHEMICAL

C. Mercury has a density of 13.6 g/mL. - PHYSICAL

D. Human blood is red. - PHYSICAL

E. The boiling point of isopropyl alcohol, which is used to sterilize cuts and scrapes, is lower than the boiling point of water. - PHYSICAL

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

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

A. xenon

B. Sprite

C. solid glucose, $C_6H_{12}O_6$

D. gaseous hydrogen molecules, H_2

E. dirt, a combination of rocks and decaying plant matter

F. air (on Earth)

4. What word(s) describes each phase change?

A. solid to liquid

B. liquid to gas

C. solid to gas

Answers (Section 1.2)

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.

E. The boiling point of isopropyl alcohol, which is used to sterilize cuts and scrapes, is lower than the boiling point of water.

2. Define *element*. How does it differ from a compound? - An element is a substance that cannot be broken down into chemically simpler components. Compounds can be broken down into simpler substances.

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

A. xenon - element

B. Sprite - homogeneous mixture (if no ice and cap is on bottle so cannot see bubbles); heterogeneous mixture (if can see ice cubes or bubbles separate from the rest of the liquid solution)

C. solid glucose, $C_6H_{12}O_6$ - compound

D. gaseous hydrogen molecules, H_2 - element

E. dirt, a combination of rocks and decaying plant matter - heterogeneous mixture

F. air (on Earth) - homogeneous mixture (mostly nitrogen and oxygen)

4. What word(s) describes each phase change?

A. solid to liquid - melting or fusion

B. liquid to gas - boiling or evaporation

C. solid to gas - sublimation

1.3: Measurements

Exercises for Section 1.3

1. Why are both parts of a quantity important when describing it?
2. You ask a classmate how much homework your chemistry professor assigned. Your classmate answers, “twenty.” Is that a proper answer? Why or why not?

Answers (Section 1.3)

1. The number states how much, and the unit states of what. Without the number and the unit, a quantity cannot be properly communicated.
2. No, it is not a proper answer; you do not know whether the professor meant homework problem number 20 or 20 homework problems.

1.4: Expressing Numbers: Scientific Notation

Exercises for Section 1.4

1. Why is scientific notation useful in expressing numbers?
2. Express each number in scientific notation.

A. 0.00064

B. 5,230,000

C. −56,200

D. 0.000000000220

E. 1.0

3. Express each number in standard form.

A. 6.72×10^{4}

B. 2.088×10^{-4}

C. -3×10^{6}

D. 9.98×10^{-7}

4. Complete the following table:

Incorrect Scientific Notation	Correct Scientific Notation
54.7×10^{4}	
0.0066×10^{3}	
$3,078 \times 10^{0}$	

Answers (Section 1.4)

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

2.

A. 6.4×10^{-4}

B. 5.23×10^{6}

C. -5.62×10^{4}

D. 2.20×10^{-10}

E. 1.0×10^{0}

3.

A. 67,200

B. 0.0002088

C. −3,000,000

D. 0.000000998

4.

Incorrect Scientific Notation	Correct Scientific Notation
54.7×10^{4}	5.47×10^{5}
0.0066×10^{3}	6.6×10^{0}
$3,078 \times 10^{0}$	3.078×10^{3}

1.5: Expressing Numbers: Significant Figures

Exercises for Section 1.5

1. Define *significant figures*. Why are they important?

2. How many significant figures are in each number?

A. 140

B. 0.009830

C. 220,560,000

D. 5.67×10^{3}

E. 2.9600×10^{-5}

3. Round each number to three significant figures.

A. 34,705

B. 34,750

C. 0.001996

4. Perform each operation and express the answer to the correct number of significant figures.

A. 467.88 + 23.0 + 1,306 = ?

B. 0.00565 + 0.002333 + 0.0991 = ?

C. 439 × 8,767 = ?

D. 23.09 ÷ 13.009 = ?

5. Use your calculator to solve each equation. Express each answer in proper scientific notation and with the proper number of significant figures. If you do not get the correct answers, you may not be entering scientific notation into your calculator properly, so ask your instructor for assistance.

A. $(5.6 \times 10^{3}) \times (9.04 \times 10^{-7}) = ?$

B. $(8.331 \times 10^{-2}) \times (2.45 \times 10^{5}) = ?$

C. $983.09 \div (5.390 \times 10^{5}) = ?$

6. Perform each calculation and express your answer using the correct number of significant digits. (Hint: Think about the appropriate rule as you do each step in the calculation.)

A. 6.78 x 5.903 x (5.489 - 5.01) = ?

B. (4.562 x 3.99870) / (452.6755 - 452.33) = ?

C. (14.82 x 0.44) – 6.1111 = ?

Answers (Section 1.5)

1. Significant figures represent all the known digits plus the first estimated digit of a measurement; they are the only values worth reporting in a measurement.

2.

A. two

B. four

C. five

D. three

E. five

3.

A. 34,700

B. 34,800

C. 0.00200

4.

A. 1,797

B. 0.1071

C. 3,850,000

D. 1.775

5.

A. 5.1×10^{-3}

B. 2.04×10^{4}

C. 1.824×10^{-3}

6.

A. 19

B. 53

C. 0.4

1.6: The International System of Units

Questions for Section 1.6

1. What property is represented by each of the following measurements? A) 273 K; B) 725 nm; C) 55 cm^3; D) 8.1×10^4 µs
2. Complete the following table:

Unit	Abbreviation	Exponent & Base Unit
nanogram		
		10^{-3} s
	Mm	
kiloliter		
	µm	
		10^{-2} L

Answers (Section 1.6)

1. What property is represented by each of the following measurements? A) 273 K = temperature; B) 725 nm = length; C) 55 cm^3 = volume; D) $8.1x10^4$ µs = time

2. Complete the following table:

Unit	Abbreviation	Exponent & Base Unit Abbr.
nanogram	ng	10^{-9} g
milliseconds	ms	10^{-3} s
megameters	Mm	10^{6} m
kiloliter	kL	10^{3} L
micrometers	µm	10^{-6} m
centiliters	cL	10^{-2} L

1.7: Converting Units

Exercises for Section 1.7

1. Give the two conversion factors you can construct using each pair of units.
   A. meters and kilometers
   B. liters and nanoliters
   C. seconds and milliseconds
2. How many meters are in 56.2 km?
3. How many microliters (µL) are in 44.1 L?
4. Convert 109.6 kg into micrograms. Express your final answer in scientific notation.
5. Convert 3.009×10^{-5} ML into centiliters. Express your final answer in scientific notation.
6. The density of ethyl alcohol is 0.79 g/mL. What is the mass of 340 mL of ethyl alcohol?
7. The density of ethyl alcohol is 0.79 g/mL. What is the volume of 340 g of ethyl alcohol?
8. Convert 55 miles per hour (mph or mi/hr) into meters per second (m/s). (Hints: 1 mi = 1609 m; 1 hr = 60 min; 1 min = 60 s)
9. Vitamin C tablets can come in 500 mg tablets. How many of these tablets are needed to obtain 10 g of vitamin C?
10. Some brands of aspirin have 81 mg of aspirin in each tablet. If a person takes 8 tablets per day, how many grams of aspirin is that person consuming every day?

Answers (Section 1.7)

1.

A. $\frac{1\text{ km}}{10^3\text{ m}}$ or $\frac{10^3\text{ m}}{1\text{ km}}$ or $\frac{1\text{ km}}{1000\text{ m}}$ or $\frac{1000\text{ m}}{1\text{ km}}$

B. $\frac{1\text{ nL}}{10^{-9}\text{ L}}$ or $\frac{10^{-9}\text{ L}}{1\text{ nL}}$ or $\frac{1000000000\text{ nL}}{1\text{ L}}$ or $\frac{1\text{ L}}{1000000000\text{ nL}}$

C. $\frac{1\text{ ms}}{10^{-3}\text{ s}}$ or $\frac{10^{-3}\text{ s}}{1\text{ ms}}$ or $\frac{1000\text{ ms}}{\text{s}}$ or $\frac{\text{s}}{1000\text{ ms}}$

2. 5.62×10^4 m

3. 4.41×10^7 µL

4. 1.096×10^{11} µg

5. 3.009×10^3 cL

6. 270 g

7. 430 mL

8. 25 m/s

9. 20 tablets [10 g x $\frac{1\text{ mg}}{10^{-3}\text{ g}}$ x $\frac{1\text{ tablet}}{81\text{ mg}}$ = 20 tablets]

10. 0.65 g [$\frac{8\text{ tablets}}{1\text{ day}}$ x $\frac{81\text{ mg}}{1\text{ tablet}}$ x $\frac{10^{-3}\text{ g}}{1\text{ mg}}$ = 0.65 g]

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2: ELEMENTS, ATOMS, AND THE PERIODIC TABLE

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

2.1: The Elements

2.2: Atomic Theory

2.3: The Structure of Atoms

2.4: Nuclei of Atoms

2.5: Atomic Masses

2.6: Arrangements of Electrons

2.7: The Periodic Table

2.8: Chapter Summary

2.E: Exercises

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2.1: The Elements

Skills to Develop

- 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

Earth's Crust		Earth (overall)	
Element	Percentage	Element	Percentage
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 28.5%. 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.

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

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

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

chlorine	Cl	potassium	K*
chromium	Cr	silicon	Si
copper	Cu*	silver	Ag*
fluorine	F	sodium	Na*
gold	Au*	strontium	Sr
helium	He	sulfur	S
hydrogen	H	tin	Sn*
iron	Fe	tungsten	W†
iodine	I	uranium	U
lead	Pb*	zinc	Zn
lithium	Li	zirconium	Zr
***The symbol comes from the Latin name of element.**			
†The symbol for tungsten comes from its German name—*wolfram*.			

Note

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 by consulting Table 2.1.3 "Element Names and Symbols".

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

SOLUTION

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

Example 2.1.2

What element is represented by each chemical symbol?

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

SOLUTION

a. sodium
b. mercury
c. phosphorus
d. potassium
e. iodine

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. The first letter in the symbol is always upper-case and, if there is a second letter, it is always lower-case.

Contributors

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2.2: Atomic Theory

Skills to Develop

- Explain how all matter is composed of atoms.
- Describe the modern atomic theory.

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).

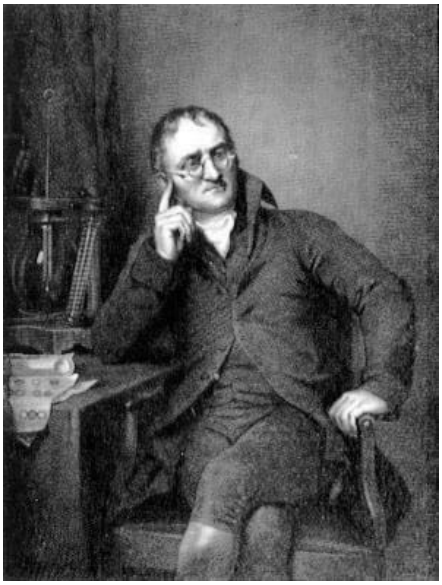


Figure 2.2.1 *John Dalton was an English scientist who enunciated the modern atomic theory.*

Most elements in their pure form exist as individual atoms. For example, a macroscopic chunk of iron 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), oxygen (O_2), nitrogen (N_2), fluorine (F_2), chlorine (Cl_2), bromine (Br_2), and iodine (I_2).

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.

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2.3: The Structure of Atoms

Skills to Develop

- 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 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. 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)
proton	p or p^+	1.673×10^{-27}
neutron	n or n^0	1.675×10^{-27}
electron	e or e^-	9.109×10^{-31}

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.

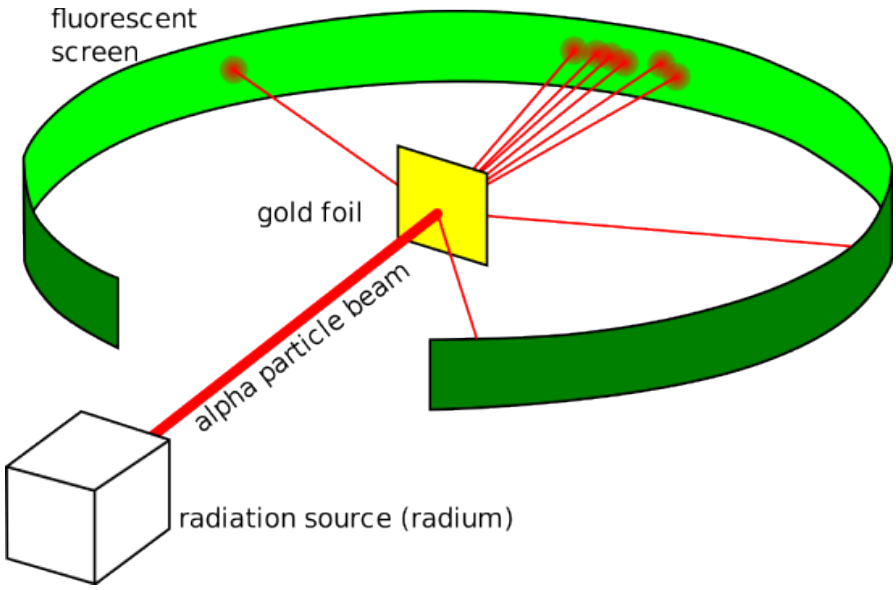


Figure 2.3.1***:*** *The Geiger-Marsden Experimental Setup. Experiments using this setup were used to investigate the structure of atoms. Most of the particles traveled straight through the foil, but some alpha particles were deflected off to one side. Some were even deflected back toward the source. 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." Image used with permission (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.

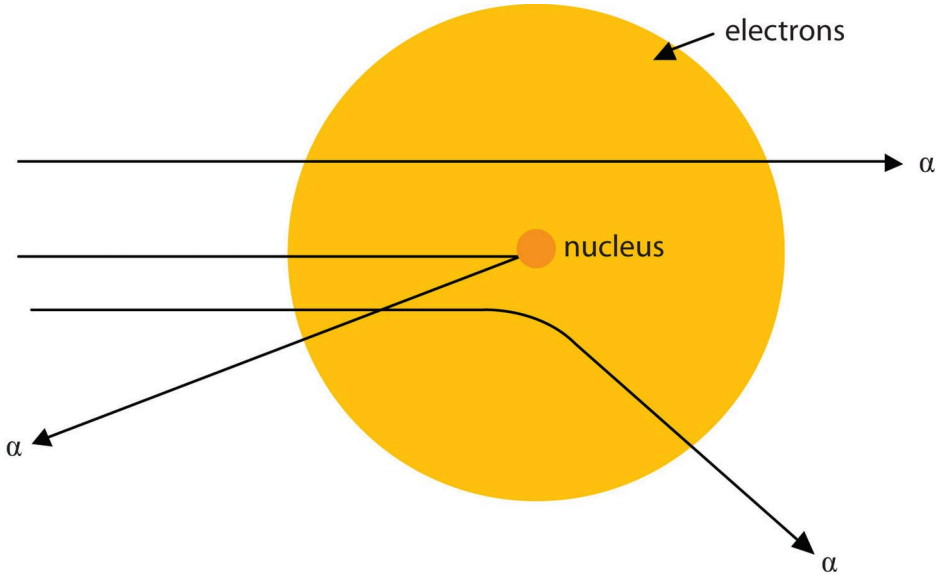


Figure 2.3.2***:*** *Rutherford's Metal-Foil Experiments. Rutherford explained the results of the metal-foil experiments by proposing that most of the mass and the positive charge of an atom are located in its nucleus, while the relatively low-mass electrons orbit about the nucleus. Most alpha particles 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.

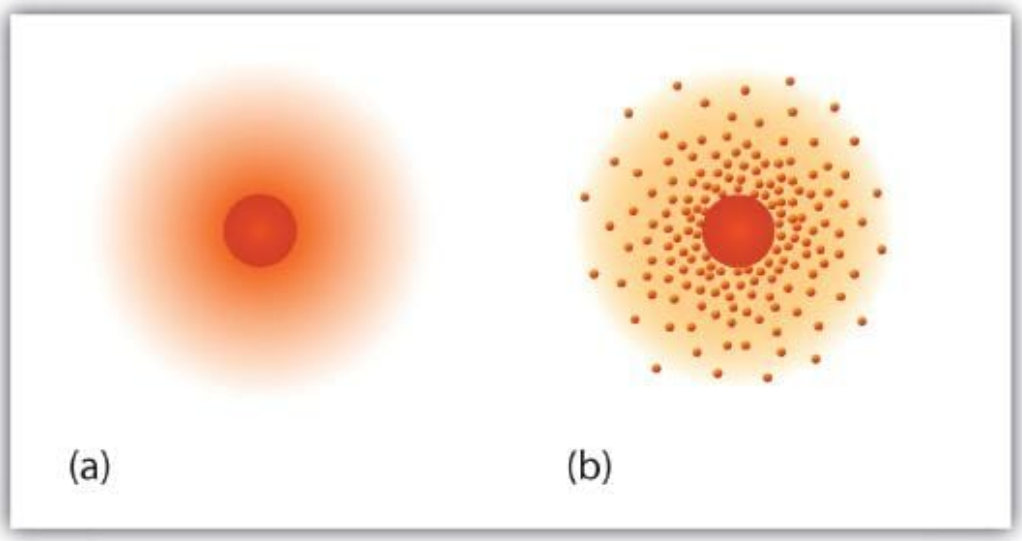


Figure 2.3.3*: A Modern Depiction of Atomic Structure. A more modern understanding of atoms, reflected in these representations of the electron in a hydrogen atom, is that electrons occupy regions of space about the nucleus; they are not in discrete orbits like planets around the sun. (a) The darker 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 relative 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 charge, 1 amu; neutron: 0 charge, 1 amu; electron: –1 charge, negligibly small
2. Protons and neutrons are located in a central nucleus, while electrons orbit about the nucleus.

Key Takeaways

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

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2.4: Nuclei of Atoms

kills to Develop

- 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.

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. Chapter 21 lists the elements and their atomic numbers. From this table, you can determine the number of protons in the nucleus of any element. The largest atoms have over 100 protons in their nuclei.

Example 2.4.1

Consult a periodic table to determine the number of protons in the nucleus of each element.

a. aluminum
b. iron
c. carbon

SOLUTION

a. According to the table, aluminum has an atomic number of 13. Therefore, every aluminum atom has 13 protons in its nucleus.
b. Iron has an atomic number of 26. Therefore, every iron atom has 26 protons in its nucleus.
c. Carbon has an atomic number of 6. Therefore, every carbon atom has 6 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

Consult a periodic table to determine how many electrons are present in the atoms of each element.

a. sulfur

b. tungsten
c. argon

SOLUTION

a. The atomic number of sulfur is 16. Therefore, in a neutral atom of sulfur, there are 16 electrons.
b. The atomic number of tungsten is 74. Therefore, in a neutral atom of tungsten, there are 74 electrons.
c. The atomic number of argon is 18. Therefore, in a neutral atom of argon, there are 18 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 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 2.6 compares the three isotopes of hydrogen.

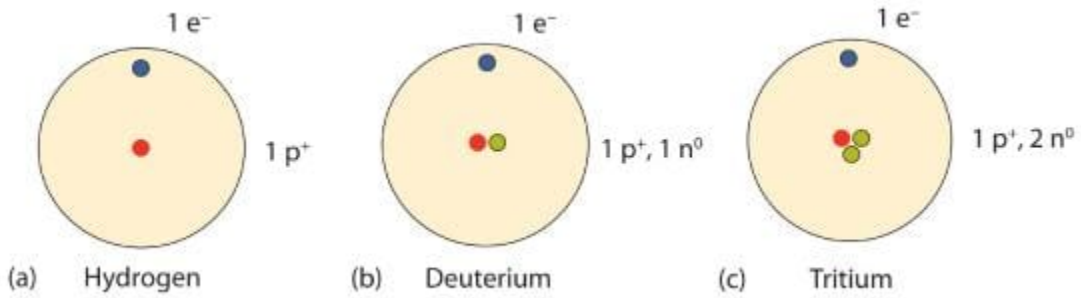


Figure 2.4.1***:*** *Isotopes of Hydrogen. Most hydrogen atoms have only a proton in the nucleus (a). A small amount of hydrogen exists as the isotope deuterium, which has one proton and one neutron in its nucleus (b). A tiny amount of the hydrogen isotope tritium, with one proton and two neutrons in 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 of an atom is the sum of the numbers of protons and neutrons in the nucleus. Given the mass number for a nucleus (and knowing the atomic number of that particular atom), you can determine the number of neutrons by subtracting the atomic number from the mass number.

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

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

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

SOLUTION

a. In $^{35}_{17}\mathrm{Cl}$ there are 17 protons, and 35 − 17 = 18 neutrons in each nucleus.
b. In $^{127}_{53}\mathrm{I}$ there are 53 protons, and 127 − 53 = 74 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}C or ^{235}U. You may also see isotopes represented in print as, for example, carbon-13 or uranium-235.

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 by the number of protons in the nucleus.
2. In an electrically neutral atom, the number of protons equals the number of electrons.
3. Isotopes 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

- Elements can be identified by their atomic number and mass number.
- Isotopes are atoms of the same element that have different masses.

Contributors

- Anonymous

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2.5: Atomic Masses

Skills to Develop

- To define atomic mass and atomic mass unit.

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.

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.

For example, boron exists as a mixture that is 19.9% ^{10}B and 80.1% ^{11}B. The atomic mass of boron would be calculated as (0.199 × 10.0 u) + (0.801 × 11.0 u) = 10.8 u. Similar average atomic masses can be calculated for other elements. Carbon exists on Earth as about 99% ^{12}C and about 1% ^{13}C, so the weighted average mass of carbon atoms is 12.01 u.

Example 2.5.1: Average Atomic Mass of Isotopes

Use the following information to determine the atomic mass of magnesium. (Do not look at the value on the periodic table.)

Isotope	Exact Mass (atomic mass units)	Relative Abundance (percentage)
^{24}Mg, magnesium-24	23.9850 u	78.99 %
^{25}Mg, magnesium-25	24.9858 u	10.00 %
^{26}Mg, magnesium-26	25.9826 u	11.01 %

SOLUTION

Atomic masses are the average of the naturally occuring isotopes. The fraction of each is the percentage, divided by 100.

= (fraction of ^{24}Mg)(exact mass ^{24}Mg) + (fraction of ^{25}Mg)(exact mass ^{25}Mg) + (fraction of ^{26}Mg)(exact mass ^{26}Mg)

= (78.99/100)(23.9850 u) + (10.00/100)(24.9858 u) + (11.01/100)(25.9826 u)

= (0.7899)(23.9850 u) + (0.1000)(24.9858 u) + (0.1101)(25.9826 u)

= (18.94<u>57515</u> u) + (2.49<u>858</u> u) + (2.860<u>68426</u> u)

= 24.30<u>501576</u> u = **24.31 u**

The digits underlines are not significant. When multiplying, the answers are known to the fewest total significant figures (four). When adding, the answer is known to the fewest decimal places (two).

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 exactly 1/12th of the mass of a ^{12}C atom (and very close to the mass of one proton or one neutron).

Key Takeaway

- Atoms have a mass that is based largely on the number of protons and neutrons in their nucleus.

Contributors

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2.6: Arrangements of Electrons

Skills to Develop

- To 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. 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 an *s* subshell, the second shell has an *s* and a *p* subshell, the third shell has *s*, *p*, and *d* subshells, and so forth.
- Different subshells hold a different maximum number of electrons. Any *s* subshell can hold up to 2 electrons; *p* supshell up to 6 electrons; *d* subshell up to 10; and *f* subshell up to 14.

It is the arrangement of electrons into shells that has the most effect on chemical properties, so we will focus on mainly on shells here.

We use numbers to indicate which shell an electron is in. The first shell, closest to the nucleus and with the lowest-energy electrons, is shell 1. This first shell has only one subshell (labeled 1s) and can hold a maximum of 2 electrons. This is why there are two elements in the first row of the periodic table (H & He).

Because the first shell can only hold a maximum of 2 electrons, the third electron must go into the second shell. Therefore the lithium (Li), which has three total electrons, will have two electrons in the first shell and one electron in the second shell. Notice that lithium is the first element in the second row of the periodic table.

The second shell has two subshells (labeled 2*s* and 2*p)*. The 2*s* subshell holds a maximum of 2 electrons, and the 2*p* subshell holds a maximum of 6 electrons. This means that the second shell can hold a maximum of eight electrons (2+6=8). Notice that there are eight elements in the second row of the periodic table.

It is only the electrons in the outer-most shell, called the VALENCE shell, that tend to react (be gained, lost, or shared). You might imagine that, if two atoms bumped into each other, it would be the outer electrons that would interact first. The following is a list of total electrons, electrons by shell, and valence electrons for the first 10 elements.

1. Hydrogen has 1 electron in the first shell (so one valence electron).
2. Helium has 2 electrons --- both in the first shell (so two valence electrons).
3. Lithium has 3 electrons --- 2 in the first shell, and 1 in the second shell (so one valence electron).
4. Beryllim has 4 electrons --- 2 in the first shell, and 2 in the second shell (so two valence electrons).
5. Boron has 5 electrons --- 2 in the first shell, and 3 in the second shell (so three valence electrons).
6. Carbon has 6 electrons --- 2 in the first shell, and 4 in the second shell (so four valence electrons).
7. Nitrogen has 7 electrons --- 2 in the first shell, and 5 in the second shell (so five valence electrons).
8. Oxygen has 8 electrons --- 2 in the first shell, and 6 in the second shell (so six valence electrons).
9. Fluorine has 9 electrons --- 2 in the first shell, and 7 in the second shell (so seven valence electrons).
10. Neon has 10 electrons --- 2 in the first shell, and 8 in the second shell (so eight valence electrons).

Figure 2.6.1 below lists the atomic number for the main group elements. The atomic number defines the number of protons in the nucleus of each atom. For neutral atoms, the number of positive protons will equal the total number of negative electrons (zero net charge). For example, bromine (Br) has 35 protons and 35 total electrons. Periodic tables always list the atomic number.

Atomic Number for the Main Group Elements (listed in each box with the elemental symbol)

The atomic number gives the number of protons. For neutral atoms, the number of protons and electrons are equal.

IA															VIIIA
1 H	IIA										IIIA	IVA	VA	VIA	VIIA	2 He
3 Li	4 Be										5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg										13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca										31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr										49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba										81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra															

Figure 2.6.1 - Atomic Number for Each of the Main Group Elements

The number of valence electrons for each main group element can be determined by the column, or group, it occupies on the periodic table. Table 2.6.2 below summarizes the number of valence electrons for each main group column of elements. For example, the elements in the first column (sometimes labeled IA), all have one valence electron. The second column (IIA) has two valence electrons. We skip the short block of ten elements in the middle because this is where a subshell fills out of order. The elements in columns IIIA, IVA, VA, VIA, and VIIA, and VIIIA* have three, four, five, six, seven, and eight* valence electrons, respectively.

*Note that helium (He) only has two valence electrons. Some periodic tables place helium in column IIA, others place it in VIIIA, and some in both locations.

Number of Outer **Valence Electrons** for Each Group (Column) of Main Group Elements

one	two										three	four	five	six	seven	eight
IA																VIIIA
H	IIA										IIIA	IVA	VA	VIA	VIIA	He
Li	Be										B	C	N	O	F	Ne
Na	Mg										Al	Si	P	S	Cl	Ar
K	Ca										Ga	Ge	As	Se	Br	Kr
Rb	Sr										In	Sn	Sb	Te	I	Xe
Cs	Ba										Tl	Pb	Bi	Po	At	Rn
Fr	Ra										Nh	Fl	Mc	Lv	Ts	Og

Figure 2.6.2 - Number of Valence Electrons for Main Group Elements

Example 2.6.1: Electrons of Phosphorus

How many total and valence electrons are in a neutral phosphorus atom?

SOLUTION

A neutral phosphorus atom has 15 total electrons. Two electrons can go into first shell, eight in the second shell, and it has five more in the third shell. The third shell is the outer valence shell, so it has 5 valence electrons.

The number of electrons in each shell becomes more complicated as more electrons are added because there are more subshells being used and because the shell start to fill out of order. For elements with larger atomic number than 20 (beyond calcium), we will just focus on how many total and how many valence electrons, not the number in each shell. We have stated that the outer-shell electrons are called valence. The inner (non-valence) shells and electrons are often called the core.

Example 2.6.2: Counting total and Valence Electrons in Xenon

How many total, valence, and core electrons are there in a neutral xenon atom?

SOLUTION

Xenon has 54 total, 8 valence, and 46 core electrons.

Concept Review Exercises

1. How are electrons organized in atoms?
2. What is the maximum number of electrons that can fit into the first two shells of an atom?
3. What is the difference between core electrons and valence electrons?

Answers

1. Electrons are organized into shells and subshells around nuclei.
2. The first shell can fit a maximum of two and the second shell can fit a maximum of eight electrons.
3. Valence electrons are in the highest-numbered (outer) shell; all other electrons are core electrons.

Key Takeaway

- Electrons are organized into shells and subshells about the nucleus of an atom.

Contributors

- Anonymous

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2.7: The Periodic Table

Skills to Develop

- 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.

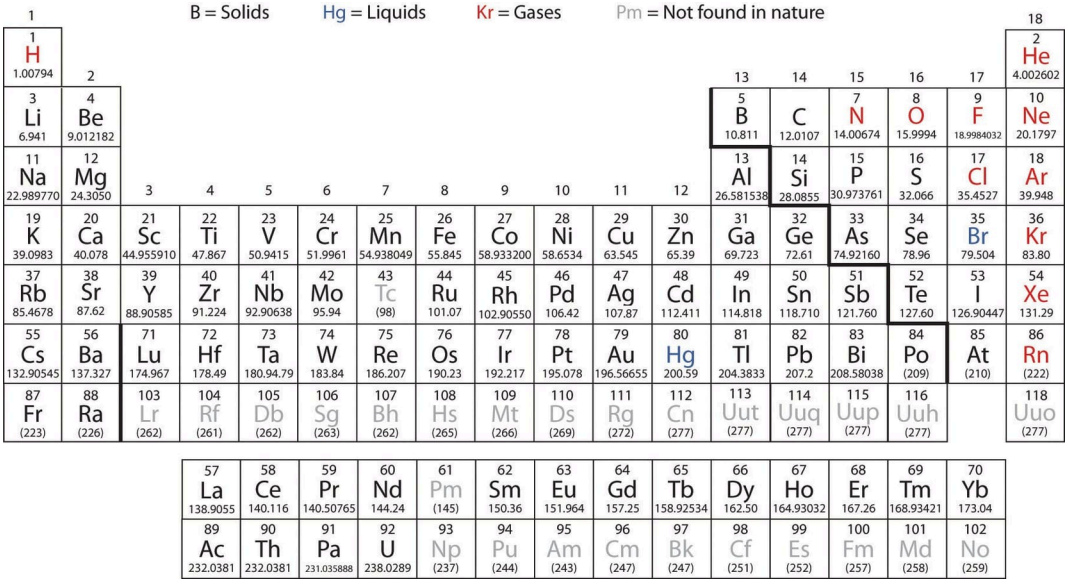


Figure 2.7.1 *A Modern Periodic Table. A modern periodic table lists elements left to right by atomic number.*

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).

The word halogen comes from the Greek for “salt maker” because these elements combine with other elements to form a group of compounds called salts.

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.

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.

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 line in the right-hand portion of the periodic table have semimetal properties.

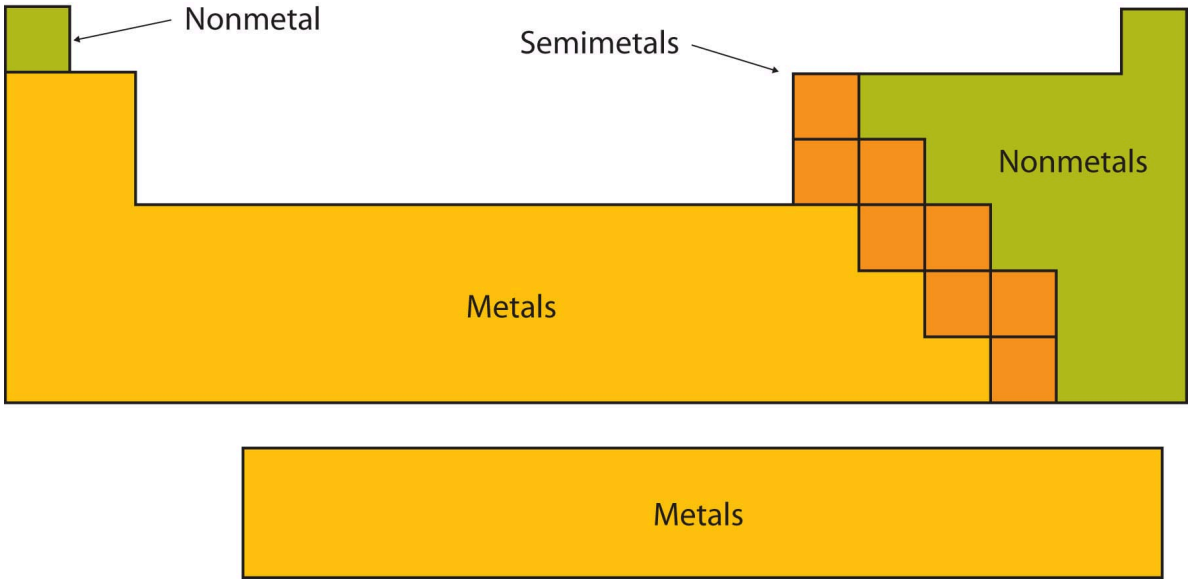


Figure 2.7.2: Types of Elements. Elements are either metals, nonmetals, or semimetals. Each group is located in a different part of the periodic table.

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 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**.

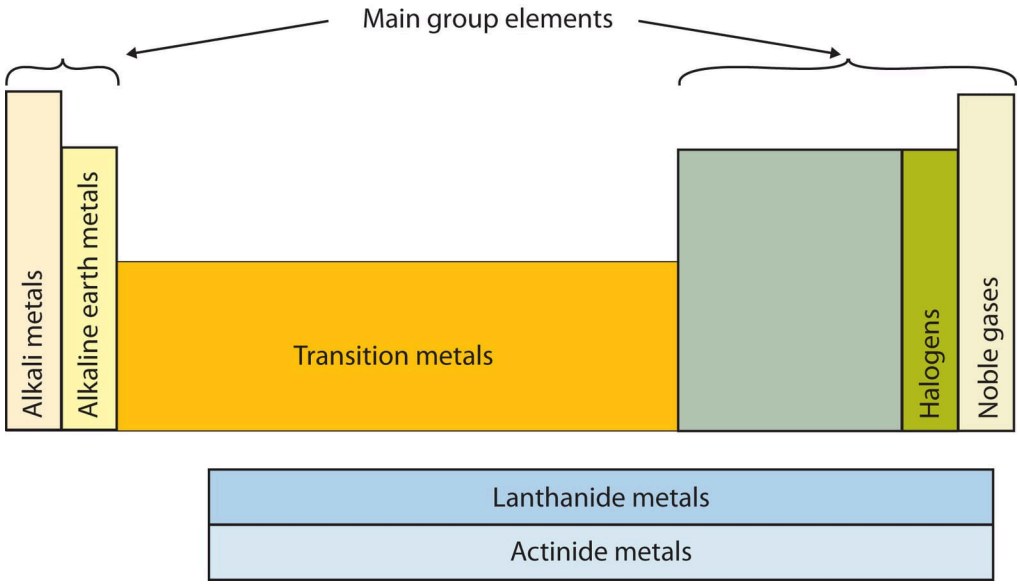


Figure 2.7.3: *Special Names for Sections of the Periodic Table. Some sections of the periodic table have special names. The elements lithium, sodium, potassium, rubidium, cesium, and francium are collectively known as alkali metals.*

To Your Health: Transition Metals in the Body

According to Table 2.2, 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 2.2, so they are present in the body in very small quantities. However, even these small quantities are required for the body to function properly.

Notice that when comparing Figure 2.7.3 and Figure 2.7.5, members of the same family have the same number of valence electrons.

- The alkali metals (Li, Na, K, Rb, Cs, Fr) all have one valence electron. (Hydrogen has one valence electron, but is a non-metal.)

- The alkaline earth metals (Be, Mg, Ca, Sr, Ba, Ra) all have two valence electrons.
- The halogens (F, Cl, Br, I, At, Ts) all have seven valence electrons.
- The noble gases (He, Ne, Ar, Kr, Xe, Rn, Og) have eight* valence electrons. (Helium is a noble gas, but only has two valence electrons.)

The elements from each family react in similar ways because they have the same number of electrons on the outside.

Number of Outer **Valence Electrons** for Each Group (Column) of Main Group Elements

one	two										three	four	five	six	seven	eight
IA																VIIIA
H	IIA										IIIA	IVA	VA	VIA	VIIA	He
Li	Be										B	C	N	O	F	Ne
Na	Mg										Al	Si	P	S	Cl	Ar
K	Ca										Ga	Ge	As	Se	Br	Kr
Rb	Sr										In	Sn	Sb	Te	I	Xe
Cs	Ba										Tl	Pb	Bi	Po	At	Rn
Fr	Ra										Nh	Fl	Mc	Lv	Ts	Og

Figure 2.7.5*: Valence Electrons for the Main Group Families of the Periodic Table*

Example 2.7.1

Which elements would have similar chemical properties to those listed below?

1. carbon, C
2. iodine, I

SOLUTION

1. Carbon is in the same family (column) as, and would have similar chemical properties to Si, Ge, Sn, Pb, and F.
2. Iodine is in the same family (column) as, and would have similar chemical properties to F, Cl, Br, At, and Ts.

Example 2.7.2

In what family do the members not all have the same number of valence electrons?

SOLUTION

The noble gases. Helium has two valence electrons but neon, argon, krypton, xenon and radon all have eight.

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). 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 electron shells; more shells of electrons stacked up on each other takes up more space. 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, the atomic radius decreases. These trends are seen clearly in Figure 2.7.5.

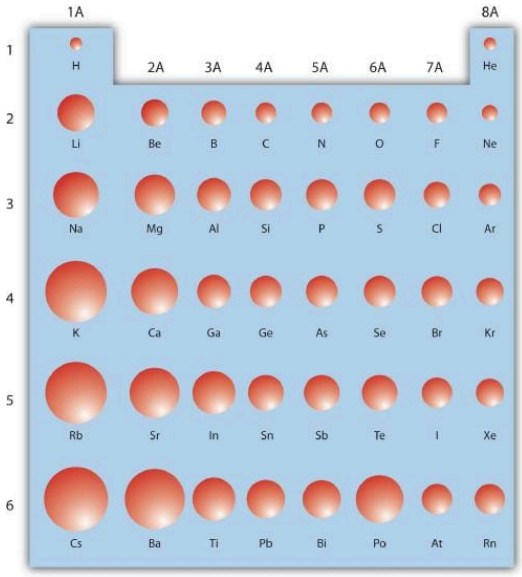


Figure 2.7.5: Trends on the Periodic Table. The relative sizes of the atoms show several trends with regard to the structure of the periodic table. Atoms become larger going down a column and smaller going across a period.

Example 2.7.3

Using the periodic table (and not Figure 2.7.5 above), which atom is larger?

a. N or Bi
b. Mg or Cl

SOLUTION

a. Because Bi is below N on the periodic table, we expect that Bi atoms are larger than N atoms. Electrons in higher-numbered shells (further down the periodic table) are further from the nucleus and thus make the atom larger.
b. Both Mg and Cl are in period 3 of the periodic table (same row). Since Mg is further to the left, we expect Mg to be larger. Both Mg and Cl have three shells of electrons, but Mg has fewer protons in the nucleus, so the electrons are not pulled in as close.

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

3. Describe the trends in atomic radii as related to an element's position on the periodic table.

Answers

1. Elements are organized by atomic number.

2. a. the left three-quarters of the periodic table
   b. the right quarter of the periodic table
   c. the next-to-last column of the periodic table
   d. the middle section 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.

Contributors

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2.8: Chapter 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. 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** and **nonmetals**. The periodic table is also separated into **main group elements**, **transition metals**, lanthanide elements, and actinide elements. The shape of the periodic table reflects the sequential filling of shells and subshells in atoms. Members of the same family have the same number of valence electrons.

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

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2.E: Exercises

Additional Exercises

1. What is the difference between the atomic symbols Si and SI?
2. How many of each subatomic particle make up a neutral bromine-80 atom, ^{80}Br? (You should be able to answer this using only a periodic table.)
3. How many electrons in each shell of a chlorine atom, Cl, and which are valence? (You should be able to answer this using only a periodic table.)
4. What are two things that protons and neutrons have in common, plus one way in which they are different?
5. A sample of the nonexistent element mythium consists of 25.59% of an isotope with mass of 580.0 u, 32.74% of an isotope with mass of 582.0 u, and 41.67% of an isotope with mass number 581.0 u. What is the atomic mass of mythium?
6. Because the distribution of isotopes is different on different planets in the solar system, the average atomic mass of any element differs from planet to planet. Assume that on Mercury, a rather hot planet, there is less of the lighter isotope left in the atmosphere than on Earth, so that 92.55% of the hydrogen on Mercury is ^{1}H, while the remainder is ^{2}H (a.k.a. deuterium). What is the atomic mass of hydrogen on Mercury? The exact masses of ^{1}H and ^{2}H are 1.0078 u and 2.0014 u, respectively.
7. The compound that sodium makes with chlorine has sodium and chlorine atoms in a 1:1 ratio. Name two other elements that should make a compound having a 1:1 ratio of atoms with sodium. (HINT: Remembers that members of the same group or family will have similar chemical properties.)

Answers

1. Si is silicon, whereas SI is sulfur and iodine.
2. 35 p, 45 n, 35 e
3. Chlorine: first shell = 2 e; second shell = 8 e; third shell = 7 e; the third shell is the (outer-most) valence shell and it contains seven valence electrons
4. They are both found in the nucleus of an atom and both have mass of about one atomic mass unit. They are different in that protons have a +1 relative charge and neutrons have zero charge.
5. The average atomic mass of mythium would be 581.1 u.
6. The average atomic mass of hydrogen on mercury would be 1.0818 u.
7. Sodium is an alkali metal and chlorine is a halogen, so any compound from the same groups should exist in the same ratio (i.e. potassium and bromine).

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3: IONIC BONDING AND SIMPLE IONIC COMPOUNDS

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

3.1: Two Types of Bonding

3.2: Ions

3.3: Formulas for Ionic Compounds

3.4: Ionic Nomenclature

3.5: Formula Mass

3.6: Chapter Summary

3.E: Exercises

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3.1: Two Types of Bonding

Skills to Develop

- 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 11 electrons: 2 in the first shell, 8 in the second shell, and 1 in the third shell. Is sodium more likely to gain or lose electrons to obtain an octet?

SOLUTION

Sodium could gain 7 electrons in the third shell to have an octet (like argon, which has 18 total and 8 valence electrons). Seven extra negative charges is a bit too much, so is not likely.

Instead, sodium would lose its one electron from the third shell. Since the third shell would be empty, now the second shell is the valence shell, and thus it would have an octet (like neon, which has 10 total and 8 valence electrons). When that happens, it becomes an ion with a net positive charge. This can be illustrated as follows:

Sodium Atom (no charge)		Sodium Ion (net positive)	
11 protons	11+	11 protons	11+
11 electrons	11–	10 electrons	10–

Sodium Atom (no charge)		Sodium Ion (net positive)	
	0 overall charge		+1 overall charge

Example 3.1.2

Is nitrogen more likely to gain or lose electrons to obtain an octet? How many electrons?

SOLUTION

Nitrogen has 7 total electrons, 2 in the first shell and 5 in the second shell. To obtain the same number of electrons as a noble gas, it could gain 3 to be like neon or lose 5 to be like helium. Gaining 3 electrons is closer and thus more likely.

After gaining three, it would have 10 total electrons, 2 in the first shell and 8 in the second shell (an octet!). When that happens, it becomes an ion with a net charge of negative three. This can be illustrated as follows:

Nitrogen Atom (no charge)		Nitrogen Ion (net negative three)	
7 protons	7+	7 protons	7+
7 electrons	7–	10 electrons	10–
	0 overall charge		-3 overall charge

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.

Contributors

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3.2: Ions

Skills to Develop

- 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.

Note

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

Electron Transfer

We can use total electrons or valence electrons to illustrate the electron transfer process between sodium atoms and chlorine atoms. First, we will look at the arrangement of electrons in sodium.

Sodium Atom, Na (11 p^+ in nucleus)	First Shell	Second Shell	Third Shell
11 e^- Total Electrons	2 e^-	8 e^-	1 e^-

As demonstrated in the previous section, sodium is likely to achieve an octet in its outermost shell by losing its one valence electron. Now it has the same number of electrons as the nearest noble gas, neon. The cation produced in this way, Na^+, is called the sodium ion to distinguish it from the neutral element. Because the ion has 11 positive protons and 10 negative electrons, there is a net positive charge. That charge is shown as a superscript at the top, right of the symbol.

Sodium Ion, Na^+ (11 p^+ in nucleus)	First Shell	Second Shell	Third Shell
10 e^- Total Electrons	2 e^-	8 e^-	empty

The third shell of the ion is empty, so the outermost shell of the sodium ion becomes the second electron shell, which has eight electrons in it. The octet rule has been satisfied. Figure 3.2.1 is a graphical depiction of this process.

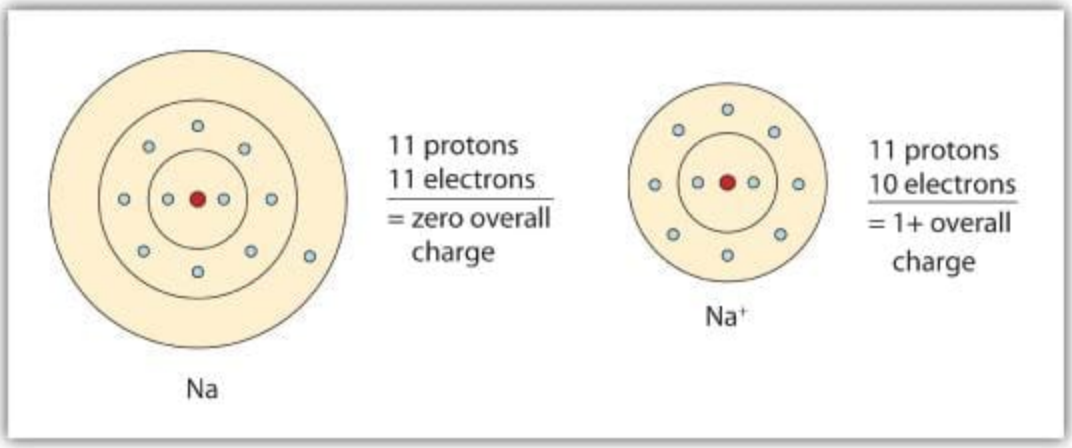


Figure 3.2.1***:*** *The Formation of a Sodium Ion. On the left, a sodium atom has 11 electrons. On the right, the sodium ion only has 10 electrons and a 1+ charge.*

A chlorine atom has the following electron arrangement:

Chlorine Atom, Cl (17 p^+ in nucleus)	First Shell	Second Shell	Third Shell
17 e^- Total Electrons	2 e^-	8 e^-	7 e^-

Only one more electron is needed to achieve an octet in chlorine's valence shell. (In table salt, NaCl, this electron comes from the sodium atom.) Now the chlorine ion has the same number of electrons as the nearest noble gas, argon. The electron arrangement of the new species that results is as follows:

Chlorine Ion, Cl^- (17 p^+ in nucleus)	First Shell	Second Shell	Third Shell
18 e^- Total Electrons	2 e^-	8 e^-	8 e^-

In this case, the ion has the same outermost shell as the original atom (third), but now that shell has eight electrons in it. Once again, the octet rule has been satisfied. By gaining an extra negative electron, the ion now has a net negative charge. 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. Figure 3.2.2 is a graphical depiction of this process.

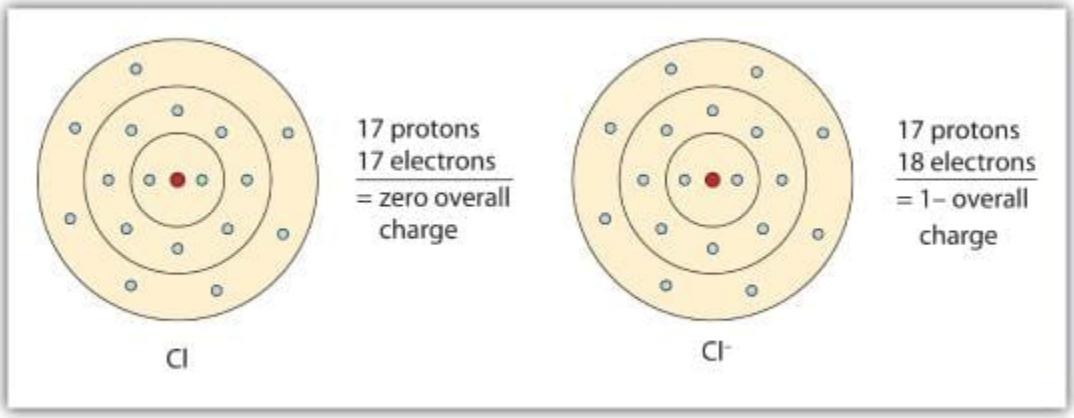


Figure 3.2.2***:*** *The Formation of a Chlorine Ion. On the left, the chlorine atom has 17 electrons. On the right, the chloride ion has*

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.

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}.

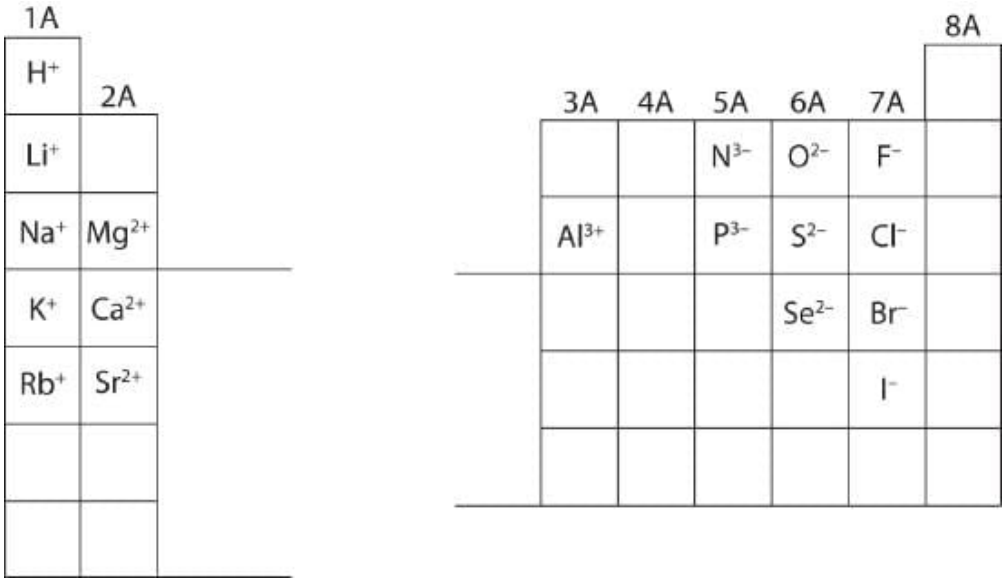


Figure 3.2.3***:*** *Predicting Ionic Charges. The charge that an atom acquires when it becomes an ion is related to the structure of the periodic table. Within a group (family) of elements, atoms form ions of a certain charge.*

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:



Note

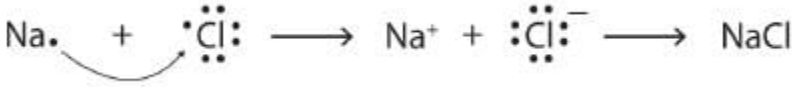
It does not matter what sides the dots are placed on in Lewis diagrams as long as each side has a maximum of two dots.

These diagrams are called **Lewis electron dot diagrams**, or simply Lewis diagrams, after Gilbert N. Lewis, the American chemist who introduced them. 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 Diagrams of the Elements Lithium through Neon

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



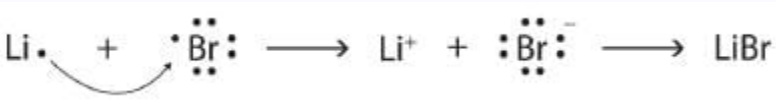
Above is shown the Lewis diagrams of sodium and chlorine atoms (on the left) exchanging an electrons to become the Lewis diagrams of the ions (in the middle), and with the formula of the compound shown (on the right). In representing the final formula, the dots are omitted (and the individual charges are not shown because they balance to zero).

Example 3.2.1

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

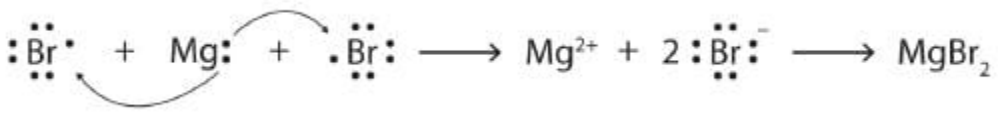
SOLUTION

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,



Lewis Diagram of Atoms → Lewis Diagram of Compound → Chemical Formula of Compound

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 $MgBr_2$:



Lewis Diagram of Atoms → Lewis Diagram of Compound → Chemical Formula of Compound

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).

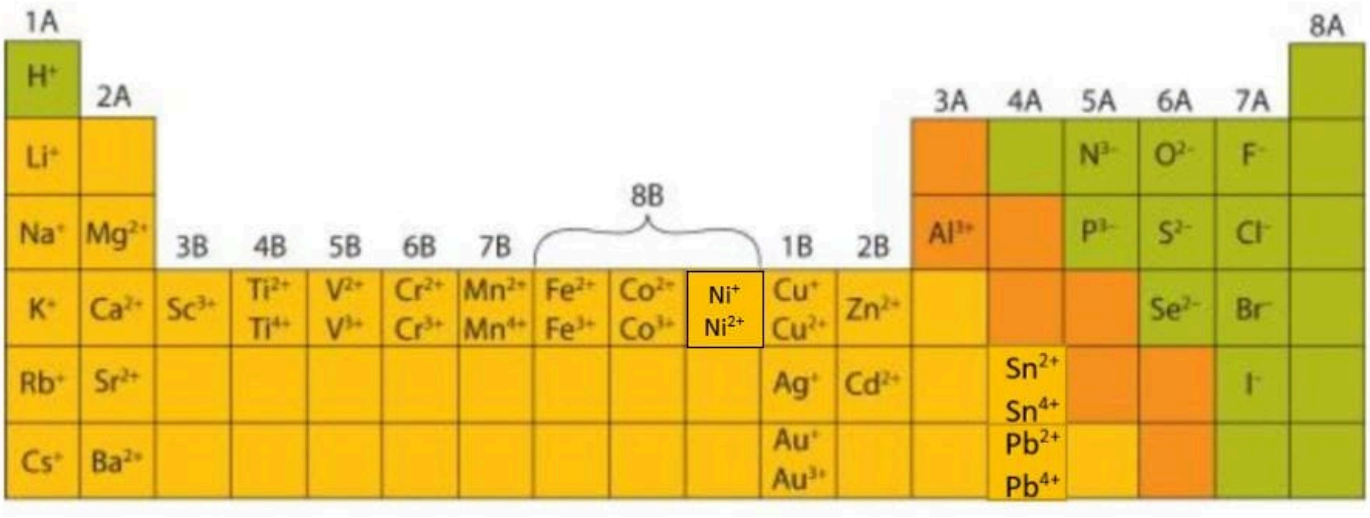


Figure 3.2.5*: Charges of the Monatomic Ions. Note that some atoms commonly form ions of different charges.*

Contributors

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3.3: Formulas for Ionic Compounds

Skills to Develop

- 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 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.

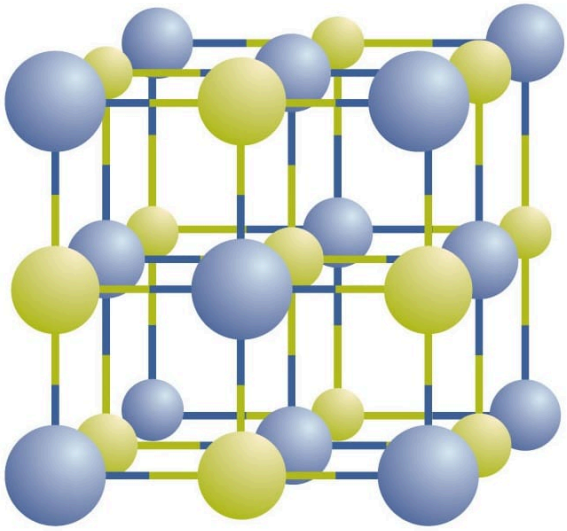


Figure $3.3.1$ A Sodium Chloride Crystal. A crystal contains a three-dimensional array of alternating positive and negative ions. The precise pattern depends on the compound. A crystal of sodium chloride, shown here, is a collection of alternating sodium and chlorine ions.

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 obeys the following rule: 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 is not correct because 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+}

Example 3.3.1

Write the chemical formula for an ionic compound formed from the following elements. (You should be able to use a periodic table and the octet rule to determine likely charges for the main group elements.)

1. Ionic compound formed from sodium and sulfur
2. Ionic compound formed from aluminum and fluorine
3. Ionic compound formed from iron and oxygen (assume the iron ion takes on a 3+ charge)

SOLUTION

1. 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 sulfide ion. Rather than writing the formula as NaNaS, we shorten it by convention to Na_2S.
2. The aluminum ion has a 3+ charge, while the fluoride ion formed by fluorine has a 1– charge. Three fluoride 1– ions are needed to balance the 3+ charge on the aluminum ion. This combination is written as AlF_3.
3. Iron can form two possible ions, but the ion with a 3+ charge is specified here. The oxygen atom will adopt 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– oxide ions will give 6–, thereby balancing the overall positive and negative charges. Thus, the formula for this ionic compound is Fe_2O_3.

Polyatomic Ions

Some ions consist of groups of atoms bonded together and have an overall electric charge. Because these ions contain more than one atom, they are called polyatomic ions. Polyatomic ions have characteristic formulas, names, and charges that should be memorized. For example, NO_3^- is the nitrate ion; it has one nitrogen atom and three oxygen atoms and an overall 1– charge. Table 3.3.1 lists the most common polyatomic ions.

Table 3.3.1***:*** *Some Polyatomic Ions*

Name	Formula
ammonium ion	NH_4^+
acetate ion	$C_2H_3O_2^-$ (also written $CH_3CO_2^-$)
carbonate ion	CO_3^{2-}
hydrogen carbonate ion (bicarbonate ion)	HCO_3^-
cyanide ion	CN^-
hydroxide ion	OH^-
nitrate ion	NO_3^-
nitrite ion	NO_2^-
phosphate ion	PO_4^{3-}
hydrogen phosphate ion	HPO_4^{2-}
dihydrogen phosphate ion	$H_2PO_4^-$
sulfate ion	SO_4^{2-}
hydrogen sulfate ion (bisulfate ion)	HSO_4^-
sulfite ion	SO_3^{2-}

The rule for constructing formulas for ionic compounds containing polyatomic ions is the same as for formulas containing monatomic (single-atom) ions: the cation is written first and 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. An example is $Ba(NO_3)_2$.

Example 3.3.2

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

1. the potassium ion and the sulfate ion
2. the calcium ion and the nitrate ion

SOLUTION

1. 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.
2. 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.

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.

1. Na_2O
2. PCl_3
3. NH_4Cl
4. OF_2

SOLUTION

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

Looking Closer: Blood and Seawater

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

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

Ion	Percent in Seawater	Percent in Blood
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.

Contributors

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3.4: Ionic Nomenclature

Skills to Develop

- 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 (Figure 3.3). 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*.

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.

Table 3.4.1***:*** *The Common & Stock Systems of Cation Names for Cations That Can Have Different Charge*

Element	Old Stem (Common System)	Charge	Old Name (Common System)	New Name (Stock System)
iron	ferr-	2+	ferrous ion	iron(II) ion
		3+	ferric ion	iron(III) ion
copper	cupr-	1+	cuprous ion	copper(I) ion
		2+	cupric ion	copper(II) ion
tin	stann-	2+	stannous ion	tin(II) ion
		4+	stannic ion	tin(IV) ion
lead	plumb-	2+	plumbous ion	lead(II) ion
		4+	plumbic ion	lead(IV) ion
chromium	chrom-	2+	chromous ion	chromium(II) ion

Element	Old Stem (Common System)	Charge	Old Name (Common System)	New Name (Stock System)
		3+	chromic ion	chromium(III) ion
gold	aur-	1+	aurous ion	gold(I) ion
		3+	auric ion	gold(III) ion

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	Ion Name	Neutral Element Symbol & Name (shown for comparison)
F^-	fluoride ion	F = fluorine
Cl^-	chloride ion	Cl = chlorine
Br^-	bromide ion	Br = bromine
I^-	iodide ion	I = iodine
O^{2-}	oxide ion	O = oxygen
S^{2-}	sulfide ion	S = sulfur
P^{3-}	phosphide ion	P = phosphorous
N^{3-}	nitride ion	N = nitrogen

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^+

SOLUTION

a. the calcium ion
b. the sulfide ion (from Table 3.4.2)
c. the sulfite ion
d. the ammonium ion

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)

Example 3.4.2

Write the formula for each ion.

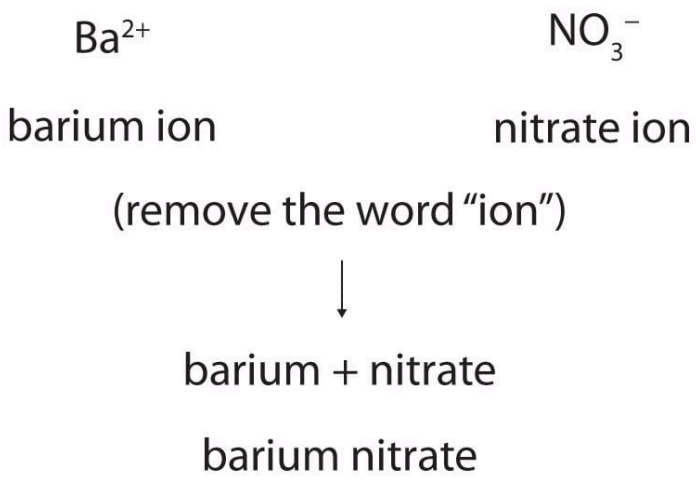
a. the bromide ion
b. the phosphate ion
c. the copper(II) ion
d. the magnesium ion

SOLUTION

a. Br^-
b. PO_4^{3-}
c. Cu^{2+}(could also be called the cupric ion)
d. Mg^{2+}

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 $Ba(NO_3)_2$?



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 $FeCl_2$ and $FeCl_3$. In the first compound, the iron ion has a 2+ charge because there are two 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 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. $(NH_4)_2SO_3$
c. GaF_3
d. CuCl
e. FeN

SOLUTION

a. calcium phosphate
b. ammonium sulfite
c. gallium fluoride
d. copper(I) chloride or cuprous chloride
e. iron(III) nitride or ferric nitride

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

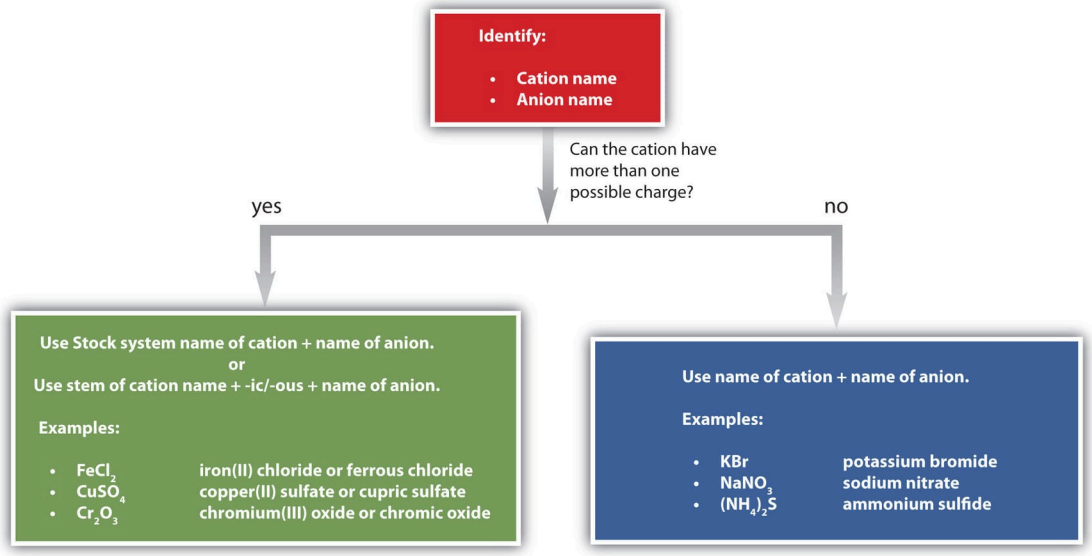


***Figure** 3.4.1**:** A Guide to Naming Simple Ionic Compounds. Follow these steps to name a simple ionic compound.*

NOTES (for Mueller's CHEM U109 courses): For tests, assume that only transition metals can have more than one possible charge (so use Roman numerals to indicate charge for transition metals only). There are exceptions, but they will not appear on the exam. On homework, you can look them up in the tables above.

KEY TAKEAWAY

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

Contributors

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3.5: Formula Mass

Skills to Develop

- 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 a compound. This quantity is often 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 (zero charge 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:

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:

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:

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:

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. When working practice problems, the measurement(s) given in the problem should be what limits the significant figures in your answer, so determine the formula mass to at least as many as the fewest given in the problem.

Example 3.5.1

Use the atomic masses (rounded to two decimal places) from the inside cover of this book to determine the formula mass for each ionic compound.

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

SOLUTION

a.

Fe:		55.85 amu
Cl:	3 × 35.45 =	+ 106.35 amu
Total:		162.20 amu

The formula mass of $FeCl_3$ is 162.20 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:

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.

To Your Health: Hydrates

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

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



Calcium sulfate hemihydrate ($CaSO_4•½H_2O$), or plaster of Paris, is used to make casts to immobilize broken bones until they heal. Figure used with permisison from Wikipedia

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

Table $3.5.1$***:*** *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/cleane

KEY TAKEAWAY

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

Contributors

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3.6: Chapter 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.

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.

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3.E: Exercises

Additional Exercises for Chapter 3:

1. Answer the following for an oxygen atom. (A) How many shells are occupied by electrons? (B) What is the number of electrons in each shell? (C) How many valence and how many core electrons?

2. Answer the following for a silicon atom. (A) How many shells are occupied by electrons? (B) What is the number of electrons in each shell? (C) How many valence and how many core electrons?

3. How many total electrons and protons in an aluminum atom? How many total electrons and protons in an aluminum ion?

4. What number shell is the valence electron shell of a sodium atom? What number shell is the valence electron shell of a sodium ion? Explain the difference.

5. Starting with neutral lithium and sulfur atoms (A) show formation of the lithium sulfide compound (B). *(Hint: Think about how many electrons each atom is likely to gain or lose. This exchange may require more than one of each atom*. *Use curved arrows for movement of electrons.)*

6. For each of the following, determine the formula and calculate the formula mass to at least three decimal places. (A) sidewalk deicing salt, caclium chloride; (B) potash, potassium oxide; (C) red-brown rust, iron(III) oxide; (D) the fertilizer, ammonium sulfate

7. Write names for each. (A) NH_4NO_3; (B) Na_3P; (C) Na_3PO_4; (D) Cu_2SO_3; (E) $CoCO_3$

Answers:

1. (A) The oxygen atom has two shells of electrons. (B) Oxygen has two electrons in the first shell and six electrons in the second shell. (C) Oxygen has six valence and two core electrons.

2. (A) The sili on atom has three shells of electrons. (B) Silicon has two electrons in the first shell, eight electrons in the second shell, and four electrons in the third shell. (C) Silicon has four valence and ten (2+8) core electrons.

3. An aluminum atom has 13 protons and 13 electrons. An aluminum ion has 13 protons and 10 electrons.

4. The third shell is valence (outer-most) for a sodium atom. The second shell is valence for a sodium ion. When the sodium atom loses its single valence electron from the third shell, the resulting sodium ion will only have electrons in two shells (so the second shell becomes valence).

5.



6. (A) $CaCl_2$, 110.984 amu; (B) K_2O, 94.195 amu; (C) Fe_2O_3, 159.687 amu; (D) $(NH_4)_2SO_4$, 132.140 amu

7. Write names for each. (A) ammonium nitrate; (B) sodium phosphide; (C) sodium phosphate; (D) copper(I)

sulfite; (E) cobalt(II) carbonate

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4: COVALENT BONDING AND SIMPLE MOLECULAR COMPOUNDS

Ionic bonding results from the transfer of electrons among atoms or groups of atoms. In this chapter, we will consider another type of bonding—covalent bonding. We will examine how atoms share electrons to form these bonds, and we will begin to explore how the resulting compounds, such as cholesterol, are different from ionic compounds.

4.1: Covalent Bonds

4.2: Multiple Covalent Bonds

4.3: Covalent Compounds: Formulas and Names

4.4: Characteristics of Covalent Bonds

4.5: Characteristics of Molecules

4.6: Organic Chemistry

4.7: Chapter Summary

4.E: Exercise

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4.1: Covalent Bonds

Skills to Develop

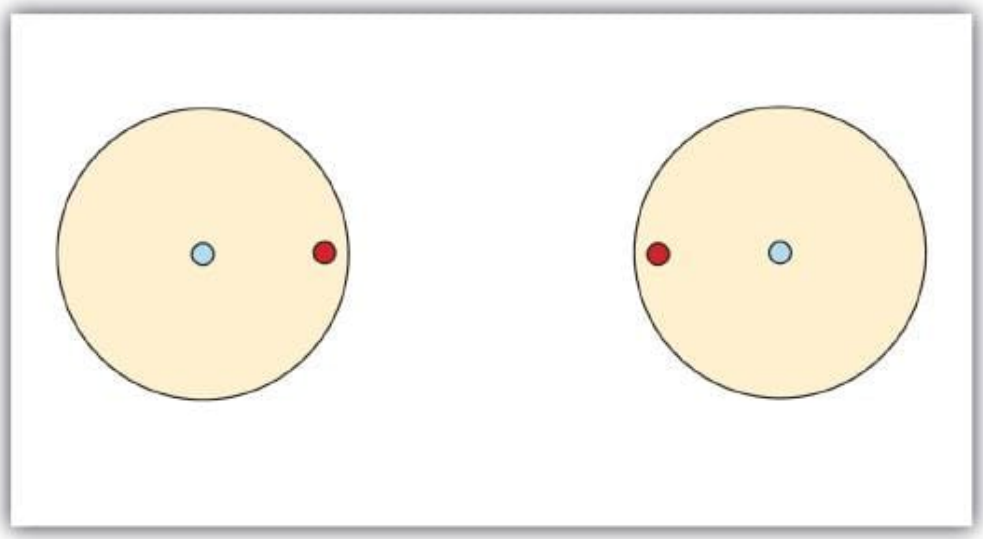
- To describe how a covalent bond forms.

You have already seen examples of substances that contain covalent bonds. One substance mentioned in Chapter 3 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.

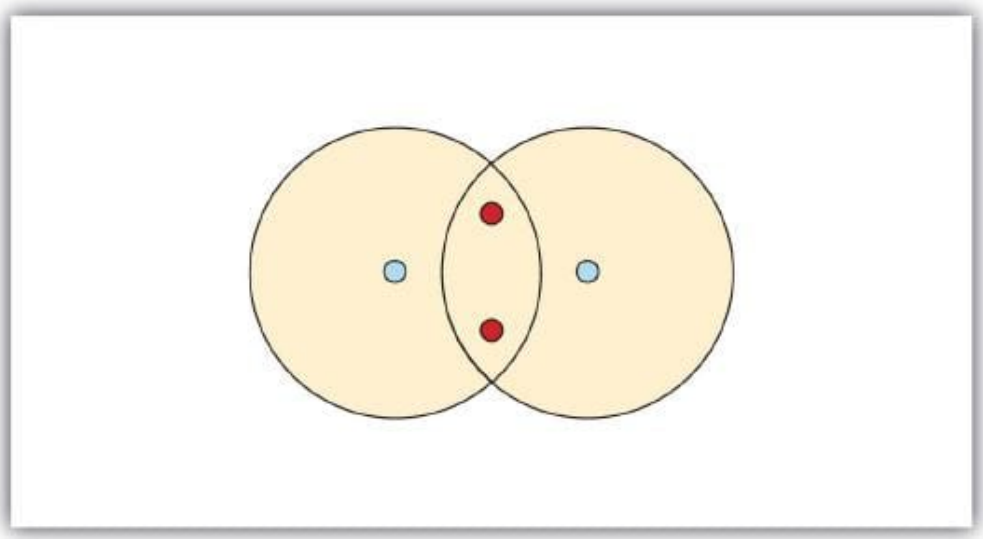
Electron Sharing

Chapter 3 described how 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. But 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:

$$H\cdot \qquad\qquad \cdot H$$

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:

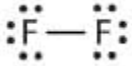
$$:\!\ddot{F}\cdot \qquad\qquad \cdot\ddot{F}\!:$$

Each fluorine atom contributes one valence electron, making a single bond and giving each atom a complete valence shell, which

fulfills the octet rule:



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



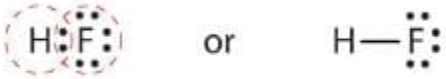
Each fluorine atom has six electrons, or three pairs of electrons, that are not participating in the covalent bond. Rather than being shared, they are considered to belong to a single atom. These are called nonbonding pairs (or lone pairs) of electrons.

Covalent Bonds between Different Atoms

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



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



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

Example 4.1.1

Draw the Lewis diagram for each compound.

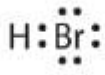
1. a molecule composed of two chlorine atoms
2. a molecule composed of a hydrogen atom and a bromine atom

SOLUTION

1. Chlorine has the same valence shell electron configuration as fluorine, so the Lewis diagram for a molecule composed of two chlorine atoms is similar to the one for fluorine:



2. Bromine has the same valence shell electron configuration as fluorine, so the Lewis diagram for a molecule composed of a hydrogen atom and a bromine atom is similar to that for hydrogen and fluorine:



Larger molecules are constructed in a similar fashion, with some atoms participating in more than one covalent bond. For example, water, with two hydrogen atoms and one oxygen atom, and methane (CH_4), with one carbon atom and four hydrogen atoms, can be represented as follows:



Atoms typically form a characteristic number of covalent bonds in compounds. Figure $4.1.1$ shows the number of covalent bonds various atoms typically form.

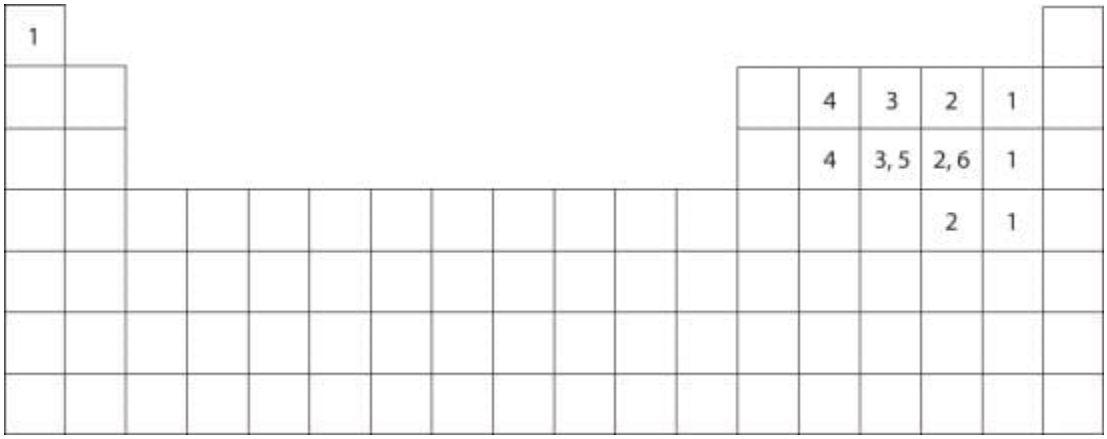


Figure $4.1.1$***:*** *How Many Covalent Bonds Are Formed? In molecules, there is a pattern to the number of covalent bonds that different atoms can form. Each block with a number indicates the number of covalent bonds formed by that atom in neutral compounds.*

Concept Review Exercises

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

Answers

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

Key Takeaway

- A covalent bond is formed between two atoms by sharing electrons.

Exercises

(Note from Mueller for CHEM 109 Courses: If you have trouble drawing the Lewis diagrams for any molecules below, try reviewing the SERIES OF STEPS FOR DRAWING LEWIS STRUCTURES given in the next section, 4.2, and then come back to these)

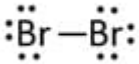
1. Define *covalent bond*.

2. Draw the Lewis diagram for the covalent bond in the Br_2 molecule.
3. What is the difference between a molecule and a formula unit?
4. Draw the Lewis diagram for the covalent bonding in H_2S. How many bonding electrons and nonbonding electrons are in the molecule?
5. Draw the Lewis diagram for the covalent bonding in CF_4. How many bonding electrons and nonbonding electrons are in the molecule?
6. How many covalent bonds does a hydrogen atom typically form? Why?
7. Tellurium atoms make covalent bonds. How many covalent bonds would a tellurium atom make? Predict the formula of a compound between tellurium and hydrogen.
8. 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?

Answers

1. A covalent bond is formed when two atoms share electrons.

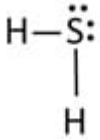
2. 

or 

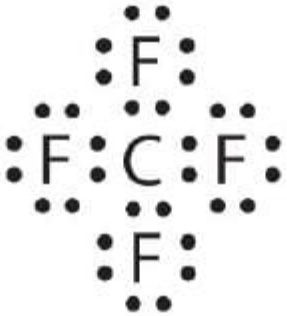
3. A molecule is a discrete combination of atoms. For example, in each water molecule (H_2O) there are two hydrogen atoms covalently bonded to one specific oxygen atom.

A formula unit is the lowest ratio of ions in a crystal. For example, in the ionic compound sodium oxide (Na_2O) the Na^+ ions are attracted to all of the surrounding O^{2-} ions by ionic bonds, not any one in particular. The ratio is ttwo Na^+ for every one O^{2-} so that the net charge balances to zero.

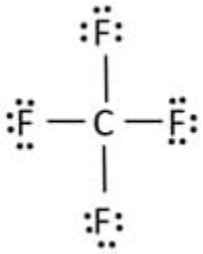
4. 

or 

Four bonding electrons (two shared pairs, or covalent bonds); Four non-bonding electrons (two lone pairs)



5. or



Eight bonding electrons (four shared pairs, or covalent bonds); 24 non-bonding electrons (12 lone pairs)

6. Hydrogen atoms form only one covalent bond because they have only one valence electron to pair (which would give hydrogen a duet, like noble helium).

7. Tellurium has six valence electrons, so it would make TWO covalent bonds to obtain eight for an octet. H_2Te

8. The halogens all have seven valence electrons, so astatine would make ONE covalent bond to obtain eight for an octet.

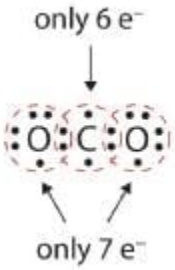
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4.2: Multiple Covalent Bonds

Skills to Develop

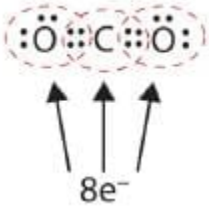
- To recognize molecules that are likely to have multiple covalent bonds.

In many molecules, the octet rule would not be satisfied if each pair of bonded atoms shares two electrons. Consider carbon dioxide (CO_2). If each oxygen atom shares one electron with the carbon atom, we get the following:

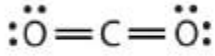


This does not give the carbon atom a complete octet; you will find only six electrons in its valence shell. In addition, each oxygen atom has only seven electrons in its valence shell. Finally, no atom makes the number of bonds it typically forms. This arrangement of shared electrons is far from satisfactory.

Sometimes more than one pair of electrons must be shared between two atoms for both atoms to have an octet. In carbon dioxide, a second electron from each oxygen atom is also shared with the central carbon atom, and the carbon atom shares one more electron with each oxygen atom:



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, covalent bonds in which *three* pairs of electrons are shared by two atoms. A simple compound that has a triple bond is acetylene (C_2H_2), whose Lewis diagram is as follows:



SERIES OF STEPS FOR DRAWING LEWIS STRUCTURES

Some students prefer a more formal series of steps for drawing Lewis structures for a molecule, given the formula. Mueller inserted these three steps below, with images of two examples that follow (HNO and NaOCl).

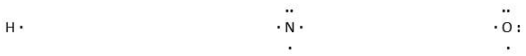
STEP 1: Draw the Lewis dot structure for each atom in the formula. (Draw a dot for each valence electron around each atomic symbol).

STEP 2: What does each atom need to do to satisfy the octet rule, like a noble gas? (Or if the closest noble is helium, which can only have a maximum of two electrons, what does it need to do to obtain a duet?)

STEP 3: How can the atoms share or exchange electrons to get there? (Metals tend to lose electrons. Non-metals tend to gain electrons from metals or share with other non-metals.)

FIRST EXAMPLE: Draw the Lewis structure for azanone, HNO.

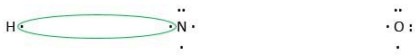
1. Hydrogen has one valence electron, nitrogen five valence electrons, and oxygen six valence electrons.



2. Hydrogen needs one more electron for a duet. Nitrogen needs three more electrons for an octet. Oxygen needs two more electrons for an octet.

3. All three atoms are non-metals, so we expect them to share electrons.

   If H and N share one pair (circled below), the duet of hydrogen is satisfied, but N & O each still need two more.



   If nitrogen and oxygen each share two pairs (circled below), they will both have eight, or octets.

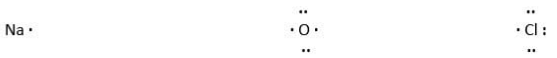


The shared pairs can be shown as pairs of dots between atoms 

Or the shared pairs can be shown as lines 

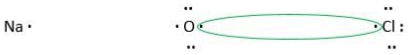
SECOND EXAMPLE: Draw the Lewis structure for sodium hypochlorite, NaOCl (bleach).

1. Sodium has one valence electron, oxygen six valence electrons, and chlorine seven valence electrons.



2. For sodium, gaining seven more for an octet is too much; that is why, as a metal, it will instead lose an electron to have the same number of electrons as the noble gas, neon (octet underneath). Oxygen needs two more electrons for an octet and chlorine needs one more for an octet.

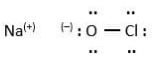
3. If O and Cl, both non-metals, share one pair (circled below), the octet of chlorine is satisfied.



   The Na metal and O non-metal will instead exchange an electron.



   Na lost a negative electron, so it now has a net positive charge.
   After gaining that extra negative electron, the oxygen has a net negative charge.



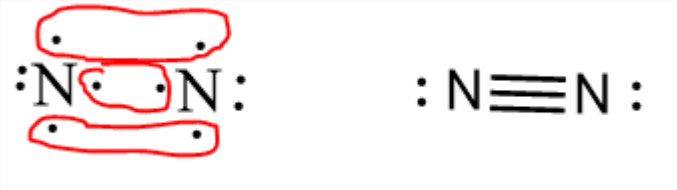
Example 4.2.1

Draw the Lewis diagram for each molecule.

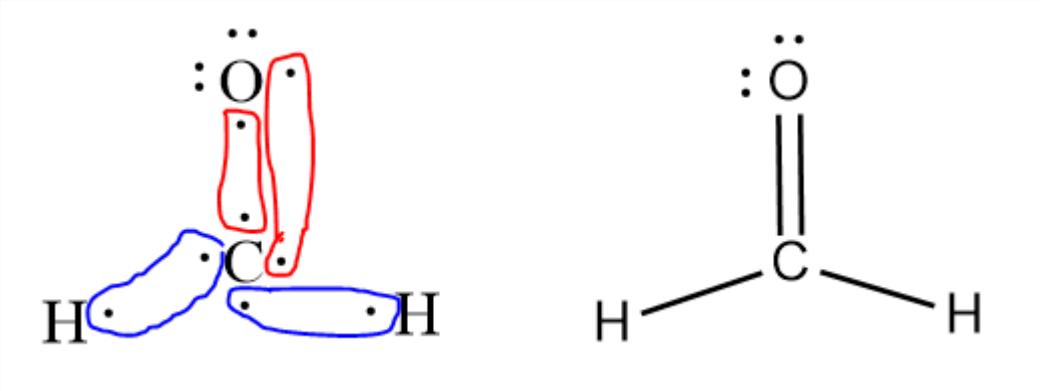
1. N_2
2. CH_2O (The carbon atom is the central atom.)

SOLUTION

1. Each lone nitrogen has five valence electrons (and needs three more for an octet). The two atoms share three pairs, a triple bond, to make the N_2 molecule.



2. By themselves, carbon has four valence electrons (and needs four more for an octet), oxgyen has six (and needs two more for octet), and each hydrogen has one (and needs one more for duet). If the carbon makes two bonds with oxygen and one to each hydrogen, all atoms will be satisfied.



Note

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.

Concept Review Exercise

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

Answer

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

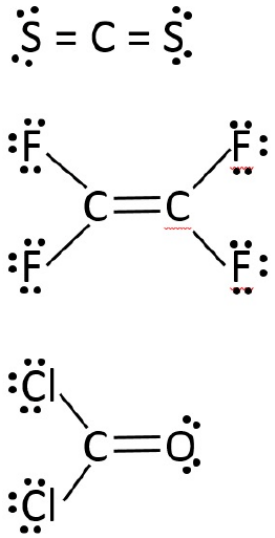
Key Takeaway

- Some molecules must have multiple covalent bonds between atoms to satisfy the octet rule.

Exercises

1. Each molecule contains multiple bonds. Draw the Lewis diagram for each.
    a. CS_2 (Carbon is the central atom.)
    b. F_2CCF_2 (Two fluorines on left bonded to carbon on left, two carbons bonded to each other, and carbon on right bonded to two fluorines on right.)
    c. Cl_2CO (Carbon is the central atom with all three other atoms bonded to carbon.)
2. Explain why hydrogen atoms do not form double bonds.
3. Why is it incorrect to draw a double bond in the Lewis diagram for MgO?

Answers

1. 

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

3. MgO an ionic compound and exchanges electrons instead of sharing them (no covalent bonds so no lines).

Contributors

- ◦ Anonymous

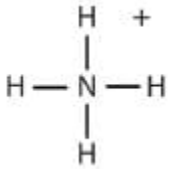
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4.3: Covalent Compounds: Formulas and Names

Skills to Develop

- Determine the chemical formula of a simple covalent compound from its name.
- Determine the name of a simple covalent compound from its chemical formula.

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. Nonmetal atoms in polyatomic ions are joined by covalent bonds, but the ion as a whole participates in ionic bonding. For example, ammonium chloride has ionic bonds between a polyatomic ion, NH_4^+, and Cl^- ions, but within the ammonium ion, the nitrogen and hydrogen atoms are connected by covalent bonds:



Example $4.3.1$

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

a. Na_2O
b. Na_3PO_4
c. N_2O_4

SOLUTION

a. The elements in Na_2O are a metal and a nonmetal, which form ionic bonds.
b. Because sodium is a metal and we recognize the formula for the phosphate ion (see Table 3.1), we know that this compound is ionic. However, polyatomic ions are held together by covalent bonds, so this compound contains both ionic and covalent bonds.
c. The elements in N_2O_4 are both nonmetals, rather than a metal and a nonmetal. Therefore, the atoms form covalent bonds.

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.

Naming *binary* (two-element) covalent compounds is similar to naming simple ionic compounds. The first element in the formula is simply listed using the name of the element. The second element is named by taking the stem of the element name and adding the suffix *-ide*. A system of numerical prefixes is used to specify the number of atoms in a molecule. Table $4.3.1$ lists these numerical prefixes. Normally, no prefix is added to the first element's name if there is only one atom of the first element in a molecule. If the second element is oxygen, the trailing vowel is usually omitted from the end of a polysyllabic prefix but not a monosyllabic one (that is, we would say "monoxide" rather than "monooxide" and "trioxide" rather than "troxide").

Table 4.3.1 *Numerical Prefixes for Naming Binary Covalent Compounds*

Number of Atoms in Compound	Prefix on the Name of the Element
1	mono-*
2	di-
3	tri-
4	tetra-
5	penta-
6	hexa-
7	hepta-
8	octa-
9	nona-
10	deca-
***This prefix is not used for the first element's name.**	

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

Example 4.3.2

Write the molecular formula for each compound.

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

SOLUTION

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

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

Note

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

Example 4.3.3

Write the name for each compound.

1. BrF_5
2. S_2F_2
3. CO

SOLUTION

1. bromine pentafluoride
2. disulfur difluoride
3. carbon monoxide

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

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

Methane is the simplest organic compound. Organic compounds are compounds with carbon atoms and are named by a separate nomenclature system that we will introduce in Section 4.6 "Introduction to Organic Chemistry".

Concept Review Exercises

1. How do you recognize a covalent compound?
2. What are the rules for writing the molecular formula of a simple covalent compound?
3. What are the rules for naming a simple covalent compound?

Answers

1. A covalent compound is usually composed of two or more nonmetal elements.
2. It is just like an ionic compound except that the element further down and to the left on the periodic table is listed first and is named with the element name.
3. Name the first element first and then the second element by using the stem of the element name plus the suffix -ide. Use numerical prefixes if there is more than one atom of the first element; always use numerical prefixes for the number of atoms of the second element.

Key Takeaways

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

Exercises

1. Identify whether each compound has ionic bonds, covalent bonds, or both.

    a. Na_3PO_4
    b. K_2O
    c. $COCl_2$
    d. $CoCl_2$

2. Write the name for each covalent compound.

    a. SiF_4
    b. NO_2
    c. CS
    d. P_2O_5

3. Write the formula for each covalent compound.

    a. iodine trichloride
    b. disulfur dibromide
    c. arsenic trioxide
    d. xenon hexafluoride

4. Write the three covalent compounds introduced in this chapter that have common rather than systematic names.

Answers

1. a. both
   b. ionic
   c. covalent
   d. ionic
2. a. silicon tetrafluoride
   b. nitrogen dioxide
   c. carbon monosulfide
   d. diphosphorus pentoxide

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

4. Water (H_2O), ammonia (NH_3), and methane (CH_4)

Contributors

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4.4: Characteristics of Covalent Bonds

Skills to Develop

- Covalent bonds have certain characteristics that depend on the identities of the atoms participating in the bond. Two characteristics are bond length and bond polarity.

Bond Length

In Section 4.1, we stated that the covalent bond in the hydrogen molecule (H_2) has a certain length, about 7.4×10^{-11} meters (m) or 74 picometers (pm). 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 (pm = 10^{-12} m)
H–H	74
F–F	142
Cl–Cl	199
Br–Br	228
I–I	267
H–C	110
H–N	100
H–O	97
H–F	92
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 (pm = 10^{-12} m)
C–C	154
C=C	134

Bond	Length (pm = 10^{-12} m)
C≡C	120
C–N	147
C=N	128
C≡N	116
C–O	143
C=O	120
C≡O	113
N–N	145
N=N	123
N≡N	110
O–O	145
O=O	121

Example 4.4.1

A. Compare the bond lengths of H-H, F-F, Cl-Cl, Br-Br, and I-I above. Based on what you learned about atomic radius in Chapter 2, what might explain this trend in bond length?

B. Compare the bond lengths of H-C, H-N, H-O, and H-F above. Based on what you learned about atomic radius in Chapter 2, what might explain this trend in bond length?

C. What is the trend you notice for single, double, and triple bonds (between the same atoms)?

SOLUTION

A. The bonds become much larger moving down from H-H (74 pm), F-F (142 pm), Cl-Cl (199 pm), Br-Br (228 pm), and I-I (267 pm) above. Hydrogen is in the first row of the periodic table and thus has only one shell of electrons, giving it the smaller atomic radius. Small atoms can get close together and make short bonds. Moving down the periodic table, the atoms have more shells of electrons and thus larger atomic radius. Larger atoms cannot get as close together and thus make longer bonds.

B. The bonds become slightly shorter moving from H-C (110 pm), H-N (100 pm), H-O (97 pm), and H-F (92 pm). They are all bonded to H, so that is not what makes the difference. Moving across the periodic table C, N, O, and F all have two shells of electrons but the number of protons increases. More protons in the nucleus pull the electrons in closer, leading to smaller radius. Smaller atomic radius leads to shorter bond length.

C. Single bonds tend to be longest and triple bonds shortest [i.e. C-C (154 pm), C=C (134 pm), C≡C (120 pm)]. The atoms must get closer to share more electrons.

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, there will always be one atom that attracts the electrons in the bond more strongly than the other atom does, as shown in Figure 4.4.1. When such an imbalance occurs, there is a resulting buildup of some negative charge (called a partial negative charge and designated δ–) on one side of the bond and some positive charge (designated δ+) on the other side of the bond. A covalent bond that has an unequal sharing of electrons,

as in part (b) of Figure 4.4.1, is called a polar covalent bond. A covalent bond that has an equal sharing of electrons (part (a) of Figure 4.4.1) is called a nonpolar covalent bond.

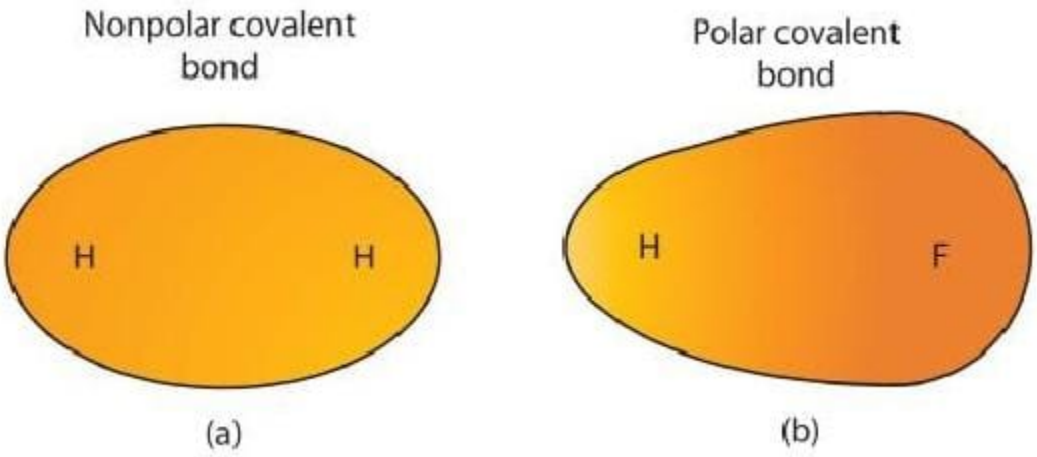


Figure 4.4.1 *Polar versus Nonpolar Covalent Bonds. (a) The electrons in the covalent bond are equally shared by both hydrogen atoms. This is a nonpolar covalent bond. (b) The fluorine atom attracts the electrons in the bond more than the hydrogen atom does, leading to an imbalance in the electron distribution.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

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 4.4.2 shows one of the most popular—the Pauling scale. 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 about 2.0 or greater), the resulting compound is considered ionic rather than covalent. An electronegativity difference of zero, of course, indicates a nonpolar covalent bond.

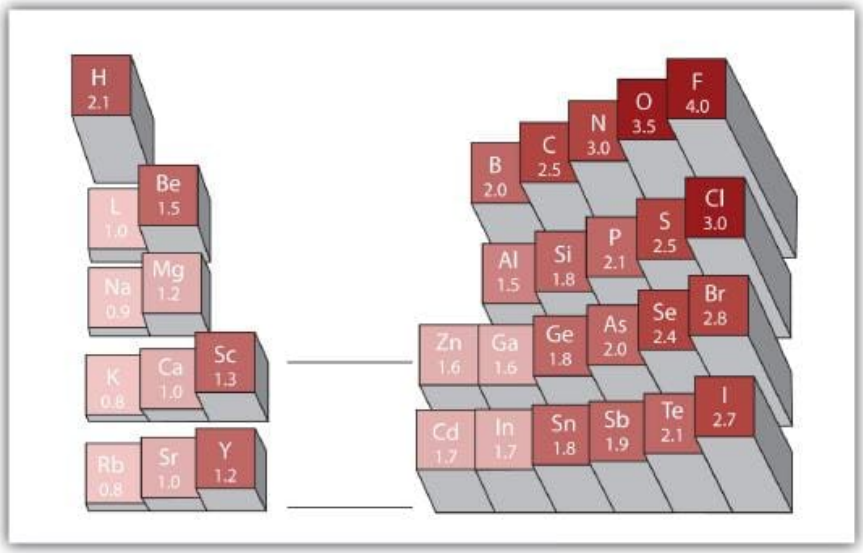
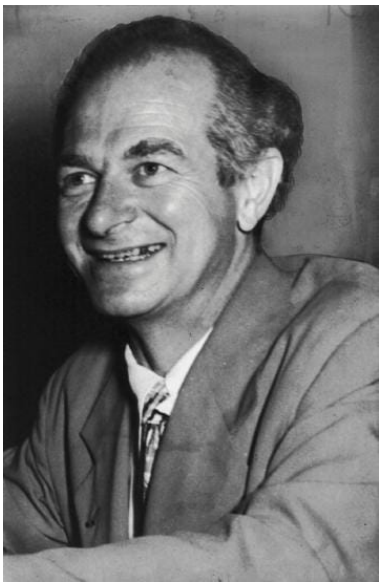


Figure 4.4.2 *Electronegativities of Various Elements. A popular scale for electronegativities has the value for fluorine atoms set at 4.0, the highest value.*

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.

Example 4.4.2

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, but not so polar that the O–H bond is considered ionic.

When a molecule's bonds are polar, the molecule as a whole can display an uneven distribution of charge, depending on how the individual bonds are oriented. For example, the orientation of the two O–H bonds in a water molecule (Figure 4.4.3) 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 and is due to the fact that polar molecules attract each other strongly.) In contrast, while the two C=O bonds in carbon dioxide are polar, they lie directly opposite each other and so cancel each other's effects. Due to this symmetry, carbon dioxide molecules are nonpolar overall. This lack of polarity influences some of carbon dioxide's properties. (For example, carbon dioxide becomes a gas at –77°C, almost 200° lower than the temperature at which water boils.)



Figure 4.4.3 *Physical Properties and Polarity. The physical properties of water and carbon dioxide are affected by their polarities.*

Concept Review Exercises

1. What is the name for the distance between two atoms in a covalent bond?
2. What does the electronegativity of an atom indicate?
3. What type of bond is formed between two atoms if the difference in electronegativities is small? Medium? Large?

Answers

1. bond length
2. Electronegativity is a qualitative measure of how much an atom attracts electrons in a covalent bond.
3. nonpolar; polar; ionic

Key Takeaways

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

Exercises

1. Which is longer: a C–H bond or a C–S bond? (Try to answer this using only position on periodic table.)
2. Which is shorter: a C-C bond or a C–F bond? (Try to answer this using only position on periodic table.)
3. A nanometer is 10^{-9} m. Using the data in Table 4.4.1 and Table 4.4.2, 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. Using a periodic table, and not Figure 4.4.2, 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

5. 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

Answers

1. A C–S bond is longer because the atomic radius of sulfur is larger than that of hydrogen.

2. A C-C bond is longer because the atomic radius of carbon is larger than that of fluorine.

3. a. 0.143 nm
    b. 0.120 nm
    c. 0.100 nm
    d. 0.116 nm
4. a. C
    b. O
    c. Na
    d. Cl
5. a. unequally toward the O
    b. equally
    c. unequally toward the N
    d. unequally toward the Cl

Contributors

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4.5: Characteristics of Molecules

Skills to Develop

- Determine the molecular mass of a molecule.
- Predict the general shape of a simple covalent molecule.

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 — 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 mass. For molecules, molecular mass and formula mass mean the same thing. Ionic compounds, however, do not involve molecules and thus formula mass is technically the only appropriate term. In practice, the terms molecular mass, formula mass, and even molecular weight or formula weight are used interchangeably.

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 masses of the atoms from the Periodic Table.

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,

2 H:	2 × 1.01 =	2.02 u
1 O:		+ 16.00 u
Total:		18.02 u

The molecular mass of H_2O is 18.02 u.

6 C:	6 × 12.01 =	72.06 u
6 H:	6 × 1.01 =	+ 6.06 u
Total:		78.12 u

The molecular mass of C_6H_6 is 78.12 u.

1 N:		14.01 u
2 O:	2 × 16.00 =	+ 32.00 u

Total:		46.01 u

The molecular mass of NO_2 is 46.01 u.

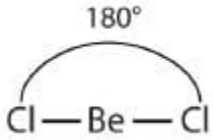
2 N:	2 × 14.01 =	28.02 u
5 O:	5 × 16.00 =	+ 80.00 u
Total:		108.02 u

The molecular mass of N_2O_5 is 108.02 u.

Note that the two different nitrogen and oxygen compounds in these examples have different molecular masses.

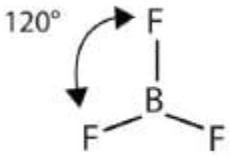
Molecular Shape: VSEPR Theory

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 negative electrons tend to repel one another. The electron groups on the central atom of a molecule tend to spread out as far apart as possible. This concept is called the valence shell electron pair repulsion (VSEPR) theory. Electron groups can be covalent bonds or lone pairs on the central atom. For example, the best way to minimize repulsions between the two bonds in $BeCl_2$ is if they are on opposite sides, ending up 180° apart from each other. The result is a *linear* molecule:



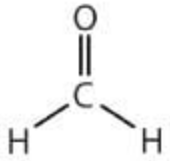
Linear molecules are often described as having an AB_2 molecular type, where A represents the central atom and each B represents other atoms covalently bonded to the central atom (subscript indicating how many).

The three covalent bonds in BF_3 repel each other to form 120° angles in a flat plane. This AB_3 molecular type makes a shape called *trigonal planar*:



The $BeCl_2$ and BF_3 molecules shown above actually violate the octet rule; however, such exceptions are rare and will not be discussed in this text.

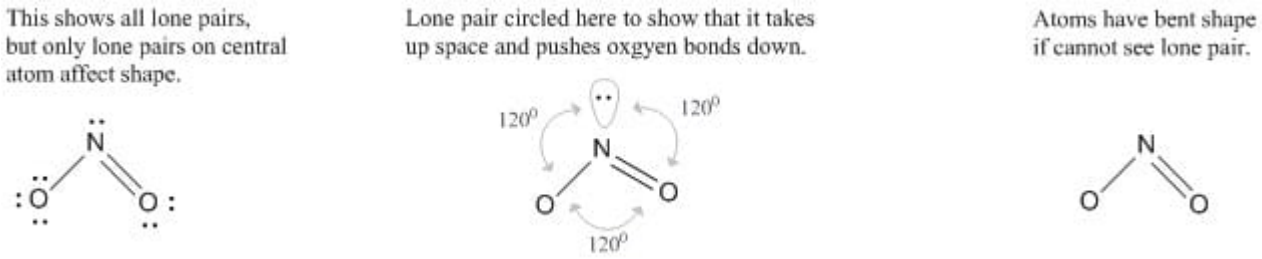
When using VSEPR theory, double and triple bonds are treated no differently than single bonds. For example, formaldehyde (H_2CO) is also AB_3 because three atoms — H, H & O — are bonded to the central carbon atom, and it also has a trigonal planar shape.



Note

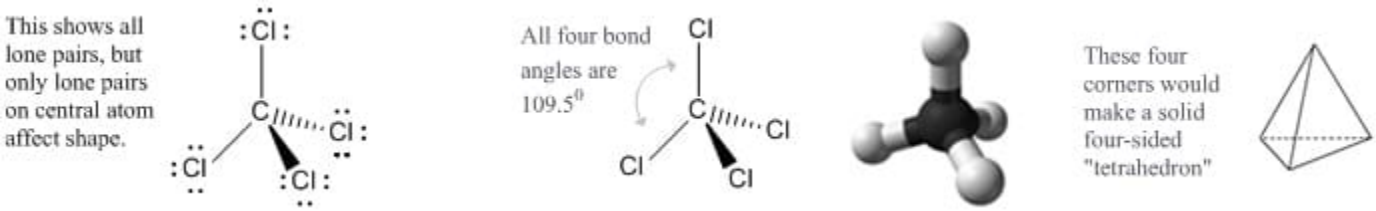
Try sticking three toothpicks into a marshmallow or a gumdrop and see if you can find different positions where your “bonds” are farther apart than the planar 120° orientation.

Molecules with lone electron pairs around the central atom have a shape based on the repulsion between both the bonds and the lone pairs on that central atom. The nitrite ion (NO_2^-), a common food preservative, is an example. The central nitrogen has one lone electron pair and two bonded electron pairs. The molecular type here would be AB_2E, where the E represents a lone pair. These three electron pairs repel each other and adopt a trigonal planar arrangement with 120^0 angles between them:



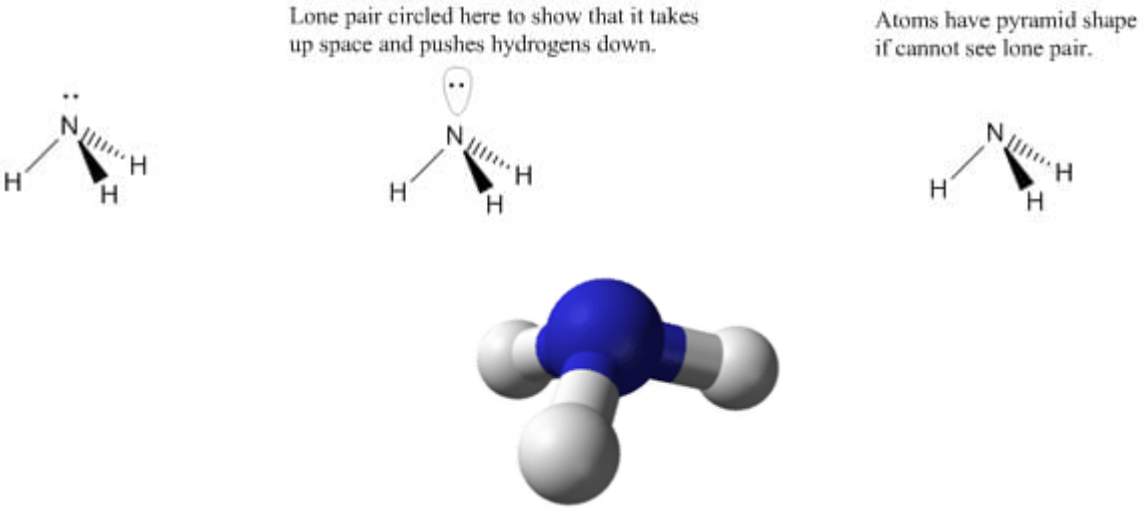
However, the shape of the molecule is described in terms of the positions of the atoms, not the lone electron pairs. Thus, NO_2^- is said to have a bent shape, not a trigonal planar one. It is assumed that the lone pair is "invisible" when describing the shape of the molecular geometry. The lone pair pushes the bonds to oxygen down in the figure above, making it appear bent.

The four covalent bonds in CCl_4 have AB_4 molecular type and arrange themselves three dimensionally, not flat. The best way to spread four groups as far apart as possible is with 109.5° angles and the shape is described as tetrahedral.



In the image above, the regular lines are meant to represent bonds that are flat against the plane of the page. The solid wedge represents a bond that is coming up from the page (toward you). The hatched wedge, also sometimes shown as just a dashed line, represents a bond going into the plane of the page (away from you).

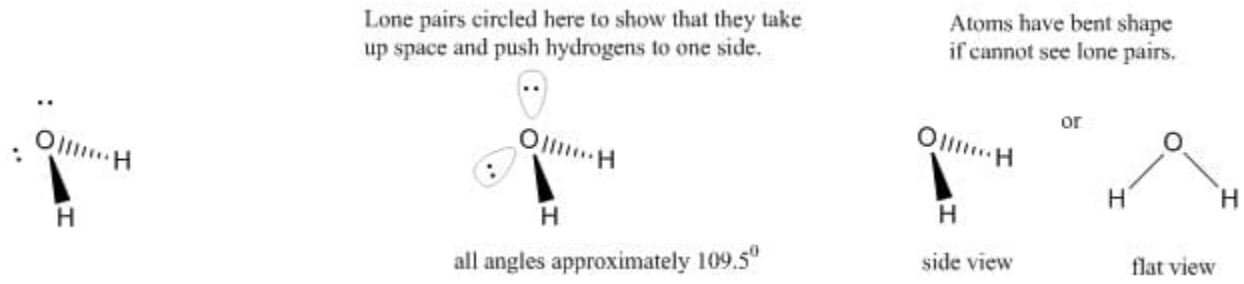
Ammonia (NH_3) has one lone electron pair and three bonded electron pairs. The molecular type here would be AB_3E, where the E represents a lone pair. These four electron pairs repel each other and adopt a tetrahedral arrangement:



The angles are again about 109.5^0, but NH_3 is said to have a *trigonal pyramidal* shape, not a tetrahedral one. The lone pair in NH_3 pushes the bonds to hydrogen down to the bottom of the pyramid in the figure above, making a triangular base. Assuming the lone pair is "invisible" when describing the shape, the nitrogen would be the top of the pyramid in the figure.

SIDE NOTE: Because bonds and lone pairs are not always the same size, they do not repel equally. This means the angles might vary slightly. In this course, we will not be concerned with these small differences. Instead, assume the angles will be approximately one of three choices: 180^0, 120^0, or 109.5^0.

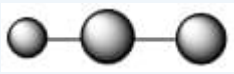
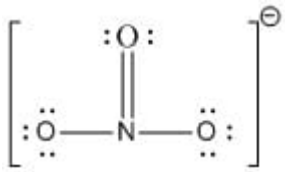
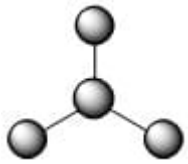
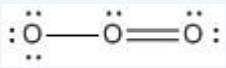
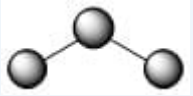
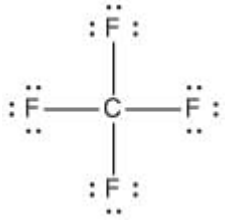
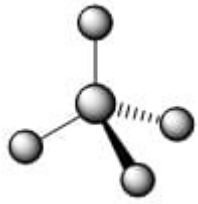
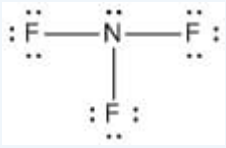
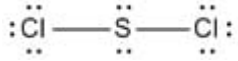
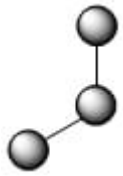
Water (H_2O) is molecular type AB_2E_2 with two lone pairs of electrons around the central oxygen atom, in addition to the two bonded pairs:



Although the four electron pairs adopt a tetrahedral arrangement due to repulsion, again the shape of the molecule is described by the positions of the atoms only. If the lone pairs are assumed invisible, the shape of H_2O appears bent. Both AB_3E and AB_2E_2 have close to 109.5^0 angles because that is the best way to spread out four electron groups.

In determining the shapes of molecules, it is important to first draw the Lewis diagram for a molecule. Only the correct Lewis structure will show how many bonds and lone pairs are associated with the central atom in the molecule, both necessary to predict shape. It is important to note that the first Lewis diagrams you draw (or the one given in in a problem) might not have the correct 3D geometry — you must be able to predict the shape and angles based on the diagram. The table below summarizes the most common molecular geometries. (There are more, but they will not be covered in this course.)

Table 4.5.1 *Molecular Geometries*

Electron Groups (see Note #1)	**Bonding Groups** (see Note #2)	**Lone Pairs** (see Note #3)	**Molecular Type** (AB_xE_y)	**Molecular Geometry** (Shape Name)	**Bond Angles** (Approximate)	**Example Lewis Structure Diagram**	**Example 3D Shape** (See Note # 4)
2	2	0	AB_2	linear	180^0	H — C ≡ N:	
3	3	0	AB_3	trigonal planar	120^0		
3	2	1	AB_2E	bent	120^0		
4	4	0	AB_4	tetrahedral	109.5^0		
4	3	1	AB_3E	trigonal pyramidal	109.5^0		
4	2	2	AB_2E_2	bent	109.5^0		

NOTE #1: Electron groups can be covalent bonds or lone pairs.

NOTE #2: Double or triple bonds each count only as one electron group, so are treated just like single bonds.

NOTE #3: Each lone pair (two dots) counts as one electron group, but **only if it is located on the central atom**.

NOTE #4: When describing the shape for molecular geometry, any lone pairs are considered invisible.

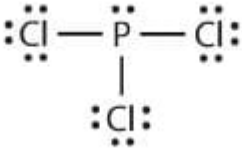
Example 4.5.2

Describe the shape of each molecule.

a. PCl_3
b. CO_2

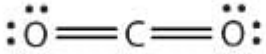
SOLUTION

a. The Lewis diagram for PCl_3 is as follows:



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 trigonal pyramidal. (Notice that the bond angles in the Lewis structure are drawn flat and at 90^0 angles; the actual pyramidal shape is not flat and has angles of about 109.5^0.

b. The Lewis diagram for CO_2 is as follows:



The multiple bonds are treated as one group. Thus, 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.

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?

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.

Key Takeaways

- A molecule has a certain mass, called the molecular mass.
- Simple molecules have geometries that can be determined from VSEPR theory.

Exercises

1. What is the molecular mass of each compound?

    a. HCl
    b. N_2O_4
    c. ICl_3
    d. Aspirin ($C_9H_8O_4$)

2. What is the shape of each molecule? *(Hint: First draw the Lewis diagram of each.)*

    a. H_2S
    b. $COCl_2$

c. SO_2

3. 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.

Answers

1. a. 36.46 u
   b. 92.02 u
   c. 233.25 u
   d. 180.17 u

2.

a. bent
b. trigonal planar
c. bent

3. linear

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4.6: Organic Chemistry

Skills to Develop

- 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 (Table 2.1.1). 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.

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. Figure 4.6.1 gives the formulas and the molecular models of the three simplest alkanes.

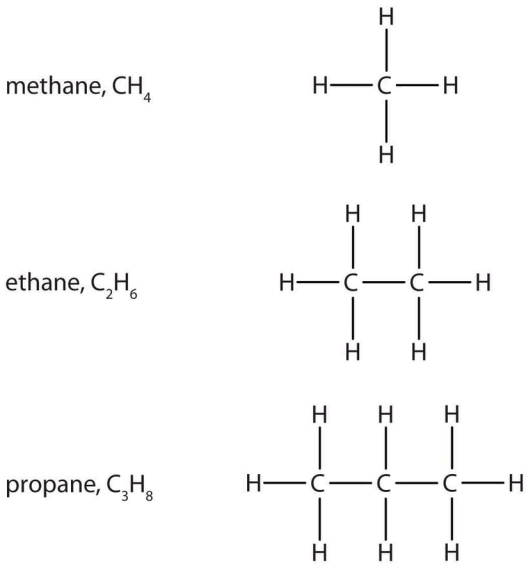


Figure 4.6.1***:*** *Formulas and Molecular Models of the Three Simplest Alkanes. The three smallest alkanes are methane, ethane, and propane.*

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.

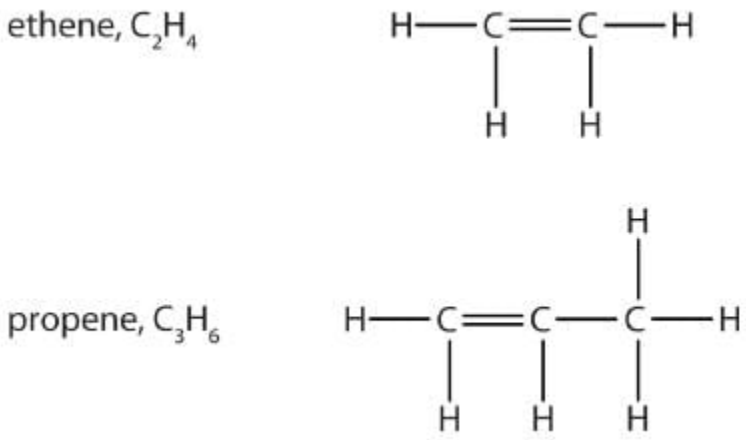


Figure 4.6.2***:*** *Formulas and Molecular Models of the Two Simplest Alkenes. Ethene is commonly called ethylene, while propene is commonly called propylene.*

Alkynes are hydrocarbons with a carbon–carbon triple bond (denoted C≡C) as part of their carbon skeleton. Figure 4.6.3 shows the formulas and the molecular models of the two simplest alkynes and their systematic names. The names for alkynes have the same stems as for alkanes but with the ending *-yne*.

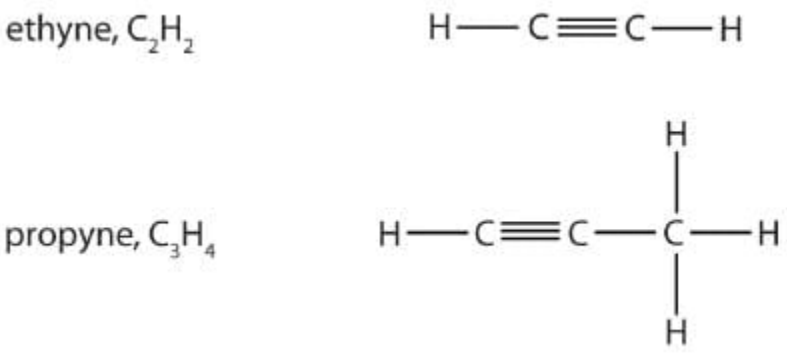


Figure 4.6.3 *Formulas and Molecular Models of the Two Simplest Alkynes. Ethyne is more commonly called acetylene.*

Note

The compound acetylene, with its carbon–carbon triple bond, was introduced in Section 4.3 and is an alkyne.

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.

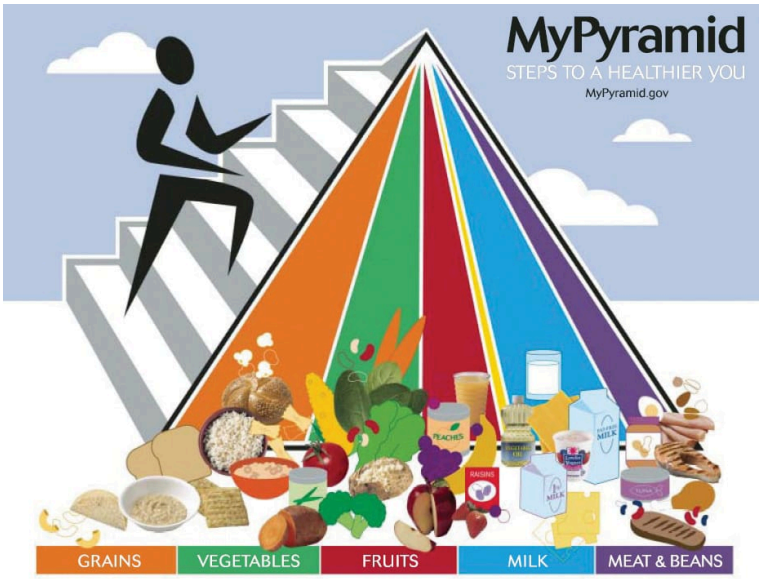
Fats are combinations of long-chain organic compounds (fatty acids) and glycerol ($C_3H_8O_3$). (For more information on fats, see Chapter 17) The long carbon chains can have either all single bonds, in which case the fat is classified as *saturated*, or one or more double bonds, in which case it is 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 1992, the US Department of Agriculture has been promoting a food pyramid that gives a simple, visual picture of how much of what kind of foods make up a good, balanced diet. It recommends eating as few fats as possible. Although nutritionists recognize that some fat is necessary (and largely unavoidable, even by strict vegetarians), they emphasize that a large proportion of any fat, saturated or unsaturated, in the diet is unhealthy. Even so, a difference as simple as the difference between a single and double carbon–carbon bond can have a significant impact on health.



The food pyramid has suggestions for the number of daily servings of each type of food. Source: Image courtesy of the USDA, http://www.mypyramid.gov/downloads/MiniPoster.pdf.

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.

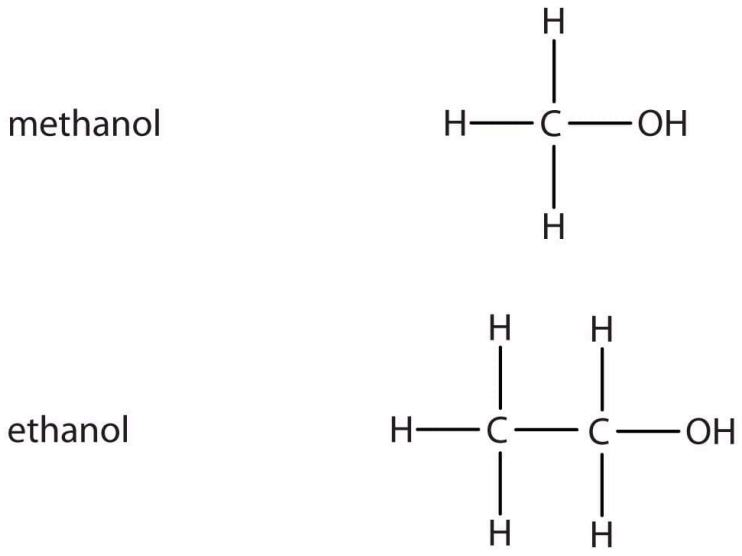


Figure 4.6.4*: The Two Simplest Organic Alcohol Compounds. Alcohols have an OH functional group in the molecule.*

Note

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

Note

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.

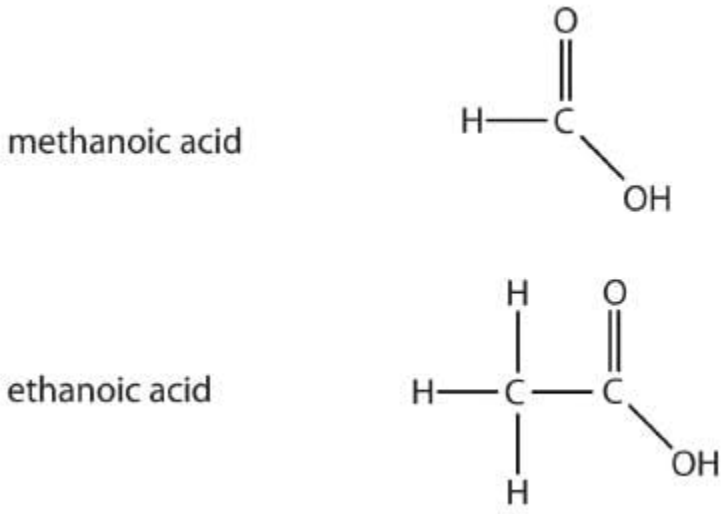
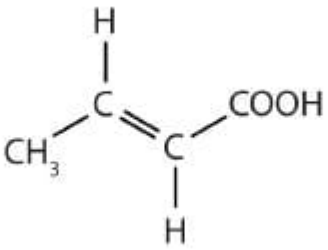


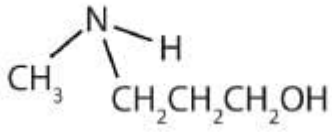
Figure 4.6.5***:*** *The Two Smallest Organic Acids. The two smallest carboxylic acids are formic acid (found in the stingers of ants) and acetic acid (found in vinegar).*

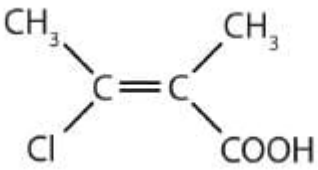
Many organic compounds are considerably more complex than the examples described here. Many compounds, such as cholesterol discussed in the chapter-opening essay, contain more than one functional group. The formal names can also be quite complex.

Example 4.6.1

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

1. $CH_3CH_2CH_2CH_2OH$
2. 

3. 

4. 

SOLUTION

1. This molecule has an alcohol functional group.
2. This molecule has a double bond and a carboxyl functional group.
3. This molecule has an alcohol functional group.
4. This molecule has a double bond and a carboxyl functional 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.

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).

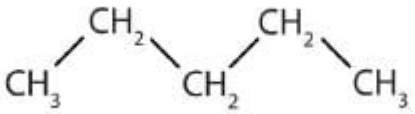
Key Takeaways

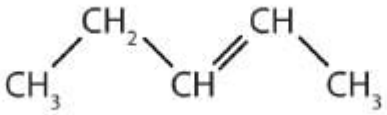
- Organic chemistry is the study of the chemistry of carbon compounds.
- Organic molecules can be classified according to the types of elements and bonds in the molecules.

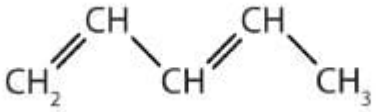
Exercises

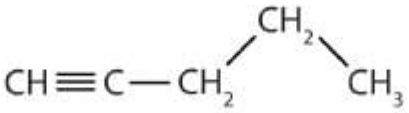
1. Give three reasons why carbon is the central element in organic chemistry.

2. Identify the type of hydrocarbon in each structure.

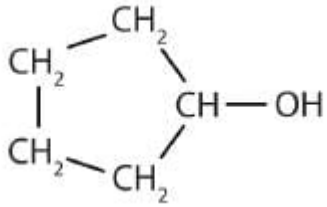
a. 

b. 

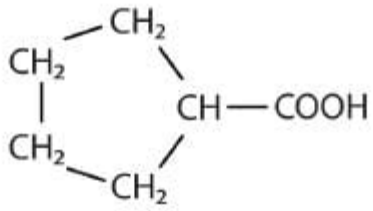
c. 

d. 

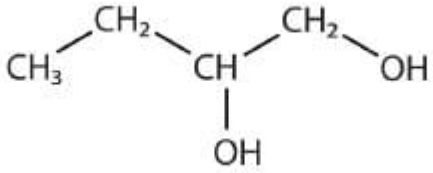
3. Identify the functional group(s) in each molecule.

a. 

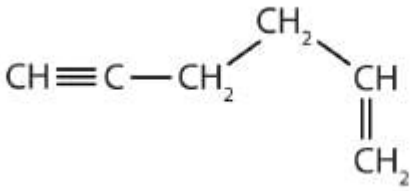
b.



c.



d.



4. How many functional groups described in this section contain carbon and hydrogen atoms only? Name them.

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.

a. alkane
b. alkene
c. alkene
d. alkyne

3.

a. hydroxyl or alcohol (OH)
b. carboxyl or carboxylic acid (COOH)
c. hydroxyl or alcohol (OH)
d. alkene (C=C) and alkyne (C≡C)

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

Contributors

- ◦ Anonymous

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4.7: Chapter 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 lines, 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 and lone pairs repel each other so spread out as much as possible.

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

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4.E: Exercise

Additional Exercises for Chapter 4:

1. For each of the following molecules, draw the Lewis structure (using lines for shared electron pairs and dots for unshared electrons), then determine the geometry and bond angles. (A) PH_3; (B) CCl_4; (C) H_2Se; (D) OCS; (E) SO_3

2. For each of the following molecules or polyatomic ions, draw the Lewis structure (using lines for shared electron pairs and dots for unshared electrons), then determine the geometry and bond angles. (A) $NH_4^{(+)}$; (B) $ClO_2^{(-)}$; (C) $HCO_2^{(-)}$; (D) $CO_3^{(2-)}$

3. Cyanogen has the formula C_2N_2, is connected with the two carbons in the middle, NCCN. Draw the Lewis structure for cyanogen, using lines for shared electron pairs and dots for unshared electrons. What are the bond angles around each carbon in this molecule?

4. Hydrogen peroxide, H_2O_2, is connected with the two oxygens in the middle, HOOH. Draw the Lewis structure for cyanogen, using lines for shared electron pairs and dots for unshared electrons. What are the bond angles around each carbon in this molecule?

5. Each of the following compounds contains both ionic and covalent bonds. Draw the Lewis structures, using lines for shared electron pairs and dots for unshared electrons. (A) KOH; (B) CsCN

6. Name these compounds. (A) NH_3; (B) CCl_4; (C) P_5O_7; (D) KOH; (E) CsCN

7. Write the formula for these compounds. (A) trinitrogen hexafluoride; (B) carbon disulfide; (C) barium chloride

8. Rank the following bonds from longest to shortest: N≡N, F-F, O=O, Br-Br.

9. Using Figure 4.4.2, classify the bonds in each molecule as non-polar, polar, or ionic. (A) NH_3; (B) CH_4; (C) $CaCl_2$; (C) CCl_4

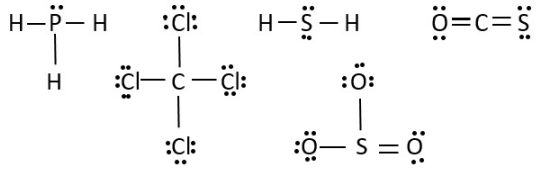
10. Explain why neither CH_4 nor CCl_4 molecules are polar.

11. Explain why the bond lenght of Br_2 was longer than F_2 in #8.

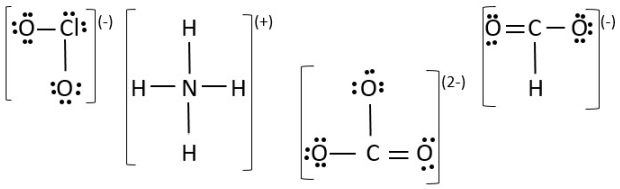
12. What is the difference between ionic and covalent bonds? Use LiCl to explain why an ionic bond keeps lithium and chlorine together. Use HCl to explain why a covalent bond keeps hydrogen and chlorine together.

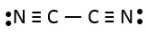
Answers:

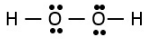
1. (A) PH_3, pyramidal, 109.5°; (B) CCl_4, tetrahedral, 109.5°; (C) H_2Se, bent, 109.5°; (D) OCS, linear, 180°; (E) SO_3, trigonal planar, 120°



2. (A) $ClO_2^{(-)}$, bent, 109.5°; (B) $NH_4^{(+)}$, tetrahedral, 109.5°; (C) $CO_3^{(2-)}$, trigonal planar, 120°; (D) $HCO_2^{(-)}$, trigonal planar, 120°



3.  180°

4.  109.5°

5. (A) $K^{(+)}$  (B) $Cs^{(+)}$ 

6. (A) ammonia *(common name)*; (B) carbon tetrachloride; (C) pentaphosphorous heptoxide; (D) potassium hydroxide; (E) cesium cyanide *(D & E are ionic compounds, not covalent molecules.)*

7. (A) N_3F_6; (B) CS_2; (C) $BaCl_2$ *(Barium chloride ionic and the formula can be predicted based on the charges, $Ba^{(2+)}$ & $Cl^{(-)}$, so no numeric prefixes are used.)*

8. (longest) Br-Br > F-F > O=O > N≡N (shortest)

9. (A) NH_3 - polar; (B) CH_4 - non-polar (C) $CaCl_2$ - ionic; (C) CCl_4 - polar

10. CH_4 cannot be polar because it does not have polar bonds. While CCl_4 has polar bonds, the tetrahedral shape spreads those bonds out evenly (symmetrical), so no one side of the molecule is more negative or positive, and thus the molecule is not polar overall.

11. Atoms further down the periodic table have more shells of electrons stacked up on the outside, thus taking up more space and extending further from the nucleus. Bromine (4 shells of electrons) has larger radius than fluorine (2 shells). The larger bromine atoms cannot get as close when they bond so have longer bond length.

12. In an ionic bond, the atoms completely exchange electrons, creating charged ions. In a covalent bond, the atoms share electrons. In LiCl the $Li^{(+)}$ cation is “bonded” to the $Cl^{(-)}$ ion due to attraction of opposite charges. In HCl the two atoms must stay close to both possess (share) the same pair of electrons.

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5: INTRODUCTION TO CHEMICAL REACTIONS

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

5.1: The Law of Conservation of Matter

5.2: Chemical Equations

5.3: Quantitative Relationships Based on Chemical Equations

5.4: Some Types of Chemical Reactions

5.5: Oxidation-Reduction (Redox) Reactions

5.6: Redox Reactions in Organic Chemistry and Biochemistry

5.7: Chapter Summary

5.E: Exercises

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5.1: The Law of Conservation of Matter

Skills to Develop

- 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*.

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 type of atoms after the chemical change as were present before the chemical change.

Before looking at explicit examples of the law of conservation of matter, we need to examine the method chemists use to represent chemical changes.

Summary

The amount of matter in a closed system is conserved.

Concept Review Exercises

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.

Answer

1. Matter may not be created or destroyed.

2. From Section 1.1, a scientific law is a "descriptive generalization about how some aspect of the natural world behaves under stated circumstances." For comparison, a scientific theory is "a well-substantiated explanation of some aspect of the natural world

that can incorporate facts, laws, inferences, and tested hypotheses." The difference between law and theory is not clear cut. Both are supported by vast amounts of evidence and generally accepted by the scientific community. A law is more narrow, like this particular description about matter, whereas a theory might be more broad and often would often include more of an explanation why. Atomic Theory explains the reason behind the law of conservation of matter; in chemical reactions, atoms just rearrange, so have same mass before and after.

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5.2: Chemical Equations

Skills to Develop

- 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.

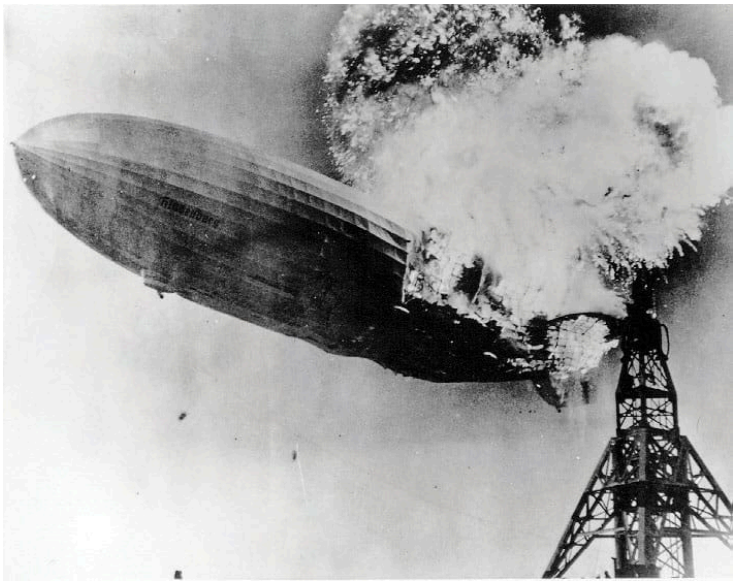


Figure $5.2.1$***:*** *The Formation of Water. Hydrogen and oxygen combine to form water. Here, the hydrogen gas in the zeppelin SS Hindenburg reacts with oxygen in the air to make water. Source: Photo courtesy of the US Navy.*

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

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

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

$$H_{2(g)} + O_{2(g)} \rightarrow H_2O_{(\ell)} \tag{5.2.2}$$

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

This equation is still not complete because *it does not satisfy the law of conservation of matter*. Count the number of atoms of each element on each side of the arrow. On the reactant side, there are two H atoms and two O atoms; on the product side, there

are two H atoms and only one oxygen atom. The equation is not balanced because the number of oxygen atoms on each side is not the same (Figure 5.2.2).

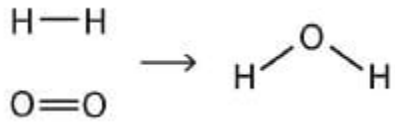


Figure 5.2.2***:*** *Balanced—Yes or No?. By counting the atoms of each element, we can see that the reaction is not balanced as written.*

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

$$H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(\ell)} \tag{5.2.3}$$

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:

$$2H_{2(g)} + O2(g) \rightarrow 2H_2O_{(\ell)} \tag{5.2.4}$$

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.

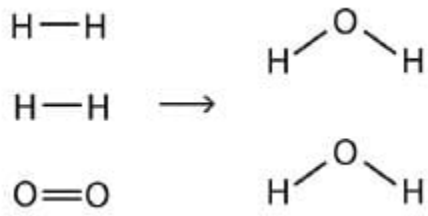


Figure 5.2.3***:*** *Balanced—Yes or No?. By counting the atoms of each element, we can see that the reaction is now balanced.*

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.

Example $5.2.2$

Balance each chemical reaction.

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

SOLUTION

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

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.

For example, to balance the equation

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

we might choose to count the carbon atoms first, finding that both sides are balanced with one carbon atom. The reactant side has four hydrogen atoms, so the product side must also have four hydrogen atoms. We fix this by putting a 4 in front of the HCl:

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

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:

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

Now we check: each side has one carbon atom, four hydrogen atoms, and eight chlorine atoms. The chemical equation is balanced.

NOTE: When balancing chemical equations, unless there is some other reason to do so, the coefficients should always be in the smallest ratio. The coefficients below are all divisible by two, so the reaction should NOT be balanced this way.

$$2CH_4 + 8Cl_2 \rightarrow 2CCl_4 + 8HCl \tag{5.2.8}$$

Summary

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.

Concept Review Exercises

1. What are the parts of a chemical equation?
2. Explain why chemical equations need to be balanced.

Answers

1. reactants and products
2. 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. (Hydrogen and iodine each form diatomic molecules in their elemental form.)

2. Mercury reacts with oxygen to make mercury(II) oxide. Write a balanced chemical equation that summarizes this reaction. (Oxygen forms diatomic molecules in the elemental form.)

3. Propyl alcohol (C_3H_7OH) reacts with oxygen to make carbon dioxide and water. Write a balanced chemical equation that summarizes this reaction.

4. 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.)

5. Balance each equation.

    a. $NH_3 + O_2 \rightarrow NO + H_2O$
    b. $Li + N_2 \rightarrow Li_3N$
    c. $AuCl \rightarrow Au + AuCl_3$

6. Chromium(III) oxide reacts with carbon tetrachloride to make chromium(III) chloride and phosgene ($COCl_2$). Write the balanced chemical equation for this reaction.

7. When sodium hydrogen carbonate is used to extinguish a kitchen fire, it decomposes into sodium carbonate, water, and carbon dioxide. Write a balanced chemical equation for this reaction.

Answers

1. $H_2(g) + I_2(s) \rightarrow 2HI(g)$

2. $2Hg + O_2 \rightarrow 2HgO$

3. $2C_3H_7OH + 9O_2 \rightarrow 6CO_2 + 8H_2O$

4.

a. $MgCl_2 + 2K \rightarrow 2KCl + Mg$
b. $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$
c. $2NaN_3 \rightarrow 2Na + 3N_2$

5.

a. $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$

b. $6Li + N_2 \rightarrow 2Li_3N$

c. $3AuCl \rightarrow 2Au + AuCl_3$

6. $Cr_2O_3 + 3CCl_4 \rightarrow 2CrCl_3 + 3COCl_2$

7. $2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$

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5.3: Quantitative Relationships Based on Chemical Equations

Skills to Develop

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

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

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

Looking Closer: Stoichiometry in Cooking

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

$$\text{2 c flour + 1 egg + 4 tbsp shortening + 1 tsp salt + 1 tsp baking soda + 1 c milk} \rightarrow \text{12 biscuits}$$

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

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

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

$$\frac{\text{12 biscuits}}{\text{2 c flour}} \tag{5.3.1}$$

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

$$\text{4 c flour} \times \frac{\text{12 biscuits}}{\text{2 c flour}} = \text{24 biscuits} \tag{5.3.2}$$

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. Image used with permission from Wikipedia.

Consider the following balanced chemical equation:

$$2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O \tag{5.3.3}$$

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:

Statement from the Balanced Chemical Reaction	
two C_2H_2 molecules react with five O_2 molecules	
two C_2H_2 molecules react to make four CO_2 molecules	
five O_2 molecules react to make two H_2O molecules	
four CO_2 molecules are made at the same time as two H_2O molecules	

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

$$26\text{C}_2\text{H}_2 \times \frac{4\text{CO}_2}{2\text{C}_2\text{H}_2} \tag{5.3.4}$$

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

$$26\mathrm{C_2H_2} \times \frac{4\mathrm{CO_2}}{2\mathrm{C_2H_2}} = 52\mathrm{CO_2} \tag{5.3.5}$$

Thus, 52 molecules of CO_2 are formed.

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

Example 5.3.1

Start with this balanced chemical equation.

$$KMnO_4 + 8HCl + 5FeCl_2 \rightarrow 5\ FeCl_3 + MnCl_2 + 4H_2O + KCl$$

A. Verify that the equation is indeed balanced.

B. Give 2 ratios that give the relationship between HCl and $FeCl_3$.

C. How many water molecules can be formed if 255 $FeCl_2$ formula units react?

SOLUTION

A. Each side has 1 K atom and 1 Mn atom. The 8 molecules of HCl yield 8 H atoms, and the 4 molecules of H_2O also yield 8 H atoms, so the H atoms are balanced. The Fe atoms are balanced, as we count 5 Fe atoms from 5 $FeCl_2$ reactants and 5 $FeCl_3$ products. As for Cl, on the reactant side, there are 8 Cl atoms from HCl and 10 Cl atoms from the 5 $FeCl_2$ formula units, for a total of 18 Cl atoms. On the product side, there are 15 Cl atoms from the 5 $FeCl_3$ formula units, 2 from the $MnCl_2$ formula unit, and 1 from the KCl formula unit. This is a total of 18 Cl atoms in the products, so the Cl atoms are balanced. All the elements are balanced, so the entire chemical equation is balanced.

B. Because the balanced chemical equation tells us that 8 HCl molecules react to make 5 $FeCl_3$ formula units, we have the following 2 ratios: $\frac{8\mathrm{HCl}}{5\mathrm{FeCl_3}}$ and $\frac{5\mathrm{FeCl_3}}{8\mathrm{HCl}}$. There are a total of 42 possible ratios. Can you find the other 40 relationships?

C. We must convert 255 $FeCl_2$ into ? H_2O, so the relationship/conversion from the balanced equation is 5 $FeCl_2$ = 4 H_2O. The 5 $FeCl_2$ goes on the bottom so that $FeCl_2$ cancels, leaving H_2O on top, which does not cancel.

$$255\ \mathrm{FeCl_2} \times \frac{4\ \mathrm{H_2O}}{5\ \mathrm{FeCl_2}} = 204\ \mathrm{H_2O} \tag{5.3.6}$$

Summary

A balanced chemical equation gives the ratios in which molecules of substances react and are produced in a chemical reaction.

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.

$$Fe_2O_3 + C \rightarrow Fe + CO_2$$

2. Balance this equation and determine how many molecules of CO_2 are formed if 15 molecules of C_6H_6 are reacted.

$$C_6H_6 + O_2 \rightarrow CO_2 + H_2O$$

3. 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?

4. 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?

Answers

1. $2Fe_2O_3 + 3C \rightarrow 4Fe + 3CO_2$; 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.

2. $2C_6H_6 + 15O_2 \rightarrow 12CO_2 + 6H_2O$; 90 molecules

3.

   a. It is balanced.
   b. 183 atoms

4.

   a. It is balanced.
   b. 1,617 atoms

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5.4: Some Types of Chemical Reactions

Skills to Develop

- 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 Reactions

A combination (a.k.a. composition or synthesis) 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

$$4Fe + 3O_2 \rightarrow 2Fe_2O_3 \tag{5.4.1}$$

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

$$Fe_2O_3 + 3SO_3 \rightarrow Fe_2(SO_4)_3 \tag{5.4.2}$$

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

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

$$2NaHCO_{3(s)} \rightarrow Na_2CO_{3(s)} + CO_{2(g)} + H_2O_{(\ell)} \tag{5.4.3}$$

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

$$2KClO_{3(s)} \rightarrow 2KCl_{(s)} + 3O_{2(g)} \tag{5.4.4}$$

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

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

Single Replacement Reactions

When an element reacts with a compound to form a new element and a new compound, it is called a single replacement, or sometimes single displacement. Essentially, one element displaces another in the compound. For example, the equation

$$3Al + 3H_2SO_4 \rightarrow 3H_2 + Al_2(SO_4)_3 \tag{5.4.5}$$

is a single replacement in which the element aluminum replaces hydrogen in sulfuric acid, H_2SO_4, to form elemental hydrogen and the new compound, $Al_2(SO_4)_3$.

Double Replacement Reactions

In a double replacement (a.k.a. double displacement or metathesis) reaction two compounds typically react with each other to produce two different compounds. This type of reaction is often an exchange of positive and negative components of the compounds. Two examples are precipitation and acid-base reactions.

In this double replacement

$$NaCl + AgNO_3 \rightarrow NaNO_3 + AgCl_{(s)} \tag{5.4.6}$$

the Na^+ from NaCl and Ag^+ from $AgNO_3$ swap partners, or replace each other. At the same time, the Cl^- in NaCl and NO_3^- in $AgNO_3$ switch and replace each other. An insoluble solid that forms from solution is called a precipitate ($AgNO_3$ here), hence this is also called a precipitation reaction.

Sulfuric acid, H_2SO_4, and magnesium hydroxide base, $Mg(OH)_2$, can also participate in a double replacement:

$$H_2SO_4 + Mg(OH)_2 \rightarrow 2H_2O + MgSO_4 \tag{5.4.7}$$

Here the sulfate and hydroxide anions, SO_4^{2-} and OH^-, trade places while two hydrogen cations, 2 H^+, replace the magnesium cation, Mg^{2+}. We will learn in more detail later how acids (which donate H^+) can react with the bases (with OH^-) to make water (H_2O) and a salt ($MgSO_4$ is the formula of Epsom salt, often used in soothing baths).

Example 5.4.1

Identify each type of reaction.

a. $2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$
b. $(NH_4)_2Cr_2O_7(s) \rightarrow N_2(g) + Cr_2O_3(s) + 4H_2O(\ell)$
c. $2K(s) + S(s) + 2O_2(g) \rightarrow K_2SO_4(s)$

SOLUTION

a. The element aluminum reacts with the compound hydrochloric acid to form the compound aluminum chloride and the element hydrogen. (Aluminum replaces hydrogen.) This is a single replacement reaction.
b. A single substance reacts to make several products, so we have a decomposition reaction.
c. Multiple reactants are combining to make a single product, so this reaction is a combination reaction.

Summary

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

Concept Review Exercises

1. How are combination and decomposition reactions similar?
2. How are single replacement and double replacement reactions different?

Answers

1. They are the reverse of each other. In combination, multiple substances make one product (in general: A + B → C). In a decomposition, one substance makes multiple substances (in general: C → B + A).
2. Single replacement reactions must have elements on both sides of the equation, one that becomes a compound and one that is formed from a compound (in general: A + BC → AB + C). Double replacement reactions require more compounds so

that two displacements can occur (in general: AB + CD → AD + CB). Other answers are possible.

Exercises

1. Identify each type of reaction.

    a. HCl + NaOH → H2O + NaCl
    b. 2Na + $CuBr_2$ → 2NaBr + Cu
    c. $2NaHCO_3$ → Na_2CO_3 + H_2O + CO_2
    d. C + $2H_2$ → CH_4
    e. $2NH_4NO_3(s)$ → $2N_2(g)$ + $4H_2O(g)$ + $O_2(g)$

Answers

1. a. double replacement
    b. single replacement
    c. decomposition
    d. combination
    e. decomposition

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5.5: Oxidation-Reduction (Redox) Reactions

Skills to Develop

- 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):

$$Zn_{(s)} + 2HCl_{(aq)} \rightarrow H_{2(g)} + ZnCl_{2(aq)} \tag{5.5.1}$$

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



Figure 5.5.1***:*** *Zinc Metal plus Hydrochloric Acid. It is fairly obvious that zinc metal reacts with aqueous hydrochloric acid! The bubbles are hydrogen gas. Source: Photo courtesy of Chemicalinterest, http://commons.wikimedia.org/wiki/File:Zn_reaction_with_HCl.JPG.*

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

$$Zn_{(s)} + 2H^{+}_{(aq)} + 2Cl^{-}_{(aq)} \rightarrow H_{2(g)} + Zn^{2+}_{(aq)} + 2Cl^{-}_{(aq)} \tag{5.5.2}$$

Viewed this way, the net reaction seems to be a charge transfer between zinc and hydrogen. (There is no net change experienced by the chloride ion.) In fact, electrons are being transferred from the zinc atoms to the hydrogen ions (which ultimately make a molecule of diatomic hydrogen), changing the charges on both elements. Note that, while HCl is not ionic, we will learn in Chapter 10 that acids like hydrochloric acid donate H^{+} ions in water.

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,

$$Zn_{(s)} + 2H^{+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_{2(g)} \tag{5.5.3}$$

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

$$Zn \rightarrow Zn^{2+} + 2e^{-} \tag{5.5.4}$$

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:

$$2H^{+} + 2e^{-} \rightarrow H_2 \tag{5.5.5}$$

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

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

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

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

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

Example 5.5.1

Write and balance the redox reaction that has silver ions and aluminum metal as reactants and silver metal and aluminum ions as products. (A silver ion will have a plus one charge. You should be able to predict the charge of an aluminum ion using the periodic table.)

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:

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

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

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

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

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

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

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:

$$Cd_{(s)} + 2NiOOH_{(s)} + 2H_2O_{(\ell)} \rightarrow Cd(OH)_{2(s)} + 2Ni(OH)_{2(s)} \tag{5.5.6}$$

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:

$$2Li_{(s)} + I_{2(s)} \rightarrow 2LiI_{(s)} \tag{5.5.7}$$

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. Image used with permission from Gerhard H Wrodnigg (via wikipedia)*

Summary

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.

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. $Al \rightarrow Al^{3+} + 3e^-$ (oxidation); $O_2 + 2e^- \rightarrow 2O^{2-}$ (reduction) (answers will vary)

Exercises

1. Which reactions are redox reactions? For those that are redox reactions, identify the oxidizing and reducing agents.

    a. $2Na + Cl_2 \rightarrow 2NaCl$
    b. $3Mg + 2AlCl_3 \rightarrow 2Al + 3MgCl_2$
    c. $KCl + AgNO_3 \rightarrow AgCl + KNO_3$

2. 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. $I^-(aq) + Br_2(\ell) \rightarrow Br^-(aq) + I_2(s)$

Answers

1. If any charges are changing, it is a redox reaction (because electrons are exchanged). If not ionic look for changes in oxygen or hydrogen to identify if redox.

    a. yes; Chlorine, Cl_2, is the oxidizing agent (Cl_2 is reduced because it gains electrons to become Cl^-, $Cl_2 + 2e^- \rightarrow 2Cl^-$); Sodium, Na, is the reducing agent (Na is oxidized because it loses electrons to become Na^+, $2Na \rightarrow 2Na^+ + 2e^-$)
    b. yes; The aluminum cation in $AlCl_3$ is the oxidizing agent (because it is reduced, $2Al^{3+} + 6e^- \rightarrow 2Al$); Magnesium, Mg, is the reducing agent (because it is oxidized, $3Mg \rightarrow 3Mg^{2+} + 6e^-$)
    c. no (no change in charges of these ions)

2.

a. $Ca \rightarrow Ca^{2+} + 2e^-$

   $2H^+ + 2e^- \rightarrow H_2$

   Combined: $Ca + 2H^+ \rightarrow Ca^{2+} + H_2$

b. $Br_2 + 2e^- \rightarrow 2Br^-$

   $2I^- \rightarrow I_2 + 2e^-$

   Combined: $Br_2 + 2I^- \rightarrow 2Br^- + I_2$

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5.6: Redox Reactions in Organic Chemistry and Biochemistry

Skills to Develop

- 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.

The carbon compounds in organic and biochemistry tend to be covalent molecules. Because they are not usually ionic, there are not usually charges, which makes it more difficult to see if negative electrons have been gained or lost (redox). In these cases, redox can be defined in terms of changes in composition. The original meaning of oxidation was “adding oxygen,” so when oxygen is added to a molecule, the molecule is being oxidized. The reverse is true for reduction: if a molecule loses oxygen atoms, the molecule is being reduced. For example, the acetaldehyde (CH_3CHO) molecule takes on an oxygen atom to become acetic acid (CH_3COOH).

$$2CH_3CHO + O_2 \rightarrow 2CH_3COOH \tag{5.6.1}$$

Thus, acetaldehyde is being oxidized.

Similarly, oxidation and reduction 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:

$$CH_3CHO + H_2 \rightarrow CH_3CH_2OH \tag{5.6.2}$$

Example $5.6.1$

In each conversion, indicate whether oxidation or reduction is occurring.

a. $N_2 \rightarrow NH_3$
b. $CH_3CH_2OHCH_3 \rightarrow CH_3COCH_3$
c. $HCHO \rightarrow HCOOH$

SOLUTION

a. Hydrogen is being added to the original reactant molecule, so reduction is occurring.
b. Hydrogen is being removed from the original reactant molecule, so oxidation is occurring.
c. Oxygen is being added to the original reactant molecule, so oxidation is occurring.

Example $5.6.2$

Rank these three one-carbon compounds in order from least to most oxidized. Methanol (CH3OH), or wood alcohol is much more toxic than beverage alcohol and used for many purposes, included antifreeze in windshield wiper fluid. Formaldehyde (H_2CO) is often used as an enbalming agent. Formic acid (HCO_2H) is what gives red ant bites their sting.

SOLUTION

The order from least to most oxidized would be CH3OH < H_2CO < HCO_2H.

CH3OH is the most reduced (least oxidized) form of the four because it has only one oxygen and the most hydrogens in the

formula. H_2CO also has one oxygen, but only two hydrogens instead of four. HCO_2H is the most oxidized of the three, as it also has only two hydrogens, but has two oxygens instead of one.

Combustion Reactions

A combustion reaction is a type of redox reaction that occurs when a substance combines with molecular oxygen to make oxygen-containing compounds of other elements in the reaction. One example is the burning of methane, the principal component of natural gas (Figure 5.6.1).

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{5.6.3}$$

Oxygen (in its elemental form) is a crucial reactant in combustion reactions, and it is also present in the products. In combustion, the oxygen (O_2) is reduced and the other elements are oxidized. Because of its abundance in the air, O_2 is the most ubiquitous oxidizing agent on Earth.

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



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. Image used with permission from Wikipedia.*

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:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \tag{5.6.4}$$

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 (C_2H_5OH) in a person's breath:

$$3C_2H_5OH + Cr_2O_7^{2-} + 8H^+ \rightarrow 3CH_3CHO + 2Cr^{3+} + 7H_2O \tag{5.6.5}$$

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:

$$3C_2H_5OH + 2Cr_2O_7^{2-} + 16H^+ \rightarrow 3CH_3COOH + 4Cr^{3+} + 11H_2O \tag{5.6.6}$$

In this reaction, the chromium atom is reduced from orange $Cr_2O_7^{2-}$ to green Cr^{3+}, and the ethanol is oxidized to acetic acid. (A Brethalyzer measures the degree of color change in these reactions to determine the amount of alcohol.)

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:

$$3CH_3CHOHCH_3 + Cr_2O_7^{2-} + 8H^+ \rightarrow 3(CH_3)_2CO + 2Cr^{3+} + 7H_2O \tag{5.6.7}$$

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.

$$CH_3COCOOH \rightarrow CH_3CHOHCOOH \tag{5.6.8}$$

(Pyruvic acid is both a carboxylic acid and a ketone; only the ketone group is reduced.) The buildup of lactic acid during vigorous exercise is responsible in large part for the fatigue that we experience.

In food chemistry, the substances known as antioxidants are reducing agents. Ascorbic acid (vitamin C; $C_6H_8O_6$) is thought to retard potentially damaging oxidation of living cells. In the process, it is oxidized to dehydroascorbic acid ($C_6H_6O_6$). In the stomach, ascorbic acid reduces the nitrite ion (NO_2^-) to nitric oxide (NO):

$$C_6H_8O_6 + 2H^+ + 2NO_2^- \rightarrow C_6H_6O_6 + 2H_2O + 2NO \tag{5.6.9}$$

> If reaction in Equation 5.6.9 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). Image used with permission 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:

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2 \tag{5.6.10}$$

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. Image used with permission (Public Domain; Wikipedia).*

Summary

Redox reactions are common in organic and biological chemistry, including the combustion of organic chemicals, respiration, and photosynthesis. When an organic compound is oxidized, the result will usually be more oxygen atoms and/or fewer hydrogen atoms in the formula.

Concept Review Exercise

1. What are two ways to determine if an organic compound has been oxidized?
2. Give some biochemical examples of oxidation and reduction reactions.

Answer

1. If the compound is more oxidized it will have more oxygen and/or less hydrogen in the formula.
2. respiration, photosynthesis, antioxidants in foods,... (answers will vary)

Exercises

1. In the combustion of methane, is the carbon reduced or oxidized? Since these are not ionic compounds and there are no charges, how can you tell? Does that make the carbon in methane the oxidizing agent or reducing agent?

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

2. List these four three-carbon organic molecules from least to most oxidized: propanal (CH_3CH_2CHO), propane ($CH_3CH_2CH_3$), propanoic acid ($CH_3CH_2CO_2H$), and propene ($CH_3CH{=}CH_2$)?

Answers

1. The carbon in methane is oxidized. Carbon gains more oxygens (more oxidized) and loses hydrogens (less reduced) when CH_4 is converted to CO_2. This means the carbon in methane is the reducing agent. (Note: O_2 is the oxidizing agent here, as is usually the case.)

2. *(least oxidized)* propane ($CH_3CH_2CH_3$) < propene ($CH_3CH{=}CH_2$) < propanal (CH_3CH_2CHO) < propanoic acid ($CH_3CH_2CO_2H$) *(most oxidized)*

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5.7: Chapter 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. Some of the types include **combination, decomposition, single replacement,** and **double replacement** reactions.

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**. 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, where the focus is on the gain or loss of oxygen atoms or hydrogen atoms. **Respiration**, the process by which we inhale and metabolize oxygen, is a series of redox reactions. **Combustion reactions** are a type of redox and combine molecular oxygen with the atoms of another reactant. 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. Oxidation of an organic compound will typically result in more oxygen, less hydrogen, or both in the formula.

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5.E: Exercises

1. Isooctane (C_8H_{18}) is used as a standard for comparing gasoline performance. (A) Write a balanced chemical equation for the combustion of isooctane. (B) if 12 isooctane molecules burn, how many CO_2 molecules will be formed?

2. Heptane (C_7H_{16}), like isooctane (see Exercise 1), is also used as a standard for determining gasoline performance. (A) Write a balanced chemical equation for the combustion of heptane. (B) How many oxygen molecules must have been used if 320 water molecules are formed by 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. 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. (A) Explain why your friend is incorrect. (B) Write and balance the half reactions and the overall reaction. (C) Which element is oxidized and which is the oxidizing agent?

5. 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. (A) $2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$; (B) 96 CO_2 molecules

2. (A) $C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O$; (B) 440 O_2 molecules

3. A combination reaction makes a new substance from more than one reactant; a redox reaction exchanges (gains & loses) electrons. Not all combination reactions are redox reactions, and not all redox reactions are combination reactions.

4. (A) Your friend is incorrect because the number of electrons transferring is not balanced.

(B) Iron Half Reaction: $Fe^{2+} + 2e^{-} \rightarrow Fe$; Sodium Half Reaction: $Na \rightarrow Na^{+} + e^{-}$; Overall Reaction: $Fe^{2+} + 2Na \rightarrow Fe + 2Na^{+}$

(C) Na is oxidized and Fe^{2+} is the oxidizing agent.

5. Zinc (Zn) is oxidized and is the reducing agent. Copper (Cu^{2+}) is reduced and is the oxidizing agent.

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6: QUANTITIES IN CHEMICAL REACTIONS

So far, we have talked about chemical reactions in terms of individual atoms and molecules. Although this works, most of the reactions occurring around us involve much larger amounts of chemicals. Even a tiny sample of a substance will contain millions, billions, or a hundred billion billions of atoms and molecules. How do we compare amounts of substances to each other in chemical terms when it is so difficult to count to a hundred billion billion? Actually, there are ways to do this, which we will explore in this chapter. In doing so, we will increase our understanding of stoichiometry, which is the study of the numerical relationships between the reactants and the products in a balanced chemical reaction.

6.1: The Mole

6.2: Atomic and Molar Masses

6.3: Mole-Mass Conversions

6.4: Mole-Mole Relationships in Chemical Reactions

6.5: Mole-Mass and Mass-Mass Problems

6.6: Chapter Summary

6.E: Exercise

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6.1: The Mole

Skills to Develop

- 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.

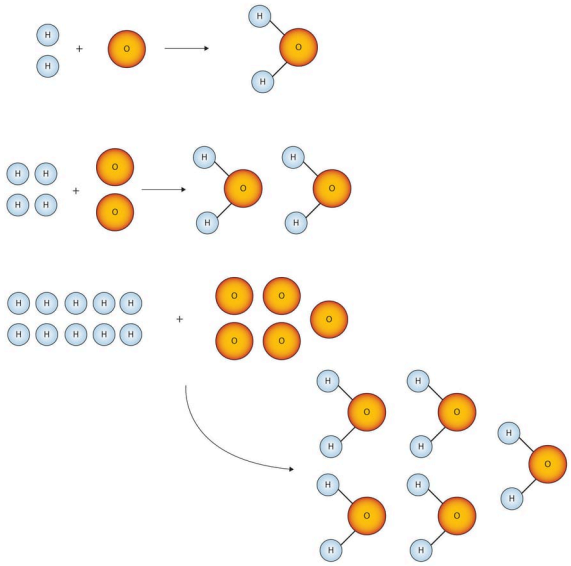


Figure 6.1.1 *Water Molecules. The ratio of hydrogen atoms to oxygen atoms used to make water molecules is always 2:1, no matter how many water molecules are being made.*

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 (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} O atoms, we say we have 1 mol of O 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.

Note

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. In these examples, we cited moles of atoms *and* moles of molecules. The word *mole* represents a number of things—6.022×10^{23} of them—but does not by itself specify what "they" are. They can be atoms, formula units (of ionic compounds), or molecules. That information still needs to be specified.

Because 1 H_2 molecule contains 2 H atoms, 1 mol of H_2 molecules (6.022×10^{23} molecules) has 2 mol of H 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:

$$2.5\ \text{mol } C_2H_6O\ \text{molecules} \times \underbrace{\frac{2\ \text{mol C atoms}}{1\ \text{mol } C_2H_6O\ \text{molecules}}}_{\text{conversion factor}} = 5.0\ \text{mol C atoms}$$

Note how the unit *mol C_2H_6O molecules* cancels algebraically. Similar equations can be constructed for determining the number of H and O atoms:

$$2.5 \text{ mol } C_2H_6O \text{ molecules} \times \frac{6 \text{ mol H atoms}}{1 \text{ mol } C_2H_6O \text{ molecules}} = 15 \text{ mol H atoms}$$

$$2.5 \text{ mol } C_2H_6O \text{ molecules} \times \frac{1 \text{ mol O atoms}}{1 \text{ mol } C_2H_6O \text{ molecules}} = 2.5 \text{ mol O atoms}$$

The fact that 1 mol equals 6.022 × 10^{23} items can also be used as a conversion factor.

Example 6.1.2

How many formula units are present in 2.34 mol of $CaCl_2$? 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:

$$2.34 \text{ mol } CaCl_2 \times \frac{6.022 \times 10^{23} \text{ } CaCl_2 \text{ units}}{1 \text{ mol } CaCl_2} = 1.41 \times 10^{24} \text{ } CaCl_2 \text{ units}$$

Because there are three ions (one Ca^{2+} cation and two Cl^- anions) per formula unit, there are

$$1.41 \times 10^{24} \text{ } CaCl_2 \text{ units} \times \frac{3 \text{ ions}}{CaCl_2 \text{ units}} = 4.23 \times 10^{24} \text{ ions}$$

in the sample.

Concept Review Exercise

1. What is a mole?

Answer

1. A mole is 6.022 × 10^{23} things.

Key Takeaway

- A mole is 6.022 × 10^{23} things.

Exercises

1. How many moles of each type of atom are in 2.58 mol of Na_2SO_4?
2. How many molecules are in 16.8 mol of H_2O?
3. A lethal dose of arsenic is 1.00 × 10^{21} atoms. How many moles of arsenic is this?
4. An intravenous solution of normal saline may contain 1.72 mol of sodium chloride (NaCl). How many sodium ions and chloride ions are present in the solution?

Answers

1. 5.16 mol of Na atoms, 2.58 mol of S atoms, and 10.32 mol of O atoms
2. 1.01×10^{25} molecules
3. 0.00166 mol (or 1.66×10^{-3} mol in scientific notation)
4. 1.04×10^{24} Na^+ ions and 1.04×10^{24} Cl^- ions

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6.2: Atomic and Molar Masses

Skills to Develop

- 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 238.03 g, so the mass of 2 mol is twice that, or 476.06 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

1 Na molar mass:	23.00 g

1 Cl molar mass:	35.45 g
Total:	58.45 g

The mass of 1 mol of NaCl is 58.45 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

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 × 14.00 =	56.00 g
6 O molar mass:	6 × 16.00 =	96.00 g
Total:		584.69 g

The mass of 1 mol of bilirubin is 584.69 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:

1 Ba molar mass:	1 × 137.33 g =	137.33 g
2 O molar mass:	2 × 16.00 g =	32.00 g
2 H molar mass:	2 × 1.01 g =	2.02 g
Total:		171.35 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 584.05 g/mol, which is read as "five hundred eighty four point zero five grams per mole."

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 with different units, grams (per one mole).
2. Molar masses of compounds are calculated by adding the molar masses of their atoms.

Key Takeaway

- The mass of moles of atoms and molecules is expressed in units of grams.

Exercises

1. What is the molar mass of Si? What is the molar mass of U?
2. What is the molar mass of $FeCl_2$? What is the molar mass of $FeCl_3$?
3. What is the molar mass of $(NH_4)_2S$? What is the molar mass of $Ca(OH)_2$?
4. Aspirin ($C_9H_8O_4$) is an analgesic (painkiller) and antipyretic (fever reducer). What is the molar mass of aspirin?

Answers

1. 28.09 g/mol; 238.00 g/mol
2. 126.75 g/mol; 162.20 g/mol
3. 68.15 g/mol; 74.10 g/mol
4. 180.17 g/mol

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6.3: Mole-Mass Conversions

Skills to Develop

- s 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). Stated mathematically,

$$1 \text{ mol Al} = 26.98 \text{ g Al}$$

We can divide both sides of this expression by either side to get one of two possible conversion factors:

$$\frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \text{ and } \frac{26.98 \text{ g Al}}{1 \text{ mol Al}} \tag{6.3.1}$$

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.

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.

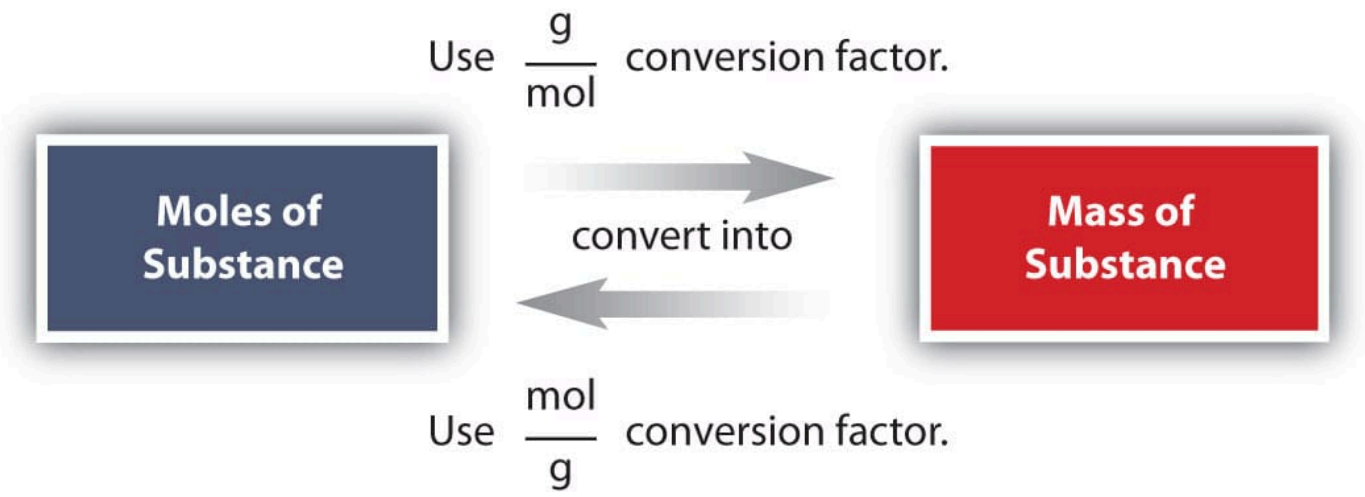


Figure 6.3.1 *A Simple Flowchart for Converting between Mass and Moles of a Substance. It takes one mathematical step to convert from moles to mass or from mass to moles.*

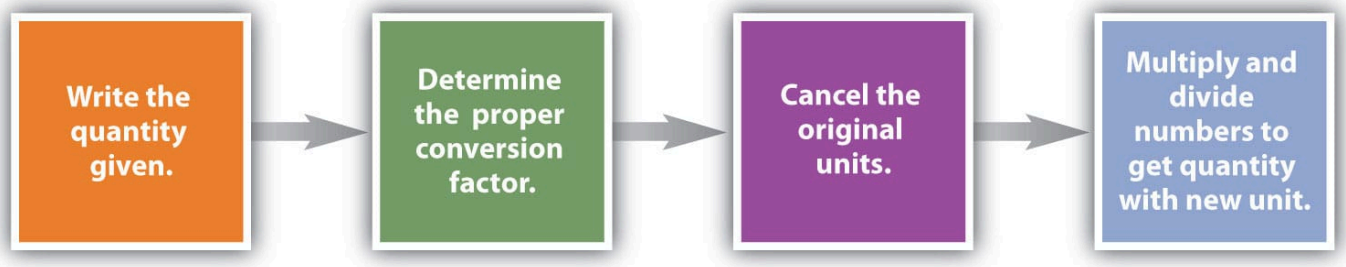


Figure 6.3.2 *A Flowchart Illustrating the Steps in Performing a Unit Conversion. When performing many unit conversions, the same logical steps can be taken.*

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:

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 × 14.00 g =	56.00 g
6 O molar mass:	6 × 16.00 g =	96.00 g
Total:		584.69 g

The molar mass of bilirubin is 584.69 g. Using the relationship

1 mol bilirubin = 584.69 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:

$$0.00655 \text{ mol bilirubin} \times \frac{584.69 \text{ g bilirubin}}{\text{mol bilirubin}} = 3.83 \text{ g bilirubin}$$

The mol bilirubin unit cancels. The biochemist needs 3.83 g of bilirubin.

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 non-carbon 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*).

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 molar mass is needed for a mole-mass conversion.
2. The unit of the initial quantity determines which conversion factor is used.

Key Takeaway

- It is possible to convert between moles of material and mass of material.

Exercises

1. What is the mass of 8.603 mol of Fe metal?
2. What is the mass of 6.24×10^4 mol of Cl_2 gas?
3. What is the mass of 20.77 mol of $CaCO_3$?
4. How many moles are present in 977.4 g of $NaHCO_3$?
5. 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?

Answers

1. 480.5 g
2. 4.42×10^6 g
3. 2,079 g
4. 11.63 mol
5. 2.77×10^{-5} mol

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6.4: Mole-Mole Relationships in Chemical Reactions

Skills to Develop

- To use a balanced chemical reaction to determine molar relationships between the substances.

In Chapter 5, 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

$$2H_2 + O_2 \rightarrow 2H_2O \tag{6.4.1}$$

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

$$4H_2 + 2O_2 \rightarrow 4H_2O \tag{6.4.2}$$

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

$$22H_2 + 11O_2 \rightarrow 22H_2O \tag{6.4.3}$$

because 22:11:22 also reduces to 2:1:2.

Suppose we want to use larger numbers. Consider the following coefficients:

$$12.044 \times 10^{23}\ H_2 + 6.022 \times 10^{23}\ O_2 \rightarrow 12.044 \times 10^{23}\ H_2O \tag{6.4.4}$$

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

$$2\ mol\ H_2 + 1\ mol\ O_2 \rightarrow 2\ mol\ H_2O \tag{6.4.5}$$

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

$$2H_2 + O_2 \rightarrow 2H_2O \tag{6.4.6}$$

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.”

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:

$$\frac{2\ \text{mol}\ \text{H}_2}{1\ \text{mol}\ \text{O}_2}\ \text{or}\ \frac{1\ \text{mol}\ \text{O}_2}{2\ \text{mol}\ \text{H}_2} \tag{6.4.7}$$

$$\frac{2\ \text{mol}\ \text{H}_2\text{O}}{1\ \text{mol}\ \text{O}_2}\ \text{or}\ \frac{1\ \text{mol}\ \text{O}_2}{2\ \text{mol}\ \text{H}_2\text{O}} \tag{6.4.8}$$

$$\frac{2\ \text{mol}\ \text{H}_2}{2\ \text{mol}\ \text{H}_2\text{O}}\ \text{or}\ \frac{2\ \text{mol}\ \text{H}_2\text{O}}{2\ \text{mol}\ \text{H}_2} \tag{6.4.9}$$

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*.

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:

$$2H_2 + O_2 \rightarrow 2H_2O$$

SOLUTION

Because we are dealing with quantities of H_2O and O_2, we will use a 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.

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.

Key Takeaway

- The balanced chemical reaction can be used to determine molar relationships between substances.

Exercises

1. List the molar ratios you can derive from this balanced chemical equation:

$$NH_3 + 2O_2 \rightarrow HNO_3 + H_2O$$

2. 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?

3. Balance the following unbalanced equation and determine how many moles of H_2O are produced when 1.65 mol of NH_3 react.

$$NH_3 + O_2 \rightarrow N_2 + H_2O$$

4. Chemical reactions are balanced in terms of molecules and in terms of moles. Are they balanced in terms of dozens? Defend your answer.

Answers

1. 1 mol NH_3:2 mol O_2:1 mol HNO_3:1 mol H_2O

3. 3.14 mol

5. $4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$; 2.48 mol

7. Yes, they are still balanced. (e.g. A ratio that is 1 dozen : 1 dozen, is the same as 12 : 12, which is the same as 1 : 1, and the same as 1 mole : 1 mole, or $6.02x10^{23} : 6.02x10^{23}$)

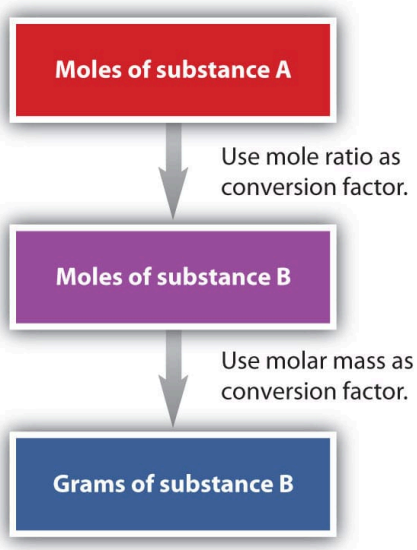
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6.5: Mole-Mass and Mass-Mass Problems

Skills to Develop

- To convert from mass or moles of one substance to mass or moles of another substance in a chemical reaction.

We have established that a balanced chemical equation is balanced in terms of moles as well as atoms or molecules. We have used balanced equations to set up ratios, now in terms of moles of materials, that we can use as conversion factors to answer stoichiometric questions, such as how many moles of substance A react with so many moles of reactant B. We can extend this technique even further. Recall that we can relate a molar amount to a mass amount using molar mass. We can use that ability to answer stoichiometry questions in terms of the masses of a particular substance, in addition to moles. We do this using the following sequence:



Collectively, these conversions are called mole-mass calculations.

As an example, consider the balanced chemical equation

$$Fe_2O_3 + 3SO_3 \rightarrow Fe_2(SO_4)_3 \tag{6.5.1}$$

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 "Mole-Mole Relationships in Chemical Reactions". As usual, we start with the quantity we were given:

$$3.59 \text{ mol } Fe_2O_3 \times \frac{3 \text{ mol } SO_3}{1 \text{ mol } Fe_2O_3} = 10.77 \text{ mol } SO_3 \tag{6.5.2}$$

The mol Fe_2O_3 units cancel, leaving mol SO_3 unit. Now, we take this answer and convert it to grams of SO_3, using the molar mass of SO_3 as the conversion factor:

$$10.77 \text{ mol } SO_3 \times \frac{80.06 \text{ g } SO_3}{1 \text{ mol } SO_3} = 862 \text{ g } SO_3 \tag{6.5.3}$$

Our final answer is expressed to three significant figures. Thus, in a two-step process, we find that 862 g of SO_3 will react with 3.59 mol of Fe_2O_3. Many problems of this type can be answered in this manner.

The same two-step problem can also be worked out in a single line, rather than as two separate steps, as follows:

$$3.59 \text{ mol } Fe_2O_3 \times \underbrace{\frac{3 \text{ mol } SO_3}{1 \text{ mol } Fe_2O_3}}_{\text{converts to moles of } SO_3} \times \underbrace{\frac{80.06 \text{ g } SO_3}{1 \text{ mol } SO_3}}_{\text{converts to grams of } SO_3} = 862 \text{ g } SO_3$$

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?

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O \tag{6.5.4}$$

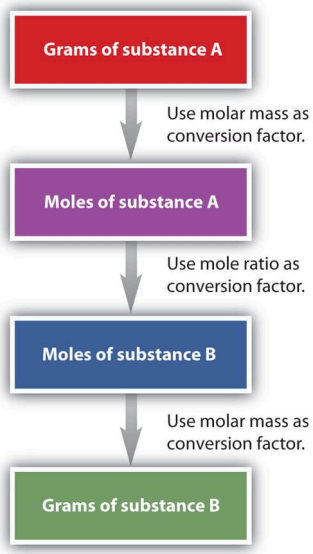
SOLUTION

Our strategy will be to convert from moles of HCl to moles of CO_2 and then from moles of CO_2 to grams of CO_2. We will need the molar mass of CO_2, which is 44.01 g/mol. Performing these two conversions in a single-line gives 46.0 g of CO_2:

$$2.09 \text{ mol HCl} \times \underbrace{\frac{1 \text{ mol } CO_2}{2 \text{ mol HCl}}}_{\text{from the coefficients of the balanced equation}} \times \frac{44.01 \text{ g } CO_2}{1 \text{ mol } CO_2} = 46.0 \text{ g } CO_2$$

The molar ratio between CO_2 and HCl comes from the balanced chemical equation.

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:

$$CH_4 + 4Cl_2 \rightarrow CCl_4 + 4HCl \tag{6.5.5}$$

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 CH_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.

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.

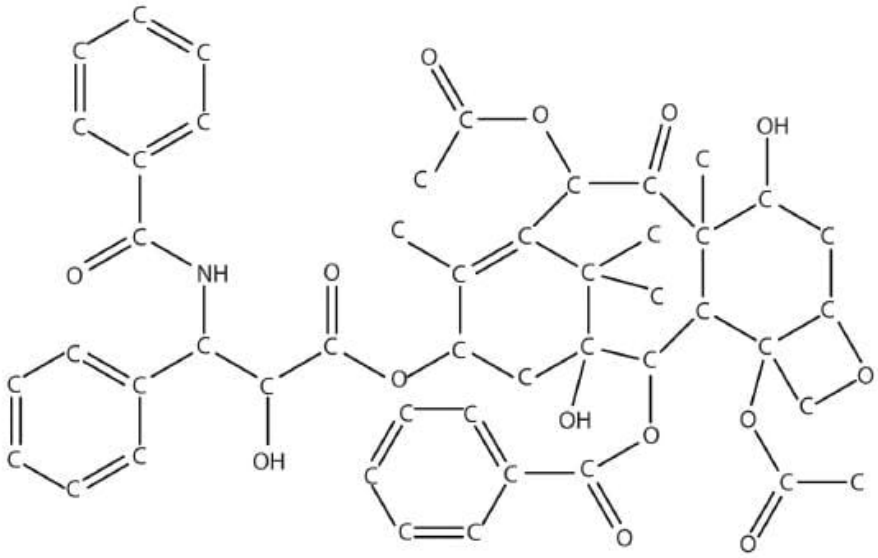


Figure 6.5.1 *The Structure of the Cancer Drug Taxol. Because of the complexity of the molecule, hydrogen atoms are not shown, but they are present on every atom to give the atom the correct number of covalent bonds (four bonds for each carbon atom).*

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

Key Takeaway

- A balanced chemical equation can be used to relate masses or moles of different substances in a reaction.

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. 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 $Ba(NO_3)_2$?

3. 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 two hundred milligram (2.00×10^2 mg) dose of $Mg(OH)_2$ neutralize?

4. 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?

Answers

1. 127 g
2. 23.9 g
3. 0.251 g
4. 1.61×10^8 g

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6.6: Chapter 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). Because not all substances have the same mass, the ratio of coefficients in the balanced equation cannot be used to convert grams of one reactant or product to grams of another --- first, the grams must be converted to moles before using the ratio.

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6.E: Exercise

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. 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) $Ga_2(SO_4)_3$
3. 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?
4. If 6.63×10^{-6} mol of a compound has a mass of 2.151 mg, what is the molar mass of the compound?
5. 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?
6. How many individual hemoglobin molecules are present in 0.034 grams of hemoglobin?
7. Plants cannot use nitrogen in air, N_2, but can use it in other forms like ammonia, NH_3. If 7.0 grams of nitrogen, N_2, completely reacts with hydrogen, H_2, (A) How many moles of H_2 are required? and (B) How many grams of ammonia, NH_3, can be formed? (Hint: You will need a balanced chemical equation.)

Answers

1. 2,330 mol (Or since the original numbers each only have one significant figure, $2x10^3$ mol)
2. 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
3. H = 1.66×10^{-24} g and O = 2.66×10^{-23} g; yes, they are in a 1:16 ratio.
4. 324 g/mol
5. $5.3x10^{-7}$ moles of hemoglobin
6. $3.2x10^{18}$ molecules of hemoglobin
7. (A) 0.75 mol H_2; (B) 8.5 g NH_3

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7: ENERGY AND CHEMICAL PROCESSES

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

7.1: Energy and Its Units

7.2: Heat

7.3: Phase Changes

7.4: Bond Energies and Chemical Reactions

7.5: The Energy of Biochemical Reactions

7.6: Energetics and Kinetics

7.7: Equilibrium

7.8: Chapter Summary

7.E: Exercises

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7.1: Energy and Its Units

Skills to Develop

- To define *energy* and *heat*.

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

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

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

$$1\ cal = 4.184\ J \tag{7.1.1}$$

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

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

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. Proteins and carbohydrates supply 4 kcal/g, while fat supplies 9 kcal/g.

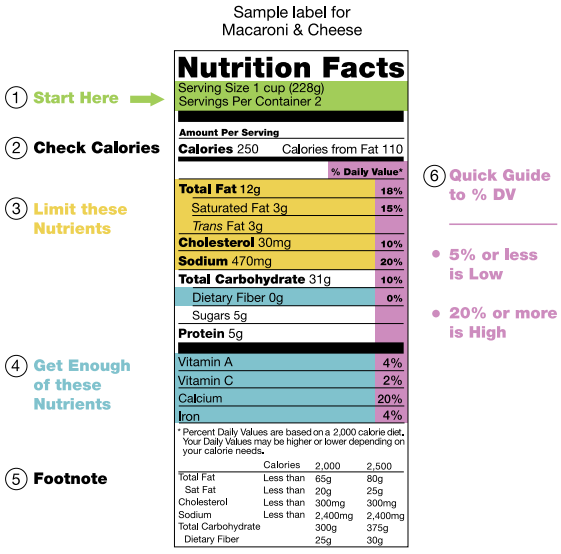


Figure 7.1.1***:*** *Nutritional Energy. A sample nutrition facts label, with instructions from the U.S. Food and Drug Administration.*

Image used with permission from Wikipedia.

Example 7.1.1

The energy content of a single serving of the macaroni and chees above is 250 Cal. What is the energy content in calories? In joules?

Based on the Nutrition Facts above, what are the positives and negatives about this food?

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:

$$250 \text{ Cal} \times \frac{1,000 \text{ cal}}{1 \text{ Cal}} = 250,000 \text{ cal}$$

Then we convert calories into joules

$$250,000 \text{ cal} \times \frac{4.184 \text{ J}}{1 \text{ cal}} = 1,050,000 \text{ J}$$

and then kilojoules

$$1,050,000 \text{ J} \times \frac{1 \text{ kJ}}{1,000 \text{ J}} = 1,050 \text{ kJ}$$

A positive about this macaroni and cheese is that it is high in calcium (20% DV). Negatives might be that a serving has no fiber and is high in sodium (20% DV). Other answers possible (like fat is 18% DV).

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 7.1.1 lists the energy expenditure for a variety of exercises.

Table 7.1.1*: 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.

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 common units of energy and heat.

Exercises

1. Define *energy*.
2. Express 1,265 cal in kilocalories and in joules.
3. Many nutrition experts say that an average person needs 2,000 Cal per day from his or her diet. How many joules is this?
4. 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. 1.265 kcal; 5,293 J
3. 8.4×10^6 J
4. Use 20.0 Cal = 1 oz as a converstion factor: $\frac{1 \text{ oz}}{20.0 \text{ Cal}}$ x 850 Cal = 42.5 oz ≈ 43 oz

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7.2: Heat

Skills to Develop

- To relate heat transfer to temperature change.

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

$$\text{heat} \propto \Delta T \tag{7.2.1}$$

where $\propto$ 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:

$$\text{heat} \propto m\Delta T \tag{7.2.2}$$

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:

$$\text{heat} = mc\Delta T \tag{7.2.3}$$

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°. 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

Substance	c (cal/g•°C)
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 7.2.1

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 heat = $mc\Delta T$ 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:

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 73.3°\text{C} - 25.0°\text{C} = 48.3°\text{C}$$

The mass is given as 150.0 g, and Table 7.3 gives the specific heat of iron as 0.108 cal/g•°C. Substitute the known values into heat = $mc\Delta T$ 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.

Example 7.2.2

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:

$$-71.7\ \text{cal} = (10.3\ \text{g})(c)(-75.5°\text{C})$$

$$c = \frac{-71.7\ \text{cal}}{(10.3\ \text{g})(-75.5^\circ\text{C})}$$

$$c = 0.0923\ \text{cal/g}\bullet°\text{C}$$

This value for specific heat is very close to that given for copper in Table 7.2.1.

Summary

Heat transfer is related to temperature change.

Concept Review Exercise

1. Describe the relationship between heat transfer and the temperature change of an object.

Answer

1. Heat is equal to the product of the mass, the change in temperature, and a proportionality constant called the specific heat.

Exercises

1. A pot of water is set on a hot burner of a stove. What is the direction of heat flow?
2. How much energy in calories is required to heat 150 g of liquid H_2O from 0°C to 100°C? (Use Table 7.2.1)

3. If 250.0 cal of heat were added to 43.8 g of Al at 22.5°C, what is the final temperature of the aluminum? (Hint: Use Table 7.2.1 and first find temperature change, ΔT.)

4. 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? (Use Table 7.2.1)

5. 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?

6. Determine the heat capacity of a substance if 23.6 g of the substance loses 199 cal of heat when its temperature changes from 37.9°C to 20.9°C. *(Hint: If it "loses" heat, what is the sign of heat, positive or negative? If the temperature is going down, what is the sign for temperature change, $\Delta T = T_f - T_i$? The sign of heat capacity should always be positive.)*

Answers

1. Heat flows from the flame of the burner into the pot of water. (i.e. The flame loses/emits/gives off heat and the water gains/absorbs/takes in heat.)
2. 15,000 cal
3. 49.0°C
4. 404 g
5. Mercury would experience the largest temperature change.
6. 0.496 cal/g•°C; *C = heat / [m ΔT] = -199 cal / [(23.6 g)(-17.0 ^{0}C)]* = 0.496 cal/g•°C

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7.3: Phase Changes

Skills to Develop

- The Learning Objective of this Module is to determine the heat associated with a phase change.

Depending on the surrounding conditions, normal matter usually exists as one of three *phases*: solid, liquid, or gas.

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 7.3.1*: The Boiling Point of Water. Nucleate boiling of water over a kitchen stove burner. Image used with permission from Wikipedia.*

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, 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.

Enthalpy, H, is a quantity that is similar to energy and has the same units. The change in enthalpy (ΔH) is equal to the amount of heat gained when pressure is constant, so enthalpy change and heat are often used interchangeably.

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. The associated values for enthalpy change and heat are positive if heat is gained.

$$\text{solid} \rightarrow \text{liquid (positive heat of fusion)} \tag{7.3.5}$$

$$\text{liquid} \rightarrow \text{gas (positive heat of vaporization)} \tag{7.3.6}$$

If heat transfers out, liquids solidify, and gases condense into liquids. The values of enthalpy change and heat will be negative for the reverse directions.

$$\text{liquid} \rightarrow \text{solid (negative heat of fusion)} \tag{7.3.7}$$

$$\text{gas} \rightarrow \text{liquid (negative heat of vaporization)} \tag{7.3.8}$$

Example 7.3.1

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 (Eq. 7.3.1b) to determine how many joules of heat are needed to melt this ice:

$$\text{heat} = m \times \Delta H_{fus}$$

$$\text{heat} = (55.8 \cancel{\text{g}}) \left(\frac{79.9 \text{ cal}}{\cancel{\text{g}}} \right) = 4,460 \text{ cal}$$

Example 7.3.2

Determine the heat associated when 5.00 grams of liquid water at 99.5°C are placed in a freezer until becoming ice (solid H_2O) at -13.5°C? Use 1440 cal/mol as the heat of fusion of H_2O, plus specific heats of 1.00 cal/g°C for liquid and 0.502 cal/g°C for solid.

SOLUTION

We can use heat = mcΔT to find the heat to bring the liquid from 99.5°C to 0°C. Heat = (5.00g)(1.00 cal/g°C)(-99.5°C) = **-498 cal**

We can use heat = $n \times \Delta H_{fus}$ to determine how many calories of heat must be removed to freeze the ice.

The molar mass of water is 16.0+1.0+1.0 = 18.0 g/mol. (5.00 g)/(18.0 g/mol) = 0.278 moles

Heat = (0.278 mol)(-1440 cal/mol) = **-400. cal** *(Note that heat must be removed to freeze, so the value is negative.)*

We can use heat = mcΔT to find the heat to bring the solid from 0°C to -13.5°C. Heat = (5.00g)(0.502 cal/g°C)(-13.5°C) = **-34.0 cal**

The sum of these values is -932 cal. The water LOST 932 calories of heat.

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

Looking Closer: Sublimation

There is also a phase change where a solid goes directly to a gas:

$$\text{solid} \rightarrow \text{gas} \tag{7.3.9}$$

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:

$$CO_2(s) \xrightarrow{-78.5^\circ C} CO_2(g) \tag{7.3.10}$$

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.

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?

Answers

1. The energy goes into changing the phase, not the temperature.
2. The amount of heat is a constant per gram of substance.

Key Takeaway

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

Exercises

1. How much energy is given off if 43.8 g of liquid gold, Au, solidifies at its melting point of 1,064°C? (You will need one of the values from Table 7.3.1.) Is this energy change a positive or negative value?
2. What mass of ice can be melted by 558 cal of energy? (You will need one of the values from Table 7.3.1.)
3. 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.
4. 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?
5. What is the heat of vaporization of gold in kilocalories per mole? *(Start with the appropriate value in Table* $7.3.1$*, then convert the units)*

Answers

1. 670. calories are given off (released) when liquid turns to solid (exothermic), which means the change in energy is – 670. cal
2. 6.98 g
3. 8,930 J/g
4. 12.0 g
5. 80.6 kcal/mol

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7.4: Bond Energies and Chemical Reactions

Skills to Develop

The Learning Objectives of this Module are to:

- Define *bond energy*.
- 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.

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. 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. 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. Table 7.4.1 lists the approximate bond energies of various covalent bonds.

Table 7.4.1***:*** *Approximate Bond Energies*

Bond	Bond Energy (kcal/mol)
C–H	100
C–O	86
C=O	190
C–N	70
C–C	85
C=C	145
C≡C	200
N–H	93

Bond	Bond Energy (kcal/mol)
H–H	105

When a chemical reaction occurs, the atoms in the reactants rearrange their chemical bonds to make products. The new arrangement of bonds almost never has the same total energy as the bonds in the reactants. Therefore, when chemical reactions occur, *there will almost always be an accompanying energy change*.

In some reactions, the energy of the products is lower than the energy of the reactants. Thus, in the course of the reaction, the substances lose energy to the surrounding environment. Such reactions are exothermic and can be represented by an *energy-level diagram* like the one in Figure 7.4.1. In most cases, the energy is given off as heat (although a few reactions give off energy as light).

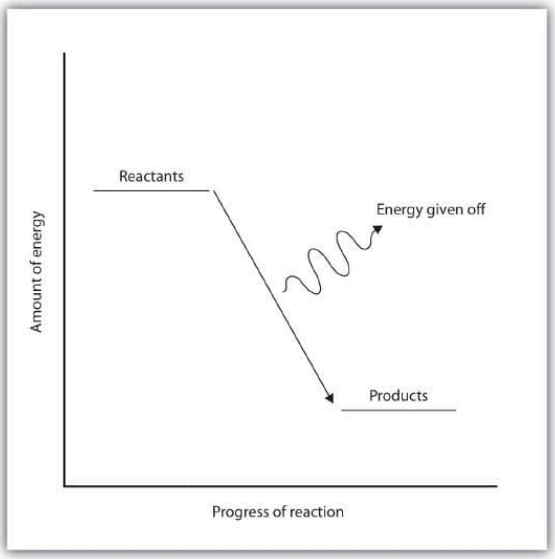


Figure 7.4.1*: Exothermic Reactions. For an exothermic chemical reaction, energy is given off as reactants are converted to products.*

In chemical reactions where the products have a higher energy than the reactants, the reactants must absorb energy from their environment to react. These reactions are endothermic and can be represented by an energy-level diagram like the one shown in Figure 7.4.2.

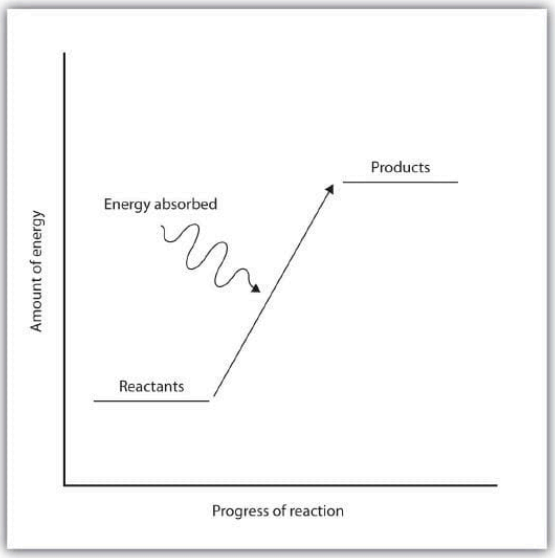


Figure 7.4.2***:*** *Endothermic Reactions. For an endothermic chemical reaction, energy is absorbed as reactants are converted to products.*

Exothermic and endothermic reactions can be thought of as having energy as either a product of the reaction or a reactant. Exothermic reactions give off energy, so energy is a product. Endothermic reactions require energy, so energy is a reactant.

Heat can also be expressed and the change in enthalpy, Δ*H*. If heat is being lost, the change is negative. If heat is gained, the change is positive. Note that the change is energy, change in enthalpy, and heat are typically similar enough that we will treat them all the same (and use those terms interchangeably).

The exothermic combustion of glucose can be expressed with the heat as a product.

$$C_6H_{12}O_{6(s)} + 6O_{2(g)} \rightarrow 6CO_{2(g)} + 6H_2O_{(\ell)} + 670 \text{ kcal} \tag{7.4.1}$$

Or the equation could be given with an accompanying enthalpy change.

$$\Delta H = -670 \text{ kcal/mol for the reaction,}$$
$$C_6H_{12}O_{6(s)} + 6O_{2(g)} \rightarrow 6CO_{2(g)} + 6H_2O_{(\ell)} \tag{7.4.2}$$

Example 7.4.1

Is each chemical reaction exothermic or endothermic?

a. $2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell) + 135$ kcal
b. $N_2(g) + O_2(g) + 45$ kcal $\rightarrow 2NO(g)$
c. $2C(s) + H_2(g) \rightarrow C_2H_2(g)$; $\Delta H = 22$ kJ/mol

SOLUTION

a. Because energy is a product, energy is given off by the reaction. Therefore, this reaction is exothermic.
b. Because energy is a reactant, energy is absorbed by the reaction. Therefore, this reaction is endothermic.
c. Because the enthalpy change is positive, heat is absorbed by the reaction. Therefore, this reaction is endothermic.

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?

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.

Key Takeaways

- Atoms are held together by a certain amount of energy called bond energy.
- Chemical processes are labeled as exothermic or endothermic based on whether they give off or absorb energy, respectively.

Exercises

1. Using the Table of Approximate Bond Energies from earlier in this section, calculate the energy of one C–H bond (as opposed to 1 mol of C–H bonds). Remember that 1 mole = 6.022×10^{23} things (and the "things" are bonds here).
2. Is a bond-making process exothermic or endothermic?
3. Is each chemical reaction exothermic or endothermic?
   a. $2SnCl_2(s) + 33 \text{ kcal} \rightarrow Sn(s) + SnCl_4(s)$
   b. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell) + 213 \text{ kcal}$
   c. The enthalpy change for the reaction, $H_2(g) + F_2(g) \rightarrow 2HF(g)$, is $\Delta H = -130$ kcal.

Answers

1. 1.661×10^{-22} kcal or 1.661×10^{-19} cal

2. exothermic

3. a. endothermic; b. exothermic; c. exothermic

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7.5: The Energy of Biochemical Reactions

Skills to Develop

- The Learning Objective of this Module is to relate the concept of energy change to chemical reactions that occur in the body.

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

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

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

$$C_6H_{12}O_{6(s)} + 6O_{2(g)} \rightarrow 6CO_{2(g)} + 6H_2O_{(\ell)} + 670 \text{ kcal} \tag{7.5.1}$$

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.

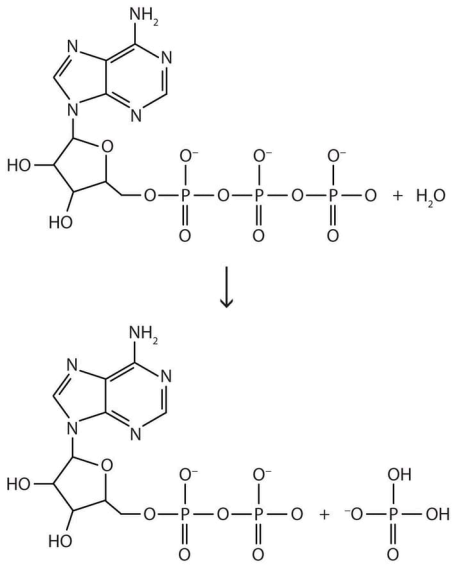


Figure 7.5.1***:*** *ATP to ADP. The conversion of ATP (top) to ADP (bottom) provides energy for the cells of the body.*

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.

Concept Review Exercise

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

Answer

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

Key Takeaway

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

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. 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?
3. 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 one mole of glucose (Equation 7.5.1).
4. The overall reaction shown in Equation 7.5.1 takes place in many steps in the metabolism. If it were to occur all at once, what type of reaction would it be? (Hint: See the Chapter 5 Summary to see a list of the reaction types.)

Answers

1. 156 kcal
2. exothermic (The metabolic reaction in our bodies give off heat, increasing our body temperature.)
3. 89 mol
4. Combustion (also redox)

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7.6: Energetics and Kinetics

Skills to Develop

- The Learning Objective of this Module is to review how energy changes can effect the direction (how far) and rate (how fast) of chemical reactions.

Energetics (Thermodynamics)

In chemistry, thermodynamics (from the Greek roots for heat and force, power, or energy) is the field that studies the energetics of chemical reactions. There are several different energy-related quantities. Section 7.1 discussed that energy, work, and heat are inter-related and share the same units (e.g. calories or joules). Enthalpy, H, and Gibbs free energy, G, can also be expressed in those same energy units. The change in enthalpy is usually equal to the amount of heat gained or lost, so those two are often used interchangeably. Thermodynamics can tell us both if a reaction is likely to proceed and how far it is likely to go.

A system that is lower in energy is considered more stable. A ball at the top of a ramp is higher-energy (less stable), whereas that ball on the floor is lower-energy (more stable). A system will tend to move from higher to lower energy to become more stable --- the ball will spontaneously roll down the ramp.

The degree disorder or randomness, often called entropy, S, can also affect chemical reactions. A process is more likely to take place of everything becomes more disordered. For example, in a game of Yatzee, the odds of getting all five dice with the same number --- all ones, all twos, all threes, all fours, all fives, or all sixes --- in one roll is 6 out of 46 656 (very low). The odds that the roll will be less ordered (not five of a kind) will be the remaining 46 650 out of 46 656 (very high). There are just more ways to be random, so you are more likely to end up that way.

Gibbs free energy takes into account enthalpy (heat), temperature, and entropy (randomness). Because it takes into account more factors, the change is Gibbs free energy is the best for predicting which way a reaction will go and how far. A reaction will take place spontaneously from left to right (reactants to products) if the Gibbs free energy change is negative (going down in energy to become more stable). The more negative the change, the further the reaction will go. If the Gibbs free energy change is positive (going up in energy to become less stable), it will not take place spontaneously; instead it will go backward. Sometimes it is difficult to determine the change in Gibbs free energy, so we often use things like enthalpy change, or even the term “energy change” in a general sense instead.

A reaction energy diagram can summarize the energetics taking place. These diagrams show some type of energy on the vertical axis --- higher up is higher in energy. They show reaction progress, or time, on the horizontal axis --- further to the right means the reaction has gone further, or more time.

Figure 7.6.1 below shows a reaction in which the reactants are higher in energy and the products are lower in energy. If looking at energy (E) or enthalpy (H), the reaction would be described as “exothermic” because it would give off (lose or emit) heat. Reactions with negative changes in energy or enthalpy are more likely to be spontaneous. If examining Gibbs free energy, the reaction would be described instead as “exergonic” and would spontaneously proceed to the right (favors products).

Figure 7.6.1 – Exothermic (or exergonic) Reaction Energy Diagram

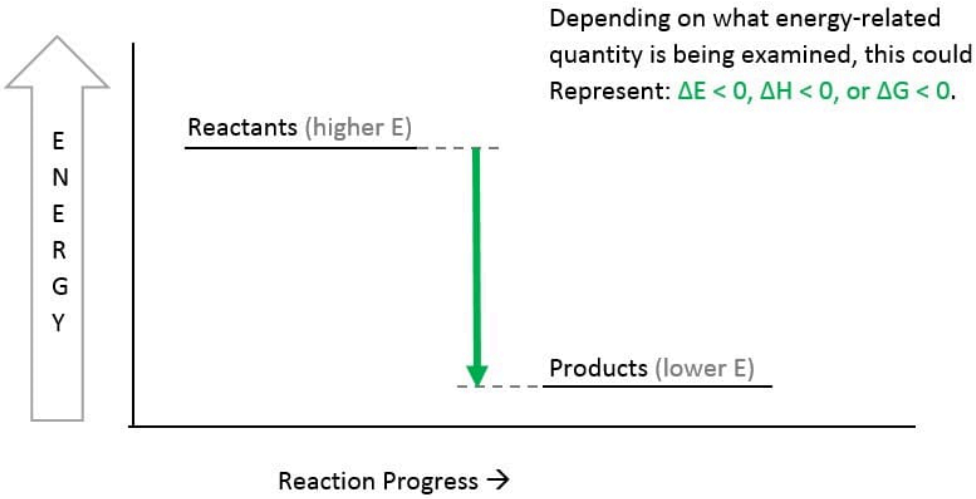
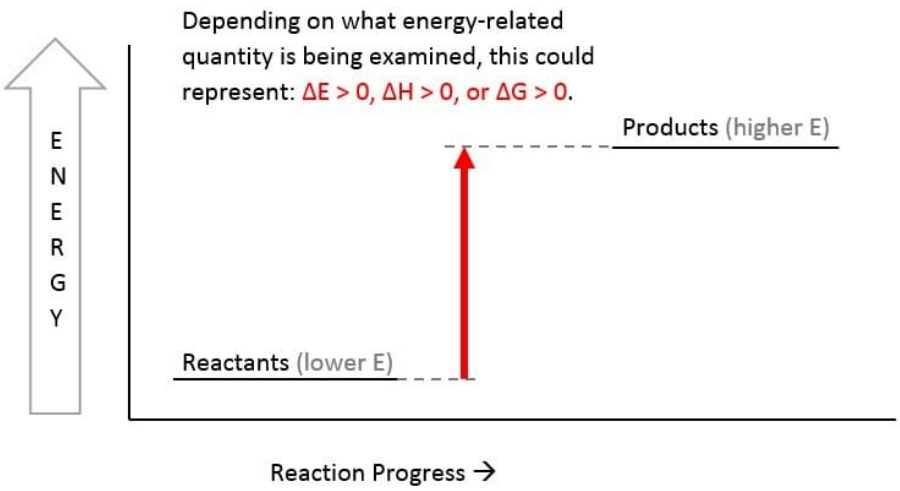


Figure 7.6.2 below shows a reaction in which the reactants are lower in energy and the product are higher in energy. If looking at energy (E) or enthalpy (H), the reaction would be described as “endothermic” because it would take in (gain or absorb) heat. Reactions with positive changes is energy or enthalpy are less likely to be spontaneous. If examining Gibbs free energy, the reaction would be described instead as “endergonic” and would not spontaneously proceed to the right; instead it would spontaneously proceed in reverse to the left (favors reactants).

Figure 7.6.2 – Endothermic (or Endergonic) Reaction Energy Diagram



Kinetics

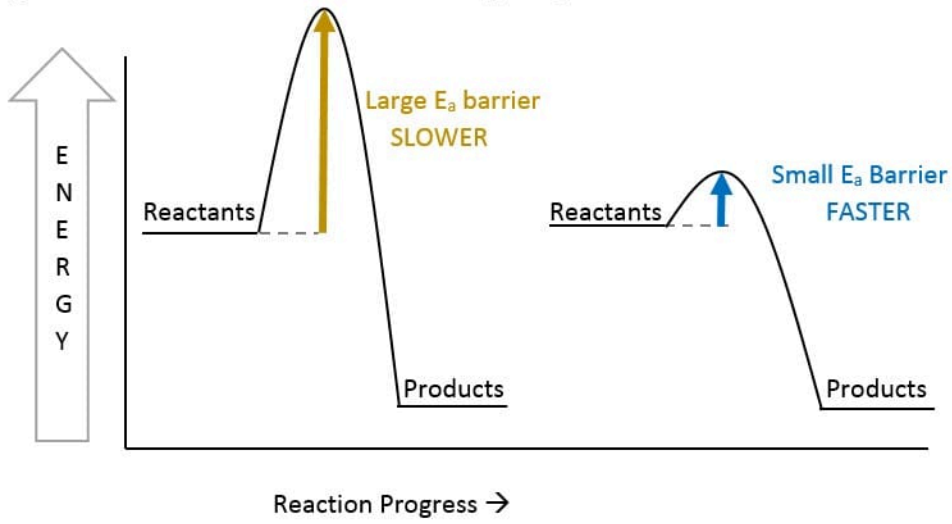
The energetics (or thermodynamics) tell us if a reaction is likely to proceed and how far. Another important factor to consider is how FAST a reaction will go, also called KINETICS.

Two common forms of carbon are diamond and graphite. Diamond is less stable and, under normal conditions, is spontaneously being converted to the more stable graphite form. However, you do not need to rush out and sell your diamond jewelry. This reaction is terribly slow and will not take place in your lifetime. There is a barrier to getting a reaction started called the activation energy. Before the new bonds can form, some of the old bonds must be broken. (This is also why a spark is required to start a flame.) If the reaction energy barrier is larger, the reaction will be slower.

In Figure 7.6.3 below, the reaction energy diagram on the left has a larger activation energy barrier and would be slower. The

smaller activation energy shown on the right would have a faster rate of reaction.

Figure 7.6.3 – Fast and Slow Reaction Energy Diagrams



Activation energy also incorporates other factors that we are not discussing here. Nonetheless, it can help us understand other phenomena. Several things can increase the rate of a reaction. Here, we will look at three factors that can help reactants get over the activation energy barrier faster: temperature, concentration, and catalysts.

You likely know that food cooks faster at higher temperature. In general, reactions proceed at higher rate at higher temperature. Temperature is proportional to average kinetic energy, or how fast the reactants are moving. At higher temperatures, more of the reactants have enough energy to climb the activation energy barrier and thus can proceed to products faster.

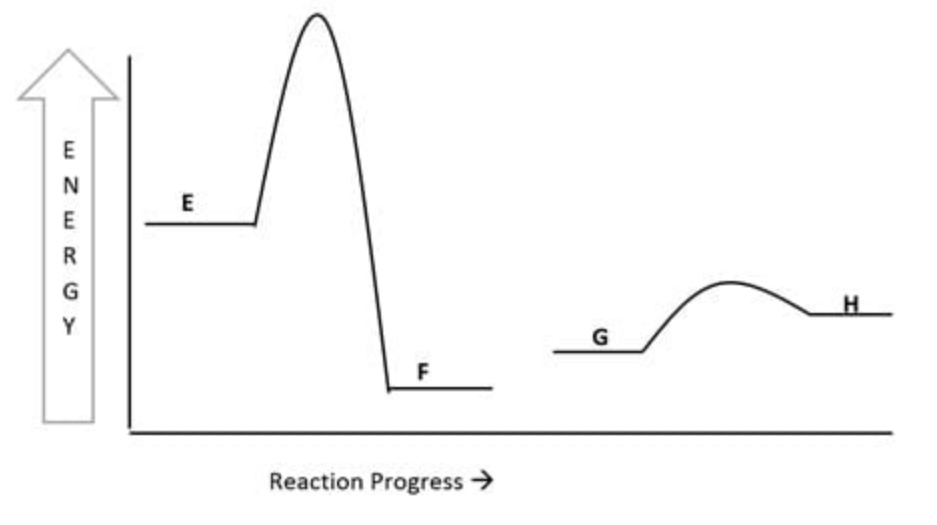
Another way to increase the rate of a reaction is by increasing concentration of the reactants. Most reactions require the reactants to collide before they become products. If the concentration of reactants is higher, they are more crowded and thus collide more frequently. It was not mentioned in the previous paragraph but, at higher temperatures, faster-moving reactants also collide more frequently.

Catalysts are substances that speed up a reaction without being used up themselves. Because a catalyst is not consumed in a reaction, only a small amount is required. Catalysts make a reaction faster by lowering the activation energy barrier for the reaction. Instead of climbing the highest peak, a catalyst provide an easier pathway to the other side. If the two reaction energy diagrams shown previously in Figure 7.6.3 were the same reaction, the diagram on the left might represent the reaction without a catalyst. The diagram on the right might represent the same reaction, but in the presence of a catalyst (and with a lower energy of activation).

Example 7.6.1

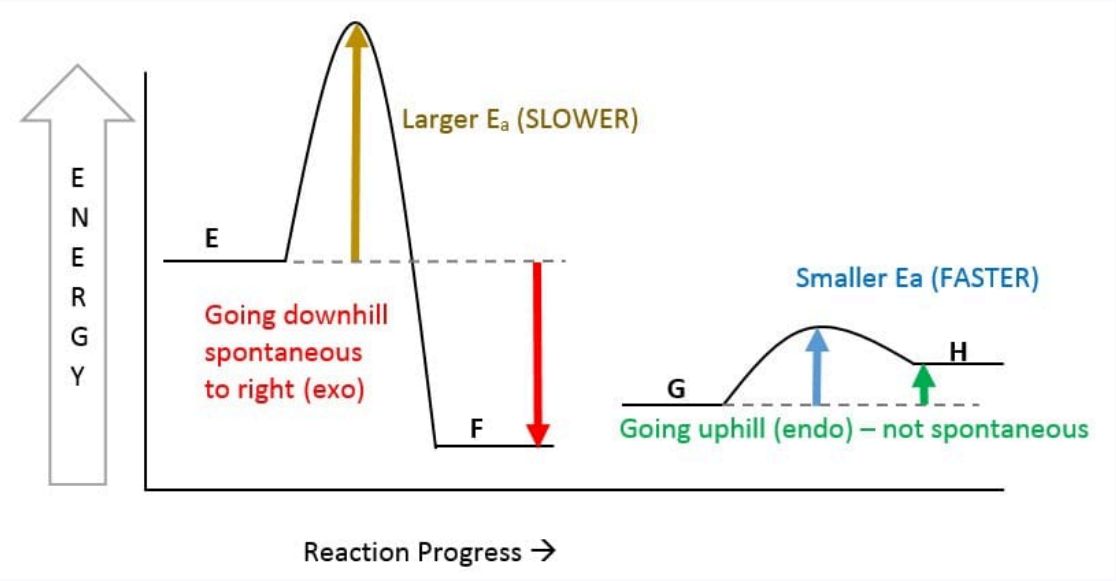
(A) Which of the two reaction energy diagrams shown below is more likely to proceed to products?

(B) Which of the two reaction energy diagrams shown would be the fastest?



SOLUTION

A. The reaction, E --> F, is more likely to proceed to products. The products are more stable (exothermic or exergonic).
B. The reaction, G --> H, would be faster. It has a smaller activation energy barrier.



Concept Review Exercise

1. What word is used to describe a reaction with (a) positive enthalpy change or with (b) positive gibbs free energy change?
2. What quantity determines the rate of reaction?

Answer

1. (a) $\Delta H > 0$ is endothermic; (b) $\Delta G > 0$ is endergonic
2. Activation energy, E_a

Key Takeaway

- Reactions are more likely to proceed spontaneously if the products are more stable (negative ΔE, ΔH, ΔG).
- The reaction rate will be faster if it has a lower activation energy barrier (E_a).

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7.7: Equilibrium

Skills to Develop

- The Learning Objective of this Module is to establish that chemical reactions are reversible and to relate equilibrium constant to energy change.

Chemical Equilibrium

When first looking at chemical reactions, we typically say that reactants form products (proceed from left to right). Once products are present, however, they can go back to reactants. Reactions that go a significant amount in both directions are sometimes called *reversible*.

$$\text{Reactants} \rightarrow \text{Products } \textit{and/or } \text{Reactants} \leftarrow \text{Products}$$

Eventually, there is a balance between the two opposing processes, and no additional change occurs. The reversible chemical reaction is better represented at this point with a double arrow:

$$\text{Reactants} \rightleftharpoons \text{Products}$$

When the forward and reverse reactions are occurring at equal rate, their effects cancel each other out. A process at this point is considered to be at chemical equilibrium (or equilibrium). While the amounts of reactants and products seems to be unchanging, 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*. Imagine 20 people in a room and every time one person leaves, another person enters; even though there is movement, the number of people stays constant.

If the reaction is faster to the right, the concentration of products (on the right) will be larger at equilibrium. If the reaction is faster to the left, there will be a higher concentration of reactants (on the left) at equilibrium. If neither direction is faster, the concentrations will be roughly equal at equilibrium. The ratio of products to reactants at equilibrium is called the *equilibrium constant*, K.

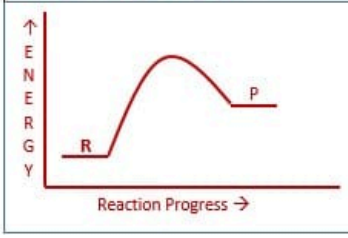
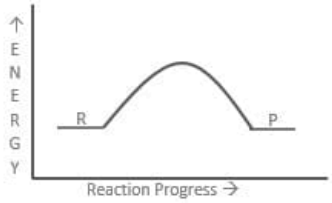
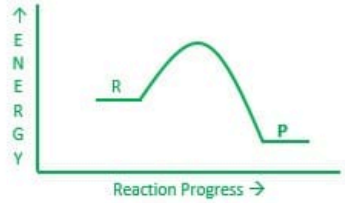
The equilibrium constant expression always has products on top and reactants on bottom. The amounts of each are usually expressed as either concentrations, [brackets], or as pressures, P, if gases. (Note: We are simplifying this by assuming only one reactant and one product. The expression is typically more complicated.)

$$K = \frac{[\text{products}]}{[\text{reactants}]} \qquad \textit{or} \qquad K = \frac{P_{\text{products}}}{P_{\text{reactants}}}$$

A K-value that is close to one will result in roughly equal amounts of reactants and products at equilibrium. Large K-values favor products and small K-values favor reactants. Thus equilibrium constants indicate *how far* a reaction will go to the right or left. This should sound familiar. Remember that energy, in particular Gibbs free energy (G), also indicates how far a reaction will go. While we will not do the calculations, K can be calculated from ΔG and temperature. Figure 7.7.1

below summarizes the relationship.

Figure 7.7.1 - The Relationship Between Reaction, Energy, and Equilibrium

Reaction goes far LEFT	Neither side favored	Reaction goes far RIGHT
REACTANTS ⇌ products	Reactants ⇌ Products	reactants ⇌ PRODUCTS
$\Delta G > 0$ (positive, endergonic) Reactants lower-energy (more stable)	$\Delta G \approx 0$ (close to zero) Both about the same energy and stability	$\Delta G < 0$ (negative, exergonic) Products lower-energy (more stable)
$K << 1$ (much smaller than one) Much higher concentration of REACTANTS at equilibrium	$K \approx 1$ (close to one) Significant amounts of both reactants and products present at equilibrium	$K >> 1$ (much larger than one) Much higher concentration of PRODUCTS at equilibrium
		

Concept Review Exercise

1. What can be determined about the equilibrium constant and direction of a reaction if it has a negative Gibbs free energy change (exergonic)?

Answer

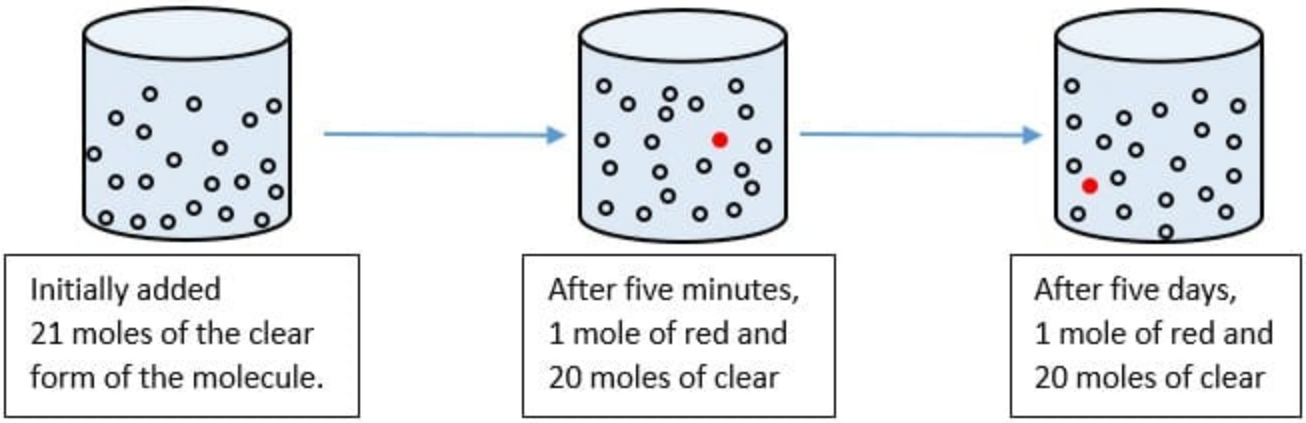
1. The reaction is likely to favor products and the equilibrium constant will be large.

Key Takeaway

- Many reactions are reversible and exist in equilibrium.
- The equilibrium constant is the ratio of the concentration of products over concentration of reactants.

Exercises

1. A particular molecule converts between clear and red forms in an equilibrium reaction, clear ⇌ red. In the images below, each clear dot represents one mole of the molecules in clear form and each red colored dot represents one mole of the molecules in the red form (always in a constant one-liter volume). If the reaction takes place as shown below (starting with 21 moles clear, then ending with 20 moles clear and 1 mole red at equilibrium), what is the value of the equilibrium constant? Is this reaction endergonic or exergonic?



2. What would exist in the container at equilibrium if 42 moles of the clear form of the molecule were added initially? (Same reaction and conditions as above.)
3. What would exist in the container at equilibrium if 21 moles of the RED form of the molecule were added initially? (Same reaction and conditions as above.)

Answers

1. K = [products] / [reactants] = [red] / [clear] = [1] / [20] = 0.05

   A small K value (0.05 < 1) indicates that the reaction is endergonic (positive ΔG).

2. At equilibrium, there would be 2 moles of the red form and 40 moles of the clear form (to keep the same ratio). K = [red] / [clear] = [2] / [40] = 0.05

3. At equilibrium, there would be 1 moles of the red form and 20 moles of the clear form (to keep the same ratio). K = [red] / [clear] = [1] / [20] = 0.05

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7.8: Chapter 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.

We often use the generic term "energy" but heat, work, enthalpy (H), and Gibbs free energy (G) are related and have the same units. Reactions with negative changes in energy (going down) are more likely proceed spontaneously to products. The speed of reactions (kinetics) is determined by the height of the **activation energy** barrier between reactants and products. Larger activation energies result in slower rates of reaction. Reaction rate can be increased with higher temperature, higher concentration of reactants, or presence of a catalyst.

Reactions can go both forward and backward in a process called equilibrium. The **equilibrium constant**, K, gives the ratio of products to reactants that will exist when the forward and reverse rates are equal. A large value for equilibrium constant (K >> 1) indicates that the reaction goes far to the right before reaching equilibrium, and thus favors products. Equilibrium and energy change are related. Reactions with large K-values are exergonic ($\Delta G < 0$).

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7.E: Exercises

Additional Exercises

1. Ammonia (NH_3) is made by the direct combination of H_2 and N_2 gases according to this reaction:

   $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) + 22.0$ 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?

2. A 5.69 g sample of iron metal was heated in boiling water, then dropped into a beaker containing 100.0 g of H_2O at 22.6°C, both reaching a final temperature of 23.1°C. Assuming that the water gained all the heat lost by the iron, what is the temperature change for the iron? (Hint: You will first need to find the heats.)

3. (A) When 1 g of steam condenses, how much energy (heat) is released. (B) How many grams of ice can be melted with this amount of heat? (Hint: You will need the heats of vaporization and fusion for water.)

4. The change in energy is +65.3 kJ for each mole of calcium hydroxide [$Ca(OH)_2$] according to the following reaction:

   $Ca(OH)_2(s) \rightarrow CaO(s) + H_2O(g)$

   If 652 grams of $Ca(OH)_2$ react, calculate the amount of heat absorbed.

5. The volume of the world's oceans is approximately 1.3×10^{24} cm^3.

   (A) How much heat energy would be needed to increase the temperature of the world's oceans by 1°C? Assume that, for the oceans, the heat capacity is 4.2 J/g^0C and the density is 1.0 g/mL. (B) If Earth receives 6×10^{22} J of heat energy per day from the sun, how much could the ocean be warmed by the sun in one day (temperature change), assuming all the energy went into warming the water?

6. Section 7.5 indicates that the conversion of ATP to ADP gives off about 7.5 kcal/mol. (A) What is the sign of that change, and is that process exothermic or endothermic? (B) What would be the value of ΔH if the reaction is reversed? (C) What is the maximum number of ADP that could be converted to ATP using the energy of oxidation of glucose, Reaction 7.5.1?

7. The molecule borneol can rearrange to a different form called isoborneol in a process called isomerization. A container initially contains only borneol gas at a pressure of 553 torr. At equilibrium, the pressure of borneol is 500.0 torr and the pressure of isoborneol is 53.0 torr. (A) Calculate the value of the equilibrium constant for the reaction, borneol $\Leftrightarrow$ isoborneol. (B) Is the isomerization reaction exergonic or endergonic? (C) Which is more stable at this temperature, borneol or isoborneol?

Answers

1. (A) Exothermic; (B) –1200 kcal
2. ΔT = 80°C (for iron), rounded to one significant figure based on the water temperature change
3. (A) 540 cal; (B) 6.76 g
4. 575 kJ
5. (A) 5.5×10^{24} J to increase 1 ^0C; (B) ΔT = 0.01 °C; the heat from the sun per day is about a hundred times less than what is required to change the oceans by 1 ^0C.
6. (A) Negative because "gives off" so ΔH = - 7.5 kcal/mol, exothermic. (B) ΔH = + 7.5 kcal/mol, endothermic (C) (670 kcal/mol) / (7.5 kcal/mol) = 89.3, so the maximum number would be eighty nine.
7. (A) K = (pressure of product) / (pressure of reactant) = (P isoborneol) / (P borneol) = (53.0) / (500.0) = 0.106; (B) Small equilibrium constant (K < 1) means endergonic ($\Delta G > 0$); (C) Positive energy change means the product is higher-energy, so

the reactant (borneol) is lower-energy and more stable.

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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 picture on this page shows the substance we are probably most familiar with as having those three phases: water. In everyday life, we commonly come in contact with water as a solid (ice), as a liquid, and as a gas (steam). All we have to do is change the conditions of the substance—typically temperature—and we can change the phase from solid to liquid to gas and back again. Under the proper conditions of temperature and pressure, many substances—not only water—can experience the three different phases. An understanding of the phases of matter is important for our understanding of all matter. In this chapter, we will explore the three phases of matter.

8.1: Intermolecular Interactions

8.2: Solids and Liquids

8.3 Gases and Pressure

8.4: Gas Laws

8.5: Chapter Summary

8.E: Exercises

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8.1: Intermolecular Interactions

Skills to Develop

- 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. 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 interactions between the particles of substances. (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.

Covalent Network Substances

Substances with the highest melting and boiling points have covalent network bonding. This substances are held together by covalent bonds. In these substances, all the atoms in a sample are covalently bonded to other atoms. In effect, the entire sample

is essentially one large molecule so the term intermolecular (or between molecules) is often not used for these interactions (since there are not multiple, discreet molecules). 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 8.1.1), which is a form of pure carbon. At temperatures over 3,500°C, diamond finally vaporizes into gas-phase atoms.

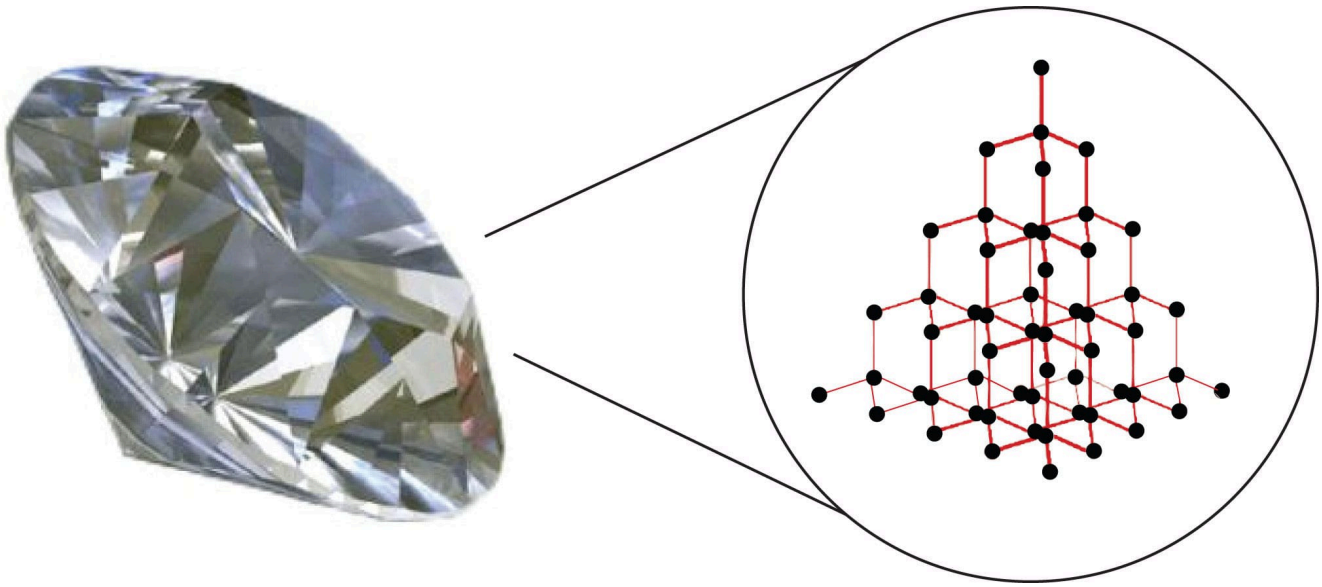


Figure 8.1.1*: Diamond. Diamond, a form of pure carbon, has covalent network bonding. It takes a very high temperature—over 3,500°C—for diamond to leave the solid state. Source: Photo © Thinkstock*

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. While not ions are not technically molecules, ionic interactions between particles are usually classified as a 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 8.1.2) is an example of a substance whose particles experience ionic interactions (Table 8.1.1).

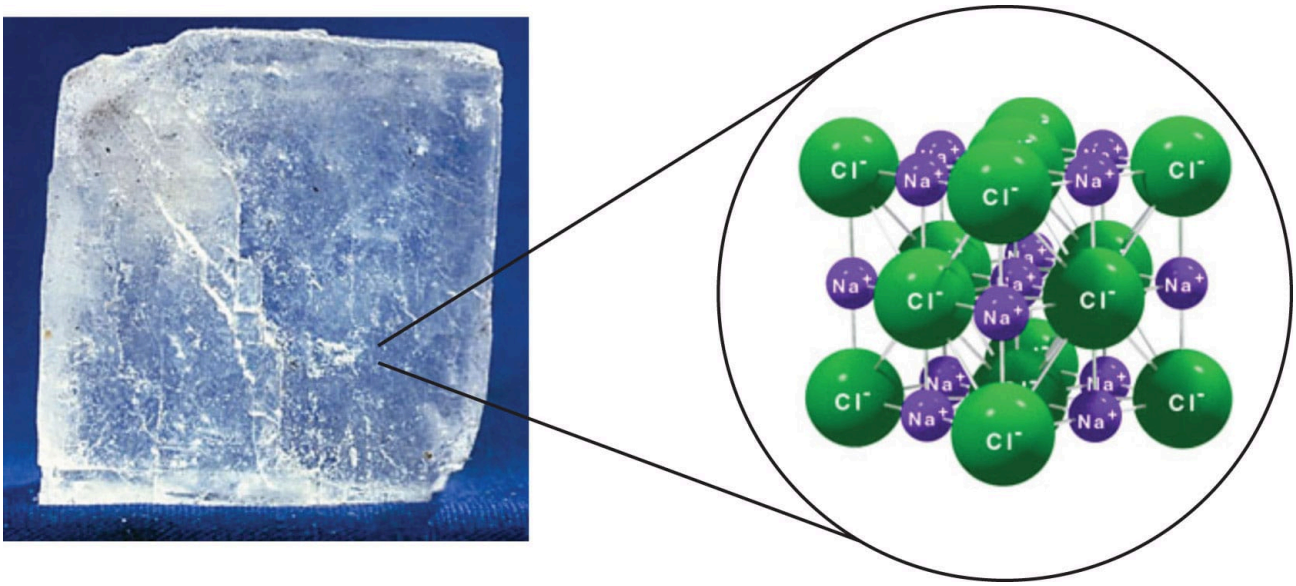


Figure 8.1.2***:*** *Sodium Chloride. Solid NaCl is held together by ionic interactions. Source: Photo © Thinkstock*

Covalent Compounds (also called Molecular Compounds)

Many substances that experience covalent bonding exist as discrete molecules. Very strong covalent bonds within the molecule hold the atoms together to make each molecule. It is not, however, covalent bonds that are responsible for bringing the separate molecules together to make liquids and solids. Instead, there are three types of intermolecular interactions that exist between molecules that hold liquids and solids together. All thee types result from the attractions between partial opposite charges and are weaker than covalent or ionic bonds.

In many molecules, the electrons that are shared in a covalent bond are not shared equally among the two atoms in the bond. Typically, one of the atoms attracts the electrons more strongly than the other, leading to an unequal sharing of electrons in the bond. This idea is illustrated in Figure 8.1.3, which shows a diagram of the covalent bond in hydrogen fluoride (HF). The fluorine atom attracts the electrons in the bond more than the hydrogen atom does. An arrow is often used to show in which direction the electrons are pulled. The result is an unequal distribution of electrons in the bond, favoring the fluorine side of the covalent bond. Because of this unequal distribution, the fluorine side of the covalent bond actually takes on a partial negative charge (indicated by the δ– in Figure 8.1.3), while the hydrogen side of the bond, being electron deficient, takes on a partial positive charge (indicated by the δ+ in Figure 8.1.3). A 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.

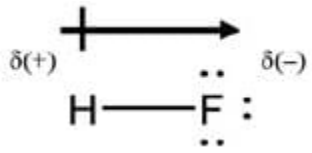


Figure 8.1.3***:*** *Polar Covalent Bonds. The electrons in the HF molecule are not equally shared by the two atoms in the bond. Because the fluorine atom has nine protons in its nucleus, it attracts the negatively charged electrons in the bond more than the hydrogen atom does with its one proton in 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. These types of intermolecular interactions are called a dipole-dipole forces. Many molecules with polar covalent bonds experience dipole-dipole forces. The covalent bonds in some molecules are oriented in space symmetrically so that the bonds in the molecules cancel each other out. The individual bonds are polar, but the overall molecule is not polar; rather, the molecule is *nonpolar* due to its overall symmetry. Such molecules experience little or no dipole-dipole interactions. Carbon dioxide (CO_2) and carbon tetrachloride (CCl_4) are examples of such molecules (Figure 8.1.4).

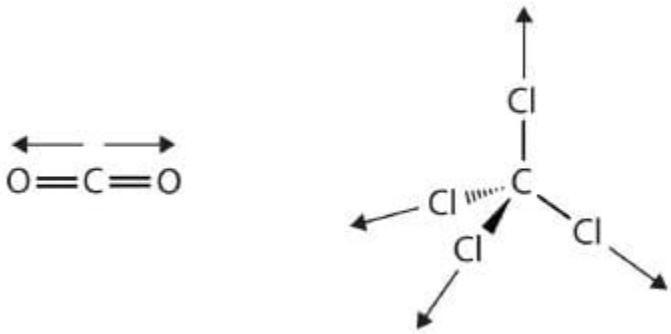


Figure 8.1.4***:*** *Nonpolar Molecules. Although the individual bonds in both CO_2 and CCl_4 are polar, their effects cancel out because of the symmetrical distribution of the bonds in each molecule. As a result, such molecules experience little or no dipole-dipole interaction.*

The H–F, O–H, and N–H bonds are strongly polar; in molecules that have these bonds, particularly strong dipole-dipole interactions (as strong as 10% of a true covalent bond) can occur. Because of this strong interaction, the term hydrogen bonding is used to describe this dipole-dipole interaction. The physical properties of water, which has two O–H bonds, are strongly affected by the presence of hydrogen bonding forces of attraction between water molecules. Figure 8.1.5 shows how molecules experiencing hydrogen bonding can interact. Hydrogen-bonding forces between water molecules (illustrated below as green dashes) are different than the covalent O-H bonds within a water molecule (illustrated as solid orange lines below). Hydrogen-bonding forces between molecules are stronger than dipole-dipole forces between molecules, but not as strong as covalent bonds within molecules.

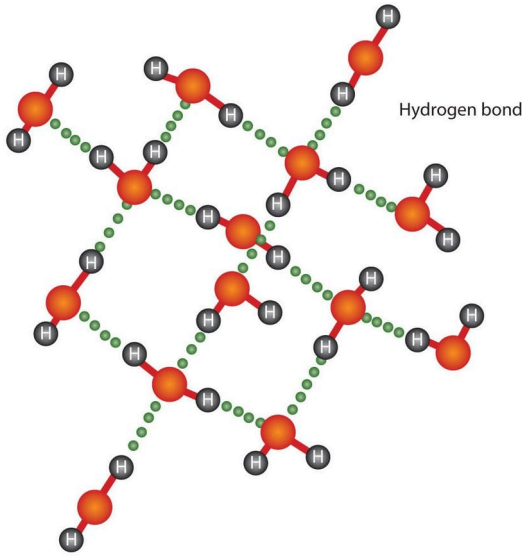


Figure 8.1.5*: Hydrogen-Bonding forces between Water Molecules (dashed green lines). The presence of hydrogen bonding in molecules like water can have a large impact on the physical properties of a substance.*

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. Because dispersion forces are caused by the instantaneous distribution of electrons in a molecule, larger molecules with a large number of electrons can experience substantial dispersion forces. 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.

The phase that a substance adopts depends on the type and magnitude of the intermolecular interactions the particles of a substance experience. If the intermolecular interactions are relatively strong, then a large amount of energy—in terms of temperature—is necessary for a substance to change phases. If the intermolecular interactions are weak, a low temperature is all that is necessary to move a substance out of the solid phase.

Example 8.1.1: Intermolecular Forces

What intermolecular interactions 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 fully charged ions, so the intermolecular interactions in potassium chloride are ionic bonds. Because ionic bonds 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 forces. It is also polar so has dipole-dipole forces, but the H-bonding forces are more significant. 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.

Concept Review Exercise

1. What types of interactions might cause a gas to stick together as liquid or solid in:

   A. a covalent network substance

   B. an ionic compound

   C. a molecular compound?

Answer

1. A. covalent bonds (sharing of electrons)

   B. ionic bonds (attraction between full opposite charges of ions)

   C. All molecules will have London-dispersion forces, polar molecules will have dipole-dipole forces, and molecules with H directly bonded to N, O, or F will have hydrogen-bonding forces. (All three are attractions of partial opposite charges between molecules.)

Key Takeaways

- A phase is a form of matter that has the same physical properties throughout.
- Atoms and molecules interact with each other through various forces: ionic and covalent bonds, dipole-dipole interactions, hydrogen bonding, and dispersion forces.

Exercises

1. List the three common phases in the order you are likely to find them—from lowest temperature to highest temperature.

2. List these intermolecular interactions from weakest to strongest: London forces, hydrogen-bonding forces, dipole-dipole forces and ionic interactions.

3. What type of intermolecular interaction is predominate in each substance?

   a. ammonia (NH_3)
   b. sodium sulfate (Na_2SO_4)
   c. decane ($C_{10}H_{22}$)

4. Explain how a molecule like carbon dioxide (CO_2) can have polar covalent bonds but be nonpolar overall.

5. What types of intermolecular forces would exist in a sample of sulfur dichloride (SCl_2)?

6. What are some of the physical properties of substances that experience covalent network bonding?

7. What are some of the physical properties of substances that experience only dispersion forces?

8. Heat is required to boil water (endothermic). What types of interactions are being overcome when water is boiled?

Answers

1. solid, liquid, and gas
2. London forces < dipole-dipole forces < hydrogen-bonding forces < ionic interactions
3. a. hydrogen-bonding forces predominate (but NH_3 also has dipole-dipole and London-dispersion); b. ionic interactions; c. dipsersion forces (C-C and C-H bonds are not polar)
4. In linear carbon dioxide, the two covalent bonds are oriented on opposite sides (symmetrically) such that the polarity of each bond cancels out.
5. Sulfur dichloride has polar bonds, and because of the two lone pairs on the central sulfur atom, would have a bent geometry. The molecule is not symmetrical so one side is more negative and the other more positive. Like all molecules, it would have London-dispersion forces and, because it is polar, also dipole-dipole forces.
6. very hard, high melting point
7. low melting point and low boiling point
8. London-dispersion, dipole-dipole, and hydrogen-bonding forces of attraction are being overcome to separate the liquid water molecules into gaseous water molecules. *(Covalent bonds bind oxygen to the two hydrogens in each water, but these are not broken when water is boiled.)*

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8.2: Solids and Liquids

Skills to Develop

- 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. Image used with permission 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. Image used with permission 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.

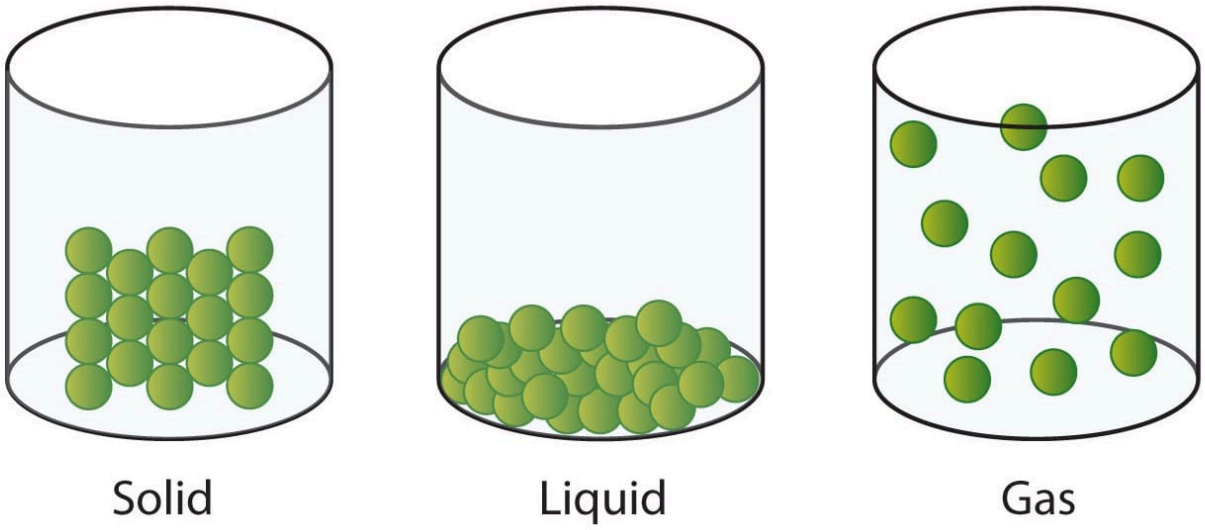


Figure 8.2.3*: A Representation of the Solid, Liquid, and Gas States. A solid has definite volume and shape, a liquid has a definite volume but no definite shape, and a gas has neither a definite volume nor shape.*

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.

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. In colder weather, lakes and rivers freeze from the top, allowing animals and plants to continue to live underneath. 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.

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 gases?
3. What phase or phases have a definite volume? What phase or phases do not have a definite volume?
4. Are substances with strong intermolecular interactions likely to be solids at higher or lower temperatures? Explain.
5. State two similarities between the solid and liquid states.
6. 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.
7. 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. variable volume and shape, low density, compressible
3. Solids and liquids have definite volume, whereas gases do not have definite volume. *NOTE: Solids and liquids can expand and contract a very small amount, like when changing temperature, but the differences are negligible compared to gases (so we assume a solid or liquid sample does not change volume).*
4. At higher temperatures, their intermolecular interactions are strong enough to hold the particles in place.
5. high density; definite volume
6. If individual particles are moving around with respect to each other, a substance may be in either the _gas_ or _liquid_ state but probably not in the _solid_ state. *(Particles in a solid can only vibrate a bit, whereas particles in gases and liquids are in constant motion throught the sample.)*
7. If individual particles are in contact with each other, a substance may be in either the __solid__ or __liquid___ state but probably not in the __gas___ state.

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8.3 Gases and Pressure

Skills to Develop

- 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 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.

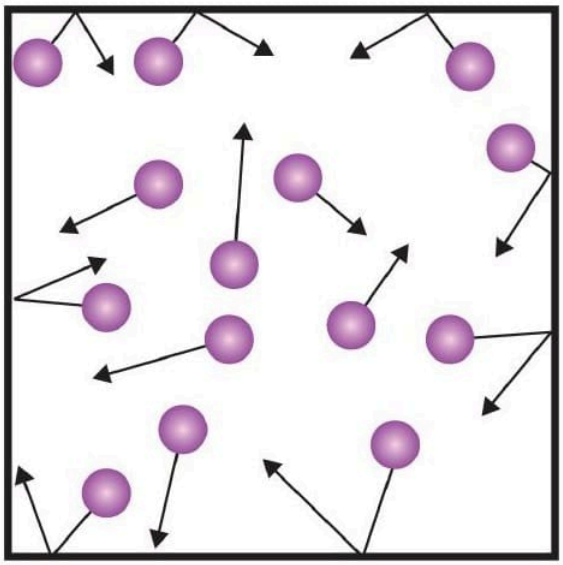


Figure 1: *Gas Pressure. Pressure is what results when gas particles rebound off the walls of their container.*

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. One atmosphere is expressed in five other pressure units below.

$$1 \text{ atm} = 760 \text{ torr (exact)} = 760.000 \text{ mmHg} = 101\,325 \text{ Pa} = 1.01325 \text{ barr} = 14.6959 \text{ psi}$$

Example 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.

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.

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.

Key Takeaway

- The gas phase has certain general properties characteristic of that phase.

Exercises

1. What is the kinetic theory of gases?
2. Why does a gas exert pressure?
3. Arrange the following pressure quantities in order from smallest to largest: 1 mmHg, 1 Pa, and 1 atm.
4. How many torr are there in 1.56 atm?
5. 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.")

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. A gas exerts pressure as its particles rebound off the walls of its container.
3. 1 Pa < 1 mmHg < 1 atm
4. 1,190 torr
5. 0.158 atm; 0.108 atm

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8.4: Gas Laws

Skills to Develop

- 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

$$\mathrm{P} \propto \frac{1}{\mathrm{V}} \tag{8.4.1}$$

where the "$\propto$" symbol means "is proportional to." This is one form of Boyle's law, which relates the pressure of a gas to its volume. Because the volume is inverted (1/V), we say that pressure and volume are inversely proportional.

A more useful form of Boyle's law involves a change in conditions of a gas. For a given amount of gas at a constant temperature, if we know the initial pressure and volume of a gas sample and the pressure or volume changes, we can calculate what the new volume or pressure will be. That form of Boyle's law is written

$$P_i V_i = P_f V_f \tag{8.4.2}$$

where the subscript i refers to initial conditions and the subscript f refers to final conditions.

To use 8.4.2, 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.

Example 8.4.2: Gas Compression

If a sample of gas has an initial pressure of 1.56 atm and an initial volume of 7.02 L, what is the final volume if the pressure is reduced to 0.987 atm? Assume that the amount and the temperature of the gas remain constant.

SOLUTION

The key in problems like this is to be able to identify which quantities represent which variables from the relevant equation. The way the question is worded, you should be able to tell that 1.56 atm is P_i, 7.02 L is V_i, and 0.987 atm is P_f. What we are

looking for is the final volume—V_f. Therefore, substituting these values into $P_iV_i = P_fV_f$:

$$(1.56\text{ atm})(7.02\text{ L}) = (0.987\text{ atm}) \times V_f$$

The expression has atmospheres on both sides of the equation, so they cancel algebraically:

$$(1.56)(7.02\text{ L}) = (0.987) \times V_f$$

Now we divide both sides of the expression by 0.987 to isolate V_f, the quantity we are seeking:

$$\frac{(1.56)(7.02\text{ L})}{0.987} = \text{V}_\text{f}$$

Performing the multiplication and division, we get the value of V_f, which is 11.1 L. The volume increases. This should make sense because the pressure decreases, so pressure and volume are inversely related.

If the units of similar quantities are not the same, one of them must be converted to the other quantity's units for the calculation to work out properly. It does not matter which quantity is converted to a different unit; the only thing that matters is that the conversion and subsequent algebra are performed properly. The following example illustrates this process.

Example 8.4.3

If a sample of gas has an initial pressure of 1.56 atm and an initial volume of 7.02 L, what is the final volume if the pressure is changed to 1,775 torr? Does the answer make sense? Assume that the amount and the temperature of the gas remain constant.

SOLUTION

This example is similar to Example 8.4.2, except now the final pressure is expressed in torr. For the math to work out properly, one of the pressure values must be converted to the other unit. Let us change the initial pressure to torr:

$$1.56\text{ atm} \times \frac{760\text{ torr}}{1\text{ atm}} = 1,190\text{ torr}$$

Now we can use Boyle's law:

$$(1,190\text{ torr})(7.02\text{ L}) = (1,775\text{ torr}) \times V_f$$

Torr cancels algebraically from both sides of the equation, leaving

$$(1,190)(7.02\text{ L}) = (1,775) \times V_f$$

Now we divide both sides of the equation by 1,775 to isolate V_f on one side. Solving for the final volume,

$$\text{V}_\text{f} = \frac{(1,190)(7.02\text{ L})}{1,775} = 4.71\text{ L}$$

Because the pressure increases, it makes sense that the volume decreases.

The answer for the final volume is essentially the same if we converted the 1,775 torr to atmospheres: $1,775\text{ torr} \times \frac{1\text{ atm}}{760\text{ torr}} = 2.336\text{ atm}$. Using Boyle's law: (1.56 atm)(7.02 L) = (2.335 atm) × V_f; $\text{V}_\text{f} = \frac{(1.56\text{ atm})(7.02\text{ L})}{2.336\text{ atm}} = 4.69\text{ L}$.

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. They are directly proportional. The way to write this mathematically is

$$V \propto T \tag{8.4.3}$$

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:

$$\text{Kelvin temperature} = \text{Celsius temperature} + 273.15$$

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.

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:

$$\frac{\mathrm{V_i}}{\mathrm{T_i}} = \frac{\mathrm{V_f}}{\mathrm{T_f}} \tag{8.4.4}$$

where V_i and T_i are the initial volume and temperature, and V_f and T_f are the final volume and temperature. This is Charles's law. The restriction on its use is that the pressure of the gas and the amount of gas must remain constant. (Charles's law is sometimes referred to as Gay-Lussac's law, after the scientist who promoted Charles's work.)

Example 8.4.5

A gas sample at 20.°C has an initial volume of 20.0 L. What is its volume if the temperature is changed to 60.°C? Does the answer make sense? Assume that the pressure and the amount of the gas remain constant.

SOLUTION

Although the temperatures are given in degrees Celsius, we must convert them to the kelvins before we can use Charles's law. Thus,

$$20.°C + 273.15 = 293\ K = T_i\ 60.°C + 273.15 = 333\ K = T_f$$

Now we can substitute these values into Charles's law, along with the initial volume of 20.0 L:

$$\frac{20.0\ \mathrm{L}}{293\ \mathrm{K}} = \frac{\mathrm{V_f}}{333\ \mathrm{K}}$$

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).

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:

$$PV = nRT \tag{8.4.5}$$

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:

$$\mathrm{R} = 0.08206\ \frac{\mathrm{L \cdot atm}}{\mathrm{mol \cdot K}} \tag{8.4.6}$$

This may seem like a strange unit, but that is what is required for the units to work out algebraically.

Example 8.4.6

What is the volume in liters of 1.45 mol of N_2 gas at 298 K and 3.995 atm?

SOLUTION

Using the ideal gas law where *P* = 3.995 atm, *n* = 1.45, and *T* = 298,

$$(3.995\ \mathrm{atm}) \times \mathrm{V} = (1.45\ \mathrm{mol}) \left(0.08206\ \frac{\mathrm{L \cdot atm}}{\mathrm{mol \cdot K}}\right) (298\ \mathrm{K})$$

On the right side, the moles and kelvins cancel. Also, because atmospheres appear in the numerator on both sides of the equation, they also cancel. The only remaining unit is liters, a unit of volume. So

$$3.995 \times V = (1.45)(0.08206)(298)\ \text{L}$$

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.

For convenience, scientists have selected 273 K (0°C) and 1.00 atm pressure as a set of standard conditions for gases. This combination of conditions is called standard temperature and pressure (STP). Under these conditions, 1 mol of any gas has about the same volume. We can use the ideal gas law to determine the volume of 1 mol of gas at STP:

$$(1.00\ \text{atm}) \times \text{V} = (1.00\ \text{mol}) \left(0.08206\ \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right) (273\ \text{K}) \tag{8.4.7}$$

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 8.4.7

Cyclopropane (C_3H_6) is a gas that formerly was used as an anesthetic. How many moles of gas are there in a 100.0 L sample if the gas is at STP?

SOLUTION

We can set up a simple, one-step conversion that relates moles and liters:

$$100.0\ \text{L}\ \text{C}_3\text{H}_6 \times \frac{1\ \text{mol}}{22.4\ \text{L}} = 4.46\ \text{mol}\ \text{C}_3\text{H}_6$$

There are almost 4.5 mol of gas in 100.0 L.

Note: Because of its flammability, cyclopropane is no longer used as an anesthetic gas.

Combined Gas Law

Boyle's and Charles's laws compare initial and final situations, but not for every possible change of pressure, temperature, mole of gas, and temperature. Memorizing all the possible equations is not necessary because they can all be derived from the ideal gas law. First, rearrange PV = nRT to solve for R, the gas constant.

$$\text{R} = \frac{\text{PV}}{\text{nT}} \tag{8.4.8}$$

Under the initial conditions, $R = \frac{P_i V_i}{n_i T_i}$ and under final conditions, $R = \frac{P_f V_f}{n_f T_f}$. Since both expressions are equal to R, they are equal to each other.

Double subscripts: use braces to clarify

This equation is typically used when one or more of the variables is constant. As a result, that variable is canceled from the equation. For example, the equation $2x^2 = 2y$ can be simplified to $x^2 = y$ since the 2 is on both sides of the equation.

What happens to the combined gas law equation when the initial and final pressures are equal ($P_i = P_f$)? Since they are equal, P_i can replace P_f.

$$\frac{P_iV_i}{n_iT_i} = \frac{P_iV_f}{n_fT_f}$$

which simplifies to

$$\frac{V_i}{n_iT_i} = \frac{V_f}{n_fT_f}$$

If two variables are constant, the equation can be simplified even more. For Boyle's law, only pressure and volume change, so the other variables cancel out. For Charles's law, everything but volume and temperature cancel.

If temperature and volume are constant, then $T_i = T_f$ and $V_i = V_f$. Then,

$$\frac{P_iV_i}{n_iT_i} = \frac{P_fV_i}{n_fT_i}$$

simplifies to

$$\frac{P_i}{n_i} = \frac{P_f}{n_f}$$

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 or four 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 8.4.8

A sample of gas has P_i = 1.50 atm, V_i = 10.5 L, and n_i = 1.66 mol. What is the final volume if P_f = 0.750 atm and n_f = 2.33 mol?

SOLUTION

We are not told that temperature changes, so assume it is constant (and will cancel out of the combined gas law).

$$\frac{P_iV_i}{n_iT_i} = \frac{P_iV_f}{n_fT_f}$$

simplifies to

$$\frac{P_iV_i}{n_i} = \frac{P_iV_f}{n_f}$$

Plugging in the known values gives

$$\frac{(1.50\ \text{atm})(10.5\ \text{L})}{1.66\ \text{mol}} = \frac{(0.750\ \text{atm})(\text{V}_\text{f})}{2.33\ \text{mol}}$$

We algebraically rearrange this expression to isolate V_f on one side of the equation:

$$\text{V}_\text{f} = \frac{(1.50\ \text{atm})(10.5\ \text{L})(2.33\ \text{mol})}{(1.66\ \text{mol})(0.750\ \text{atm})} = 29.5\ \text{L}$$

Note how all the units cancel except the unit for volume.

Example 8.4.9

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°C + 273.15 = 295 K = T_i

11°C + 273.15 = 284 K = T_f

$$1.09\ \text{atm} \times \frac{760\ \text{torr}}{1\ \text{atm}} = 828\ \text{torr} = \text{P}_\text{i}$$

We are not told that the sample of gas changed moles (balloon did not leak), so assume moles constant and it will cancel out of the equation.

$$\frac{P_iV_i}{n_iT_i} = \frac{P_iV_f}{n_fT_f}$$

simplifies to

$$\frac{P_iV_i}{T_i} = \frac{P_iV_f}{T_f}$$

Now we can substitute the quantities into the combined has law:

$$\frac{(828\ \text{torr})(1,070\ \text{mL})}{295\ \text{K}} = \frac{(655\ \text{torr}) \times \text{V}_\text{f}}{284\ \text{K}}$$

To solve for V_f, we multiply the 284 K in the denominator of the right side into the numerator on the left, and we divide 655 torr in the numerator of the right side into the denominator on the left:

$$\frac{(828\ \text{torr})(1,070\ \text{mL})(284\ \text{K})}{(295\ \text{K})(655\ \text{torr})} = \text{V}_\text{f}$$

Notice that torr and kelvins cancel, as they are found in both the numerator and denominator. The only unit that remains is milliliters, which is a unit of volume. So V_f = 1,300 mL. The overall change is that the volume of the balloon has increased by 230 mL.

Dalton's Law of Partial Pressures

The ideal gas equation of state applies to mixtures just as to pure gases. It was in fact with a gas mixture, ordinary air, that Boyle, Gay-Lussac and Charles did their early experiments. The only new concept we need in order to deal with gas mixtures is the *partial pressure*, a concept invented by the famous English chemist John Dalton (1766-1844). Dalton reasoned that the low density and high compressibility of gases indicates that they consist mostly of empty space; from this it follows that when two or more different gases occupy the same volume, they behave entirely independently. The contribution that each component of a gaseous mixture makes to the total pressure of the gas is known as the *partial pressure* of that gas.

The definition of Dalton's Law of Partial Pressures that address this is:

The total pressure of a gas is the sum of the partial pressures of its components

which is expressed algebraically as

$$P_{total} = P_1 + P_2 + P_3... = \sum_i P_i \tag{8.4.9}$$

or, equivalently

$$P_{total} = \frac{RT}{V}\sum_i n_i \tag{8.4.10}$$

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

A 2.00 liter bottle initially contains 0.0801 moles of nitrogen and 0.0199 moles of oxygen. Without allowing the other gases to escape, 1.00 grams of dry ice (solid carbon dioxide) is added to the bottle and completely sublimates. Find the total pressure of the three gases in the bottle at 25 degrees Celsius.

SOLUTION

We are given volume and temperature. We can look up the value of the ideal gas constant. PV = nRT can be rearranged to P = nRT/V to solve for pressure if we we can find moles, n. The total number of moles of gases will be proportional to the total pressure exerted by those gases.

Mass of CO_2, can be converted to moles if divided by the molar mass. (From periodic table: C + O + O = 12.0 + 16.0 + 16.0 = 44.0 g/mol)

(1.00 g CO_2) / (44.0 g/mol) = 0.0227 mol CO_2

Total Moles = $n_T = n_{N2} + n_{H2} + n_{CO2}$ = (0.0801 mol N_2) + (0.0199 mol O_2) + (0.0227 mol CO_2) = 0.1227 mol gases

T = 25 ^{0}C + 273 = 298 K

Total Pressure = $P_T = n_TRT/V$ = (0.1227 mol)(0.08206 Latm/molK)(298 K)/(2.00 L) = **1.50 atm**

Dalton's law states that in a gas mixture (P_{total}) each gas will exert a pressure independent of the other gases (P_n) and each gas will behave as if it alone occupies the total volume. By extension, the partial pressure of each gas can be calculated by multiplying the total pressure (P_{total}) by the gas percentage (%).

$$P_{Total} = P_1 + P_2 + P_3 + P_4 + ... + P_n \tag{8.4.11}$$

or

$$P_n = \frac{n}{P_{Total}} \tag{8.4.12}$$

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

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:

$$C = kP_{gas} \tag{8.4.13}$$

where

- 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)

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).

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.

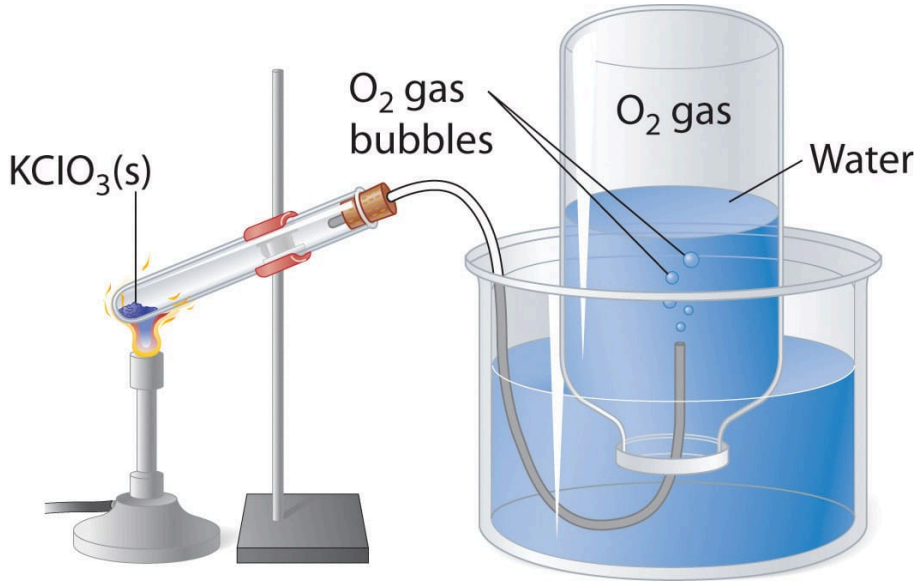


Figure 8.4.1:*An Apparatus for Collecting Gases by the Displacement of Water*

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

$$n = \frac{PV}{RT} = \frac{(0.966\ atm)(0.155\ L)}{(0.082\ Latmmol^{-1}K^{-1})(295\ K)} = 0.00619\ mol$$

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.

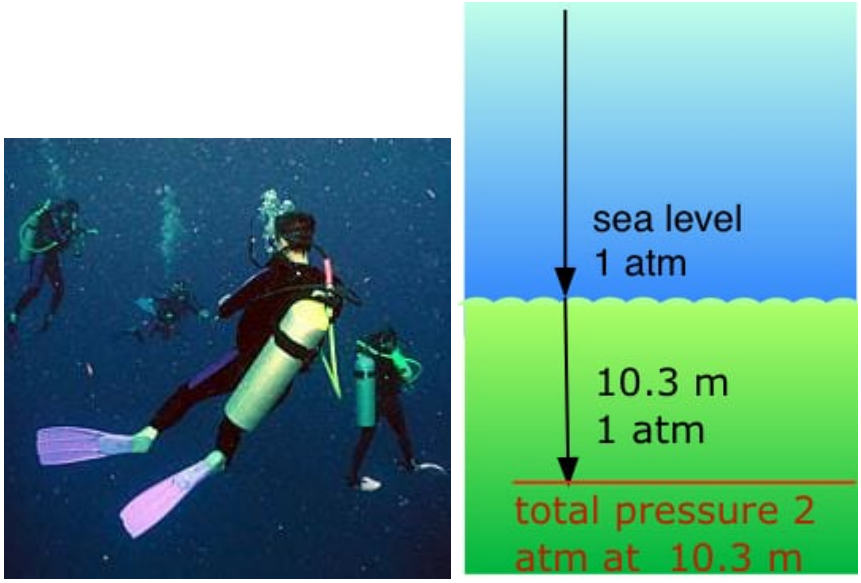


***Figure** 8.4.2**:** Scuba Dviging actively takes into account both Henry's and Dalton's Laws*

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.

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.

Key Takeaway

- The physical properties of gases are predictable using mathematical formulas known as gas laws.

Exercises

1. What conditions of a gas sample should remain constant for Boyle's law to be used?

2. Does the identity of a gas matter when using Boyle's law? Why or why not?

3. 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.

4. 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.

5. 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.

6. 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?

7. 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?

8. Use the ideal gas law to show that 1 mol of a gas at STP has a volume of about 22.4 L.

9. How many moles of gas are there in a 27.6 L sample at 298 K and a pressure of 1.44 atm?

10. 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?

11. What is the pressure of 0.0456 mol of Ne gas contained in a 7.50 L volume at 29°C?

12. 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?

13. Soda water has an unusually high pressure of dissolved carbon dioxide. Apply Henry's Law to explain how soda water is made.

Answers

1. temperature and amount of the gas
2. The identity does not matter because the variables of Boyle's law do not identify the gas.
3. 3.79 L
4. 89.7 mL
5. 1.07 L
6. 23.7 cm^3
7. 206 mL
8. The ideal gas law confirms that 22.4 L equals 1 mol.
9. 1.63 mol
10. 405 K; 132°C
11. 0.151 atm
12. 70 mmHg
13. According to Henry's Law the Concentration of dissolved carbon dioxide (C) would be proportional to the pressure of carbon dioxide gas above the liquid. Soda water (with high concentration) is made by exposing water to high pressure carbon dioxide gas (from a tank).

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8.5: Chapter 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** substances, like those in diamond, are held together by strong covalent bonds. **Ionic interactions**, the forces of attraction due to oppositely charged ions, are also relatively strong.

Strong covalent bonds within a each molecule hold atoms together as one molecular unit. There are three weaker types of intermolecular forces (attractions between molecules) that attract molecules to other molecules, and are responsible for liquid and solid formation. If the bonds within a molecule 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 0°C, and standard pressure is 1.00 atm.

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8.E: Exercises

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. The balanced chemical equation for the combustion of propane is as follows:

   $C_3H_{8(g)} + 5O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(\ell)}$

   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?
3. At 20°C, 1.000 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?
4. Predict whether HCl or LiCl will have the higher melting point. Explain. (Hint: consider the relative strengths of the intermolecular interactions of the two compounds.)
5. 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.

Answers

1. 31.9 g
2. A) 11.4 mol; B) 255 L
3. 57.81 L; an expansion of 57,700 times
4. LiCl; the attractions between full charges (ionic bonds) are stronger than those between the partial charges of HCl (London-dispersion and dipole-dipole forces)
5. 12 mol

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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.

9.1: Solutions

9.2: Concentration

9.3: The Dissolution Process

9.4: Properties of Solutions

9.5: Chapter Summary

9.E: Exercises

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9.1: Solutions

Skills to Develop

- To understand what causes solutions to form.
- Distinguish among suspensions. colloids, and solutions.

Solutions

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 solute, 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.

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 that only have non-polar C-C and C-H bonds, octane is nonpolar, so we expect that it would not be soluble in water.

Suspensions

Take a glass of water and throw in a handful of sand or dirt. Stir it and stir it and stir it. Have you made a solution? Sand and dirt do not dissolve in water, and, though it may look homogenous for a few moments, the sand or dirt gradually sinks to the bottom of the glass (see figure below). Some medications are delivered as suspensions and must be mixed well before the doses measured to make sure the patient is receiving the correct amount of medication.



Figure $9.1.2$ *: A mixture of sand and water forms a suspension.*

A **suspension** *is a heterogeneous mixture in which some of the particles settle out of the mixture upon standing*. The particles in a suspension are far larger than those of a solution, so gravity is able to pull them down out of the dispersion medium (water). The diameter for the dispersed particles in a suspension, such as the sand in the suspension described above, is typically at least 1000 times greater than those in a solution. Solutions are typically transparent, whereas the particles in a suspension will block some or all light from passing through. Unlike a solution, the dispersed particles can be separated from the dispersion medium by filtering. Suspensions are considered heterogeneous because the different substances in the mixture will not remain uniformly distributed if they are not actively being mixed.

Colloids

A colloid is a heterogeneous mixture in which the dispersed particles are intermediate in size between those of a solution and a suspension. The particles are spread evenly throughout the dispersion medium, which can be a solid, liquid, or gas. Because the dispersed particles of a colloid are not as large as those of a suspension, they do not settle out upon standing. The table below summarizes the properties and distinctions between solutions, colloids, and suspensions.

Table $9.1.2$***:*** *Properties of Solutions, Colloids, and Suspensions*

Solution	Colloids	Suspensions
Homogeneous	Heterogeneous	Heterogeneous
Particle size: 0.01-$1\ \text{nm}$; atoms, ions or molecules	Particle size: 1-$1000\ \text{nm}$, dispersed; large molecules or aggregates	Particle size: over $1000\ \text{nm}$, suspended: large particles or aggregates
Do not separate on standing	Do not separate on standing	Particles settle out
Cannot be separated by filtration	Cannot be separated by filtration	Can be separated by filtration
Do not scatter light (transparent)	Usually scatter light, but may block (translucent or opaque)	Usually block light, but may scatter (opaque or translucent)

Colloids are unlike solutions because their dispersed particles are much larger than those of a solution. The dispersed particles of a colloid cannot be separated by filtration, but they scatter light, a phenomenon called the Tyndall effect.

Tyndall Effect

Colloids are often confused with true homogenous solutions because the individual dispersed particles of a colloid cannot be seen. When light is passed through a true solution, the dissolved particles are too small to deflect the light. However, the dispersed particles of a colloid, being larger, do deflect light (see figure below). The **Tyndall effect** *is the scattering of visible light by colloidal particles*. You have undoubtedly "seen" a light beam as it passes through fog, smoke, or a scattering of dust particles suspended in air. All three are examples of colloids. Suspensions may scatter light, but if the number of suspended particles is sufficiently large, the suspension may simply be opaque, and the light scattering will not occur.



Figure 9.1.3***:*** *Light passes through a colorless solution and is not scattered. When it passes through a diluted milk solution, the light is scattered by colloidal particles, an observation of the Tyndall effect. The Tyndall effect allows sunlight to be seen as it passes through a fine mist.*

Examples of Colloids

Listed in the table below are examples of colloidal systems, most of which are very familiar. Some of these are shown below (see figure below). The dispersed phase describes the particles, while the dispersion medium is the material in which the particles are distributed.

Table 9.1.3***:*** *Classes of Colloids*

Class of Colloid	Dispersed Phase	Dispersion Medium	Examples
Solid and gel	solid	liquid	paint, jellies, blood, gelatin, mud
Solid aerosol	solid	gas	smoke, dust in air
Solid emulsion	liquid	solid	cheese, butter
Liquid emulsion	liquid	liquid	milk, mayonnaise
Liquid aerosol	liquid	gas	fog, mist, clouds, aerosol spray
Foam	gas	solid	marshmallow
Foam	gas	liquid	whipped cream, shaving cream



Figure 9.1.4***:*** *Some common colloids (A) gelatin dessert, (B) smoke (solid aerosol), (C) butter (solid emulsion), (D) mayonnaise (liquid emulsion), (E) fog (liquid aerosol), (F) marshmallows (foam), (G) whipped cream (foam)*

Emulsions

Butter and mayonnaise are examples of a class of colloids called emulsions. An **emulsion** *is a colloidal dispersion of a liquid in either a liquid or a solid.* A stable emulsion requires an emulsifying agent to be present. Mayonnaise is made in part of oil and vinegar. Since oil is nonpolar, and vinegar is a polar aqueous solution, the two do not mix and would quickly separate into layers. However, the addition of egg yolk causes the mixture to become stable and not separate. Egg yolk is capable of interacting with both the polar vinegar and the nonpolar oil. The egg yolk is called the emulsifying agent. Soap acts as an emulsifying agent because one end of a soap molecule is polar, and the other end is nonpolar. This allows the grease to be removed from your hands or your clothing by washing with soapy water.

Concept Review Exercises

1. What causes a solution to form?
2. How does the phrase *like dissolves like* relate to solutions?
3. How can you distinguish between a solution, a suspension, and a colloid?

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.
3. A suspension can be separated from the solvent by filtration while a solution and colloid cannot. Suspensions and colloids block or scatter light, whereas typically do not.

Key Takeaway

- Solutions form because a solute and a solvent experience similar intermolecular interactions.

Exercises

1. Define *solution*.

2. What is the difference between a solvent and a solute?

3. 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)

4. 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.

5. Identify each of the following descriptions or examples as being representative of a solution, suspension, or colloid. More than one answer may apply.

    a. dispersed particles can be filtered out
    b. heterogeneous
    c. particles are not visible to the unaided eye
    d. paint
    e. lemonade with no pulp
    f. particle size larger than 1 nm
    g. milk
    h. particles do not settle upon standing
    i. fog

Answers

1. a homogeneous mixture
2. A solvent is the majority component of a solution; a solute is the minority component of a solution.
3. a. probably soluble; b. probably not soluble; c. probably soluble; d. probably not soluble
4. Small alcohol molecules have strong polar intermolecular interactions (polar C-O bond and very polar O-H bond), so they dissolve in water. In large alcohol molecules, the nonpolar hydrocarbon portion overwhelms the polar end, so they do not dissolve very well in water.
5.

    a. suspension

    b. colloids and suspensions

    c. solution

    d. colloid

    e. solution

    f. colloids and suspensions

    g. colloid

    h. solutions and colloids

    i. colloids

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9.2: Concentration

Skills to Develop

- Express the amount of solute in a solution in various concentration units.
- Use molarity to determine quantities in chemical reactions.
- Determine the resulting concentration of a diluted solution.

There are several ways to express the amount of solute present in a solution. The **concentration** *of a solution is a measure of the amount of solute that has been dissolved in a given amount of solvent or solution*. A **concentrated solution** *is one that has a relatively large amount of dissolved solute*. A **dilute solution** *is one that has a relatively small amount of dissolved solute*. However, these terms are relative, and we need to be able to express concentration in a more exact, quantitative manner. Still, concentrated and dilute are useful as terms to compare one solution to another (see figure below). Also, be aware that the terms "concentrate" and "dilute" can be used as verbs. If you were to heat a solution, causing the solvent to evaporate, you would be concentrating it, because the ratio of solute to solvent would be increasing. If you were to add more water to an aqueous solution, you would be diluting it because the ratio of solute to solvent would be decreasing.

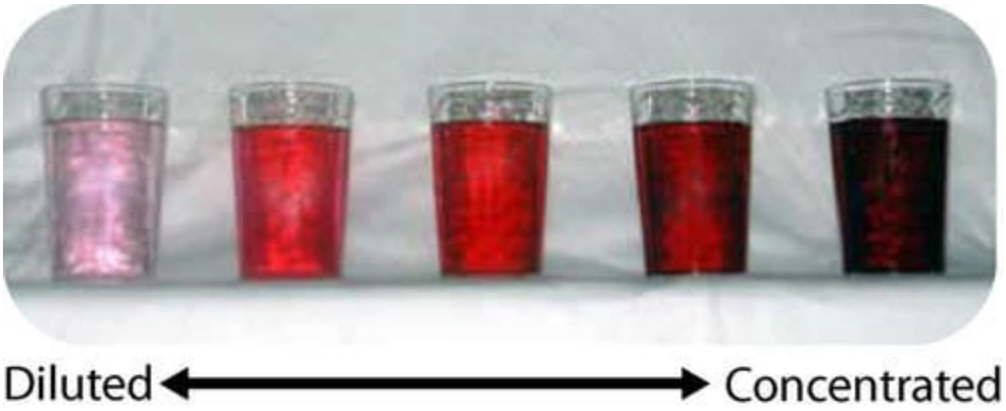


Figure 8.1.1: *Solutions of a red dye in water from the most dilute (on the left) to the most concentrated (on the right).*

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

Substance	Solubility (g in 100 mL of H2O)
$Ca(NO_3)_2(s)$	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.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Most solutions we encounter are unsaturated, so knowing the solubility of the solute does not accurately express the amount of solute in these solutions. There are several common ways of specifying the concentration of a solution.

Percent Composition

There are several ways of expressing the concentration of a solution by using a percentage. The mass/mass percent (% m/m) is defined as the mass of a solute divided by the mass of a solution times 100:

$$\%\ \mathrm{m/m} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\% \tag{9.2.1}$$

If you can measure the masses of the solute and the solution, determining the mass/mass percent is easy. Each mass must be expressed in the same units to determine the proper concentration.

Example 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:

$$\%\ \mathrm{m/m} = \frac{36.5\ \mathrm{g}}{355\ \mathrm{g}} \times 100\% = 10.3\%$$

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:

$$\%\ \mathrm{v/v} = \frac{\text{volume of solute}}{\text{volume of solution}} \times 100\% \tag{9.2.2}$$

Again, the units of the solute and the solution must be the same. A hybrid concentration unit, mass/volume percent (% m/v), is commonly used for intravenous (IV) fluids (Figure 9.2.1). It is defined as the mass in grams of a solute, divided by volume in milliliters of solution times 100:

$$\%\ \mathrm{m/v} = \frac{\text{mass of solute (g)}}{\text{volume of solution (mL)}} \times 100\% \tag{9.2.3}$$



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*

Each percent concentration can be used to produce a conversion factor between the amount of solute, the amount of solution, and the percent. Furthermore, given any two quantities in any percent composition, the third quantity can be calculated, as the following example illustrates.

Example 9.2.2

A sample of 45.0% v/v solution of ethanol (C_2H_5OH) in water has a volume of 115 mL. What volume of ethanol solute does the sample contain?

SOLUTION

A percentage concentration is simply the number of parts of solute per 100 parts of solution. Thus, the percent concentration of 45.0% v/v implies the following:

$$45.0\%\ \text{v/v} \rightarrow \frac{45\ \text{mL}\ C_2H_5OH}{100\ \text{mL solution}}$$

That is, there are 45 mL of C_2H_5OH for every 100 mL of solution. We can use this fraction as a conversion factor to determine the amount of C_2H_5OH in 115 mL of solution:

$$115\ \text{mL solution} \times \frac{45\ \text{mL}\ C_2H_5OH}{100\ \text{mL solution}} = 51.8\ \text{mL}\ C_2H_5OH$$

The highest concentration of ethanol that can be obtained normally is 95% ethanol, which is actually 95% v/v.

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.

$$\%\ \text{m/v} = \frac{9.0\ \text{g NaCl}}{1,000\ \text{mL solution}} \times 100\% = 0.90\%\ \text{m/v}$$

In addition to percentage units, the units for expressing the concentration of extremely dilute solutions are parts per million (ppm) and parts per billion (ppb). Both of these units are mass based and are defined as follows:

$$\text{ppm} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 1,000,000 \tag{9.2.4}$$

$$\text{ppb} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 1,000,000,000 \tag{9.2.5}$$

Similar to parts per million and parts per billion, related units include parts per thousand (ppth) and parts per trillion (ppt).

Concentrations of *trace elements* in the body—elements that are present in extremely low concentrations but are nonetheless necessary for life—are commonly expressed in parts per million or parts per billion. Concentrations of poisons and pollutants are also described in these units. For example, cobalt is present in the body at a concentration of 21 ppb, while the State of Oregon's Department of Agriculture limits the concentration of arsenic in fertilizers to 9 ppm.

In aqueous solutions, 1 ppm is essentially equal to 1 mg/L, and 1 ppb is equivalent to 1 µg/L.

Example 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.

Molarity

Another way of expressing concentration is to give the number of moles of solute per unit volume of solution. Such concentration units are useful for discussing chemical reactions in which a solute is a product or a reactant. Molar mass can then be used as a conversion factor to convert amounts in moles to amounts in grams.

Molarity is defined as the number of moles of a solute dissolved per liter of solution:

$$\text{molarity} = \frac{\text{number of moles of solute}}{\text{number of liters of solution}} \tag{9.2.6}$$

Molarity is abbreviated M (often referred to as “molar”), and the units are often abbreviated as mol/L. It is important to remember that “mol” in this expression refers to moles of solute and that “L” refers to liters of solution. For example, if you have 1.5 mol of NaCl dissolved in 0.500 L of solution, its molarity is therefore

$$\frac{1.5 \text{ mol NaCl}}{0.500 \text{ L solution}} = 3.0 \text{ M NaCl} \tag{9.2.7}$$

which is read as “three point oh molar sodium chloride.” Sometimes (aq) is added when the solvent is water, as in “3.0 M NaCl(aq).”

Before a molarity concentration can be calculated, the amount of the solute must be expressed in moles, and the volume of the solution must be expressed in liters, as demonstrated in the following example.

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:

$$\text{M} = \frac{0.625 \text{ mol NaOH}}{0.750 \text{ L}} = 0.833 \text{ M NaOH}$$

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. The following example illustrates this.

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

In both parts, we will use the definition of molarity (mol/L) to solve for the desired quantity.

1. Molarity, 0.0753 mol/L, can be used as a conversion factor (0.0753 mol = 1 L)

   The moles can be on top with liters on bottom, or it can be inverted.

   $$\frac{0.0753\ mol}{1\ L} \text{ or } \frac{1\ L}{0.0753\ mol}$$

   The inverted verstion has volume units (L) on top. The moles on bottom can be cancelled with the given 0.450 moles.

   $$0.450 \text{ mol} \times \frac{1 \text{ L}}{0.0753 \text{ mol}} = 5.98 \text{ L}$$

2. The molar mass of $C_2H_6O_2$ is 62.08 g/mol., so

   $$6.00 \text{ M} = \frac{6.00 \text{ mol}}{1 \text{ L}}$$

   To solve for the number of moles of solute, we multiply molarity (mol/L) by the volume (L):

   moles of solute = (6.00 mo/L)(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.

   Note: Dimethylamine has a “fishy” odor. In fact, organic compounds called amines cause the odor of decaying fish.

Using Molarity in Stoichiometry Problems

Of all the ways of expressing concentration, molarity is the one most commonly used in stoichiometry problems because it is directly related to the mole unit. Consider the following chemical equation:

$$HCl(aq) + NaOH(s) \rightarrow H_2O(\ell) + NaCl(aq)$$

Suppose we want to know how many liters of aqueous HCl solution will react with a given mass of NaOH. A typical approach to

answering this question is as follows:

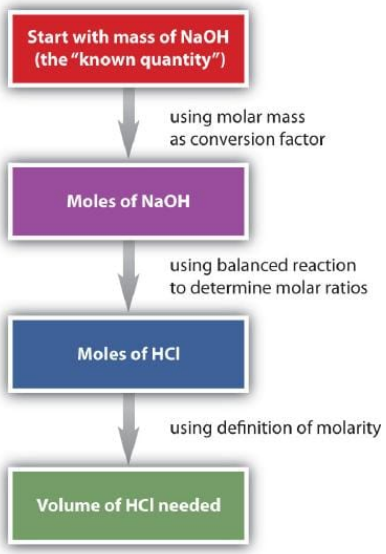


Figure 9.2.2: *Typical approach to solving Molarity problems*

In itself, each step is a straightforward conversion. It is the combination of the steps that is a powerful quantitative tool for problem solving. Note that in the last step, molarity is used to convert moles HCl to volume HCl. Some problems instead give the volume and ask for molarity. In that case, moles of HCl divided by volume of solution (in liters) would give molarity (mol/L).

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:

$$\text{HCl(aq)} + \text{NaOH(s)} \rightarrow \text{H}_2\text{O}(\ell) + \text{NaCl(aq)}$$

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. Notice that, like in Example 9.2.6, the molarity must be inverted to get volume (L) on top and moles on the bottom (so moles will cancel).

$$2.75 \text{ M HCl} = \frac{2.75 \text{ mol HCl}}{1 \text{ L of HCl solution}}$$

$$4.63 \text{ mol HCl} \times \frac{1 \text{ L HCl solution}}{2.75 \text{ mol HCl}} = 1.68 \text{ L} \times \frac{1,000 \text{ mL}}{1 \text{ L}} = 1,680 \text{ mL}$$

We need 1,680 mL of 2.75 M HCl to react with the NaOH.

The 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.

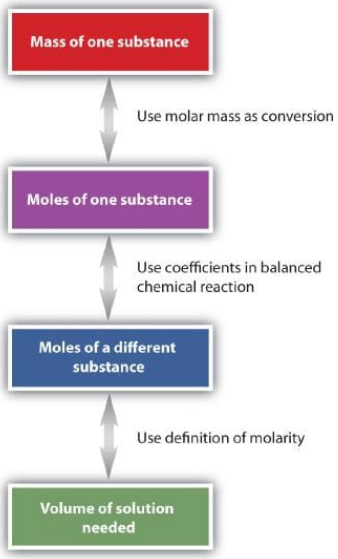


Figure 9.2.3*: Diagram of Steps for Using Molarity in Stoichiometry Calculations. When using molarity in stoichiometry calculations, a specific sequence of steps usually leads you to the correct answer.*

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
blood plasma	Na^+
	K^+
	Ca^{2+}
	Mg^{2+}
	Cl^-
	HCO_3^-
stomach acid	HCl
urine	NaCl
	PO_4^{3-}
	NH_2CONH_2 (urea)
***Note: Concentrations are approximate and can vary widely.**	

Looking Closer: The Dose Makes the Poison

Why is it that we can drink 1 qt of water when we are thirsty and not be harmed, but if we ingest 0.5 g of arsenic, we might die? There is an old saying: *the dose makes the poison*. This means that what may be dangerous in some amounts may not be dangerous in other amounts.

Take arsenic, for example. Some studies show that arsenic deprivation limits the growth of animals such as chickens, goats, and pigs, suggesting that arsenic is actually an essential trace element in the diet. Humans are constantly exposed to tiny amounts of arsenic from the environment, so studies of completely arsenic-free humans are not available; if arsenic is an essential trace mineral in human diets, it is probably required on the order of 50 ppb or less. A toxic dose of arsenic corresponds to about 7,000 ppb and higher, which is over 140 times the trace amount that may be required by the body. Thus, arsenic is not poisonous in and of itself. Rather, it is the amount that is dangerous: the dose makes the poison.

Similarly, as much as water is needed to keep us alive, too much of it is also risky to our health. Drinking too much water too fast can lead to a condition called water intoxication, which may be fatal. The danger in water intoxication is not that water itself becomes toxic. It is that the ingestion of too much water too fast dilutes sodium ions, potassium ions, and other salts in the bloodstream to concentrations that are not high enough to support brain, muscle, and heart functions. Military personnel, endurance athletes, and even desert hikers are susceptible to water intoxication if they drink water but do not replenish the salts lost in sweat. As this example shows, even the right substances in the wrong amounts can be dangerous!

Equivalents

Concentrations of ionic solutes are occasionally expressed in units called equivalents (Eq). One equivalent equals 1 mol of positive or negative charge. Thus, 1 mol/L of $Na^+(aq)$ is also 1 Eq/L because sodium has a 1+ charge. A 1 mol/L solution of $Ca^{2+}(aq)$ ions has a concentration of 2 Eq/L because calcium has a 2+ charge. Dilute solutions may be expressed in milliequivalents (mEq)—for example, human blood plasma has a total concentration of about 150 mEq/L. (For more information about the ions present in blood plasma, see Chapter 3 "Ionic Bonding and Simple Ionic Compounds", Section 3.3 "Formulas for Ionic Compounds".)

Dilution

When solvent is added to dilute a solution, the volume of the solution changes, but the amount of solute does not change. Before dilution, the amount of solute was equal to its original concentration times its original volume:

$$\text{amount in moles} = (\text{concentration} \times \text{volume})_{\text{initial}}$$

After dilution, the same amount of solute is equal to the final concentration times the final volume:

$$\text{amount in moles} = (\text{concentration} \times \text{volume})_{\text{final}}$$

To determine a concentration or amount after a dilution, we can use the following equation:

$$(\text{concentration} \times \text{volume})_{\text{initial}} = (\text{concentration} \times \text{volume})_{\text{final}}$$

or simply

$$C_i V_i = C_f V_f$$

Any units of concentration and volume can be used, as long as both concentrations and both volumes have the same unit.

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)$_{initial}$ = (concentration × volume)$_{final}$:

$$(0.900\ M \times 125\ mL) = (concentration \times 1{,}125\ mL)$$

We solve by isolating the unknown concentration by itself on one side of the equation. Dividing by 1,125 mL gives

$$\text{concentration} = \frac{0.900\ \text{M} \times 125\ \text{mL}}{1,125\ \text{mL}} = 0.100\ \text{M}$$

as the final 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.

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.

Exercises

1. Define *solubility*. Do all solutes have the same solubility?
2. How many grams of NaCl can be dissolved in 250.0 mL of H_2O? (Use solubility table at beginning of section.)
3. 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.
4. 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?
5. What is the molarity of a 2.66 L aqueous solution containing 56.9 g of NaBr?
6. What mass of HCl is present in 825 mL of a 1.25 M solution?
7. What volume of 0.345 M NaCl solution is needed to obtain 10.0 g of NaCl?
8. 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?

9. 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?

10. What is the concentration of a 0.75 M solution of aqueous calcium ion in equivalents/liter? (Look at calcium on a periodic table to determine it's likely ionic charge.)

11. 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?

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. 90.0 g
3. 0.203%
4. 0.00321 g
5. 0.208 M
6. 37.6 g
7. 0.496 L
8. 0.262 mol; 37.5 g
9. 1.13 M C_2H_5OH; 1.13 mol of CO_2; 49.7 g of CO_2
10. 1.5 Eq/L
11. 0.200 M

Extra Exercises

If you did not answer the questions above correctly the first time and/or want more practice, try working these also.

12. 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? (Use solubility table at beginning of section.)

13. Calculate the mass/mass percent of a saturated solution of NaCl. Use the data from Table $9.2.1$ "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 the water (0.997 g/mL) as a conversion factor.

14. What volume of water must be added to 150 mL of 5.0% hydrogen peroxide to dilute it to 1.0%?

15. 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?

Answers (to extra exercises)

12. 12.6 g

13. Since density of water is 0.997 g/mL, 100 mL of water has mass of 99.7 g. The total mass of solution will be 99.7 g water plus 36.0 g NaCl, or 135.7 g solution. So the percent NaCl is (mass NaCl / mass solution)x100% = (36.0g/135.7g)x100% = **26.5%**.

14. 600 mL (The total volume at the end, V_2, would need to be 750 mL, so 600 mL of water must be added to the 150 mL of original solution.)

15. 52.4 mL

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9.3: The Dissolution Process

Skills to Develop

- 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.

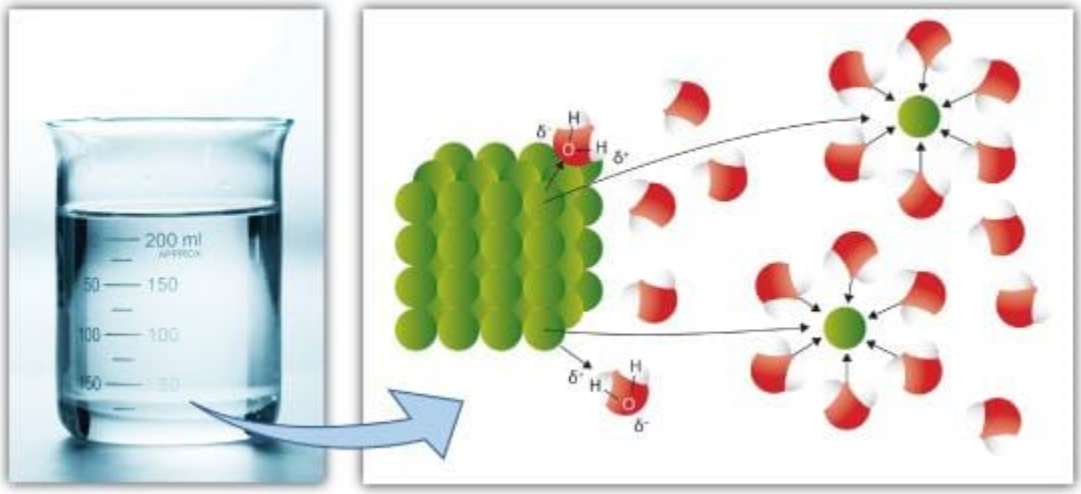


Figure 9.3.1***:*** *Solvation. When a solute dissolves, the individual particles of solute become surrounded by solvent particles. Eventually the particle detaches from the remaining solute, surrounded by solvent molecules in solution. Source: Photo © Thinkstock*

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. Substances that only make covalent bonds (usually compounds of only non-metals), like table sugar ($C_{12}H_{22}O_{11}$) and ethanol

($CH3CH_2OH$), are examples of a nonelectrolytes.

> 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.

Concept Review Exercise

1. Explain how the solvation process describes the dissolution of a solute in a solvent.

Answer

1. Each particle of the solute is surrounded by particles of the solvent, carrying the solute from its original phase.

Key Takeaway

- When a solute dissolves, its individual particles are surrounded by solvent molecules and are separated from each other.

Exercises

1. Describe what happens when an ionic solute like Na_2SO_4 dissolves in a polar solvent.

2. 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

3. Will solutions of each solute conduct electricity when dissolved?

a. $AgNO_3$
b. $CHCl_3$
c. $BaCl_2$
d. Li_2O

Answers

1. The solid, $Na_2SO_{4(s)}$, dissociates into $Na^+_{(aq)}$ and $SO_4^{2-}{}_{(aq)}$ ions (which can move independently in solution).

2.

a. electrolyte
b. nonelectrolyte
c. nonelectrolyte
d. electrolyte

3.

a. yes
b. no
c. yes
d. yes

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9.4: Properties of Solutions

Skills to Develop

- 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.

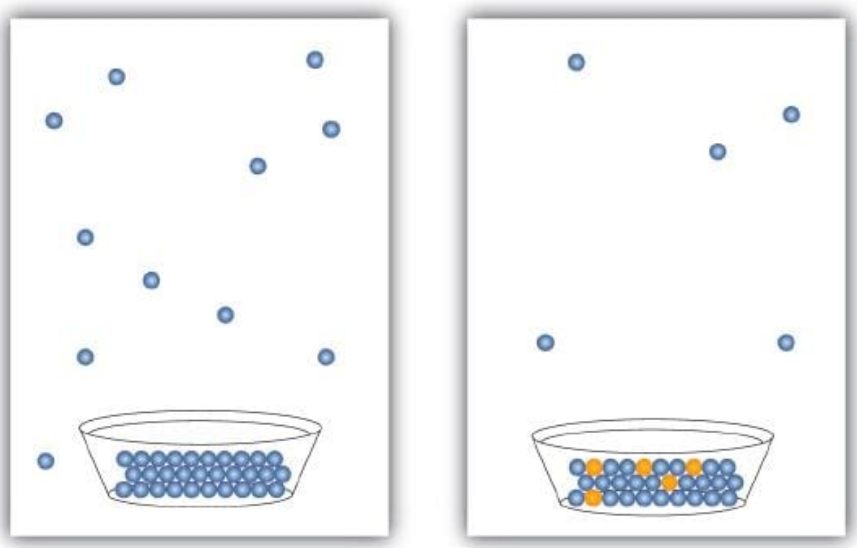


Figure 9.4.1***:*** *Vapor Pressure Depression. The presence of solute particles blocks some of the ability for liquid particles to evaporate. Thus, solutions of solid solutes typically have a lower vapor pressure than the pure solvent.*

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.

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.

Both boiling point elevation and freezing point depression have practical uses. For example, solutions of water and ethylene glycol ($C_2H_6O_2$) are used as coolants in automobile engines because the boiling point of such a solution is greater than 100°C, the normal boiling point of water. In winter, salts like NaCl and $CaCl_2$ are sprinkled on the ground to melt ice or keep ice from forming on roads and sidewalks (Figure 9.4.2). This is because the solution made by dissolving sodium chloride or calcium chloride in water has a lower freezing point than pure water, so the formation of ice is inhibited.



Figure 9.4.2***:*** *Effect of Freezing Point Depression. The salt sprinkled on this sidewalk makes the water on the sidewalk have a lower freezing point than pure water, so it does not freeze as easily. This makes walking on the sidewalk less hazardous in winter. © Thinkstock*

Example 9.4.1

Which solution's freezing point deviates more from that of pure water—a 1 M solution of NaCl or a 1 M solution of $CaCl_2$?

SOLUTION

Colligative properties depend on the number of dissolved particles, so the solution with the greater number of particles in solution will show the greatest deviation. When NaCl dissolves, it separates into two ions, Na^+ and Cl^-. But when $CaCl_2$ dissolves, it separates into three ions—one Ca^{2+} ion and two Cl^- ions. Thus, mole for mole, $CaCl_2$ will have 50% more impact on freezing point depression than NaCl.

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 9.4.2

A 0.50 M NaCl aqueous solution and a 0.30 M $Ca(NO_3)_2$ aqueous solution are placed on opposite sides of a semipermeable membrane. Determine the osmolarity of each solution and predict the direction of solvent flow.

SOLUTION

The solvent will flow into the solution of higher osmolarity. The NaCl solute separates into two ions—Na^+ and Cl^-—when it dissolves, so its osmolarity is as follows:

$$\text{osmol (NaCl)} = 0.50\ \text{M} \times 2 = 1.0\ \text{osmol}$$

The $Ca(NO_3)_2$ solute separates into three ions—one Ca^{2+} and two NO_3^-—when it dissolves, so its osmolarity is as follows:

$$\text{osmol [Ca(NO}_3)_2\text{]} = 0.30\ \text{M} \times 3 = 0.90\ \text{osmol}$$

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.

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.



A patient undergoing hemodialysis depends on osmosis to cleanse the blood of waste products that the kidneys are incapable of removing due to disease. Image used with permission 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.

Concept Review Exercises

1. What are the colligative properties of solutions?

2. Explain how the following properties of solutions differ from those of the pure solvent: vapor pressure, boiling point, freezing point, and osmotic pressure.

Answers

1. Colligative properties are characteristics that a solution has that depend on the number, not the identity, of solute particles.

2. In solutions, the vapor pressure is lower, the boiling point is higher, the freezing point is lower, and the osmotic pressure is higher.

Exercises

1. In each pair of aqueous systems, which will have the lower vapor pressure?

    a. pure water or 1.0 M NaCl
    b. 1.0 M NaCl or 1.0 M $C_6H_{12}O_6$
    c. 1.0 M $CaCl_2$ or 1.0 M $(NH_4)_3PO_4$

2. In each pair of aqueous systems, which will have the higher boiling point?

    a. pure water or a 1.0 M NaCl
    b. 1.0 M NaCl or 1.0 M $C_6H_{12}O_6$
    c. 1.0 M $CaCl_2$ or 1.0 M $(NH_4)_3PO_4$

3. Estimate the boiling point of each aqueous solution. The boiling point of pure water is 100.0°C. (As noted earlier in this section, "For every mole of particles dissolved in a liter of water, the boiling point of water increases by about 0.5°C.")

    a. 0.5 M NaCl
    b. 0.4 M Na_2SO_4
    c. 2.0 M $C_6H_{12}O_6$

4. Explain why salt (NaCl) is spread on roads and sidewalks to inhibit ice formation in cold weather.

5. What is the osmolarity of each aqueous solution?

    a. 0.500 M NH_2CONH_2
    b. 0.500 M NaBr
    c. 0.500 M $Ca(NO_3)_2$

6. A 1.0 M solution of an unknown soluble salt has an osmolarity of 3.0 osmol. What can you conclude about the salt?

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 NaCl
b. 1.0 M NaCl
c. 1.0 M $(NH_4)_3PO_4$

3. The normal boiling point of water, 100.0°C, will elevate (increase) by 0.5°C/M, where M is the molarity of particles dissolved (a.k.a. osmolarity).

a. Answer = **100.5°C** (0.5 M NaCl x 2 particles/1NaCl = 1 M particles --> 1M x 0.5°C/M = 0.5°C ---> 100.0°C + 0.5°C = 100.5°C)
b. Answer = **100.6°C** (0.4 M Na_2SO_4 x 3 particles/1Na_2SO_4 = 1.2 M particles --> 1.2M x 0.5°C/M = 0.6°C ---> 100.0°C + 0.6°C = 100.6°C)
c. Answer = **101.0°C** (2.0 M $C_6H_{12}O_6$ x 1 particles/1$C_6H_{12}O_6$= 2.0 M particles --> 2.0M x 0.5°C/M = 1.0°C ---> 100.0°C + 1.0°C = 101.0°C)

4. NaCl lowers the freezing point of water (i.e. freezing point depression), so it needs to be colder for the water to freeze.

5.

a. 0.500 osmol
b. 1.000 osmol
c. 1.500 osmol

6. It must separate into three ions when it dissolves.

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9.5: Chapter 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. **Suspensions** and **colloids** seem homogeneous, but are actually heterogeneous solutions with undissolved particles that may be too small to see individually, but large enough to block or scatter light.

The amount of solute in a solution is represented by the **concentration** of the solution. The maximum amount of solute that will dissolve in a given amount of solvent is called the **solubility** of the solute. Such solutions are **saturated**. Solutions that have less than the maximum amount are **unsaturated**. Most solutions are unsaturated, and there are various ways of stating their concentrations. **Mass/mass percent**, **volume/volume percent**, and **mass/volume percent** indicate the percentage of the overall solution that is solute. **Parts per million (ppm)** and **parts per billion (ppb)** are used to describe very small concentrations of a solute. **Molarity**, defined as the number of moles of solute per liter of solution, is a common concentration unit in the chemistry laboratory. **Equivalents** express concentrations in terms of moles of charge on ions. When a solution is diluted, we use the fact that the amount of solute remains constant to be able to determine the volume or concentration of the final diluted solution.

Dissolving occurs by **solvation**, the process in which particles of a solvent surround the individual particles of a solute, separating them to make a solution. For water solutions, the word **hydration** is used. If the solute is molecular, it dissolves into individual molecules. If the solute is ionic, the individual ions separate from each other, forming a solution that conducts electricity. Such solutions are called **electrolytes**. If the dissociation of ions is complete, the solution is a **strong electrolyte**. If the dissociation is only partial, the solution is a **weak electrolyte**. Solutions of molecules do not conduct electricity and are called **nonelectrolytes**.

Solutions have properties that differ from those of the pure solvent. Some of these are **colligative** properties, which are due to the number of solute particles dissolved, not the chemical identity of the solute. Colligative properties include **vapor pressure depression**, **boiling point elevation**, **freezing point depression**, and **osmotic pressure**. Osmotic pressure is particularly important in biological systems. It is caused by **osmosis**, the passage of solvents through certain membranes like cell walls. The **osmolarity** of a solution is the product of a solution's molarity and the number of particles a solute separates into when it dissolves. Osmosis can be reversed by the application of pressure; this reverse osmosis is used to make fresh water from saltwater in some parts of the world. Because of osmosis, red blood cells placed in hypotonic or hypertonic solutions lose function through either hemolysis or crenation. If they are placed in isotonic solutions, however, the cells are unaffected because osmotic pressure is equal on either side of the cell membrane.
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9.E: Exercises

ADDITIONAL EXERCISES

1. Calcium nitrate reacts with sodium carbonate to precipitate solid calcium carbonate:

   $Ca(NO_3)_2(aq) + Na_2CO_3(aq) \rightarrow CaCO_3(s) + 2NaNO_3(aq)$

   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) What was the osmolarity of the 50.0 mL of 0.450 M $Ca(NO_3)_2$ solution before the reaction?

2. 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. (The normal freezing point of water is zero celsius. For every mole of particles in a liter of water, the freezing point decreases by about 1.9°C.)

3. 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. (Hint: Think about the units on top and on bottom of each concentration, then how to convert the top and bottom.)

4. 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?

5. 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?

Answers

1. A) $Ca(NO_3)_2(aq) + Na_2CO_3(aq) \rightarrow CaCO_3(s) + 2NaNO_3(aq)$; B) 2.39 g; C) 1.35 osmol
2. –45.6°C
3. 3.0% (m/m) is 3.0 g NaCl per 100 g solution. The 3.0 g NaCl can be converted to moles using molar mass. The 100 g solution can be converted to mL using density, and then to liters. Moles NaCl, divided by liters of solution gives **0.51 M**. Since each NaCl breaks up into two ions (i = 2), the molarity is doubled to get the molarity of particles (a.k.a. osmolarity), **1.0 osmol**.

4. The final volume needs to be 100. mL total. This means that **75.0 mL** of water must be added to the initial 25.0 mL of solution.

5. 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 collapsing and killing the cells (crenation).

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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.

10.1: Arrhenius Definition of Acids and Bases

10.2 Brønsted-Lowry Definition of Acids and Bases

10.3: Water - Both an Acid and a Base

10.4: The Strengths of Acids and Bases

10.5: Buffers

10.6: Chapter Summary

10.E: Exercises

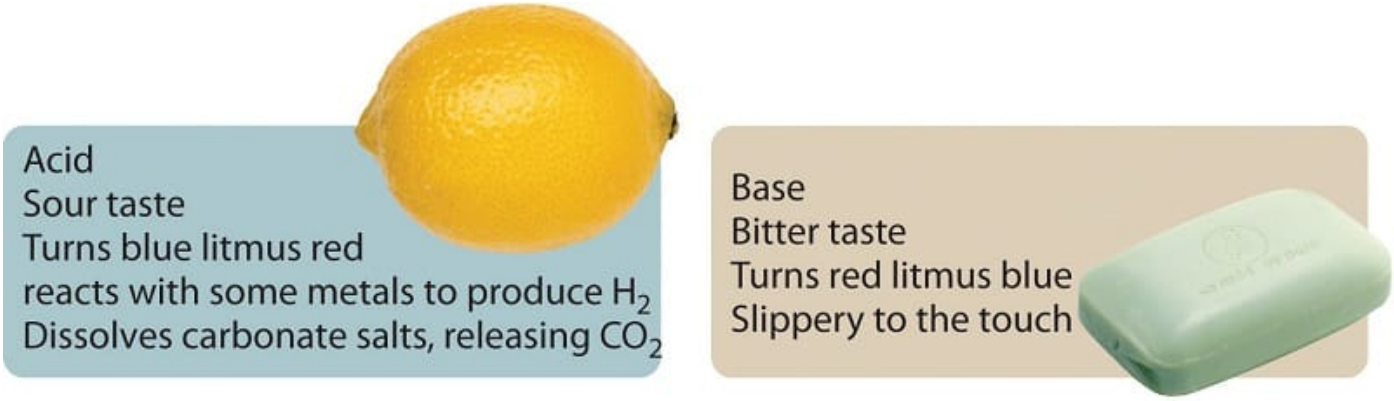
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10.1: Arrhenius Definition of Acids and Bases

Skills to Develop

- To recognize a compound as an Arrhenius acid or an Arrhenius base.

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		
HNO_2(aq)	nitrous acid		
H_2SO_4(aq)	sulfuric acid		

Acids		Bases	
$H_2SO_3(aq)$	sulfurous acid		
$HClO_3(aq)$	chloric acid		
$HClO_4(aq)$	perchloric acid		
$HClO_2(aq)$	chlorous acid		
$H_3PO_4(aq)$	phosphoric acid		
$H_3PO_3(aq)$	phosphorous 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.

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:

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

The reaction of acid and base to make water and a salt is called **neutralization**, which is a type of double replacement reaction. 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 HCl provides H^+ and Cl^- ions. The NaOH provides Na^+ and OH^- ions. The H^+ and OH^- ions combine to form H_2O. The Na^+ and Cl^- ions are the salt, NaCl (essentially left-over ions).

The neutralization reaction between sodium hydroxide and sulfuric acid is as follows:

$$2NaOH_{(aq)} + H_2SO_{4(aq)} \rightarrow Na_2SO_{4(aq)} + 2H_2O_{(\ell)} \tag{10.1.3}$$

The H_2SO_4 provides H^+ and SO_4^{2-} ions. The NaOH provides Na^+ and OH^- ions. The H^+ and OH^- ions combine to form H_2O. The Na^+ and SO_4^{2-} ions are the salt, with formula Na_2SO_4. Remember from Chapter 3 that in the formula of an ionic compound, the charges should balance to zero (so two Na^+ ions for every one SO_4^{2-} ion). Once a neutralization reaction is properly balanced, we can use it to perform stoichiometry calculations, such as the ones we practiced earlier.

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. Notice that, since two OH^- ions react with two H^+ ions, we get two H_2O.

b. This calculation is much like the calculations we did in Chapter 6 "Quantities in Chemical Reactions". First we convert the mass of HNO_3 to moles using its molar mass of 1.01 + 14.00 + 3(16.00) = 63.01 g/mol. Second, we use the ratio from the balanced chemical equation to determine the related number of moles of $Ca(OH)_2$ needed to neutralize it. Third, 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.

$$16.8\ \text{g HNO}_3 \times \frac{1\ \text{mol HNO}_3}{63.01\ \text{g HNO}_3} \times \frac{1\ \text{mol Ca(OH)}_2}{2\ \text{mol HNO}_3} \times \frac{74.10\ \text{g Ca(OH)}_2}{1\ \text{mol Ca(OH)}_2} = 9.88\ \text{g Ca(OH)}_2\ \text{needed}$$

c. Having concentration information allows us to employ the skills we developed in Chapter 9. First, we use the molarity (mol/L) and volume data to determine the number of moles of $Ca(OH)_2$ present. Recognizing that 805 mL = 0.805 L,

$$\frac{0.672\ \text{mol Ca(OH)}_2}{1\ \text{L soln}} = \frac{?\text{mol Ca(OH)}_2}{0.805\ \text{L soln}}$$

$$\frac{0.672\ \text{mol Ca(OH)}_2}{1\ \text{L soln}} \text{x}\ 0.805\ \text{L soln} = ?\ \text{mol Ca(OH)}_2 = 0.541\ \text{mol Ca(OH)}_2$$

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 (number of moles per one liter) one more time, we determine the volume of acid solution needed:

$$\frac{0.432\ \text{mol HNO}_3}{1\ \text{L soln}} = \frac{1.08\text{mol HNO}_3}{?\ \text{L soln}}$$

$$?\text{volume of HNO}_3\ \text{soln} = \frac{1\ \text{L soln}}{0.432\ \text{mol HNO}_3} \text{x}\ 1.08\ \text{mol HNO}_3 = 2.50\ \text{L soln} = 2.50 \times 10^3\ \text{mL HNO}_3\ \text{soln}$$

Example 10.1.3

Oxalic acid [$H_2C_2O_4$(aq)] can be neutralized by potassium hydroxide [KOH(aq)].

a. Write a balanced chemical equation for the reaction between these two compounds.
b. If 0.250 L of aqueous potassium hydroxide are required to neutralize 45.0 g of oxalic acid, find the concentration (M) of the original 0.250 L of potassium hydroxide solution.

SOLUTION

a. Because there are two H^+ ions in the formula for $H_2C_2O_4$, we need two moles of KOH to provide OH^- ions (and form two waters). The balanced chemical equation is as follows:

$$H_2C_2O_4(aq) + 2KOH(aq) \rightarrow K_2C_2O_4(aq) + 2H_2O(\ell)$$

b. The molar mass of oxalic acid from the periodic table, 90.03 g/mol, can be used to convert grams to moles.

$$\frac{1\ \text{mol H}_2\text{C}_2\text{O}_4}{90.03\ \text{g H}_2\text{C}_2\text{O}_4} \text{x}\ 45.0\ \text{g H}_2\text{C}_2\text{O}_4 = 0.500\ \text{mol H}_2\text{C}_2\text{O}_4$$

We combine this information with the proper ratio from the balanced chemical equation to determine the number of moles of KOH needed:

$$0.500\ \text{mol H}_2\text{C}_2\text{O}_4 \times \frac{2\ \text{mol KOH}}{1\ \text{mol H}_2\text{C}_2\text{O}_4} = 1.00\ \text{mol KOH}$$

Now that we have moles of KOH, we can divide by the volume of KOH solution (0.250 L) to obtain molairty (mol/L).

$$\frac{0.432\ \text{mol KOH}}{1\ \text{L soln}} = \frac{1.08\text{mol KOH}}{?\ \text{L soln}}$$

$$?\text{molarity of KOH soln} = \frac{1.00\ \text{mol KOH}}{0.250\ \text{L KOH soln}} = 4.00\ \text{M KOH soln}$$

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

Key Takeaway

- An Arrhenius acid increases the H^+ ion concentration in water, while an Arrhenius base increases the OH^- ion concentration in water.

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10.2 Brønsted-Lowry Definition of Acids and Bases

Skills to Develop

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.

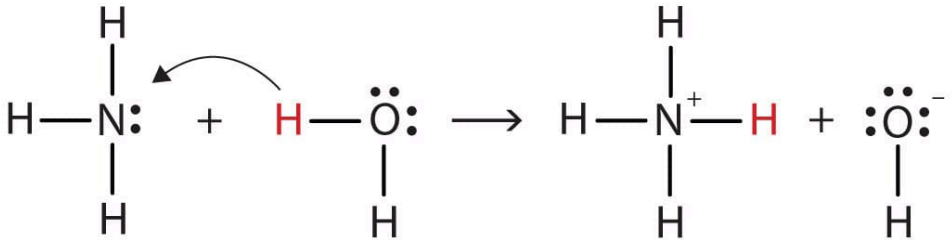
Ammonia (NH_3) increases the hydroxide ion concentration in aqueous solution by reacting with water rather than releasing hydroxide ions directly. In fact, the Arrhenius definitions of an acid and a base focus on hydrogen ions and hydroxide ions. Are there more fundamental definitions for acids and bases?

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:

$$NH_{3(aq)} + H_2O_{(\ell)} \rightarrow NH^+_{4(aq)} + OH^-_{(aq)} \tag{1}$$

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.

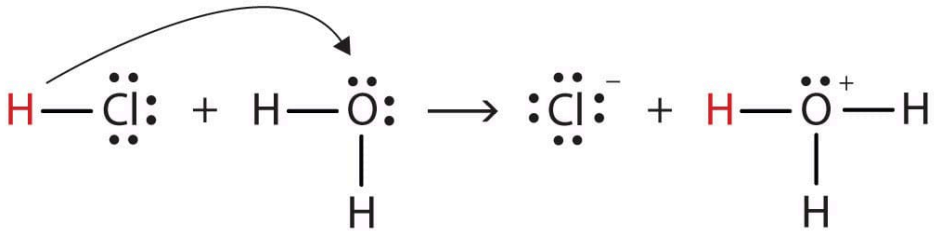
Is an Arrhenius acid like hydrochloric acid still an acid in the Brønsted-Lowry sense? Yes, but it requires us to understand what really happens when HCl is dissolved in water. Recall that the hydrogen *atom* is a single proton surrounded by a single electron. To make the hydrogen *ion*, we remove the 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:

$$HCl_{(g)} + H_2O_{(\ell)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)} \tag{2}$$

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.

CONJUGATE BASE AND ACID

After the acid loses a proton, it is often referred to as the conjugate base. For example, if the monoprotic acid HCl loses a proton, it becomes Cl^-. The Cl^- no longer has a proton so is no longer an acid, so we call it the conjugate base. An acid like H_2SO_4, is called diprotic because it has two protons that can be donated. After losing one proton, H_2SO_4 becomes HSO_4^-. The HSO_4^- is still called a conjugate base because it was formed from an acid and will be less acidic than H_2SO_4.

After the base loses a proton, it is often referred to as the conjugate base. For example, if NH_3 base gains a proton, it becomes NH_4^+. The NH_4^+ now has extra protons and is more acidic, so we call it the conjugate acid.

Below are two examples that label the acid, base, conjugate acid and conjugate base for each.

NH_3	+	H_2O	→	NH_4^+	+	OH-
base		acid		conjugate acid		conjugate base

HCl	+	H_2O	→	Cl^-	+	H_3O^+
acid		base		conjugate base		conjugate acid

Example 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, plus conjugates.

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 $C_6H_5NH_3^+$ product is therefore the conjugate acid.

The H_2O molecule, because it donates a proton, is the Brønsted-Lowry acid. The OH^- product is therefore the conjugate base.

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 2

Sodium amide ($NaNH_2$) dissolves in methanol (CH_3OH) and separates into sodium ions and amide ions (NH_2^-). Normally alcohols, like methanol, are not significantly acidic. However in the presence of an extremely strong base, like the amide anion, alcohols will behave as acids. Write a balanced chemical equation for the reaction NH_2^- with CH_3OH. Identify the Brønsted-Lowry acid and base, plus conjugates. Hint: *Pay attention to changes in charges as the proton (H^+) is exchanged.*

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, NH_2^- gains H^+ to make NH_3. As the proton acceptor, NH_2^- is the Brønsted-Lowry base. The NH_3 product is therefore the conjugate acid.

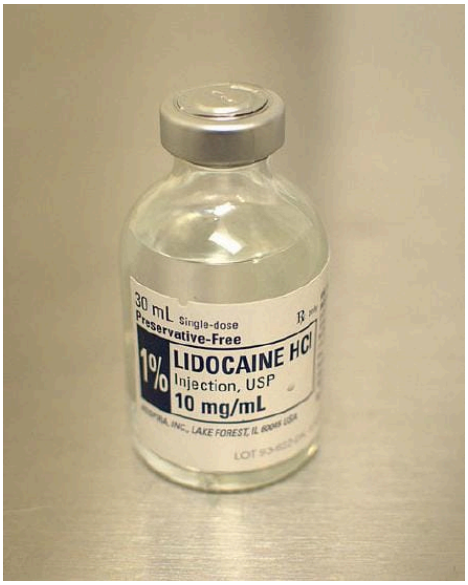
CH_3OH loses H^+ to make CH_3O^-. As the proton donor, CH_3OH is the Brønsted-Lowry acid. The CH_3OH^- product is therefore the conjugate base.

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:

$$\mathrm{RN(sl\,aq) + H^+(aq) \rightarrow RNH^+(aq) \xrightarrow{Cl^-(aq)} RNHCl(s)} \quad (3)$$

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 as a hydrochloride salt.



The name of this medicine makes it clear that it exists as the hydrochloride salt. Figure used with permission from Wikipedia.

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.

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.

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10.3: Water - Both an Acid and a Base

Skills to Develop

- 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:

$$\mathrm{HCl} + \mathrm{H_2O}_{(\ell)} \rightarrow \mathrm{H_3O^+_{(aq)}} + \mathrm{Cl^-_{(aq)}} \tag{10.3.1}$$

In other circumstances, a water molecule can donate a proton and thus act as a Brønsted-Lowry acid. For example, in the presence of the amide ion (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.)

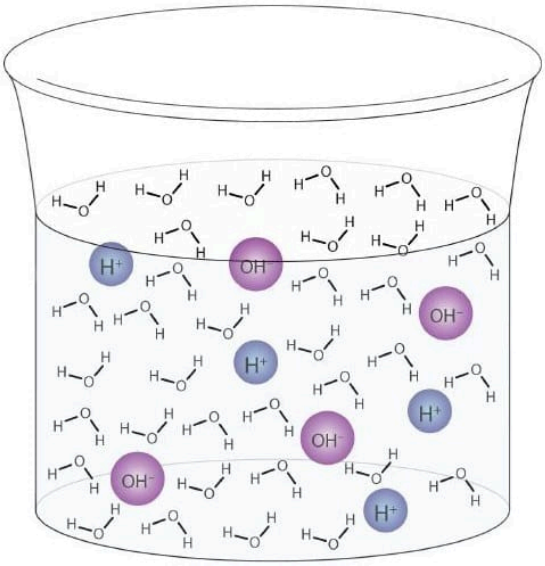


Figure 10.3.1 *Autoionization. A small fraction of water molecules—approximately 6 in 100 million—ionize spontaneously into hydronium ions and hydroxide ions. This picture necessarily overrepresents the amount of autoionization that really occurs in pure water.*

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.

Concept Review Exercises

1. Explain how water can act as an acid.
2. Explain how water can act as a base.

Answers

1. Under the right conditions, H_2O can donate a proton, making it a Brønsted-Lowry acid.
2. Under the right conditions, H_2O can accept a proton, making it a Brønsted-Lowry base.

Key Takeaway

- Water molecules can act as both an acid and a base, depending on the conditions.

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10.4: The Strengths of Acids and Bases

Skills to Develop

- 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:

$$\mathrm{HCl_{(g)} + H_2O_{(l)} \xrightarrow{\sim 100\%} H_3O^+_{(aq)} + Cl^-_{(aq)}} \tag{10.4.1}$$

Because the subscripts indicate that the reaction is taking place in water, aqueous (aq), sometimes the water is not explicitly shown.

$$\mathrm{HCl_{(g)} \xrightarrow{water} H^+_{(aq)} + Cl^-_{(aq)}} \tag{10.4.2}$$

These first two chemical equations are equivalent. The aqueous proton ($H^+_{(aq)}$) is dissolved in water, or hydrated, so is assumed to be the same as writing it as the hydronium ion ($H_3O^+_{(aq)}$). (i.e. H_3O^+ is essentially H_2O bonded to H^+, and "aq" can represent the water.)

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:

$$HC_2H_3O_{2(aq)} + H_2O_{(\ell)} \rightarrow H_3O^+_{(aq)} + C_2H_3O^-_{2(aq)} \tag{10.4.3}$$

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:

$$NH_{3(aq)} + H_2O_{(\ell)} \rightarrow NH^+_{4(aq)} + OH^-_{(aq)} \tag{10.4.4}$$

Many soaps are also slightly basic because they contain compounds that act as Brønsted-Lowry bases, accepting protons from water and forming excess hydroxide ions. This is one reason that soap solutions are slippery.



Figure 10.4.1*: (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

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 $HC_2H_3O_2$ (aq) is as follows:

$$HC_2H_3O_{2(aq)} + H_2O_{(\ell)} \rightarrow H_3O^+_{(aq)} + C_2H_3O^-_{2(aq)} \tag{10.4.5}$$

The reverse process also begins to occur:

$$H_3O^+_{(aq)} + C_2H_3O^-_{2(aq)} \rightarrow HC_2H_3O_{2(aq)} + H_2O_{(\ell)} \tag{10.4.6}$$

Eventually, there is a balance between the two opposing processes, and no additional change occurs. The chemical reaction is better represented at this point with a double arrow:

$$HC_2H_3O_{2(aq)} + H_2O_{(\ell)} \rightleftharpoons H_3O^+_{(aq)} + C_2H_3O^-_{2(aq)} \tag{10.4.7}$$

The $\rightleftharpoons$ implies that both the forward and reverse reactions are occurring, and their effects cancel each other out. A process at this point is considered to be at chemical equilibrium (or equilibrium). It is important to note that the processes do not stop. They balance out each other so that there is no further net change; that is, chemical equilibrium is a *dynamic equilibrium*.

Example 10.4.1: Partial Ionization

Write the equilibrium chemical equation for the partial ionization of each weak acid or base.

a. HNO_2(aq)
b. C_5H_5N(aq)

SOLUTION

a. $HNO_2(aq) + H_2O(\ell) \diamond NO_2^-(aq) + H_3O^+(aq)$ or $HNO_2(aq) \diamond NO_2^-(aq) + H^+(aq)$
b. $C_5H_5N(aq) + H_2O(\ell) \diamond C_5H_5NH^+(aq) + OH^-(aq)$

Finally, you may realize that the autoionization of water is actually an equilibrium process, so it is more properly written with the double arrow:

$$H_2O_{(\ell)} + H_2O_{(\ell)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)} \tag{10.4.8}$$

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. Again, H^+ and H_3O^+ are assumed to be equivalent in water (aqueous).

$$pH = -\log[H^+] \tag{10.4.9}$$

or

$$pH = -\log[H_3O^+] \tag{10.4.10}$$

A neutral (neither acidic nor basic) solution, one that has the same concentration of hydrogen and hydroxide ions, 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. Table 10.4.2 lists the pH of several common solutions. Notice that some biological fluids are nowhere near neutral.

Table 10.4.2***:*** *The pH Values of Some Common Solutions*

Solution	pH
battery acid	0.3
stomach acid	1–2
lemon or lime juice	2.1
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

Weak acids and bases are relatively common. You may notice from Table $10.4.2$ 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.

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 pH scale is used to succinctly communicate the acidity or basicity of a solution.

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10.5: Buffers

Skills to Develop

- 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. Buffers do so by being composed of certain pairs of solutes: either a weak acid plus a salt derived from that weak acid or a weak base plus a salt of that weak base. For example, a buffer can be composed of dissolved acetic acid ($HC_2H_3O_2$, a weak acid) and sodium acetate ($NaC_2H_3O_2$, a salt derived from that acid). Another example of a buffer is a solution containing ammonia (NH_3, a weak base) and ammonium chloride (NH_4Cl, a salt derived from that base).

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.

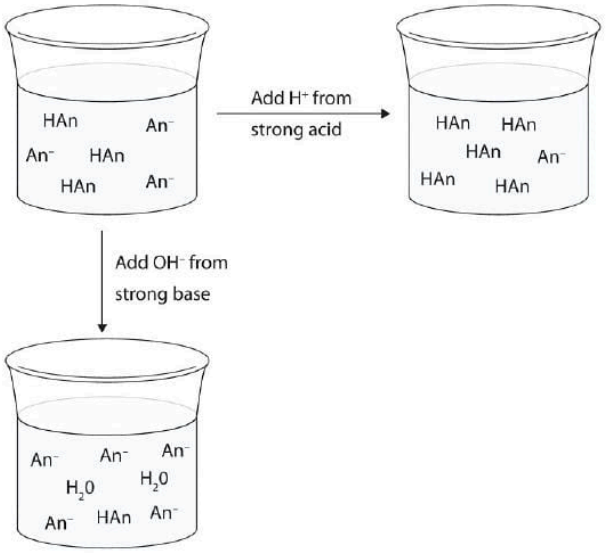


Figure 10.5.1: *The Action of Buffers. Buffers can react with both strong acids (top) and strong bases (bottom) to minimize large changes in pH.*

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:

$$NH^+_{4(aq)} + OH^-_{(aq)} \rightarrow NH_{3(aq)} + H_2O_{(\ell)} \tag{10.5.4}$$

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 the salt made from the anion of the weak acid—the formate ion (CHO_2^-). The combination of these two solutes would make a buffer solution.
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 with one of its hydrogen atoms substituted with a CH_3 (methyl) group. Because it is not on our list of strong bases, we can assume that it is a weak base. The compound CH_3NH_3Cl is a salt made from that weak base, so the combination of these two solutes would make a buffer solution.
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.

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.

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.

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.

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10.6: Chapter 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.

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10.E: Exercises

10.1 Arrhenius Definition of Acids and Bases

Exercises

1. Give two examples of Arrhenius acids and two of Arrhenius bases.
2. List the general properties of acids.
3. List the general properties of bases.
4. Write a balanced chemical equation for the neutralization of $Ba(OH)_2(aq)$ with $HNO_3(aq)$.
5. 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.)
6. Hydrazoic acid (HN_3) can be neutralized by a base. (The azide ion, N_3^-, is a polyatomic ion with three nitrogen atoms and a -1 charge.)

   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?
7. Magnesium hydroxide [$Mg(OH)_2$] is an ingredient in some antacids. How is the molarity of 101 mL of $Mg(OH)_2$ solution if it can neutralize 158 mL of 0.106 M HCl(aq)? You will need to write the balanced chemical equation.

Answers

1. HCl and HNO_3 are acids and NaOH and NH_3 are bases. (answers will vary)
2. sour taste, react with metals, react with bases, and turn litmus red
3. bitter taste, turns red litmus blue, slippery to the touch
4. $2HNO_3(aq) + Ba(OH)_2(aq) \rightarrow Ba(NO_3)_2(aq) + 2H_2O(\ell)$
5. 0.844 mol
6. A) $2HN_3(aq) + Ca(OH)_2 \rightarrow Ca(N_3)_2 + 2H_2O$; B) 268 mL
7. (0.106 mol HCl / L HCl soln) (0.158 L HCl soln) (1 mol $Mg(OH)_2$ / 2 mol HCl) (1 / 0.101 L $Mg(OH)_2$ soln) = 0.0829 mol $Mg(OH)_2$ / L $Mg(OH)_2$ soln = 0.0829 M $Mg(OH)_2$

10.2 Brønsted-Lowry Definition of Acids and Bases

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. Explain why a Brønsted-Lowry acid can be called a proton donor.
3. Write the chemical equation of the reaction of ammonia in water and label the Brønsted-Lowry acid and base.
4. 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.

Answers

1. HCl: Brønsted-Lowry acid; NH_3: Brønsted-Lowry base
2. A Brønsted-Lowry acid gives away an H^+ ion—nominally, a proton—in an acid-base reaction.
3. $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$; NH_3: Brønsted-Lowry base; H_2O: Brønsted-Lowry acid
4. $HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$; HNO_3: Brønsted-Lowry acid; H_2O: Brønsted-Lowry base

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10.3 Water: Both an Acid and a 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. 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?

Answers

1. base
2. acid

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. Is each compound a strong acid or a weak acid? Assume all are in aqueous solution. (Hint: Consult Table 10.4.1)

(A) HF; (B) $HC_2H_3O_2$; (C) HCl; (D) $HClO_4$

2. Is each compound a strong base or a weak base? Assume all are in aqueous solution. (Hint: Consult Table 10.4.1)

   (A) NH_3; (B) NaOH; (C) $Mg(OH)_2$; (D) $Cu(OH)_2$

3. Write the chemical equation for the equilibrium process for $HC_2H_3O_2$.

4. Write the chemical equation for the equilibrium process for NH_3.

5. Consider two different solutions, 0.15 M HCl and 0.15 M HF. (A) Which would have lower pH? (B) Which would have lower freezing point?

Answers

1. (A) weak; (B) weak; (C) strong; (D) strong
2. (A) weak; (B) strong; (C) strong; (D) weak
3. $HC_2H_3O_2(aq) \diamondsuit H^+(aq) + C_2H_3O_2^-(aq)$
4. $NH_3(aq) + H_2O \diamondsuit NH_4^+(aq) + OH^-(aq)$
5. (A) The HCl solution will have lower pH (because larger concentration of H+). (Both are the same concentration, but HF is a weak acid so does not ionize completely so there will be a lower $[H^+]$ and thus higher pH for HF.) (B) The HCl will have lower freezing point because there is a larger concentration of dissolved particles (since it completely ionizes).

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. Which solute combinations can make a buffer? Assume all are aqueous solutions.

   A) HCl and NaCl; B) HNO_2 and $NaNO_2$; C) NH_4NO_3 and HNO_3; D) NH_4NO_3 and NH_3

3. For each combination in Exercise 2 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.

4. 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?

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. A) not a buffer; B) buffer; C) not a buffer; D) buffer
3. #2b: strong acid: $H^+ + NO_2^- \rightarrow HNO_2$; strong base: $OH^- + HNO_2 \rightarrow H_2O + NO_2^-$; #2d: strong acid: $H^+ + NH_3 \rightarrow NH_4^+$; strong

base: $OH^- + NH_4^+ \rightarrow H_2O + NH_3$

4. 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-}.

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11: ORGANIC CHEMISTRY

We begin our study of organic chemistry with the alkanes, compounds containing only two elements, carbon and hydrogen, and having only single bonds. There are several other kinds of hydrocarbons, distinguished by the types of bonding between carbon atoms and by the properties that result from that bonding. We will examine several other types of hydrocarbons, then look at other organic functional groups including those with atoms like oxygen and nitrogen. Finally, we focus on organic acids and bases, after which we will be ready to look at the chemistry of life itself—biochemistry—in the remaining chapters.

11.1: Organic Chemistry

11.2: Alkanes

11.3: Condensed Structural and Line-Angle Formulas

11.4: Cycloalkanes

11.5: Alkenes

11.6: IUPAC Nomenclature

11.7: Organic Compounds with Functional Groups

11.8: Physical Properties of Organic Compounds

11.9: Chemical Properties: Carboxylic Acids

11.10: Chemical Properties: Amines as Bases

11.E: Organic Chemistry (Exercises)

11.S: Organic Chemistry (Summary)

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11.1: Organic Chemistry

Skills to Develop

- 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.

$$AgOCN + NH_4Cl \rightarrow AgCl + NH_4OCN \tag{11.1.1}$$

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 11.1.1.

Table 11.1.1*: General Contrasting Properties and Examples of Organic and Inorganic Compounds*

Organic	Hexane		Inorganic
low melting points	–95°C		high melting points
low boiling points	69°C		high boiling points

Organic	Hexane		Inorganic
low solubility in water; high solubility in nonpolar solvents	insoluble in water; soluble in gasoline		greater solubility in water; low solubility in nonp
flammable	highly flammable		nonflammable
aqueous solutions do not conduct electricity	nonconductive		aqueous solutions conduct electricit
exhibit covalent bonding	covalent bonds		exhibit ionic bonding

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 11.1.1 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 11.1.1.

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11.2: Alkanes

Skills to Develop

- To identify and name simple (straight-chain) alkanes given formulas and write formulas for straight-chain alkanes given their names.
- To learn how alkane molecules can have branched chains and recognize compounds that are isomers.

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 11.2.1.

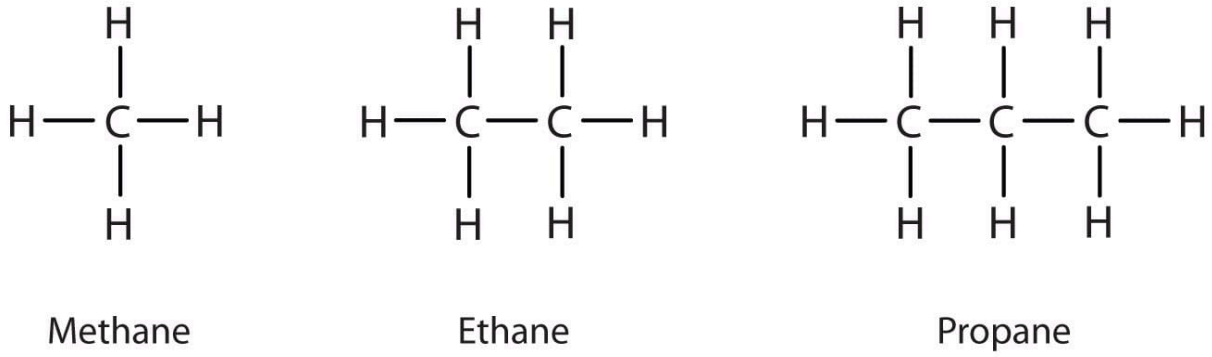


Figure 11.2.1***:*** *The Three Simplest Alkanes*

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 11.2.2).

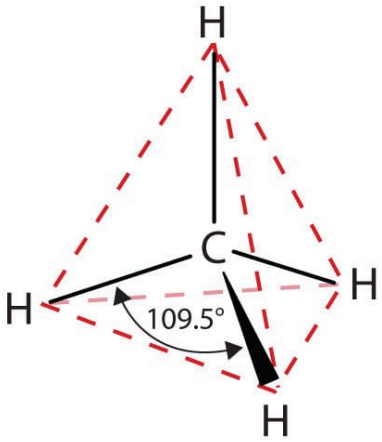


Figure 11.2.2**:** The Tetrahedral Methane Molecule

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 11.2.1.

Table 11.2.1***:*** *The First 10 Straight-Chain Alkanes*

Name	Molecular Formula (C_nH_{2n+2})	C
methane	CH_4	
ethane	C_2H_6	
propane	C_3H_8	
butane	C_4H_{10}	
pentane	C_5H_{12}	
hexane	C_6H_{14}	
heptane	C_7H_{16}	
octane	C_8H_{18}	Cl
nonane	C_9H_{20}	CH_3
decane	$C_{10}H_{22}$	CH_3Cl

Consider the series in Figure 11.2.3. 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.

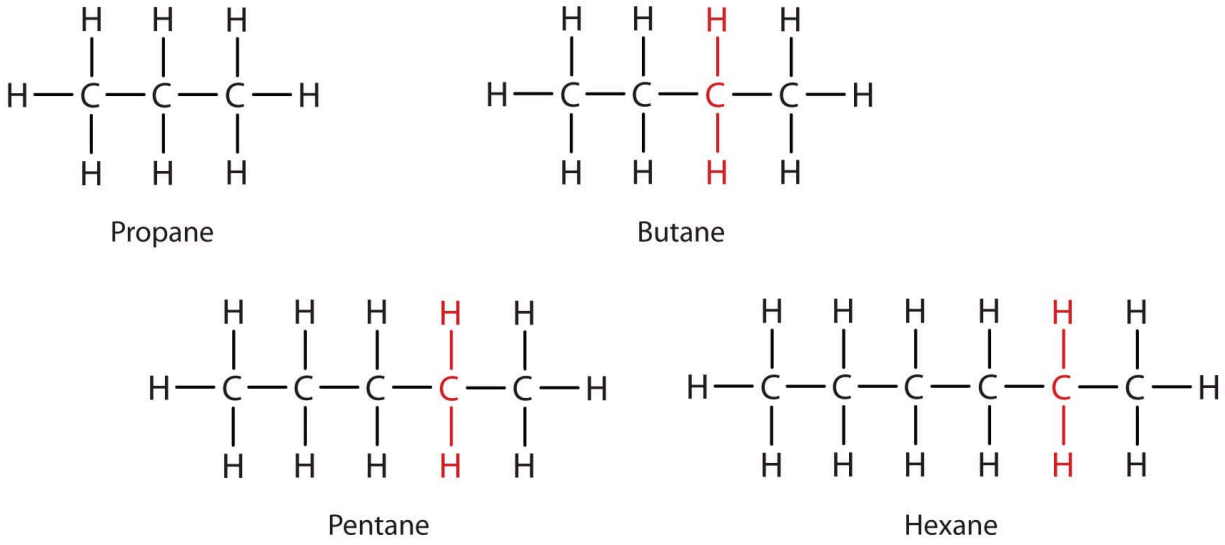


Figure 11.2.3*: Members of a Homologous Series. Each succeeding formula incorporates one carbon atom and two hydrogen atoms more than the previous formula.*

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 $C_8H_{(2\,\times\,8)\,+\,2} = C_8H_{18}$.

Example 11.2.1

Determine the formula for dodecane, an alkane with twelve carbons.

SOLUTION

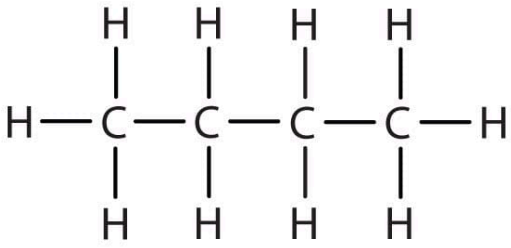
The general formula will be $C_nH_{2n\,+\,2}$. It has twelve carbons, so n = 12. The number of hydrogens is 2n+2 = 2(12)+2 = 26. The formula is therefore $C_{12}H_{26}$.

Branched-Chain Alkanes

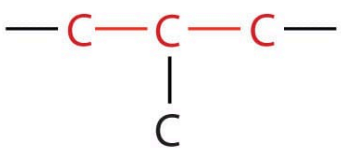
As seen above, we can write the structure of butane (C_4H_{10}) by stringing four carbon atoms in a row,

–C–C–C–C–

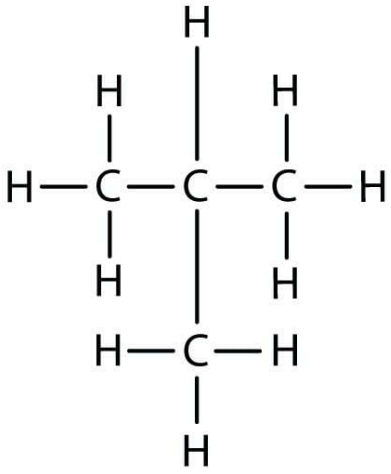
and then adding enough hydrogen atoms to give each carbon atom four bonds:



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.



There is a hydrocarbon that corresponds to this structure, which means that two different compounds have the same molecular formula: C_4H_{10}. The two compounds have different properties—for example, one boils at −0.5°C; the other at −11.7°C. Different compounds having the same molecular formula are called isomers. The compound with this branched chain is called *isobutane* (Figure 11.2.4).

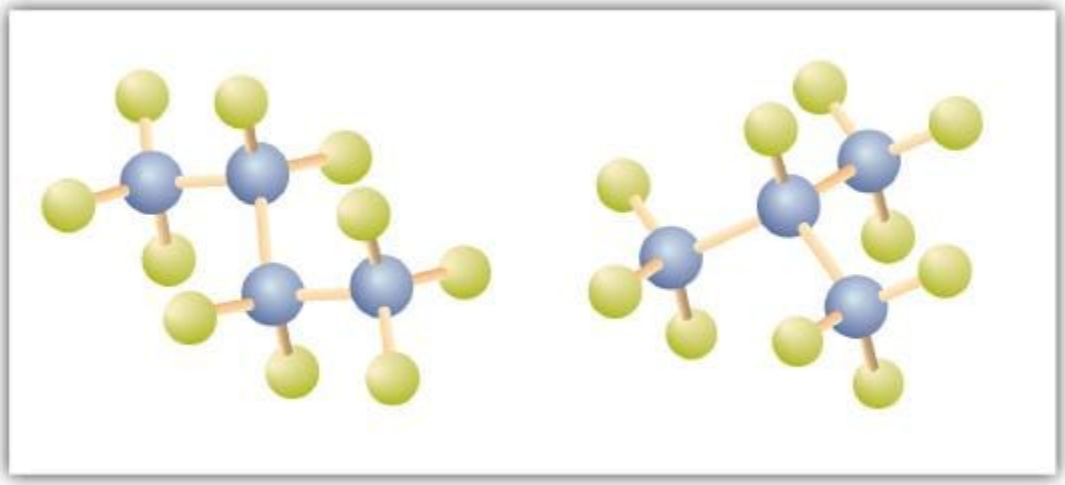
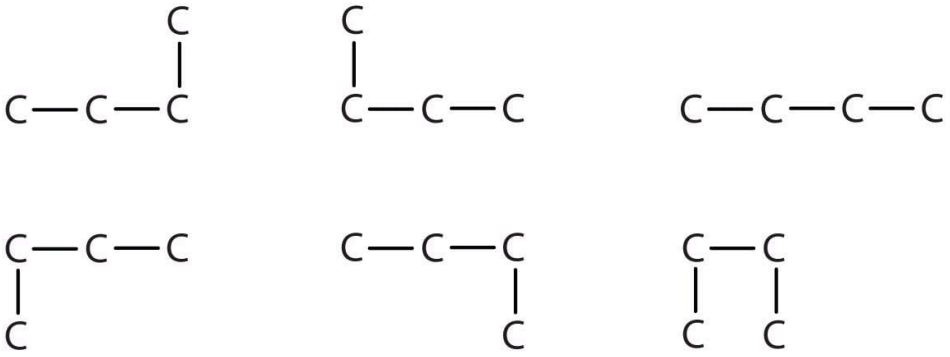


Figure 11.2.4***:*** *Butane and Isobutane. The ball-and-stick models of these two compounds show them to be isomers; both have the molecular formula C_4H_{10}.*

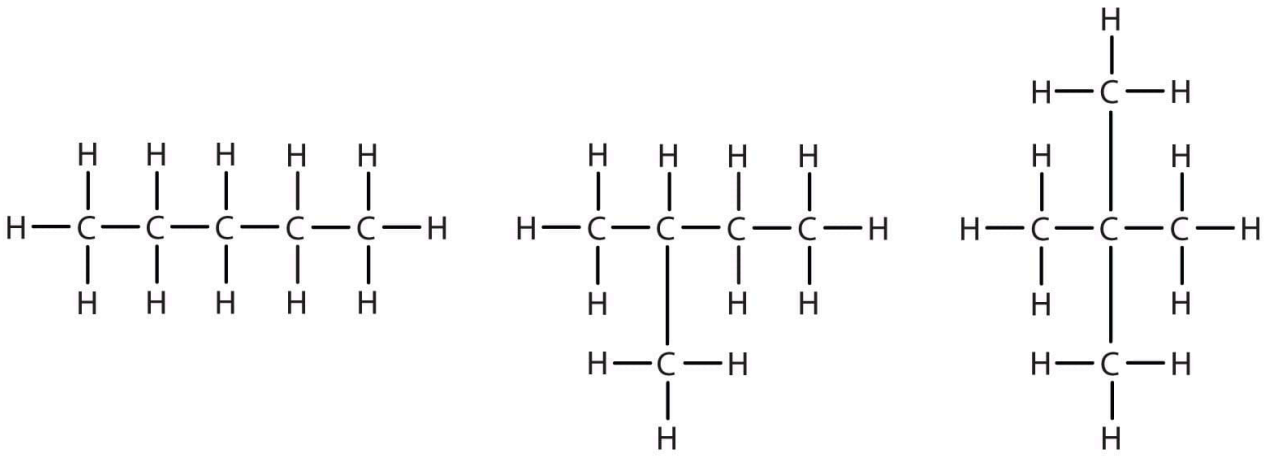
Notice that C_4H_{10} is depicted with a bent chain in Figure 11.2.1. The four-carbon chain may be bent in various ways because the groups can rotate freely about the C–C bonds. However, this rotation does not change the identity of the compound. It is important to realize that bending a chain does *not* change the identity of the compound; all of the following represent the same compound:



The formula 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.

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 12.2 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 nt use that prefix here because it is not a part of the system established by the International Union of Pure and Applied Chemistry.

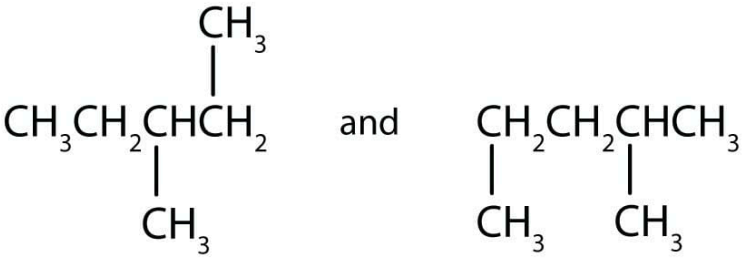
Example 11.2.2

Indicate whether the structures in each pair represent the same compound, isomers, or neither.

A)



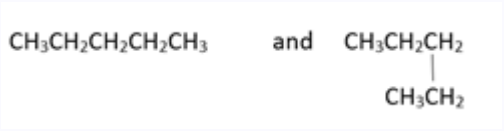
B)



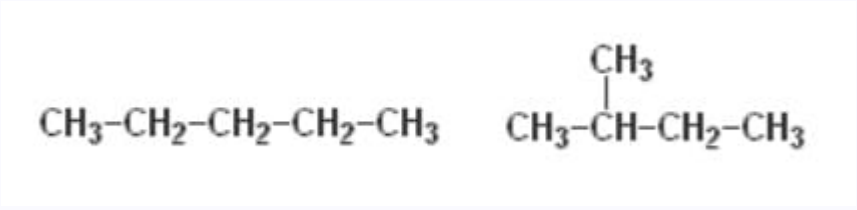
C)



D)



E)



SOLUTION

A) same

B) isomers

C) isomers

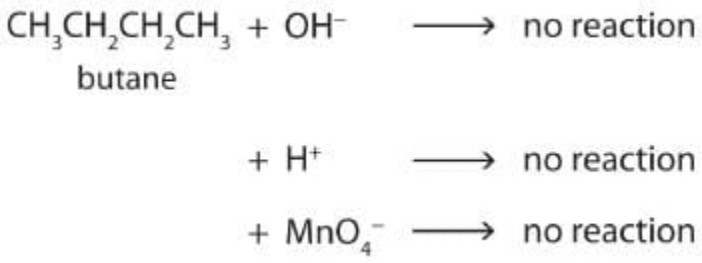
D) same

E) isomers

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:



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.”

One important reactions that the alkanes do undergo is combustion. Nothing happens when alkanes are merely mixed with oxygen (O_2) at room temperature, but when a flame or spark provides the activation energy, a highly exothermic combustion reaction proceeds vigorously. For methane (CH_4), the reaction is as follows:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + \text{heat} \tag{11.2.1}$$

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:

$$2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O \tag{11.2.2}$$

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.)

Key Takeaways

- Simple alkanes exist as a homologous series, in which adjacent members differ by a CH_2 unit.
- If the carbon chain of an alkane can branch to make different connections but with the same formula, the different versions are called isomers.
- Because of the non-polar nature of alkanes, they are relatively unreactive; one important exception is combustion with oxygen.

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11.3: Condensed Structural and Line-Angle Formulas

Skills to Develop

- 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:



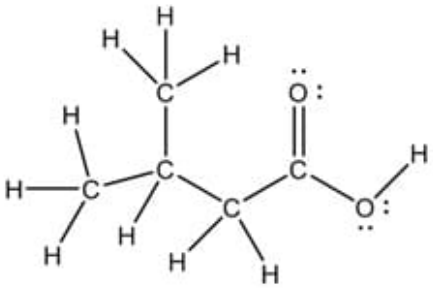
Even more abbreviated is a **line-angle** formula, also called a *skeletal* structure, in which carbon atoms are implied at the corners and ends of lines, and each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds. All other types of atoms are shown and hydrogens bonded to atoms other than carbon are shown. For example, we can represent pentane ($CH_3CH_2CH_2CH_2CH_3$) and isopentane [$(CH_3)_2CHCH_2CH_3$] as follows:



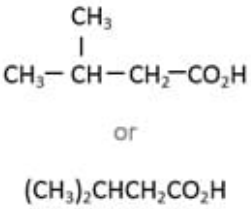
Parentheses in condensed structural formulas indicate that the enclosed grouping of atoms is attached to the adjacent carbon atom.

Below is an example of a more complicated molecule. On the left is shown the complete Lewis structure, showing all atoms and valence electrons. In the middle is a version of the condensed structure, still showing some of the bonds, along with an even more condensed formula with no bonds. Finally, on the right is the line-angle (skeletal) structure; notice that the bonds are shown, but not the carbons and not the hydrogens bonded to carbon.

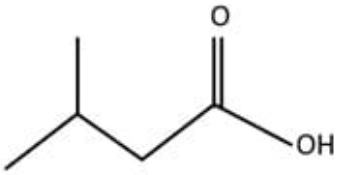
Complete Lewis Structure



Condensed Structure/Formula

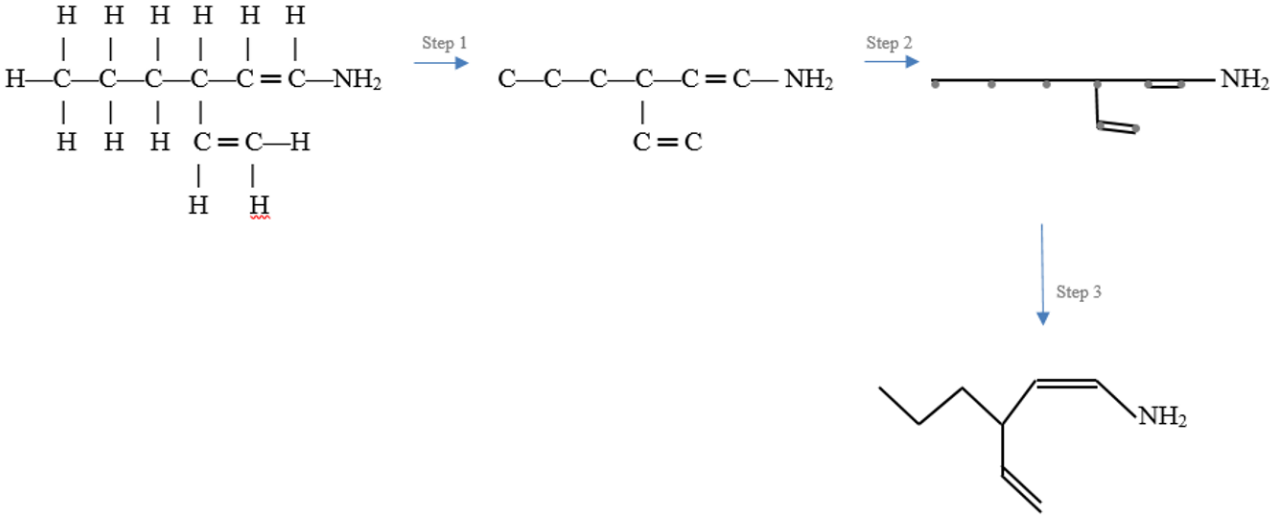


Line-Angle Structure



The following are suggested steps for drawing a line-angle structure (also known as a skeletal structure).

1. Remove all hydrogens bonded to carbons.
2. Remove all carbons.
3. Because the carbons on the left are drawn straight across, we cannot see corners easily, so bend your lines (zig-zag) so that the corners are apparent.



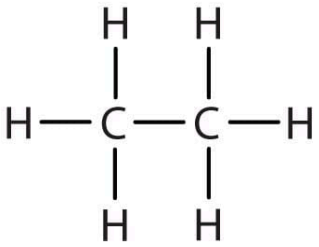
Key Takeaways

- 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.

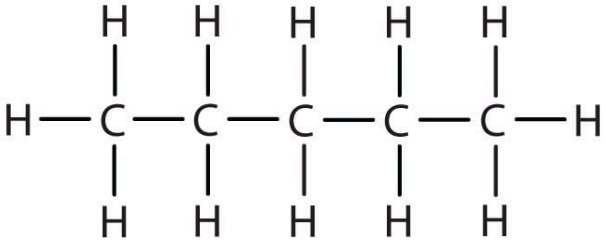
Exercises

1. Write the condensed formula for each Lewis structure.

A.

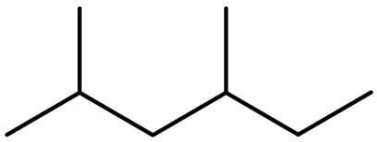


B.

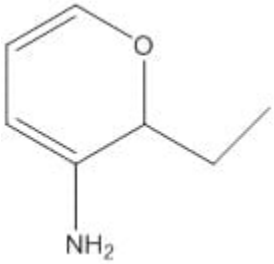


2. Draw a line-angle structure for the compound $CH_3CH_2CH(CH_3)CH_2CH_2CH_3$.

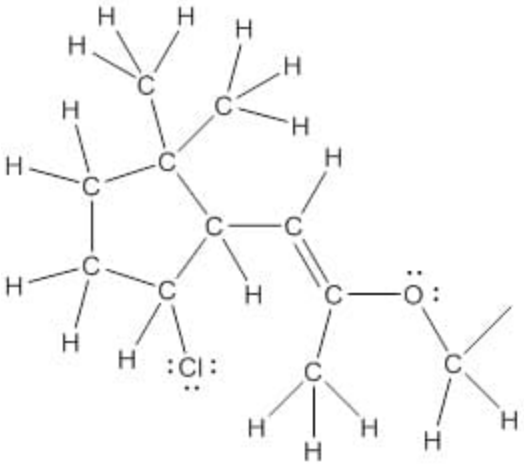
3. Give the condensed formula for the compound represented by this line-angle structure:



4. Draw the Lewis structure of the molecule below, showing all atoms and all valence electrons (bonds and lone pairs).



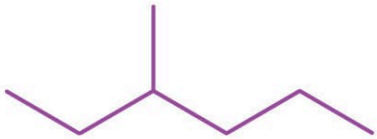
5. Draw the Line-Angle structure for the molecule below.



Answers

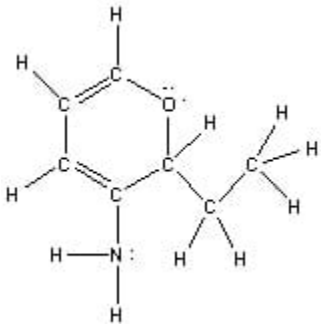
1. A. CH_3CH_3 B. $CH_3CH_2CH_2CH_2CH_3$

2

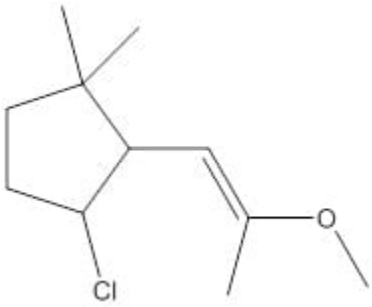


3. $(CH_3)_2CHCH_2CH(CH_3)CH_2CH_3$

4.



5.



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11.4: Cycloalkanes

Skills to Develop

- To draw and name basic cycloalkanes.
- Recognize that alkenes that can exist as geometric isomers and classify isomers as cis or trans.

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 11.4.1) and is called cyclopropane.

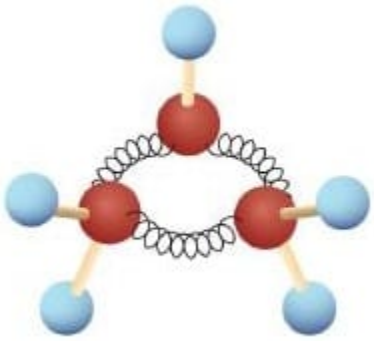


Figure 11.4.1***:*** *Ball-and-Spring Model of Cyclopropane. The springs are bent to join the carbon atoms.*

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.

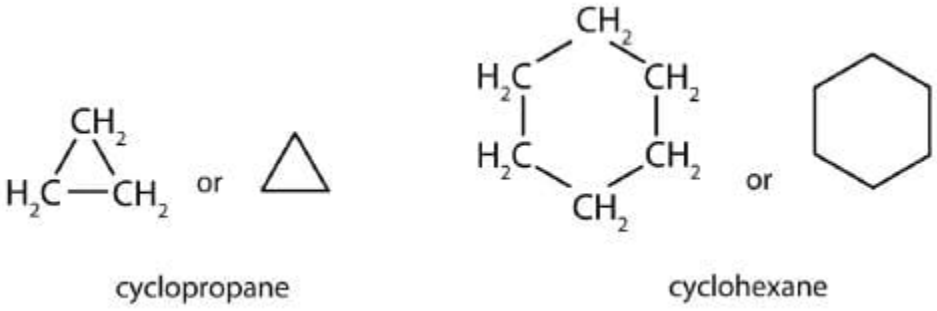
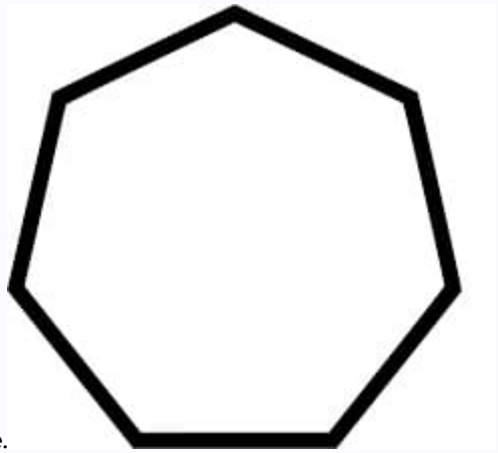


Figure 11.4.2***:*** *Condensed structures and line-angle structures of two cycloalkanes*

Example 11.4.1

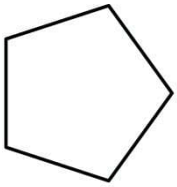
a. Draw the structure of cyclopentane.



a. Propose a name for this structure.

SOLUTION

a. The name *cyclopentane* indicates a cyclic (cyclo) alkane with five (pent-) carbon atoms. It can be represented as a pentagon.



b. The name would be cylcoheptane for this ring of seven carbons (seven-cornered heptagon).

Cis-Trans Geometric Isomers

To obtain tetrahedral 109.5^{0} bond angles around each carbon in a cyclohexane, most rings bend or "pucker" slightly in three dimenstions. Despite this, it will be easier for us to show all cycloalkanes as planar (flat) here. Every carbon a cylcoalkane must have two bonds to other carbons in the ring, plus two other bonds (to make four bonds for an octet). Of the two bonds that are not a part of the ring, one will point up from the plane of the ring and one will point down.

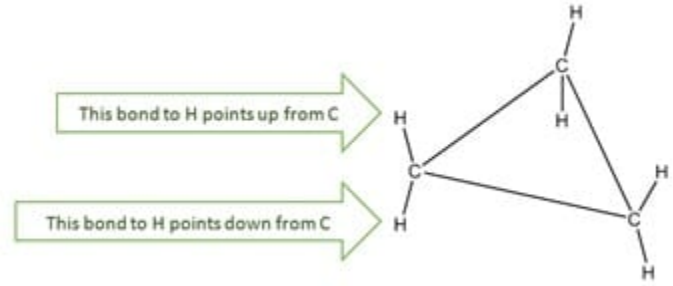
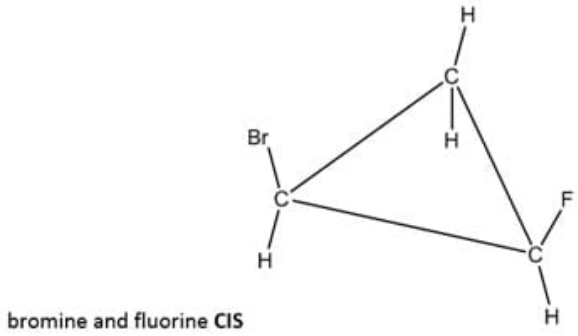


Figure 11.4.3***:*** *Lewis structure of cyclopropane, showing how each carbon has a bond to hydrogen up and down*

If two of the hydrogens on different carbons are replaced by other groups, those new groups can make two new *geometric isomers*. If both groups are pointing in the same direction, both up or both down, it is called

cis (Latin derived “on the near side of; on this side of”). If the two groups are pointing in the opposite direction, one up and one down, it is called **trans** (Latin derived "across from; on the other side of").



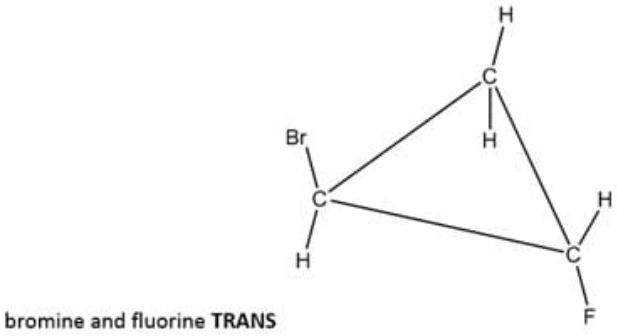
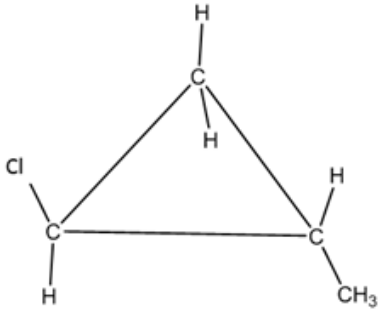


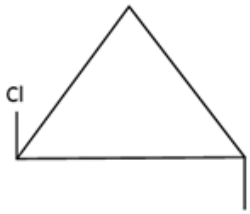
Figure 11.4.4***:*** *Cis and trans examples of a disubstituted cyclopropane ring (bromine on one carbon and fluorine on another*

The above, left image shows a bromine pointing up on one carbon and a fluorine pointing up on another carbon (cis). The above, right image shows a bromine pointing up on one carbon and a fluorine pointing down on another carbon (trans).

Note that if both non-hydrogen groups are bonded to the same carbon of the ring, cis and trans are NOT used because there are not two different ways to make those bonds. (If on the same carbon, one must be up and the other must be down; it is not called trans because there is no cis possiblity.)

When drawing line-angle (skeletal) structures for the rings, the carbons and hydrogens are not shown. To be clear if the non-H groups are up or down, we typically either use vertical lines (up/down) or wedges and dashes. For example, all three images below are different ways to show the same trans molecule (Cl up and CH_3 down).





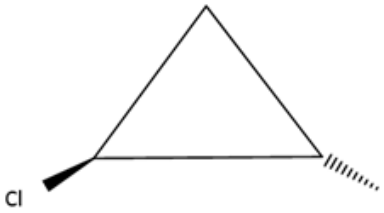


Figure 11.4.5***:*** *Three ways to show a trans disubstitured cylcopropane ring (with chlorine on one carbon and CH_3 on another carbon)*

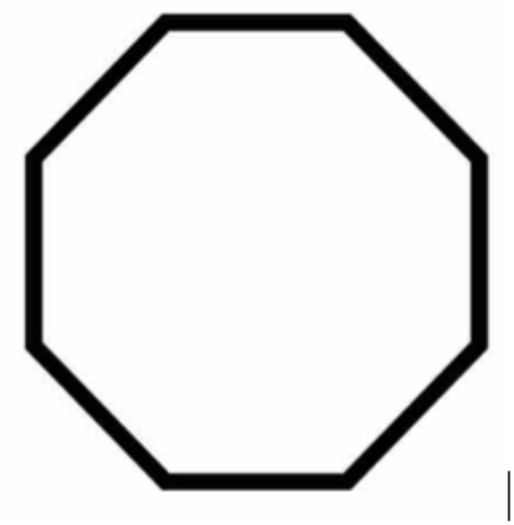
NOTE: Labeling geometric isomers of cycloalkanes with more than two non-hydrogen substituent groups is more complicated and will not be covered in this text.

Concept Review Exercises

1. What is the molecular formula of cyclooctane? Also draw a line-angle structure for cylcooctane.

Answers

1. C_8H_{16}



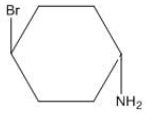
Key Takeaway

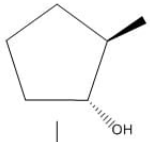
- Many organic compounds have cyclic structures.
- If a cycloalkane ring has two non-H groups on different carbons, two geometric isomers are possible --- cis and trans.

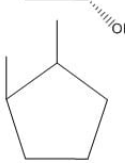
Exercises

1. Each of the following cylcoalkane rings have two hydrogens substituted for other groups (disubstituted). Label each as cis, trans, or neither.

A. 

B. 

C. 

D. 

2.

Answers

1. A. neither (both groups on same carbon); B. trans; C. trans; D. cis

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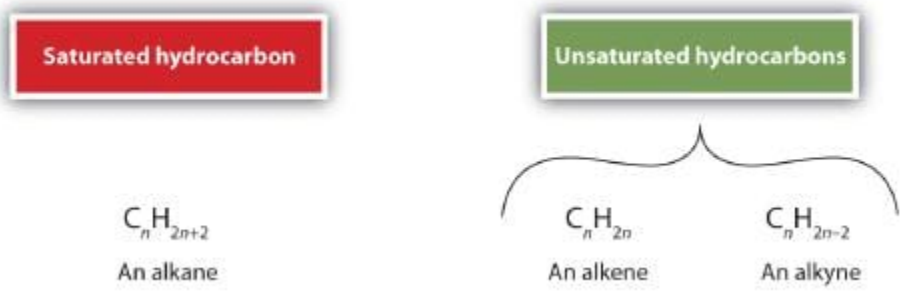
11.5: Alkenes

Skills to Develop

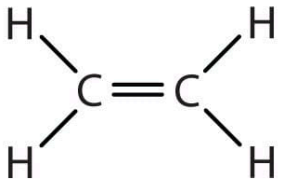
- To differentiate the structure of alkenes (and other unsaturated hydrocarbons, like alkynes and aromatics) from saturated alkanes.
- Recognize that alkenes that can exist as geometric isomers and classify isomers as cis or trans.

Our modern society is based to a large degree on the chemicals we discuss in this chapter. Most are made from petroleum. Alkanes—saturated hydrocarbons—have relatively few important chemical properties other than that they undergo combustion and react with halogens. Unsaturated hydrocarbons—hydrocarbons with double or triple bonds—on the other hand, are quite reactive. In fact, they serve as building blocks for many familiar plastics—polyethylene, vinyl plastics, acrylics—and other important synthetic materials (e.g., alcohols, antifreeze, and detergents). Aromatic hydrocarbons have formulas that can be drawn as cyclic alkenes, making them appear unsaturated, but their structure and properties are generally quite different, so they are not considered to be alkenes. Aromatic compounds serve as the basis for many drugs, antiseptics, explosives, solvents, and plastics (e.g., polyesters and polystyrene). The two simplest unsaturated compounds—ethylene (ethene) and acetylene (ethyne)—were once used as anesthetics and were introduced to the medical field in 1924. However, it was discovered that acetylene forms explosive mixtures with air, so its medical use was abandoned in 1925. Ethylene was thought to be safer, but it too was implicated in numerous lethal fires and explosions during anesthesia. Even so, it remained an important anesthetic into the 1960s, when it was replaced by nonflammable anesthetics such as halothane ($CHBrClCF_3$$CHBrClCF_3$).

As noted before, alkenes are hydrocarbons with carbon-to-carbon double bonds ($R_2C=CR_2$) and alkynes are hydrocarbons with carbon-to-carbon triple bonds (R–C≡C–R). Collectively, they are called unsaturated hydrocarbons because they have fewer hydrogen atoms than does an alkane with the same number of carbon atoms, as is indicated in the following general formulas:



Ethene condensed structural formulas, like $H_2C=CH_2$, $CH_2=CH_2$, or even CH_2CH_2 all stand 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 11.5.1, ethene and propene, are most often called by their common names—ethylene and propylene, respectively (Figure 11.5.1). 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.

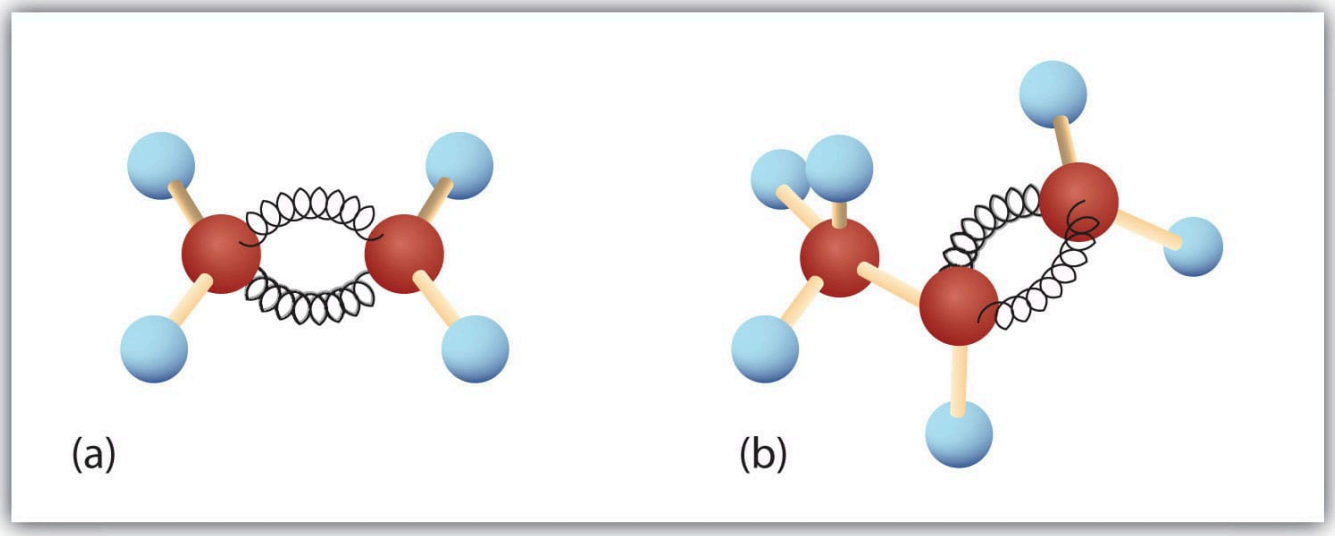


Figure 11.5.1: *Ethene and Propene. The ball-and-spring models of ethene/ethylene (a) and propene/propylene (b) show their respective shapes, especially bond angles.*

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.

Cis-Trans Geometric Isomers

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 11.5.2.

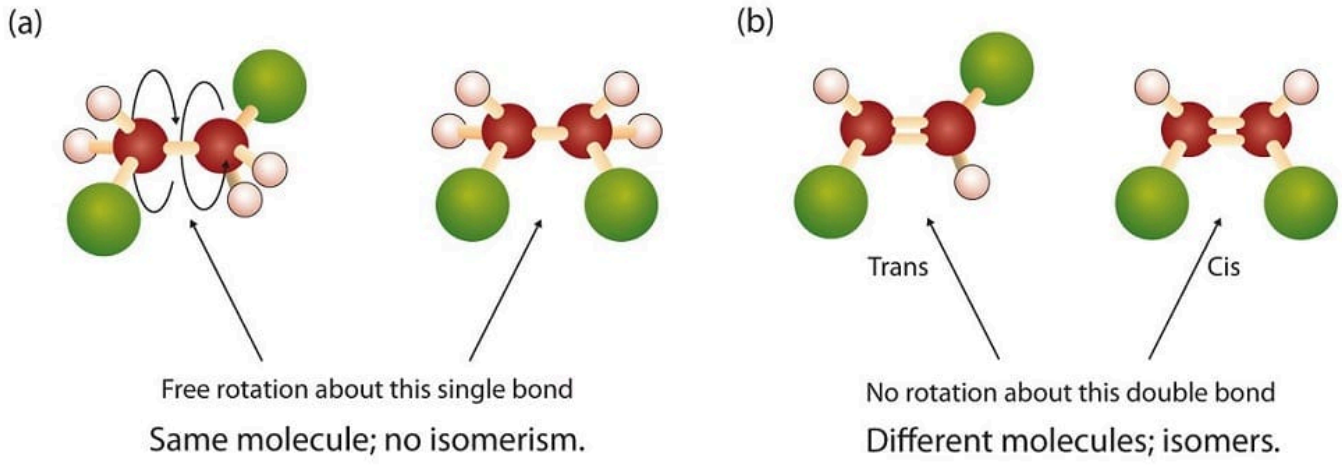


Figure 11.5.2: *Rotation about Bonds. In 1,2-dichloroethane (a), free rotation about the C–C bond allows the two structures to be interconverted by a twist of one end relative to the other. In 1,2-dichloroethene (b), restricted rotation about the double bond means that the relative positions of substituent groups above or below the double bond are significant.*

In 1,2-dichloroethane (part (a) of Figure 11.5.2), there is free rotation about the C–C bond. The two models shown represent exactly the same molecule; they are *not* isomers. You can draw structural formulas that look different, but if you bear in mind the possibility of this free rotation about single bonds, you should recognize that these two structures represent the same molecule:



In 1,2-dichloroethene (Figure 11.5.*sb*), 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 11.5.3).

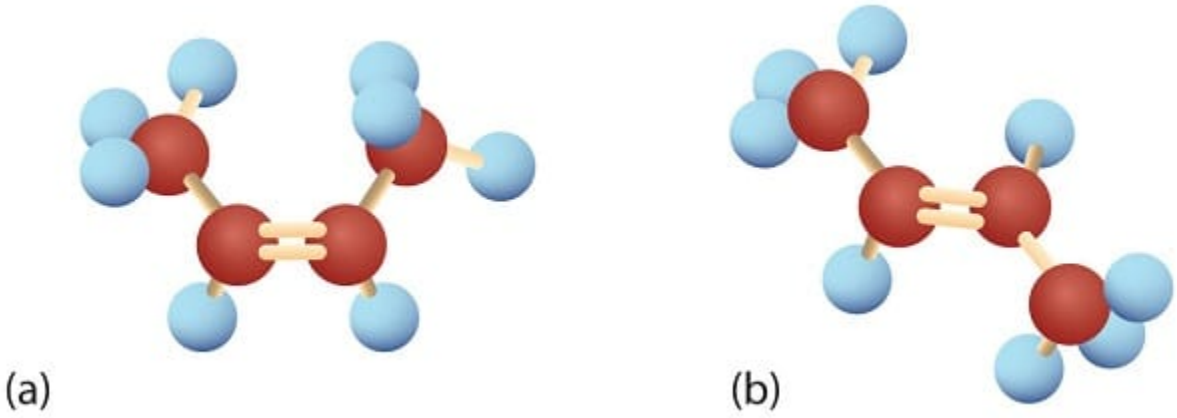


Figure 11.5.3*: Ball-and-Spring Models of (a) Cis-2-Butene and (b) Trans-2-Butene. Cis-trans isomers have different physical, chemical, and physiological properties.*

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 11.5.4*: 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 11.5.5). We can draw two *seemingly* different propenes:



Figure 11.5.5*: Different views of the propene molecule (flip vertically). These are not isomers.*

However, these two structures are not really different from each other. If you could pick up either molecule from the page and flip it over top to bottom, you would see that the two formulas are identical. Thus there are two requirements for cis-trans isomerism:

1. Rotation must be restricted in the molecule.
2. There must be **two nonidentical groups** on **each** doubly bonded carbon atom.

In these propene structures, the second requirement for cis-trans isomerism is not fulfilled. One of the doubly bonded carbon atoms does have two different groups attached, but the rules require that *both* carbon atoms have two different groups. In general, the following statements hold true in cis-trans isomerism:

- Alkenes with a $C{=}CH_2$ unit do not exist as cis-trans isomers.
- Alkenes with a $C{=}CR_2$ unit, where the two R groups are the same, do not exist as cis-trans isomers.
- Alkenes of the type R–CH=CH–R can exist as cis and trans isomers; cis if the two R groups are on the same side of the carbon-to-carbon double bond, and trans if the two R groups are on opposite sides of the carbon-to-carbon double bond.

Advanced Note: E/Z Isomerization

If a molecule has a C=C bond with one non-hydrogen group attached to each of the carbons, cis/trans nomenclature descried above is enough to describe it. However, if you have three different groups (or four), then the cis/trans approach is insufficient to describe the different isomers, since we do not know which two of the three groups are being described. For example, if you have a C=C bond, with a methyl group and a bromine on one carbon , and an ethyl group on the other, it is neither trans nor cis, since it is not clear whether the ethyl group is trans to the bromine or the methyl. This is addressed with a more advanced E/Z nomenclature discussed elsewhere.

Example 11.5.1

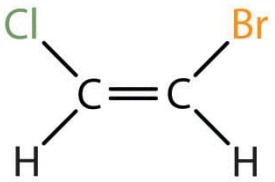
Which compounds can exist as cis-trans (geometric) isomers? Draw them.

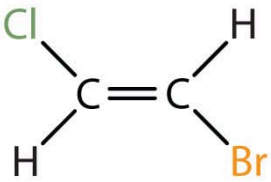
1. CHCl=CHBr
2. $CH_2{=}CBrCH_3$
3. $(CH_3)_2C{=}CHCH_2CH_3$
4. $CH_3CH{=}CHCH_2CH_3$

SOLUTION

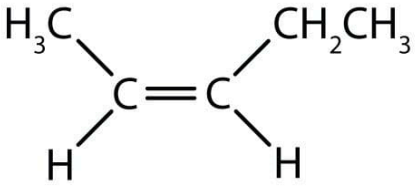
All four structures have a double bond and thus meet rule 1 for cis-trans isomerism.

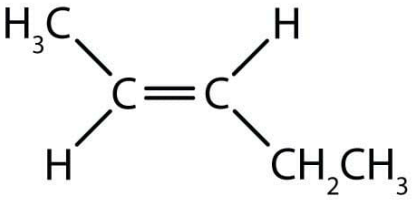
1. This compound meets rule 2; it has two nonidentical groups on *each* carbon atom (H and Cl on one and H and Br on the other). It exists as both cis and trans isomers:





2. This compound has two hydrogen atoms on one of its doubly bonded carbon atoms; it fails rule 2 and does not exist as cis and trans isomers.
3. This compound has two methyl (CH_3) groups on one of its doubly bonded carbon atoms. It fails rule 2 and does not exist as cis and trans isomers.
4. This compound meets rule 2; it has two nonidentical groups on *each* carbon atom and exists as both cis and trans isomers:



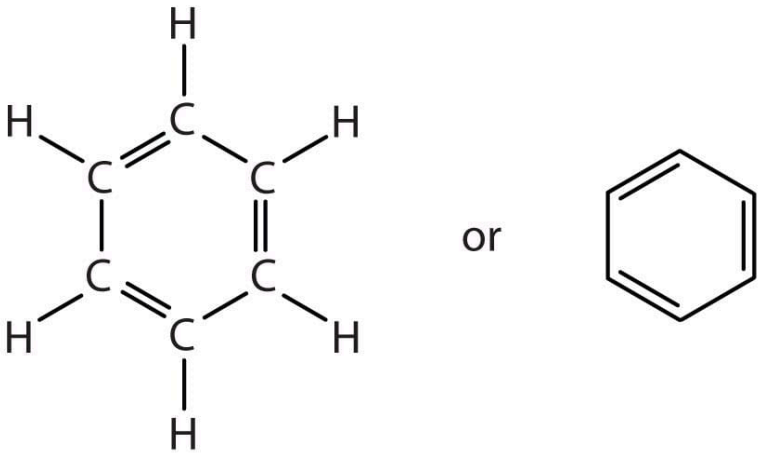


Aromatic Compounds

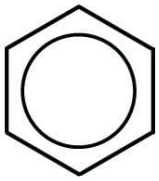
Rings of alternating double and single bonds comprise a distinct class, called aromatic hydrocarbons, with unique structures and properties different than regular alkenes. The simplest of these compounds, benzene (C_6H_6), is of great commercial importance, but it also has noteworthy health effects.

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.

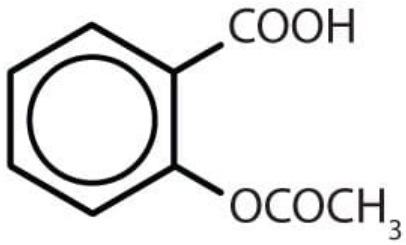
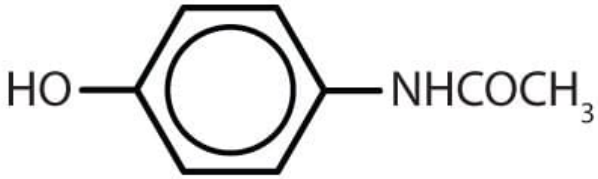
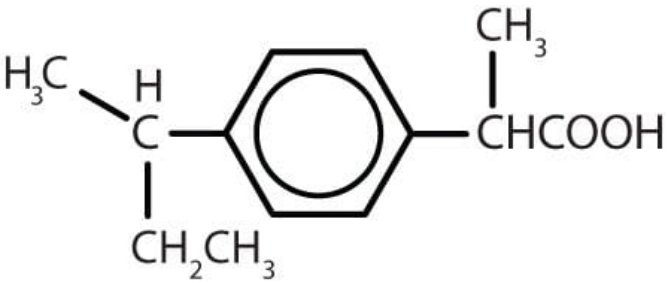
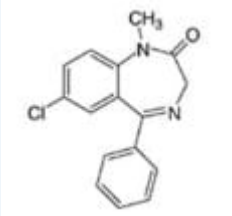
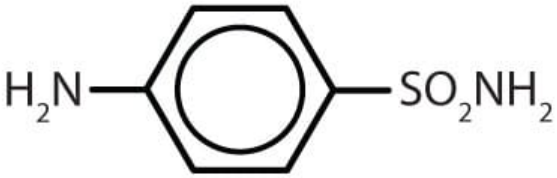
Biologically Important Compounds with Aromatic Rings

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 $11.5.2$, also feature a benzene ring.

So far we have examine only aromatic compounds with carbon-containing rings. However, many cyclic compounds have other elements, like oxygen or nitrogen, in the ring. These compounds, called *heterocyclic compounds*, will be seen in the

biochemistry chapters. For example, diazepam (Valium) below has nitrogen atoms as part of the aromatic ring system.

Table 11.5.2: Some Drugs That Contain Aromatic Rings

Name	Structure
aspirin	
acetaminophen	
ibuprofen	
diazepam (Valium)	
sulfanilamide	

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. What are cis-trans (geometric) isomers? What two types of compounds can exhibit cis-trans isomerism?

Answers

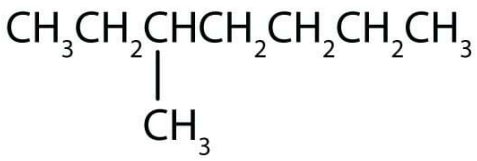
1. Unsaturated hydrocarbons have double or triple bonds and are quite reactive; saturated hydrocarbons have only single bonds and are rather unreactive.
2. An alkene has a double bond; an alkane has single bonds only.
3. Cis-trans isomers are compounds that have different configurations (groups permanently 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. The alkene must have two non-H groups, one on each double-bond carbon. The cylic compound must have two non-H groups, each on different carbons of ring.

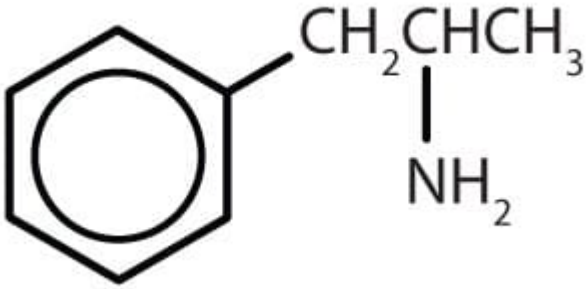
Key Takeaway

- Alkenes are hydrocarbons with a carbon-to-carbon double bond.
- Cis-trans (geometric) isomerism exists when there is restricted rotation in a molecule and there are two nonidentical groups on *each* doubly bonded carbon atom.

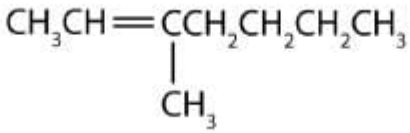
Exercises

1. Classify each compound as saturated or unsaturated. Identify each as an alkane, alkene, alkyne, or aromatic.

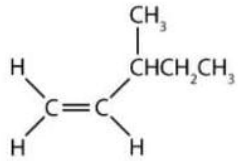
a. 

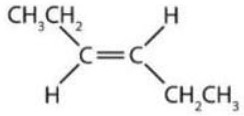
b. 

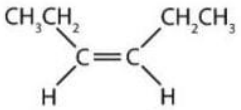
c. $CH_3CH_2C{\equiv}CCH_3$

d. 

2. Classify each compound as a cis isomer, a trans isomer, or neither.

A) 

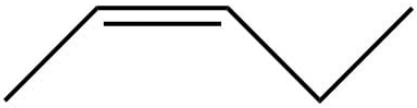
B) 

C) 

D) 

3. These are both isomers of 2-pentene. Which is cis and which is trans?

A. 

B. 

Answers

1. a. saturated; alkane b. unsaturated; aromatic c. unsaturated; alkyne d. unsaturated; alkene

2.

a. neither (fliping the bond does not change the molecule. There are no isomers for this molecule)

b. trans (the two hydrogen atoms are on different sides, as are the two ethyl groups)

c. cis (the two ethyl groups are on the same side, as are the two hydrogens)

d. trans (notice that the single bond off the double bond on the left is going down, but the other is going up)

3. A. trans-2-pentene; B. cis-2-pentene

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11.6: IUPAC Nomenclature

Skills to Develop

- To name alkanes by the IUPAC system and write formulas for alkanes given IUPAC names

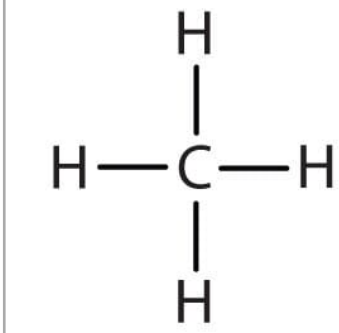
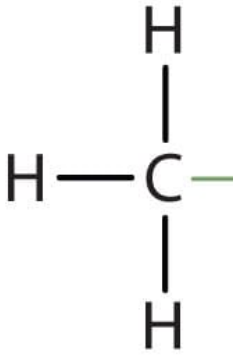
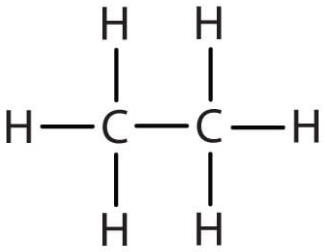
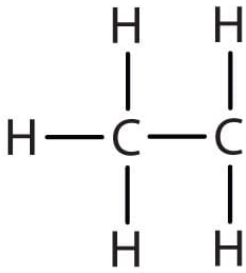
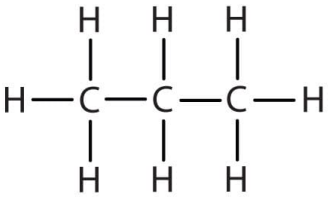
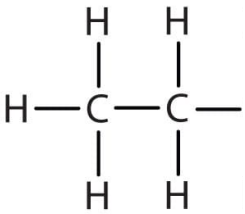
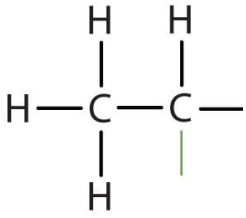
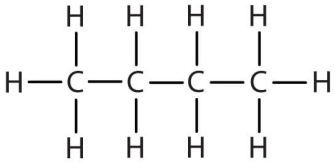
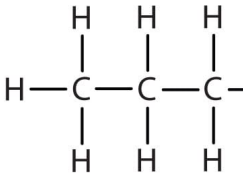
As noted in previously, the number of isomers increases rapidly as the number of carbon atoms increases. There are 3 pentanes, 5 hexanes, 9 heptanes, and 18 octanes. It would be difficult to assign unique individual names that we could remember. A systematic way of naming hydrocarbons and other organic 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 11.6.1) indicates the number of carbon atoms in the longest continuous chain (LCC). Atoms or groups attached to this carbon chain, called *substituents*, are then named, with their positions indicated by numbers. For now, we will consider only those substituents called alkyl groups.

Table 11.6.1***:*** *Stems That Indicate the Number of Carbon Atoms in Organic Molecules*

Stem	Number
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7
oct-	8
non-	9
dec-	10

An alkyl group is a group of atoms that results when one hydrogen atom is removed from an alkane. The group is named by replacing the *-ane* suffix of the parent hydrocarbon with *-yl*. For example, the CH_3 group derived from methane (CH_4) results from subtracting one hydrogen atom and is called a *methyl group*. The alkyl groups we will use most frequently are listed in Table 11.6.2. Alkyl groups are not independent molecules; they are parts of molecules that we consider as a unit to name compounds systematically.

Table 11.6.2***:*** *Common Alkyl Groups*

Parent Alkane		Alkyl Group	
methane		methyl	
ethane		ethyl	
propane		propyl	
		isopropyl	
butane		butyl*	

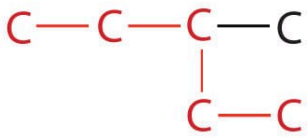
***There are four butyl groups, two derived from butane and two from isobutane. We will introduce the other three where ap**

Naming Alkanes

Simplified IUPAC rules for naming alkanes are as follows (demonstrated in Example 11.6.1).

1. **Name alkanes according to the LCC 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.)

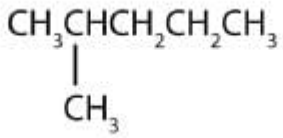
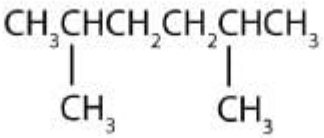
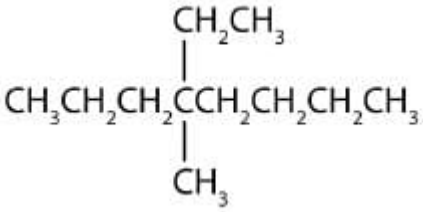


3. **Place the names of the substituent groups in alphabetical order before the name of the parent compound.** If the same alkyl group appears more than once, the numbers of all the carbon atoms to which it is attached are expressed. If the same group appears more than once on the same carbon atom, the 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 11.6.1

Name each compound.

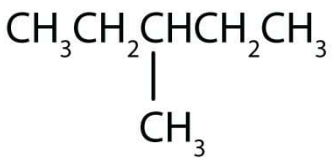
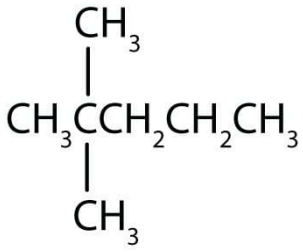
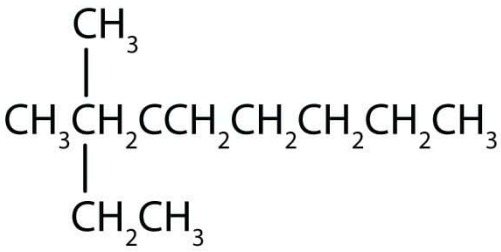
1. 
2. 
3. 

SOLUTION

1. The LCC has five carbon atoms, and so the parent compound is pentane (rule 1). There is a methyl group (rule 2) attached to the second carbon atom of the pentane chain. The name is therefore 2-methylpentane.
2. The LCC has six carbon atoms, so the parent compound is 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 11.6.1

Name each compound.

1. 
2. 
3. 

Example 11.6.2

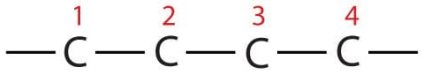
Draw the structure for each compound.

1. 2,3-dimethylbutane
2. 4-isopropyl-2-methylheptane

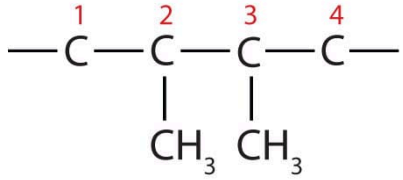
SOLUTION

In drawing structures, always start with the parent chain.

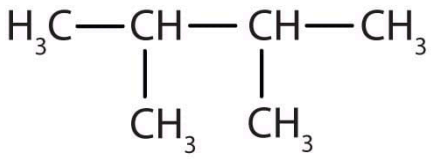
1. The parent chain is butane, indicating four carbon atoms in the LCC.



Then add the groups at their proper positions. You can number the parent chain from either direction as long as you are consistent; just don't change directions before the structure is done. The name indicates two methyl (CH_3) groups, one on the second carbon atom and one on the third.



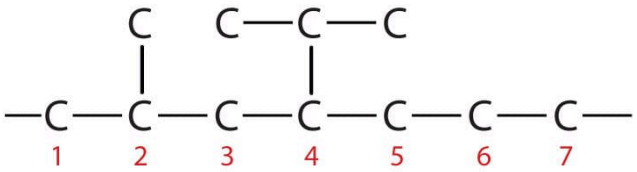
Finally, fill in all the hydrogen atoms, keeping in mind that each carbon atom must have four bonds.



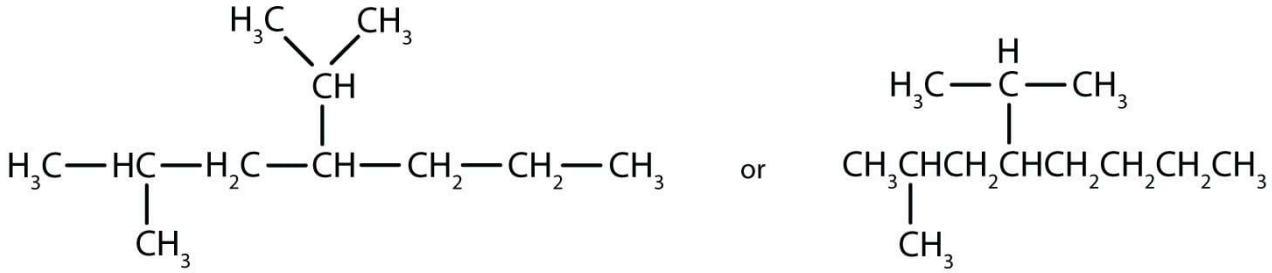
2. The parent chain is heptane in this case, indicating seven carbon atoms in the LCC.

   –C–C–C–C–C–C–C–

   Methyl is a one-carbon substituent. Isopropyl is a three-carbon substituent, with the middle of the three carbons attached. (Propyl would be a three-carbon substituent, attached at the end.) Adding the groups at their proper positions gives



   Filling in all the hydrogen atoms gives the following condensed structural formulas:



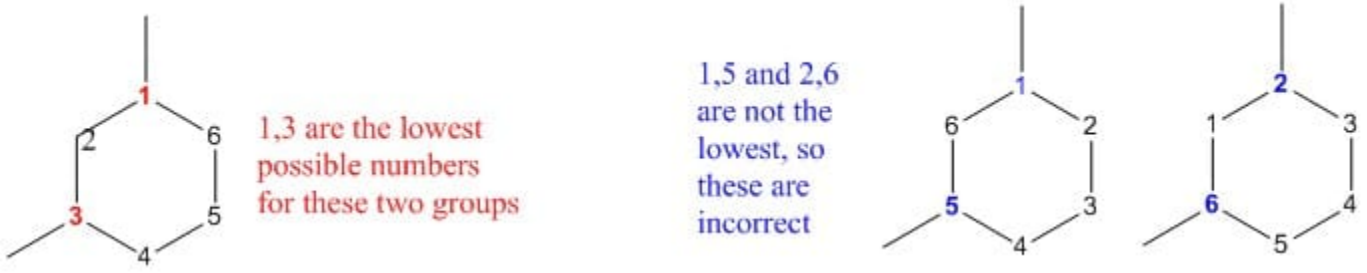
   Note that the bonds (dashes) can be shown or not; sometimes they are needed for spacing.

If a halogen substituent replaces a hydrogen, then "-gen" ending is left off and it becomes "halo" at the beginning of the name. So a chlorine substituent on the first carbon of propane ($CH_3CH_2CH_2Cl$) would be 1-chloropropane. Two bromine substituents, both on the second carbon of butane ($CH_3CBr_2CH_2CH_3$) would be 2,2-dibromobutane.

Naming Cycloalkanes

Naming cycloalkanes is essentially the same as alkanes, but the ring is the parent instead of the longest chain. If there is only one substituent, no number is required because it is always assumed to be #1 (e.g. 1-methylcyclopentane is often just methylcyclopentane). If there are multiple substituents, one of them is always #1 and you count around the ring in whichever direction gives the lowest number.

In the structure below, there are two one-carbon methyl substituents on a six-carbon cyclohexane ring. The lowest possible numbers in this example would be "1,3" so it would be named 1,3-dimethylcyclohexane. (There are many other incorrect ways to number the carbons here; two incorrect examples are shown.)



Naming Alkenes

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,

   is 5-methyl-2-hexene. Note that the numbering of the parent chain is always done in such a way as to give the double bond the lowest number, even if that causes a substituent to have a higher number. *The double bond always has priority in numbering.*

Example 11.6.1

Name each compound.

1.
2.
3. $F_2CH_2CH_2CH_2CH$=$CHCH_3$

SOLUTION

1. 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.
2. The longest chain containing the double bond has four carbon atoms, so the parent compound is a *butene* (rule 1). (The longest chain overall has five carbon atoms, but it does not contain the double bond, so the parent name is not *pentene*.)

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 1-butene. There is an ethyl group on the second carbon atom (rule 3), so the compound's name is 2-ethyl-1-butene.

3. This is a six-carbon chain so the parent is hexene (rule 1). Counting from the right (rule 2), gives the the fist carbon of the double bond the lower number (#2 < #4). Both fluorine substituents are located on the sixth carbon (rule 3), so the name is 6,6-difluoro-2-hexene.

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 11.6.2

Draw the structure for each compound.

1. 3-methyl-2-pentene
2. cyclohexene

SOLUTION

1. First write the parent chain of five carbon atoms: C–C–C–C–C. Then add the double bond between the second and third carbon atoms:

   Now place the methyl group on the third carbon atom and add enough hydrogen atoms to give each carbon atom a total of four bonds.

2. First, consider what each of the three parts of the name means. *Cyclo* means a ring compound, *hex* means 6 carbon atoms, and *-ene* means a double bond. (This could be named 1-cylohexene, but no number is necessary because the double bond is assumed to start on the first carbon.)

Key Takeaway

- Organic compounds have both common names and systematic names, specified by IUPAC.

Exercises

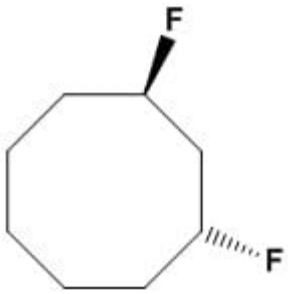
1. Draw the structure for each compound.

   a. 2-methyl-2-pentene
   b. 2,3-dimethyl-1-butene
   c. 3-bromocyclopentene
   d. cis-1-chloro-1-propene

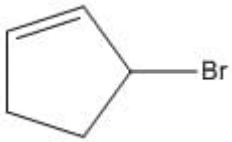
2. Name each compound according to the IUPAC system.

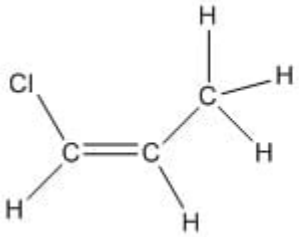
   a.
   b.
   c.
   d.

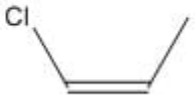
e. (Include stereochemistry, since shown in structure.)



Answers

1. a.
   b.
   c. 

   d. 

   or 

2.

a. 2-methyl-2-pentene
b. 3-methyl-2-heptene
c. 2,5-dimethyl-2-hexene
d. cis-1,3-difluorocyclooctane

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11.7: Organic Compounds with Functional Groups

Skills to Develop

- to describe functional groups and explain why they are useful in the study of organic chemistry.

With over twenty million known organic compounds in existence, it would be very challenging to memorize chemical reactions for each one. Fortunately, molecules with similar functional groups tend to undergo similar reactions. A **functional group** is defined as an atom or group of atoms within a molecule that has similar chemical properties whenever it appears in various compounds. Even if other parts of the molecule are quite different, certain functional groups tend to react in certain ways.

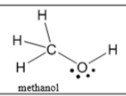
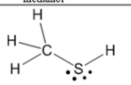
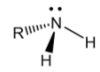
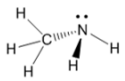
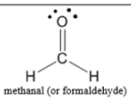
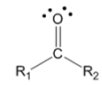
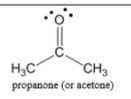
We've already looked at alkanes, but they are generally unreactive. We primarily use alkanes as a source of energy when they are combusted. While the majority of functional groups involve atoms other than carbon and hydrogen, we will also look at some that include only carbon and hydrogen. Some of the most common functional groups are presented in the following sections.

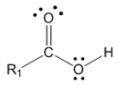
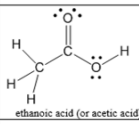
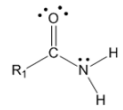
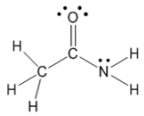
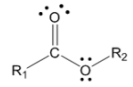
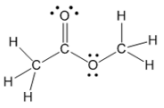
Organic molecules vary greatly in size and when focusing on functional groups, we want to direct our attention to the atoms involved in the functional group. As a result, the abbreviation R is used in some examples. The letter R is used in molecular structures to represent the "**R**est of the molecule". It consists of a group of carbon and hydrogen atoms of any size. It is used as an abbreviation since a group of carbon and hydrogen atoms does not affect the functionality of the compound. In some molecules, you will see R, R', or R'' which indicates that the R groups in the molecule can be different from one another. For example, R might be $-CH_2CH_3$ while R' is $-CH_2CH_2CH_2CH_3$.

Previously, we considered several kinds of hydrocarbons. Now we examine some of the many organic compounds that contain functional groups with atoms beyond just carbon and hydrogen. A functional group is 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 previous sections, we have looked at several classes of hydrocarbons. Saturated alkanes and cycloalkanes (with only single C-C and C-H bonds) are generally unreactive, primarily used as a source of energy when they are combusted. Unsaturated alkenes (hydrocarbons with C=C) and alkynes (hydrocarbonds with C≡C) are much more susceptible to addition reactions, in particular, and are used as precursors for the synthesis of many other compounds (like plastic polymers). Aromatic compounds (rings with alternating single and double bonds) are more stable than regular alkenes, thus less reactive, but commonly found in biological compounds (like steroids and medications). Here we add several more that include other atoms, like oxygen or nitrogen, in addition to carbon and hydrogen. Some common functional groups are listed in Table 11.7.1 below. The letter R represents the rest of the "**R**est of the molecule", typically a hydrocarbon chain or ring.

Table

:
Selected
Organic
Functional
Groups

Name	General formula (R means rest of molecule)	Line Structure	Simple Example
alcohol	R-OH		 methanol
thiol	R-SH		 methanethiol (or methyl mercaptan)
amine	$R-NH_2$ or R_2NH or R_3N		 methylamine
aldehyde	R-CHO		 methanal (or formaldehyde)
ketone	R-CO-R		 propanone (or acetone)

Name	General formula (R means rest of molecule)	Line Structure	Simple Example
carboxylic acid	R-COOH		 ethanoic acid (or acetic acid)
Amide	$R-CONH_2$ or RCONHR or $RCONR_2$		 ethanamide (or acetamide)
ester	RCOOR		 methyl ethanoate (or methyl acetate)

NOTE: There are others, but the organic functional groups introduced in this chapter are those most often discussed in later biochemistry chapters.

Alcohols

The **alcohol** functional group involves an oxygen atom that is bonded to one hydrogen atom and one carbon atom. The carbon atom will be part of a larger organic structure. One way to indicate a generic alcohol would be with the formula R–OH. R represents any organic fragment in which a carbon atom is directly bonded to the explicitly indicated functional group (in this case, OH). The R group is typically a chain of carbon atoms.

We are already familiar with several common alcohols. For example, ethanol (CH_3CH_2OH) is the alcohol present in alcoholic beverages. It is also widely used in the industrial manufacture of other chemicals. Methanol (CH_3OH) is used as a gasoline additive or alternative. Additionally, methanol can be used to manufacture formaldehyde, which is employed in the production of plastics, paints, and other useful substances. Isopropanol is commonly known as rubbing alcohol. In addition to its industrial uses, isopropanol is used to clean various surfaces, including computer monitors, whiteboards, and even skin (e.g., before getting blood drawn).

Ethers

The **ether** functional group consists of an oxygen atom that forms single bonds with two carbon atoms. The general formula is R–O–R. Ethers are good solvents for other organic compounds because of their low reactivity. They readily dissolve nonpolar molecules. Diethyl ether ($CH_3CH_2OCH_2CH_3$) is perhaps the best known ether. It is widely used as a solvent and has been used as an inhalable anesthetic.

Although ethers themselves are relatively unreactive, they can be converted to peroxides after prolonged exposure to oxygen. Peroxides are very reactive and are often explosive at elevated temperatures. Many commercially available ethers come with a small amount of a peroxide scavenger dissolved in them to help prevent this type of safety hazard.

Thiol

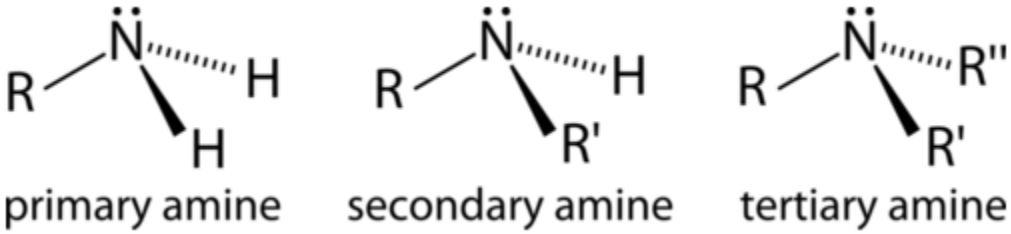
The **thiol** functional group contains a sulfur atom bonded to a hydrogen atom. It is very similar to an alcohol functional group with the sulfur replacing the O (R–S–H).

Thiols are also called mercaptans which is derived from the Latin phrase for "capturing mercury" because of the strong bonds it forms with mercury-containing compounds. Some thiol compounds have a distinctive smell similar to rotten eggs. They are often added to natural gas, which itself has no odor, as a way to detect leaks since its odor can be detected by humans in very small

amounts. A thiol group is also present in the amino acid cysteine which will be discussed later.

Amines

An **amine** consists of a nitrogen atom bonded to some combination of carbons and hydrogens.



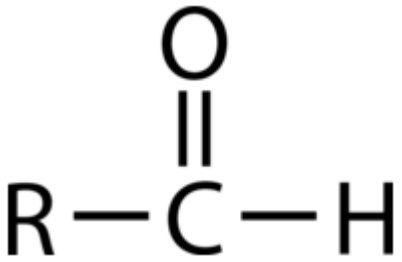
Like alcohols, amines can be classified as primary, secondary, or tertiary. However, the rules for assigning these categories are slightly different. In an alcohol, the oxygen atom is always bonded to exactly one carbon atom, so we look at the branching on the adjacent carbon, not the oxygen atom itself. In a neutral amine, the nitrogen can be bonded to one, two, or three carbon atoms, and this is how we decide whether it is called a primary, secondary, or tertiary amine.

Neutral amines are weak bases, because the lone pair on nitrogen can act as a proton acceptor. Many smaller amines have very strong and offensive odors. For example, the aptly-named compounds cadaverine and putrescine are foul-smelling amines, formed as a part of the decay process after death.

Amines serve a wide variety of uses. Diphenylamine acts as a stabilizer for certain types of explosives. Amines are found as components in some lubricating materials, in developers, and are a part of waterproofing textiles. Some amines, such as novocaine, are used as anesthetics. Many pharmaceutical compounds contain amines, including 8 of the 10 most prescribed medications in 2012.

Aldehydes

A very common structural component of organic structures is the **carbonyl**, which is simply a carbon atom and an oxygen atom connected by a double bond. The reactivity of carbonyls is primarily dictated by the polarization of the C=O bond, but the surrounding atoms also play a role in its specific reaction pathways. While carbonyl is a component of many functional groups, it is not itself a functional group.

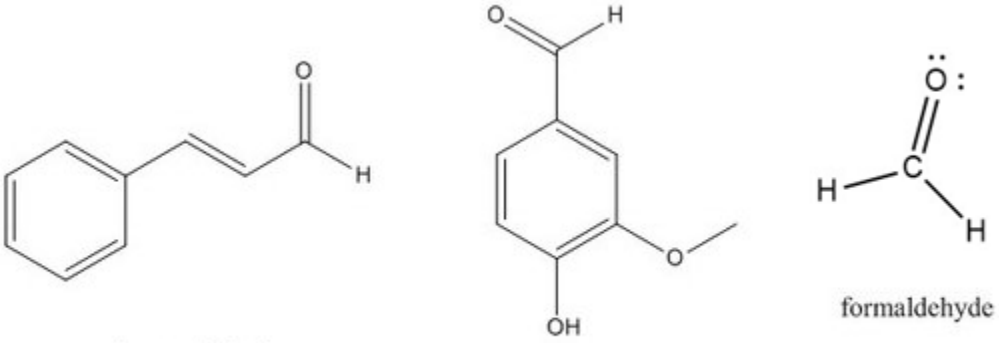


General Formula of an Aldehyde, RCHO

An **aldehyde** is a carbonyl in which the carbon atom is bonded to at least one hydrogen atom. The other group attached to the carbonyl may be an R-group or a hydrogen atom. Because the hydrogen atom is so small, the partial positive charge on the carbonyl carbon is very easy for other molecules to approach, making aldehydes a particularly reactive type of carbonyl. Aldehydes are versatile reactants for a wide variety of organic syntheses. Many aldehydes also have distinctive flavors and aromas. For example, the flavor of cinnamon is primarily due to the molecule cinnamaldehyde, and vanillin is the aldehyde most responsible for the smell and taste of vanilla extract.

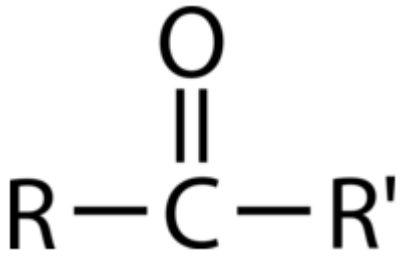
A special aldehyde is the molecule in which the carbonyl is bonded to two hydrogen atoms. This molecule, called formaldehyde, has a wide variety of uses. By itself, it can be used as a tissue preservative or as a very harsh disinfectant. It is also used as a precursor to various materials, including plastics, resins, and other polymers.

Examples of molecules with aldehyde functional groups.



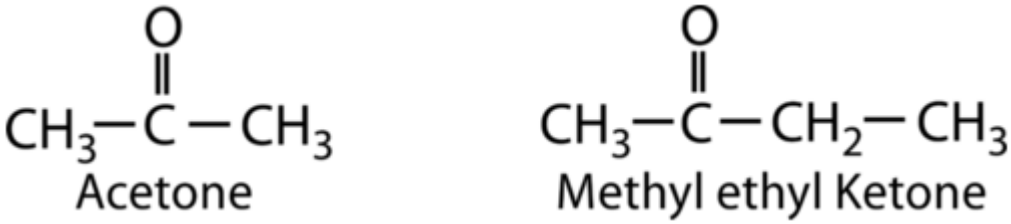
Ketones

General Formula of a Ketone



A **ketone** involves a carbonyl in which the carbon atom makes single bonds with two R-groups. Ketones undergo most of the same reactions as aldehydes, but they tend to be slightly less reactive. The simplest ketone is acetone, in which the carbonyl carbon is bonded to two CH_3 groups. This ketone is commonly used to remove fingernail polish and serves as an industrial solvent. Methyl ethyl ketone is used as a paint stripper and a solvent. Ketones are also used in the production of various polymers, either as a building block or as a solvent. The R-group in a ketone can be the same or different as seen in the example.

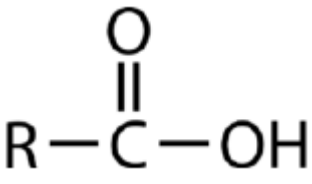
Two examples of ketones.



Carboxylic Acids

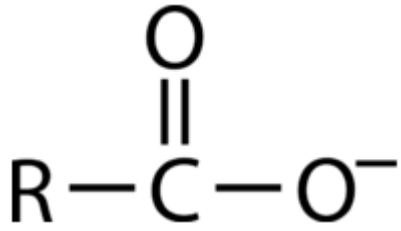
Carboxylic acids are another carbonyl-containing functional group, in which the carbon atom is bonded to an OHOH group on one side and either a carbon or hydrogen atom on the other.

General formula of a Carboxylic acid



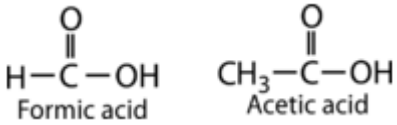
As the name implies, carboxylic acids are weak acids. An OH group that is directly connected to a carbonyl will ionize to a small extent when dissolved in water. The reason for this is the relative stability of the resulting anion. A carboxylate ion (see figure

below), in which the negative charge is spread over two different oxygen atoms through resonance structures, is more stable than an isolated oxygen-centered anion. The carboxylic acid and carboxylate ion are interchangeable. Carboxylate ions are often present in amino acids.



Carboxylate ion

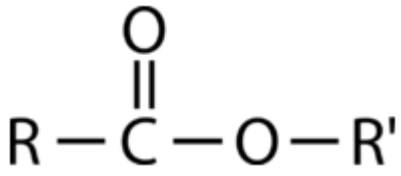
Carboxylic acids are used in a variety of environments. Formic acid acts as a protective chemical for many stinging insects and plants. Acetic acid gives vinegar its characteristic smell and flavor and is a fundamental biological and industrial building block. Carboxylic acids with longer carbon chains (fatty acids) are used by animals as a way of storing energy and are widely used in the manufacture of soaps. Some compounds contain multiple carboxylic acids within a single molecule. For example, citric acid (three carboxyl groups) is especially abundant in citrus fruits and it used as a flavoring and preservative in many foods and beverages.



Carboxylic Acid Examples

Esters

An **ester** is similar to a carboxylic acid, in that it contains a carbonyl where the carbon is bonded to one additional oxygen atom and one carbon or hydrogen atom. However, the second oxygen atom is bonded to another carbon instead of to an acidic hydrogen atom. Structurally, carboxylic acids and esters are related to one another in the same way as alcohols and ethers.



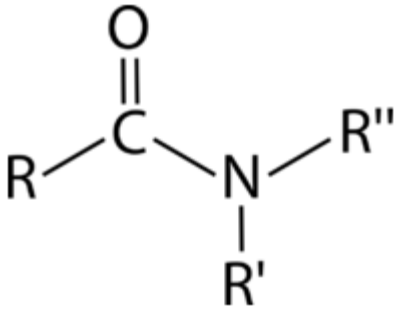
Ester

Esters can be formed by heating carboxylic acids and alcohols in the presence of an acid catalyst. This process is reversible, and the starting materials can be regenerated by reacting an ester with water in the presence of a weak base.

Some esters have very pleasant odors, so they are used in the manufacture of many perfumes. Propyl acetate contributes to the odor of pears, while isoamyl acetate gives bananas their smell. This ester also serves as an alarm signal for honeybees. Esters are employed in the manufacture of fabrics (polyesters) and Plexiglass. Anesthetics such as procaine and benzocaine also contain esters.

Amides

An **amide** is a carbonyl in which the carbon is attached to one nitrogen atom and one carbon or hydrogen atom. Alternatively, we could define an amide as an amine in which one of the carbon atoms attached to the nitrogen is part of a carbonyl.



Amide

An amide can be formed by combining a carboxylic acid and an amine. Amides are used as coloring agents in crayons, pencils, and ink. They are employed in the paper, plastic, and rubber industries. Polyacrylamide is a very widely used amide; it is involved in t he treatment of drinking water and sewage, and in plastics manufacture. The amide Kevlar is widely employed for the production of body armor, and nylon is another type of amide-based polymer.

Haloalkanes

The haloalkanes, also known as alkyl halides (R–X), are a group of chemical compounds comprised of an alkane with one or more hydrogens replaced by a halogen atom (Group 17 atom). There is a fairly large distinction between the structural and physical properties of haloalkanes and the structural and physical properties of alkanes.

Haloalkanes are found in fire extinguishers, refrigerants, propellants, solvents, and medications. They are also a significant source of pollution and their use has been reduced or eliminated in some products. Chlorofluorocarbons (CFCs) were used as refrigerants in air-conditioners but were found to be a major cause of the depletion of the ozone layer. Research and development of alternatives began in the 1970s. Hydrochlorofluorocarbons (HCFCs) have been used for many years since they cause less damage to the ozone layer, but many countries agreed to eliminate HCFCs by 2020.

Summary

The functional group, a structural arrangement of atoms and/or bonds, is largely responsible for the properties of organic compound families.

Concept Review Exercises

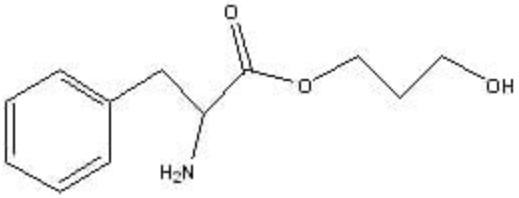
1. What is the functional group of an alkene? An thiol?
2. Does $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ have a functional group? Explain.

Answers

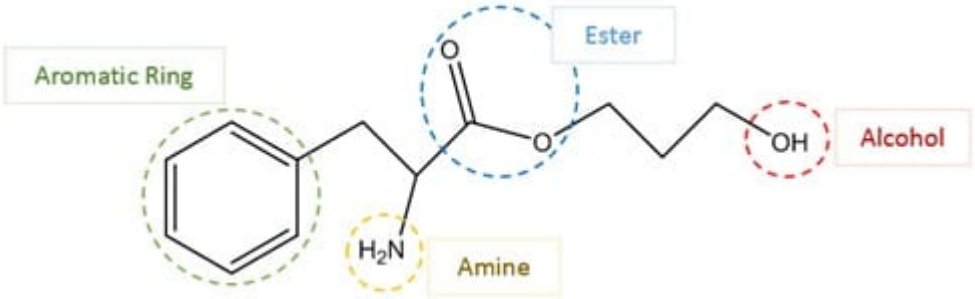
1. Alkenes contain a carbon-to-carbon double bond (C=C). Thiols have contain a sulfur bonded to hydrogen (SH).
2. No; it has nothing but carbon and hydrogen atoms and all single bonds. (Plain alkanes are often thought to be the absence of a functional group.)

Exercises

1. What is the functional group of 1-butanol ($CH_3CH_2CH_2CH_2OH$)?
2. What are the functional groups in $CH_3NHCH_2CH_2CHO$?
3. What functional group or groups are present in $CH_3COOCH_2CONHCH_3$?
4. The molecule below contains four different functional groups. Label them.



Answer

1. OH, an alcohol
2. NH, an amine, and CHO, an aldehyde
3. COOC, an ester, and CONH, and amide
4. 

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11.8: Physical Properties of Organic Compounds

Skills to Develop

- To identify the physical properties of organic compounds and describe trends in these properties.

Hydrocarbons

Hydrocarbons like alkanes, cycloalkanes, and alkenes all share similar physical properties because they only contain non-polar bonds, and thus only have London-dispersion intermolecular forces of attraction. None of the hydrocarbons are soluble in water (very polar), but are soluble in nonpolar and some slightly polar solvents.

In Table 11.8.1 several physical properties of some of the first 10 straight-chain alkanes are listed. Other hydrocarbons exhibit the same trends. 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 gasoline and oil do not mix with water but rather float on its surface.

London-dispersion interactions are typically quite weak; this is why the first few alkanes below are all gases. As the size of the molecule increases, however, the larger electron clouds become more polarizable, increasing the strength of the dispersion attractions; notice that the larger alkanes exist as liquids at room temperature (and can be solids, if even larger). The boiling points and melting point increase as size increases because more energy is required to separate them. This general trend for melting and boiling points holds true for the straight-chain homologs of all organic compound families.

Table 11.8.1*: Physical Properties of Some Alkanes*

Molecular Name	Formula	Melting Point (°C)	Boiling Poi
methane	CH_4	–182	–164
ethane	C_2H_6	–183	–89
propane	C_3H_8	–190	–42
butane	C_4H_{10}	–138	–1
pentane	C_5H_{12}	–130	36
hexane	C_6H_{14}	–95	69
octane	C_8H_{18}	–57	125
decane	$C_{10}H_{22}$	–30	174

***Gas densities are at 1 atm pressure.**

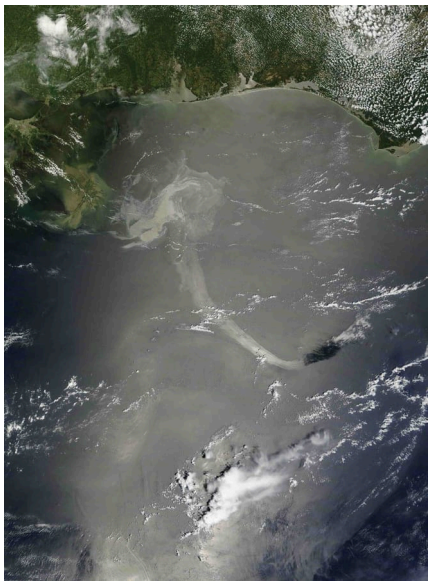


Figure 11.8.1*: Oil Spills. Crude oil coats the water's surface in the Gulf of Mexico after the Deepwater Horizon oil rig sank following an explosion. The leak was a mile below the surface, making it difficult to estimate the size of the spill. One liter of oil can create a slick 2.5 hectares (6.3 acres) in size. This and similar spills provide a reminder that hydrocarbons and water don't mix. Source: Photo courtesy of NASA Goddard / MODIS Rapid Response Team, http://www.nasa.gov/topics/earth/features/oilspill/oil-20100519a.html.*

Looking Closer: Gas Densities and Fire Hazards

Table 11.8.1 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.

Other Functional Groups

Hydrocarbons, like alkanes, are non-polar. Many other organic compounds contain contain additional highly-electronegative atoms, like oxygen or nitrogen, in functional groups with polar bonds. Table 11.8.2 compares physical properties of three organic compounds: an alkane, an alkyl halide, and an alcohol. As indicated by the mass and total electrons, all three approximately the same size. Notice that, as the number of intermolecular interactions increases, the boiling points and melting points increases. More types of attractive forces require more energy to separate the molecules (melt solid or boil liquid).

Table 11.8.2*: Physical Properties of Different Functional Groups*

SUBSTANCE **name (formula)**	**MOLECULAR MASS** (amu)	**TOTAL ELECTRONS**	**TYPES OF INTERMOLECULAR INTERACTIONS**	**MELTING POINT** (^{0}C)	**BOILING POINT** (^{0}C)	**PHYSICAL STATE** (at 20^{0}C)
ethane (CH_3CH_3)	30	18	dispersion	–183	–89	gas

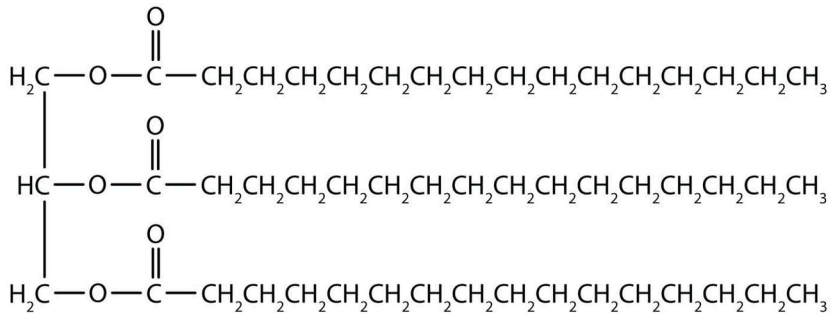
methyl fluoride (CH_3F)	34	18	dispersion dipole-dipole	–138	–78	gas
ethanol (CH_3OH)	32	18	dispersion dipole-dipole hydrogen-bonding	–98	65	liquid

The types of forces also affects solubililty. Ethanol (beverage alcohol) is completely miscible with water, as both are extremely polar and have the same types of interactions. Methylfluoride, also polar, is soluble in water, but not as completely as ethanol. Non-polar ethane does not dissolve appreciably in water.

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 fat-like 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.

(a)



(b)

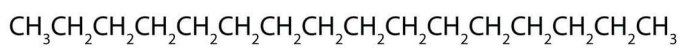


Figure 11.8.2***:*** *Tripalmitin (a), a typical fat molecule, has long hydrocarbon chains typical of most lipids. Compare these chains to hexadecane (b), an alkane with 16 carbon atoms.*

Concept Review Exercises

1. Without referring to a table, predict which has a higher boiling point:

   a. hexane or octane (explain); b. An amine or an alkane, both of similar size (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. a. octane because of its larger size; b. an amine, RNH_2, because it would have more types of forces (three compared to one for alkane)

2. b; hexane is insoluble in water and less dense than water.

Key Takeaway

- Alkanes are nonpolar compounds that are low boiling and insoluble in 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. Acetic acid (CH_3COOH) or methyl chloride (CH_3Cl)

2. Which would be more soluble in water, methanol (CH_3OH) or 1-heptanol ($CH_3CH_2CH_2CH_2CH_2CH_2CH_2OH$)? Explain.

Answer

1. a. pentane; b. acetic acid has more types of forces (three compared to two for methyl chloride)
2. Methanol would be more soluble in water. Because both are alcohols, the polar OH group will allow both to participate in dipole-dipole and hydrogen-bonding interactions with water. Because 1-heptanol has a much larger non-polar hydrocarbon portion, it is less soluble (not as much like water).

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11.9: Chemical Properties: Carboxylic Acids

Skills to Develop

- Name the typical reactions that take place with carboxylic acids.
- Describe how carboxylic acids react with basic compounds.

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.

Water-soluble carboxylic acids ionize slightly in water to form moderately acidic solutions.

$$\mathrm{RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+}$$

Their aqueous solutions exhibit the typical properties of acids, such as changing litmus from blue to red.

The anion formed when a carboxylic acid dissociates is called the *carboxylate* anion ($RCOO^-$).

Whether soluble in water or not, carboxylic acids react with aqueous solutions of sodium hydroxide (NaOH), 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) 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:

The salts of long-chain carboxylic acids are called soaps. We discuss the chemistry of soaps elsewhere.

Example 11.9.1

Write an equation for each reaction.

1. the ionization of propionic acid in water (H_2O)

2. the neutralization of propionic acid with aqueous sodium hydroxide (NaOH)

SOLUTION

Propionic acid has three carbon atoms, so its formula is CH_3CH_2COOH.

1. Propionic acid ionizes in water to form a propionate ion and a hydronium (H_3O^+) ion.

   $$CH_3CH_2COOH(aq) + H_2O(\ell) \rightarrow CH_3CH_2COO^-(aq) + H_3O^+(aq)$$

2. Propionic acid reacts with NaOH(aq) to form sodium propionate and water.

   $$CH_3CH_2COOH(aq) + NaOH(aq) \rightarrow CH_3CH_2COO^-Na^+(aq) + H_2O(\ell)$$

Example 11.9.2

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).

$$CH_3(CH_2)_8COOH + NaHCO_3(aq) \rightarrow CH_3(CH_2)_8COO^-Na^+(aq) + H_2O(\ell) + CO_2(g)$$

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.

Concept Review Exercises

1. How does the neutralization of a carboxylic acid differ from that of an inorganic acid? How are they similar?
2. What products are formed when a carboxylic acid is neutralized with a strong base? What additional product is formed when a carboxylic acid is neutralized with a carbonate or a bicarbonate?

Answers

1. Insoluble carboxylic acids often form soluble carboxylate salts. Both form a salt and water.
2. a carboxylate salt and water; carbon dioxide

Key Takeaways

- Soluble carboxylic acids are weak acids in aqueous solutions.
- Carboxylic acids neutralize bases to form salts.

Exercises

1. Write the equation for the ionization of $CH_3CH_2CH_2COOH$ in water.
2. Write the equation for the reaction of CH_3COOH with sodium carbonate [$Na_2CO_3(aq)$].
3. Write the equation for the ionization of propionic acid, CH_3CH_2COOH, in water.
4. Write an equation for the reaction of butyric acid, $CH_3CH_2CH_2COOH$, with each compound.
   a. aqueous NaOH
   b. aqueous $NaHCO_3$

Answers

1. $CH_3CH_2CH_2COOH(aq) + H_2O(\ell) \rightarrow CH_3CH_2CH_2COO^-(aq) + H_3O^+(aq)$
2. $2CH_3COOH + Na_2CO_3(aq) \rightarrow 2CH_3COO^-Na^+(aq) + H_2O(\ell) + CO_2(g)$
3. $CH_3CH_2COOH(aq) + H_2O(\ell) \rightarrow CH_3CH_2COO^-(aq) + H_3O^+(aq)$
4.

a. $CH_3CH_2CH_2COOH(aq) + NaOH(aq) \rightarrow CH_3CH_2CH_2COO^-Na^+(aq) + H_2O(\ell)$
b. $CH_3(CH_2)_2COOH + NaHCO_3(aq) \rightarrow CH_3(CH_2)COO^-Na^+(aq) + H_2O(\ell) + CO_2(g)$

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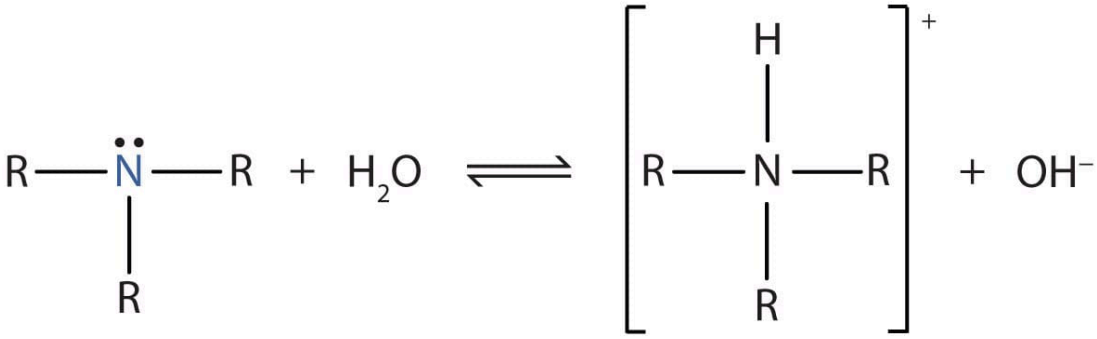
11.10: Chemical Properties: Amines as Bases

Skills to Develop

- Name the typical reactions that take place with amines.
- Describe heterocyclic amines.

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.

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.

$$CH_3NH_2(aq) + H_2O \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$$

Methylamine — Methylammonium ion

Nearly all amines, including those that are not very soluble in water, will react with strong acids to form salts soluble in water.

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2NH_2(\ell) + HNO_3(aq) \rightarrow CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2NH_2^{(+)}\ NO_3^{(-)}(aq)$$

octylamine (insoluble – mostly non-polar) — octylammonium nitrate salt (soluble – ionic)

Amine salts are named like other salts: the name of the cation is followed by the name of the anion.

Example 11.10.1

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).

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.

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.

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 is used as the salt cocaine hydrochloride and in the form of broken lumps of the free (unneutralized) base, which is called *crack cocaine*.

Because it is soluble in water, cocaine hydrochloride is readily absorbed through the watery mucous membranes of the nose when it is snorted. Crack cocaine is more volatile than cocaine hydrochloride. It vaporizes at the temperature of a burning cigarette. When smoked, cocaine reaches the brain in 15 s.

Summary

Amines are bases; they react with acids to form salts. Salts of aniline are properly named as *anilinium* compounds, but an older system is used to name drugs: the salts of amine drugs and hydrochloric acid are called “hydrochlorides.” Heterocyclic amines are cyclic compounds with one or more nitrogen atoms in the ring.

Concept Review Exercises

1. Explain the basicity of amines.
2. Contrast the physical properties of amines with those of alcohols and alkanes.
3. What is a heterocyclic compound?

Answers

1. Amines have a lone pair of electrons on the nitrogen atom and can thus act as proton acceptors (bases).
2. The solubilities of amines are similar to those of alcohols; the boiling points of primary and secondary amines are similar to those of alcohols; the boiling points of tertiary amines, which cannot engage in hydrogen bonding because they do not have a hydrogen atom on the nitrogen atom, are comparable to those of alkanes.
3. Heterocyclic compounds are ring compounds with atoms other than carbon atoms in the ring.

Exercises

1. What salt is formed in each reaction? Write its condensed structural formula.

    a. $CH_3NH_2(aq) + HBr(aq) \rightarrow$
    b. $CH_3NHCH_3(aq) + HNO_3(aq) \rightarrow$

Answer

1. a. $CH_3NH_3^+Br^-(aq)$
    b. $[CH_3NH_2CH_3]^+NO_3^-(aq)$

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11.E: Organic Chemistry (Exercises)

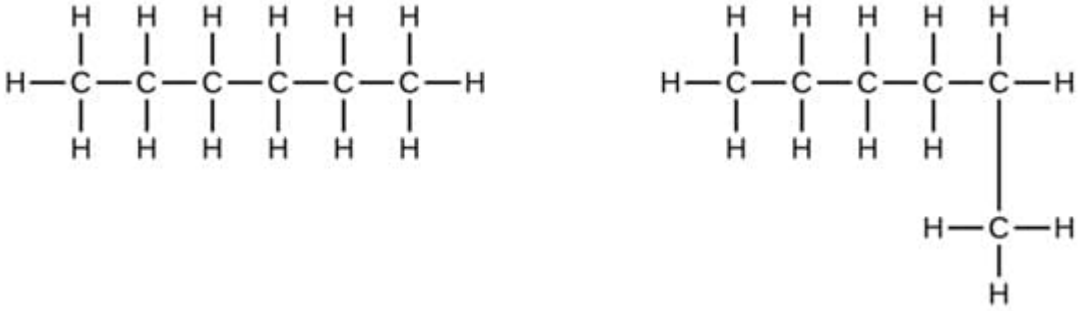
12: Organic Chemistry

Exercises

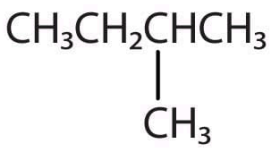
Green text involves IUPAC naming.

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
3. Which member of each pair has a higher melting point? (A) CH_3OH and NaOH; (B) CH_3Cl and CH_3OH; (C) CH_3Cl and $CH_3CH_2CH_2CH_2CH_2Cl$
4. Use the general formulas for alkanes to write the molecular formula of the alkane with 12 carbon atoms. What would the formula for an alkene with 12 carbons (just one double bond).
5. In alkanes, can there be a two-carbon branch off the second carbon atom of a four-carbon chain? Explain.
6. Indicate whether the structures in each set represent the same compound, isomers, or different. (Naming them will help.)

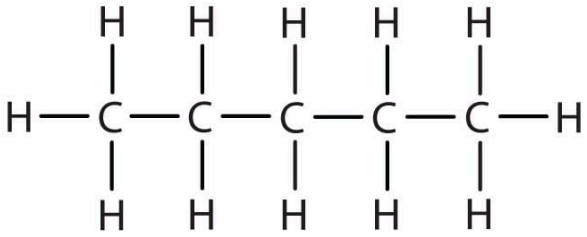
   A) and



   B) $CH_3CH_2CH_2CH_2CH_3$ and

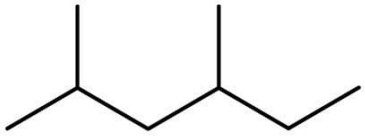


7. Name and write the condensed structural formula for the structural formula to the right.



8. Draw a line-angle formula for the compound $CH_3CH_2CH(CH_3)CH_2CH_2CH_3$. (Also give the IUPAC name.)

9. Write the structural formula for the compound represented by this line-angle formula. (Also give the IUPAC name.)



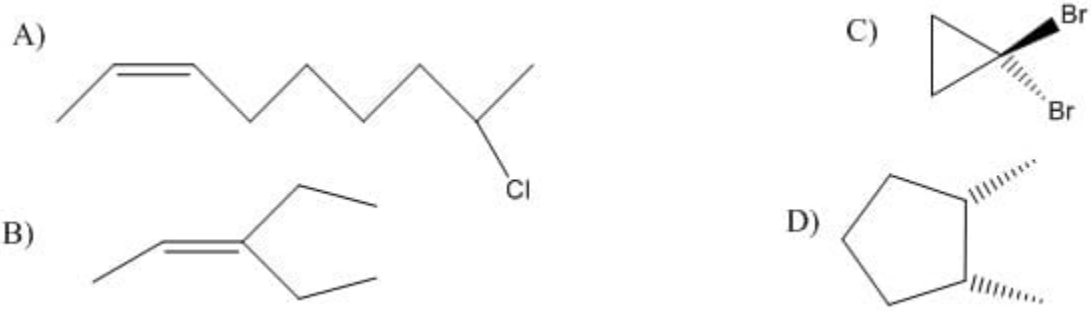
10. Draw the structure for each name. A) 4-ethyl-2-methylhexane; B) 2,2,3,3-tetramethylbutane

11. 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

12. Draw the structures for the five isomeric hexanes (C_6H_{14}). Name each by the IUPAC system.

13. Which functional group is present in each of the following? Which are also acidic or basic? A) $CH_3NHCH_2CH_3$; B) $CH_3CO_2CH_3$; C) CH_3CO_2H; D) $(CH_3)_2CHOH$

14. Is each molecule cis, trans, or neither? Also give the IUPAC name (cis- or trans- goes in front of name, when appropriate).



Answers

1. A) organic; B) inorganic; C) inorganic; D) organic

2. A) organic; B) inorganic

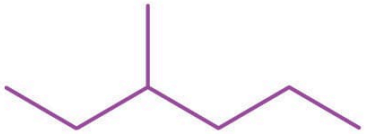
3. Which member of each pair has a higher melting point? (A) NaOH; (B) CH_3OH; (C) $CH_3CH_2CH_2CH_2CH_2Cl$

4. alkane $C_{12}H_{26}$; alkene $C_{12}H_{24}$

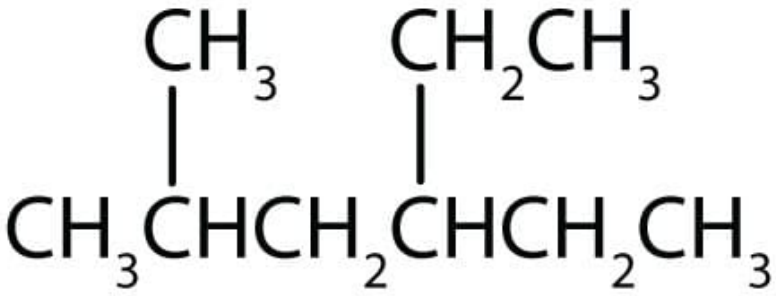
5. No; both are five-carbon continuous chains.

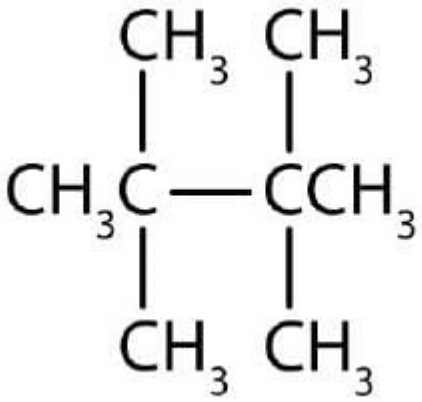
6. A) same - both pentane; B) isomers - pentane and 2-methylbutane

7. $CH_3CH_2CH_2CH_2CH_3$
8. 3-methylhexane



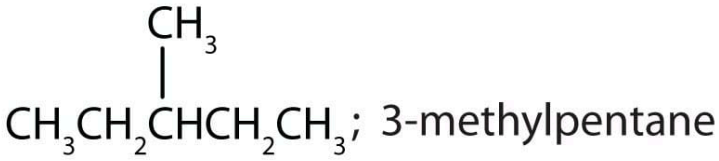
9. 2,4-dimethylhexane, $(CH_3)_2CHCH_2CH(CH_3)CH_2CH_3$
10. A)

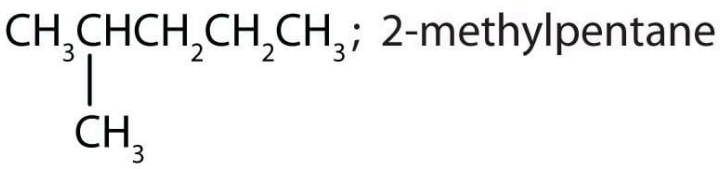


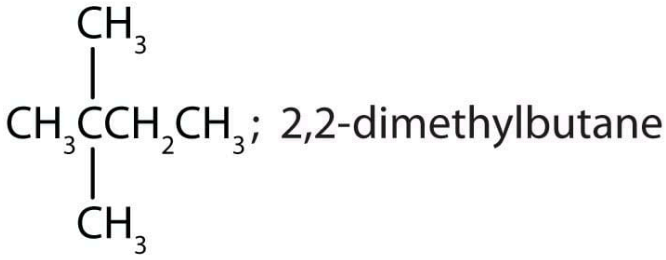


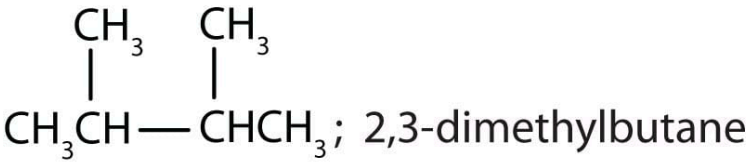
B)

11. 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.
12. $CH_3CH_2CH_2CH_2CH_2CH_3$; hexane









13. A) amine & base; B) ester; C) carboxylic acid & acid; D) alcohol

14. A) cis-8-chloro-2-nonene; B) 3-ethyl-2-pentene is not cis or trans because both groups single bonded to carbon #3 are the same; C) 1,1,-dibromocylcopropane is not cis or trans because both bromine substituents are bonded to the same carbon; D) cis-1,2-dimethylcylcopentane

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11.S: Organic Chemistry (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.

Cycloalkanes are saturated hydrocarbons whose molecules are closed rings rather than straight or branched chains. Rings restrict rotation, so if there are two non-hydrogen substituents on different carbons of a cyclohexane, two **cis-trans isomers (or geometric isomers)** can exist.

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}. Double bonds cannot rotate so if there is one non-hydrogen substituent on each of the double-bonded carbons, two cis-trans isomers can exist. **Alkynes** have a carbon-to-carbon triple bond. The general formula for alkynes is C_nH_{2n-2}.

The physical properties of hydrocarbons reflect the fact that the molecules are nonpolar. Hydrocarbons are insoluble in water and less dense than water. Size and presence of polar functional groups can affect the water solubility, melting point, and boiling point of organic compounds. 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.

A **functional group** is any atom or atom group that confers characteristic properties to a family of compounds. Alkanes are generally unreactive toward laboratory acids, bases, oxidizing agents, and reducing agents; they do burn in oxygen (undergo **combustion reactions**). Alkenes and alkynes are more reactive, susceptible to addition by halogens or water, for example. **Carboxyl** functional groups are weak acids and **amine** functional groups are weak bases.

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12: 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.

12.1: Carbohydrates

12.2: Classes of Monosaccharides

12.3: Important Hexoses

12.4: Cyclic Structures of Monosaccharides

12.5 Properties of Monosaccharides

12.6 Disaccharides

12.7 Polysaccharides

12.8: Chapter Summary

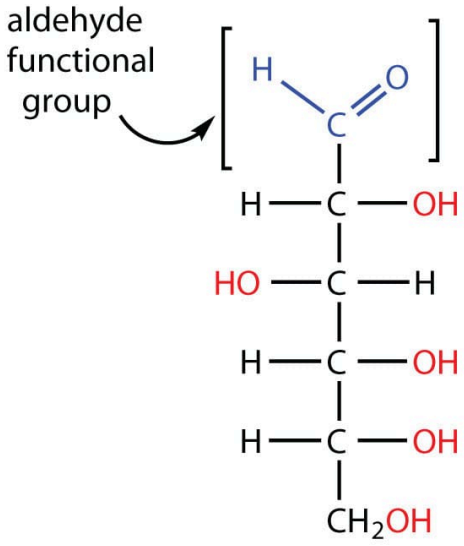
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12.1: Carbohydrates

Skills to Develop

- To recognize carbohydrates and classify them as mono-, di-, or polysaccharides.

All carbohydrates consist of carbon, hydrogen, and oxygen atoms and are polyhydroxy aldehydes or ketones or are compounds that can be broken down to form such compounds. Examples of carbohydrates include starch, fiber, the sweet-tasting compounds called sugars, and structural materials such as cellulose. The term *carbohydrate* had its origin in a misinterpretation of the molecular formulas of many of these substances. For example, because its formula is $C_6H_{12}O_6$, glucose was once thought to be a "carbon hydrate" with the structure $C_6{\cdot}6H_2O$.

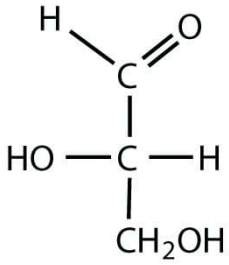


Because glucose has an aldehyde functional group and several –OH (hydroxyl) groups, it is described as a polyhydroxy aldehyde.

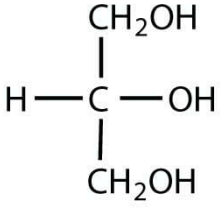
Example 12.1.1

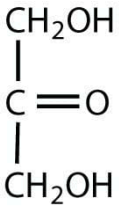
Which compounds would be classified as carbohydrates?

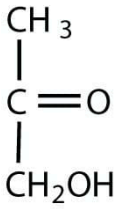
a.



b.



c. 

d. 

SOLUTION

a. This is a carbohydrate because the molecule contains an aldehyde functional group with OH groups on the other two carbon atoms.
b. This is not a carbohydrate because the molecule does not contain an aldehyde or a ketone functional group.
c. This is a carbohydrate because the molecule contains a ketone functional group with OH groups on the other two carbon atoms.
d. This is not a carbohydrate; although it has a ketone functional group, one of the other carbons atoms does not have an OH group attached.

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:

$$6CO_2 + 6H_2O + 686 \text{ kcal} \rightarrow C_6H_{12}O_6 + 6O_2 \tag{12.1.1}$$

(The 686 kcal come from solar energy.) Plants can use the glucose for energy or convert it to larger carbohydrates, such as starch or cellulose. Starch provides energy for later use, perhaps as nourishment for a plant's seeds, while cellulose is the structural material of plants. We can gather and eat the parts of a plant that store energy—seeds, roots, tubers, and fruits—and use some of that energy ourselves. Carbohydrates are also needed for the synthesis of nucleic acids and many proteins and lipids.

Animals, including humans, cannot synthesize carbohydrates from carbon dioxide and water and are therefore dependent on the plant kingdom to provide these vital compounds. We use carbohydrates not only for food (about 60%–65% by mass of the average diet) but also for clothing (cotton, linen, rayon), shelter (wood), fuel (wood), and paper (wood).

The simplest carbohydrates—those that cannot be hydrolyzed to produce even smaller carbohydrates—are called monosaccharides. Two or more monosaccharides can link together to form chains that contain from two to several hundred or thousand monosaccharide units. Prefixes are used to indicate the number of such units in the chains. Disaccharide molecules have two monosaccharide units, *trisaccharide* molecules have three units, and so on. Chains with many monosaccharide units joined together are called polysaccharides. All these so-called higher saccharides can be hydrolyzed back to their constituent monosaccharides.

> Compounds that cannot be hydrolyzed will not react with water to form two or more smaller compounds.

Summary

Carbohydrates are an important group of biological molecules that includes sugars and starches. Photosynthesis is the process by which plants use energy from sunlight to synthesize carbohydrates. A monosaccharide is the simplest carbohydrate and cannot be hydrolyzed to produce a smaller carbohydrate molecule. Disaccharides contain two monosaccharide units, and polysaccharides contain many monosaccharide units.

Concept Review Exercises

1. Why is photosynthesis important?
2. Identify the differences among monosaccharides, disaccharides, and polysaccharides.

Answers

1. Photosynthesis is the process by which solar energy is used to reduce carbon dioxide to carbohydrates, which are needed for energy by plants and other living organisms that eat plants.
2. A monosaccharide is the simplest carbohydrate and cannot be hydrolyzed to produce a smaller carbohydrate; a disaccharide is composed of two monosaccharide units; and a polysaccharide contains many saccharide units.

Exercises

1. When an aqueous solution of trehalose is heated, two molecules of glucose are produced for each molecule of trehalose. Is trehalose a monosaccharide, a disaccharide, or a polysaccharide?
2. When an aqueous solution of arabinose is heated, no other molecules are produced. Is arabinose a monosaccharide, a disaccharide, or a polysaccharide?

Answer

1. Trehalose is a disaccharide because it is hydrolyzed into two molecules of glucose (a monosaccharide).

2. Arabinose is a monosaccharide because it cannot be hydrolyzed to produce a smaller carbohydrate.

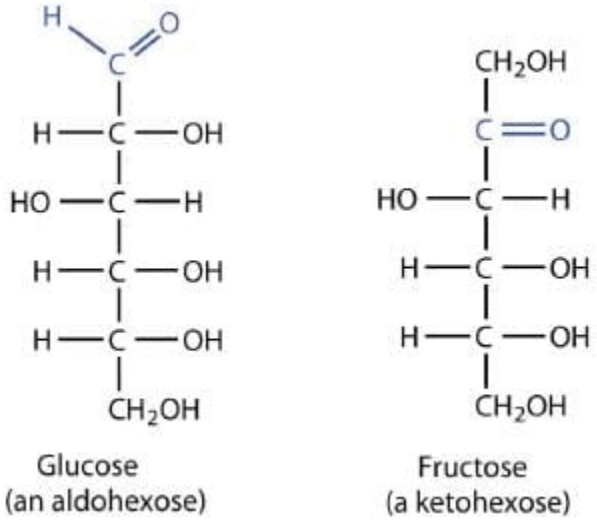
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12.2: Classes of Monosaccharides

Skills to Develop

- Classify monosaccharides as aldoses or ketoses and as trioses, tetroses, pentoses, or hexoses.
- Distinguish between a D sugar and an L sugar.

The naturally occurring monosaccharides contain three to seven carbon atoms per molecule. Monosaccharides of specific sizes may be indicated by names composed of a stem denoting the number of carbon atoms and the suffix *-ose*. For example, the terms *triose*, *tetrose*, *pentose*, and *hexose* signify monosaccharides with, respectively, three, four, five, and six carbon atoms. Monosaccharides are also classified as aldoses or ketoses. Those monosaccharides that contain an aldehyde functional group are called aldoses; those containing a ketone functional group on the second carbon atom are ketoses. Combining these classification systems gives general names that indicate both the type of carbonyl group *and* the number of carbon atoms in a molecule. Thus, monosaccharides are described as aldotetroses, aldopentoses, ketopentoses, ketoheptoses, and so forth. Glucose and fructose are specific examples of an aldohexose and a ketohexose, respectively.



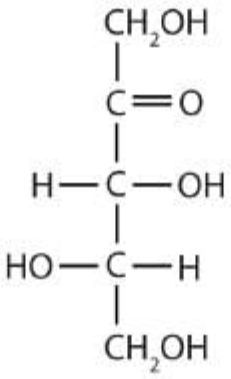
Example 12.2.1

Draw an example of each type of compound.

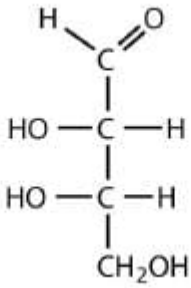
a. a ketopentose
b. an aldotetrose

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.



b. 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.

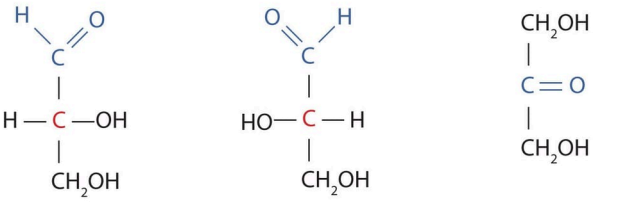


The simplest sugars are the trioses. The possible trioses are shown in part (a) of Figure 12.2.1; glyceraldehyde is an aldotriose, while dihydroxyacetone is a ketotriose. Notice that two structures are shown for glyceraldehyde. These structures are stereoisomers, and hence are isomers having the same 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 12.2.1. 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.

(a)



D–(+)–Glyceraldehyde L–(–)–Glyceraldehyde Dihydoxyacetone

(b)

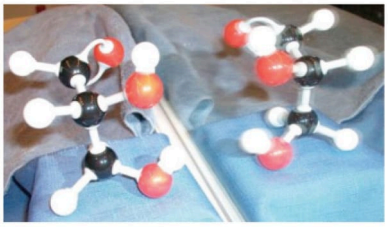


Figure 12.2.1*: Structures of the Trioses. (a) D- and L-glyceraldehyde are mirror images of each other and represent a pair of enantiomers. (b) A ball-and-stick model of D-glyceraldehyde is reflected in a mirror. Note that the reflection has the same structure as L-glyceraldehyde.*

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 12.2.1). 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°.

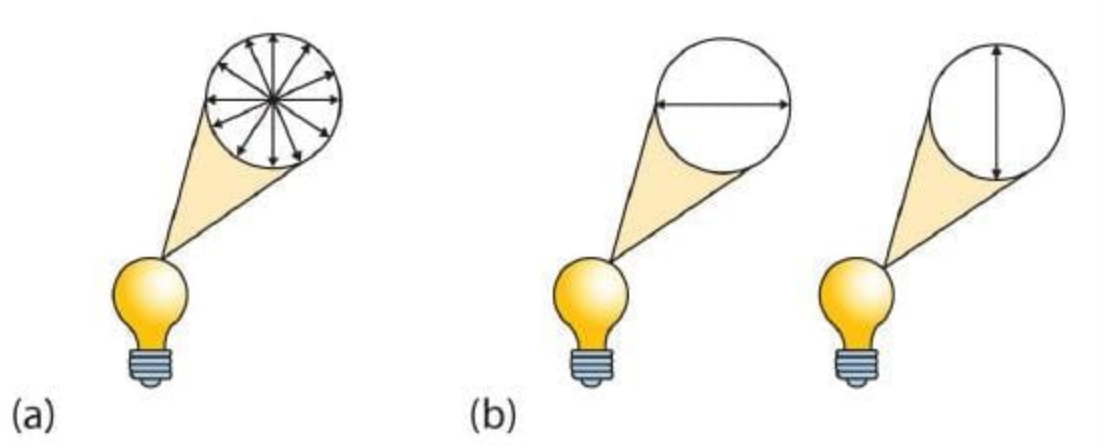
H. Emil Fischer, a German chemist, developed the convention commonly used for writing two-dimensional representations of the monosaccharides, such as those in part (a) of Figure 12.2.1. In these structural formulas, the aldehyde group is written at the top, and the hydrogen atoms and OH groups that are 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.

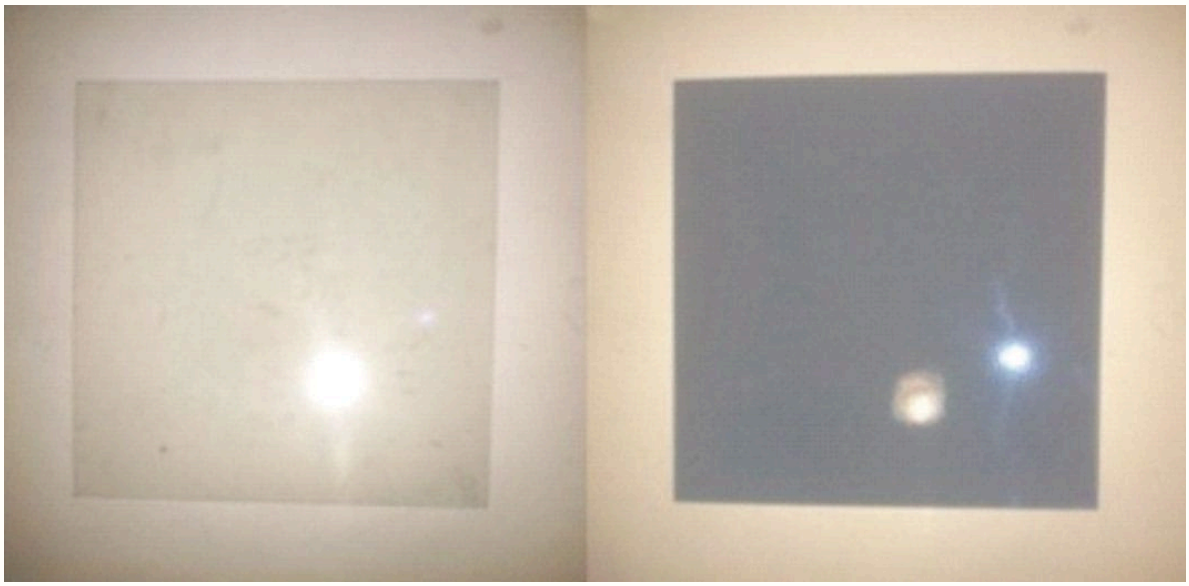
> By convention, the penultimate (next-to-last) carbon atom has been chosen as the carbon atom that determines if a sugar is D or L. It is the chiral carbon farthest from the aldehyde or ketone functional group.

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.

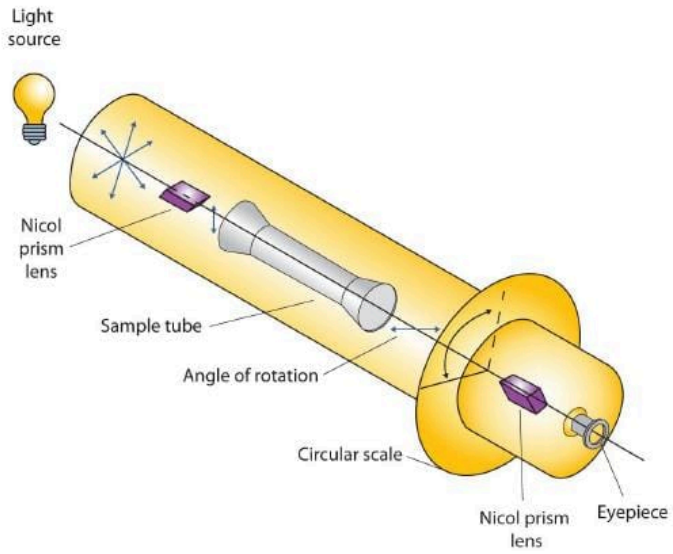


Figure 12.2.2***:*** *Diagram of a Polarimeter*

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.

Concept Review Exercises

1. What is a chiral carbon?
2. Describe how enantiomers differ.

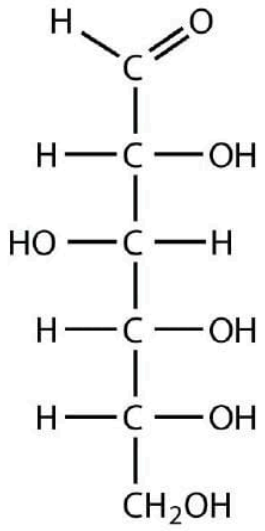
Answers

1. A chiral carbon is a carbon atom with four different groups attached to it.
2. Enantiomers are mirror images of each other; they differ in the arrangements of atoms around a chiral carbon.

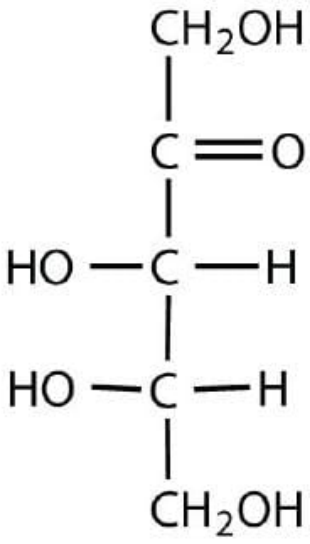
Exercises

1. Identify each sugar as an aldose or a ketose and then as a triose, tetrose, pentose, or hexose.

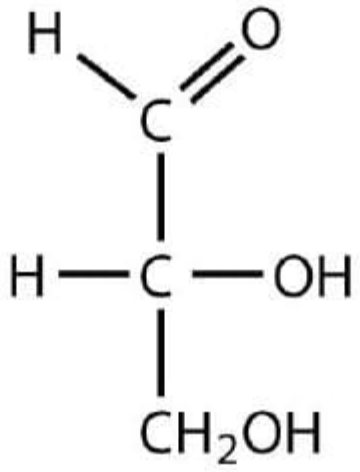
    a. D-glucose



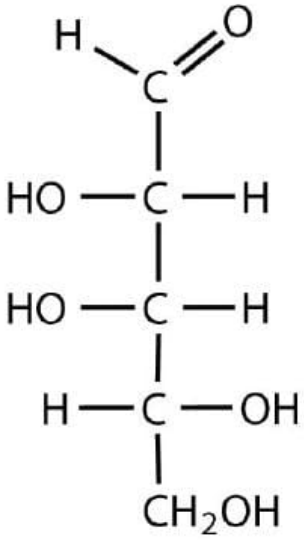
b. L-ribulose



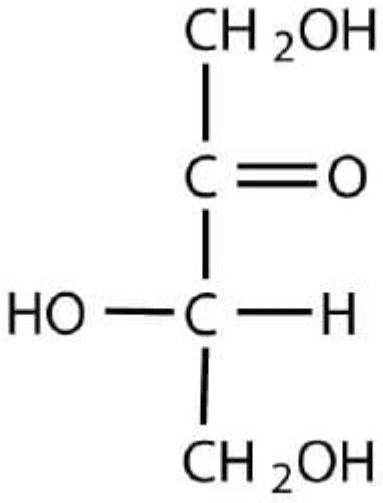
c. D-glyceraldehyde



2. Identify each sugar as an aldose or a ketose and then as a D sugar or an L sugar.



a.



b.

Answers

1. a. aldose; hexose
   b. ketose; pentose
   c. aldose; triose

2.

a. aldose; D sugar
b. ketose; L sugar

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12.3: Important Hexoses

Skills to Develop

- To identify the structures of D-glucose, D-galactose, and D-fructose and describe how they differ from each other.

Although a variety of monosaccharides are found in living organisms, three hexoses are particularly abundant: D-glucose, D-galactose, and D-fructose (Figure 12.3.1). Glucose and galactose are both aldohexoses, while fructose is a ketohexose.

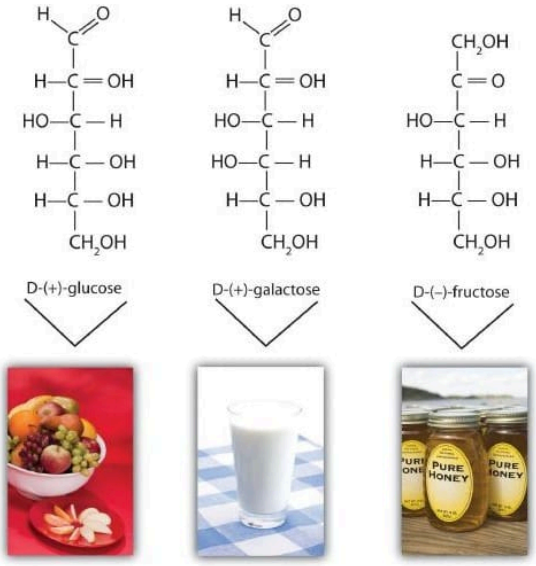


Figure 12.3.1***:*** *Structures of Three Important Hexoses. Each hexose is pictured with a food source in which it is commonly found. Source: Photos © Thinkstock.*

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.

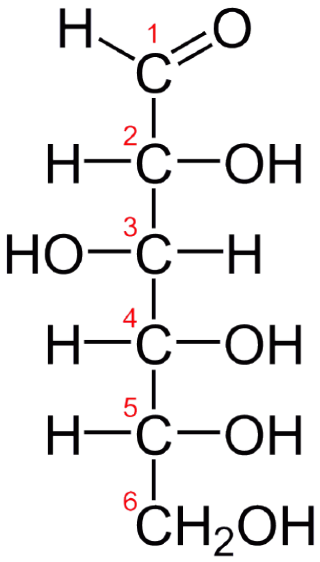


Figure 12.3.2***:*** *Fischer projection of D-glucose*

The Fischer projection of D-glucose is given in Figure 12.3.2. 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 12.3.1. Notice that the configuration differs from that of glucose only at the fourth carbon atom.

Fructose

D-Fructose, also shown in Figure 12.3.1, 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 12.3.1).

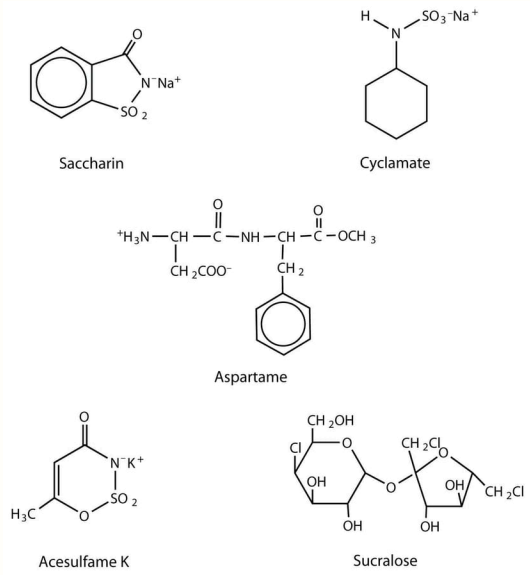
Table 12.3.1***:*** *The Relative Sweetness of Some Compounds (Sucrose = 100)*

Compound	Relative Sweetness
lactose	16
maltose	32
glucose	74
sucrose	100
fructose	173
aspartame	18,000
acesulfame K	20,000
saccharin	30,000

Compound	Relative Sweetness
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.

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.

Concept Review Exercises

1. Describe the similarities and differences in the structures of D-glucose and D-galactose.
2. Describe similarities and differences in the structures of D-glucose and D-fructose.

Answers

1. Both monosaccharides are aldohexoses. The two monosaccharides differ in the configuration around the fourth carbon atom.
2. Both monosaccharides are hexoses. D-glucose is an aldohexose, while D-fructose is a ketohexose.

Exercises

1. Identify each sugar by its common chemical name.

    a. blood sugar
    b. levulose

2. Identify each sugar as an aldohexose or a ketohexose.

    a. glucose
    b. galactose
    c. fructose

Answers

1. a. D-glucose
   b. D-fructose

2.

a. aldohexose
b. aldohexose

c. ketohexose

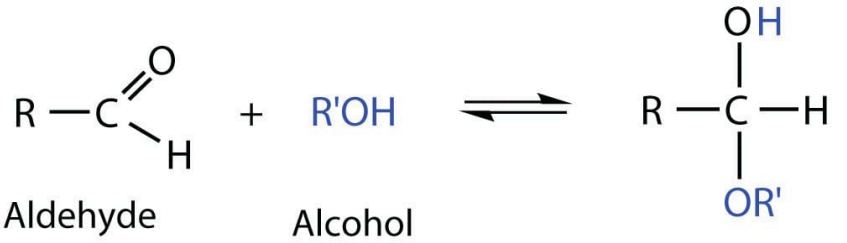
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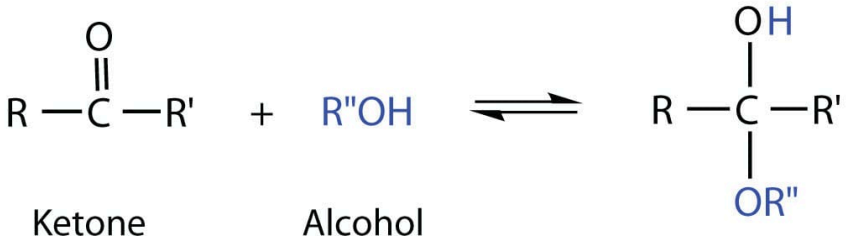
12.4: Cyclic Structures of Monosaccharides

Skills to Develop

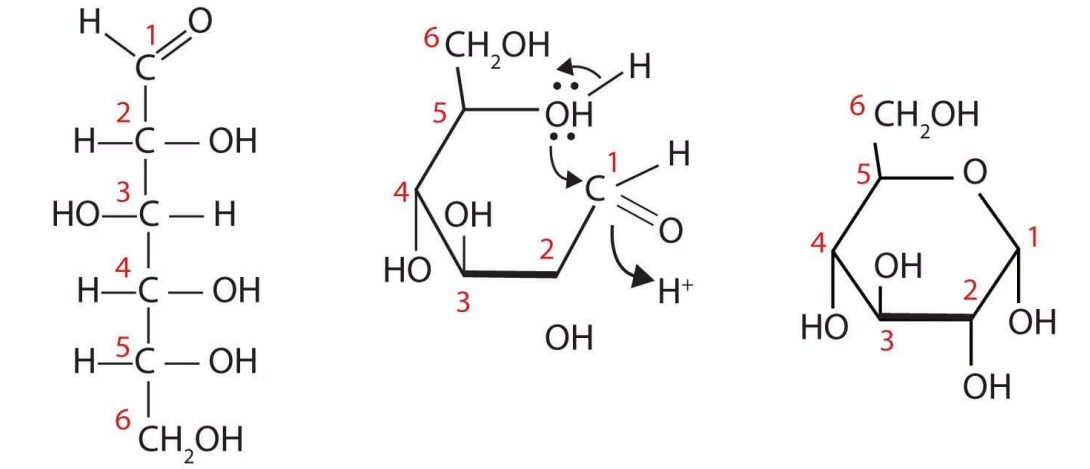
- Define what is meant by anomers and describe how they are formed.
- Explain what is meant by mutarotation.

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:





In some cases, OH and carbonyl groups on the same molecule are able to react with one another in an intramolecular reaction. Thus, monosaccharides larger than tetroses exist mainly as cyclic compounds (Figure 12.4.1). 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 12.4.1***:*** *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 12.4.1, forms a cyclic structure, the carbonyl oxygen atom may be pushed either up or down, giving rise to two stereoisomers, as shown in Figure 12.4.2. The structure shown on the left side of Figure 12.4.2, 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.

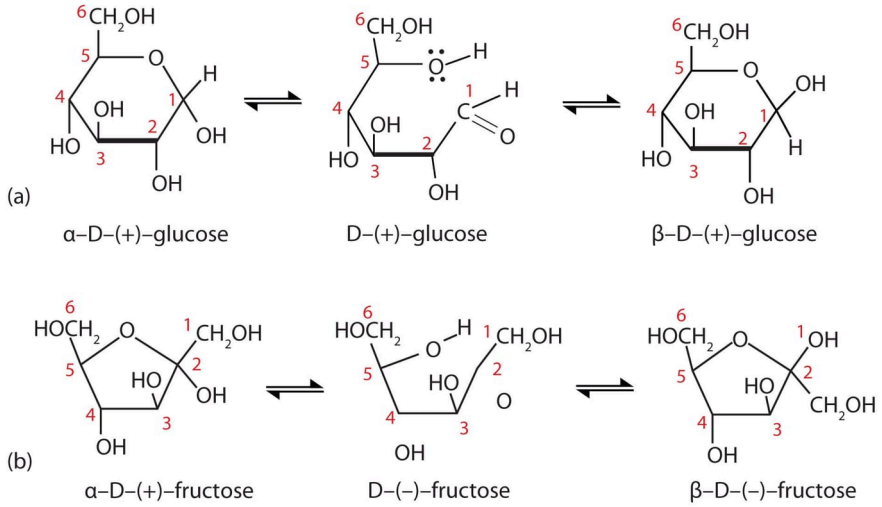


Figure 12.4.2***:*** *Monosaccharides. In an aqueous solution, monosaccharides exist as an equilibrium mixture of three forms. The interconversion between the forms is known as mutarotation, which is shown for D-glucose (a) and D-fructose (b).*

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 12.4.2). 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°.

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 12.4.1 and 12.4.2) 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.

Concept Review Exercises

1. Define each term.

    a. mutarotation
    b. anomer
    c. anomeric carbon

2. What will happen over time to a solution of α-D-glucose?

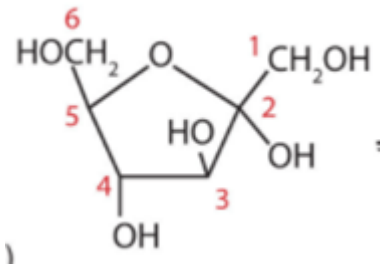
Answers

1. a. the ongoing interconversion between anomers of a particular carbohydrate to form an equilibrium mixture
    b. a stereoisomer that differs in structure around what was the carbonyl carbon atom in the straight-chain form of a monosaccharide
    c. the carbon atom that was the carbonyl carbon atom in the straight-chain form of a monosaccharide (In the ring form, the anomeric carbond is bonded to two oxgyen atoms.)

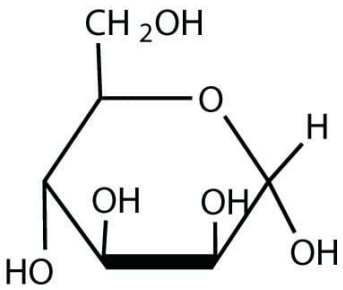
2. Over time, the α-D-glucose will undergo mutarotation, so the solution will become a mixture of alpha and beta.

Exercises

1. Identify the anomeric carbon in the structure below.



2. Is the monosaccharide shown below alpha or beta?



Answers

1.The carbon labeled "2" is anomeric (bonded to two oxygens).

2. The OH on the anomeric carbon is down, so alpha.

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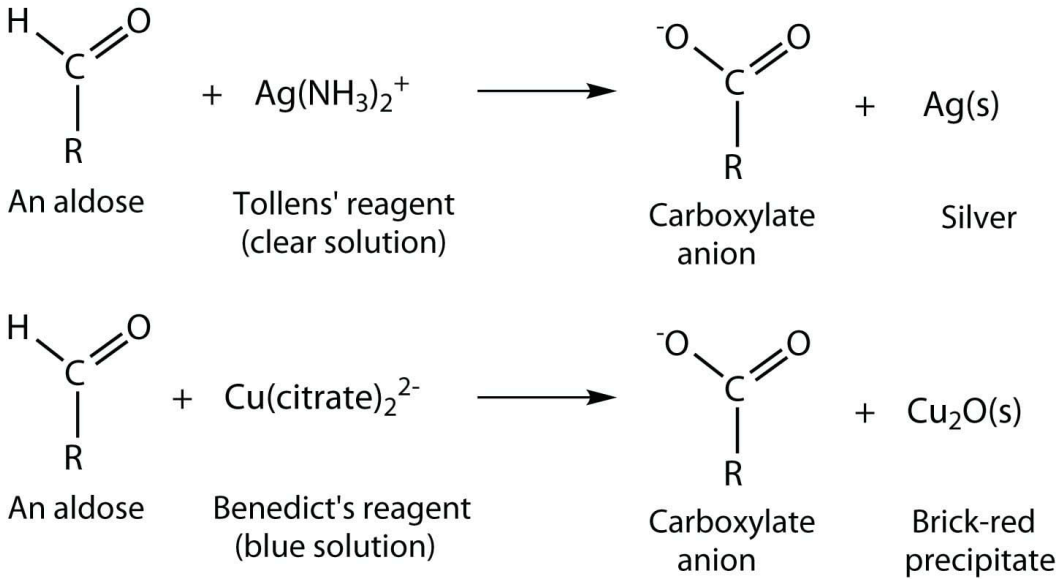
12.5 Properties of Monosaccharides

Skills to Develop

- 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 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*.

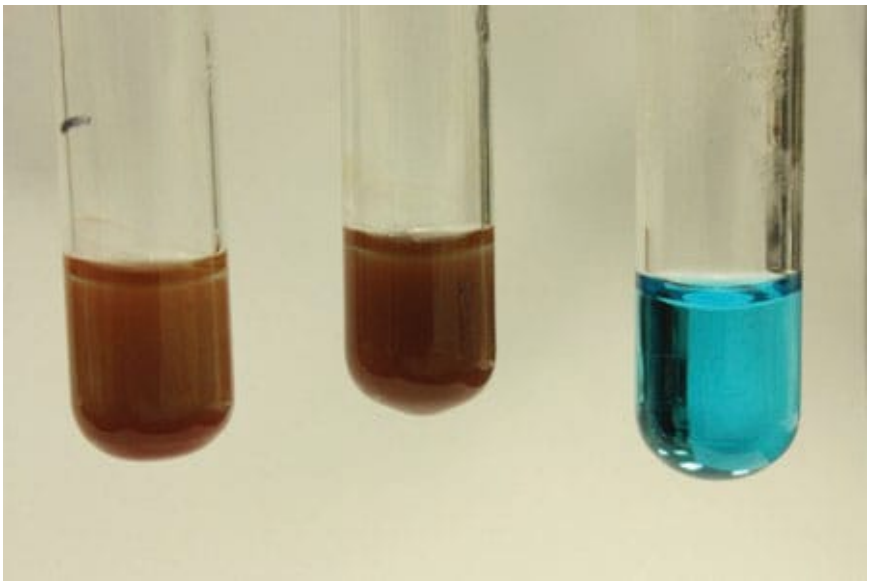


Figure 1***:*** *Benedict's Test. Benedict's test was performed on three carbohydrates, depicted from left to right: fructose, glucose, and sucrose. The solution containing sucrose remains blue because sucrose is a nonreducing sugar.*

These reactions have been used as simple and rapid diagnostic tests for the presence of glucose in blood or urine. For example, Clinitest tablets, which are used to test for sugar in the urine, contain copper(II) ions and are based on Benedict's test. A green color indicates very little sugar, whereas a brick-red color indicates sugar in excess of 2 g/100 mL of urine.

Summary

Monosaccharides are crystalline solids at room temperature and quite soluble in water. Monosaccharides are reducing sugars; they reduce mild oxidizing agents, such as Tollens' or Benedict's reagents.

Concept Review Exercises

1. Why are monosaccharides soluble in water?
2. What is a reducing sugar?

Answers

1. Monosaccharides are quite soluble in water because of the numerous OH groups that readily engage in hydrogen bonding with water.
2. any carbohydrate capable of reducing a mild oxidizing agent, such as Tollens' or Benedict's reagents, without first undergoing hydrolysis

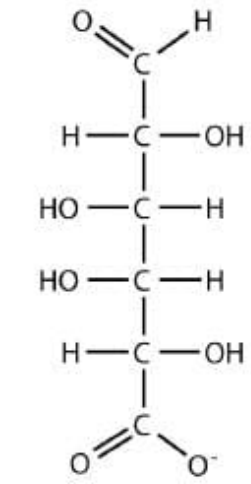
Exercises

1. Which gives a positive Benedict's test—L-galactose, levulose, or D-glucose?
2. D-Galactose can be oxidized at the sixth carbon atom to yield D-galacturonic acid and at both the first and sixth carbon atoms to yield D-galactaric acid. Draw the Fischer projection for each oxidation product.

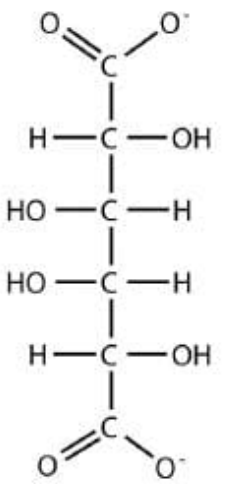
Answers

1. All three will give a positive Benedict's test because they are all monosaccharides.

2.



D-galacturonic acid



D-galactaric acid

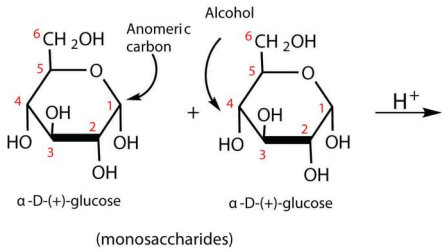
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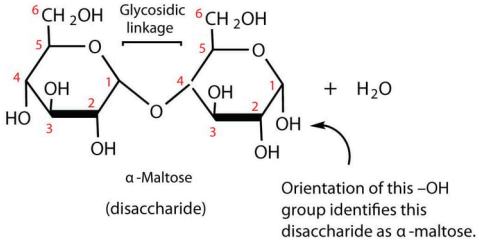
12.6 Disaccharides

Skills to Develop

- Identify the structures of sucrose, lactose, and maltose.
- Identify the monosaccharides that are needed to form sucrose, lactose, and maltose
- In Mueller's CHEM 109 course, you will not need to memorize the names or structures of the mono- or polysaccharides. Instead, you should be able to: (1) Identify the anomeric carbon; (2) Recognize a glycosidic bond and understand that water was removed from two OH groups to form it; and (3) Label a glycosidic bond as alpha or beta.
- In Mueller's CHEM 109 course, the difference between reducing and non-reducing sugars is not covered.

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.

$$\text{maltose} \xrightarrow{\text{H}^+ \text{ or maltase}} 2 \text{ D-glucose} \tag{16.6.2}$$

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 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 1.

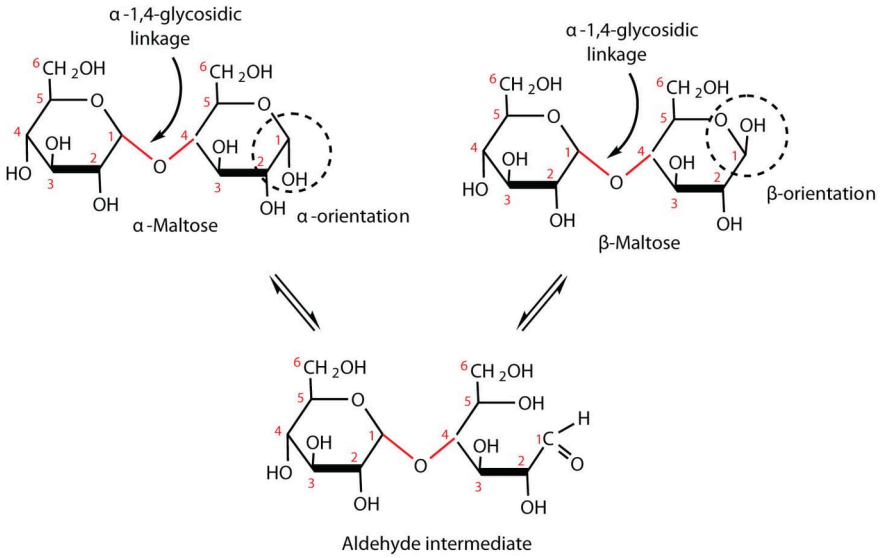
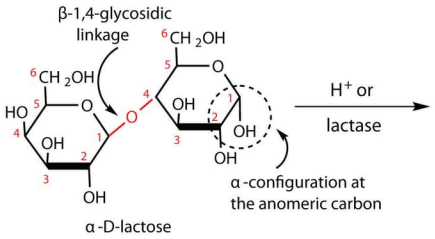


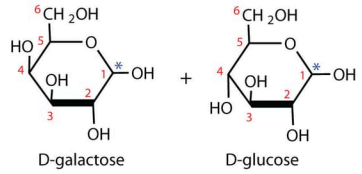
Figure 1 *An Equilibrium Mixture of Maltose Isomers*

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*:





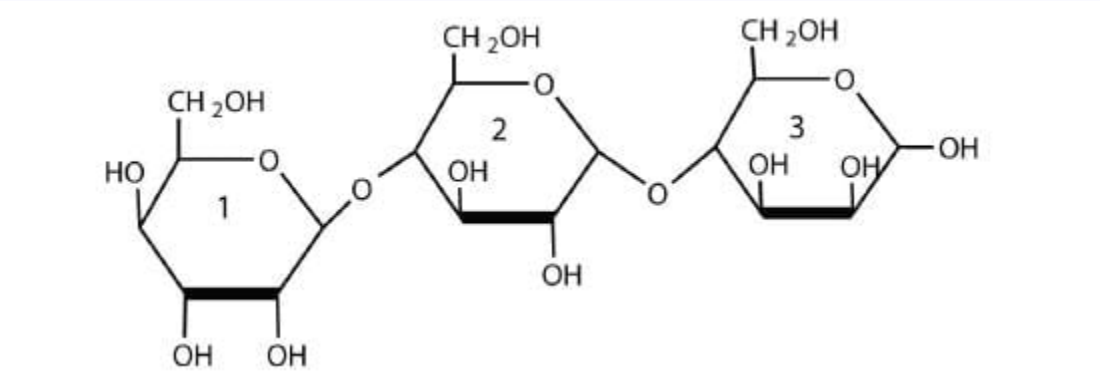
*We use this convention for writing the hydroxyl group on the anomeric carbon when we do not wish to specify either the α or the β anomer.

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 1

example* 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.

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.

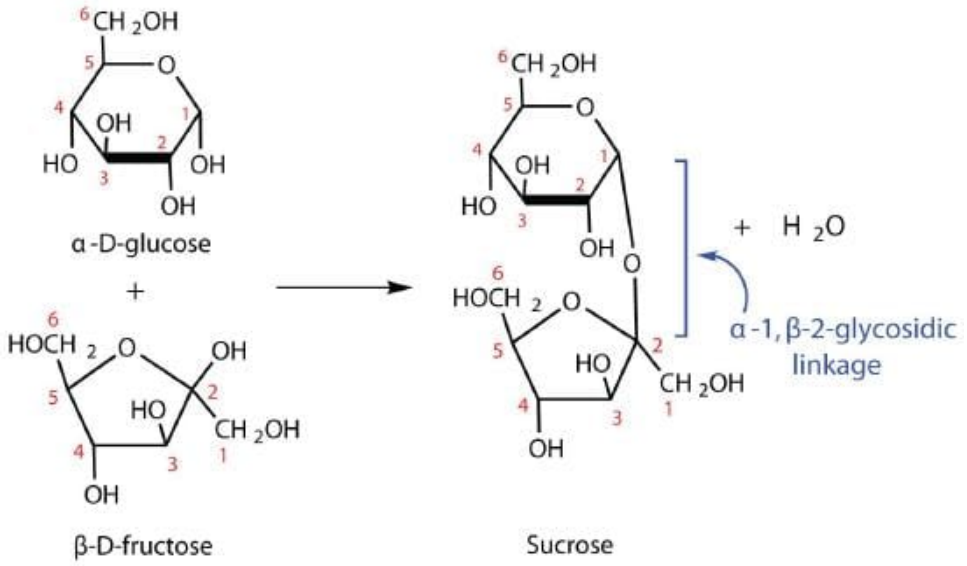
The symptoms disappear if milk or other sources of lactose are excluded from the diet or consumed only sparingly. Alternatively, many food stores now carry special brands of milk that have been pretreated with lactase to hydrolyze the lactose. Cooking or fermenting milk causes at least partial hydrolysis 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.

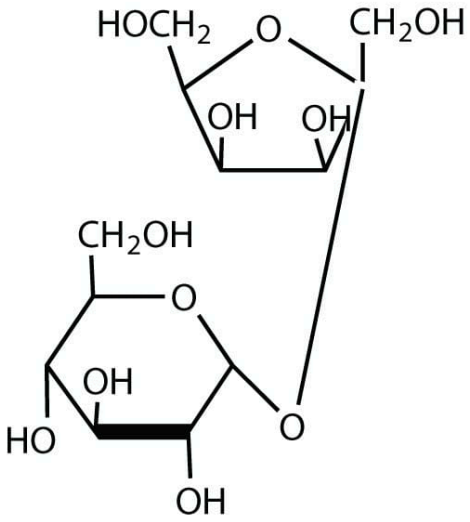
Summary

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.

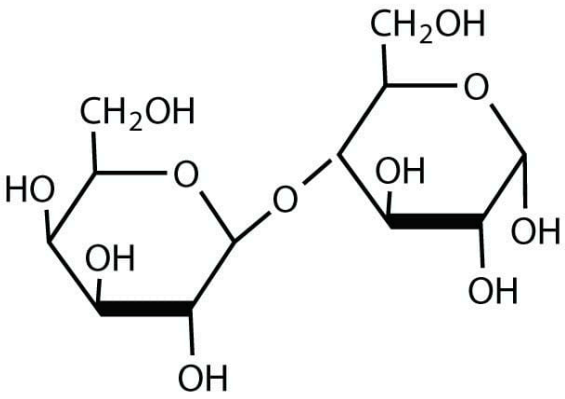
Exercises

1. Indicate whether any glycosidic linkages are α or β.

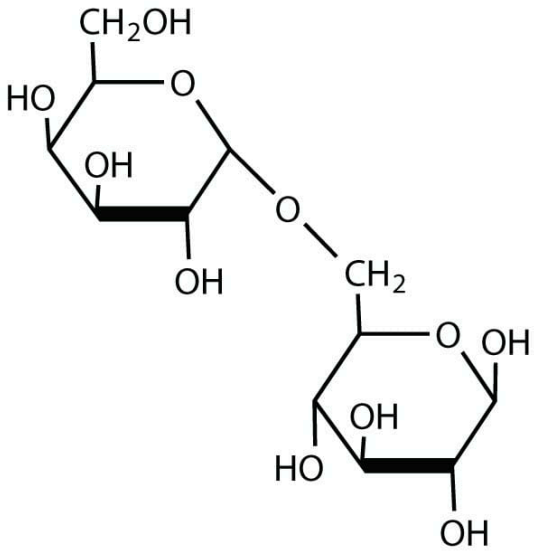
a.



b.



2. Melibiose is a disaccharide that occurs in some plant juices. Its structure is as follows:



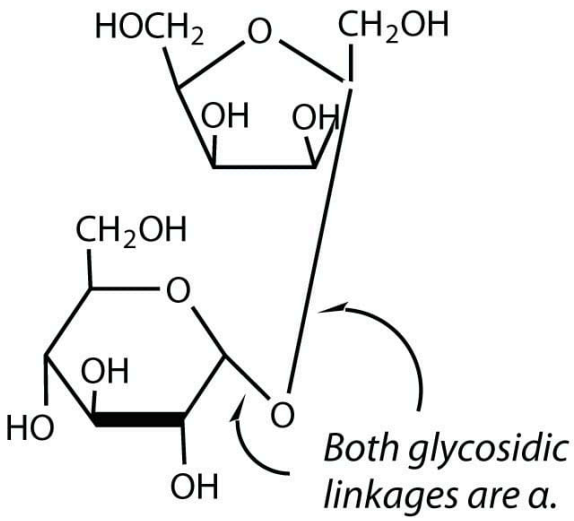
a. What type of linkage (α or β) joins the two monosaccharide units of melibiose?

b. Melibiose has a free anomeric carbon that is not involved in a glycosidic linkage. Circle the anomeric carbon and indicate whether the OH group is α or β.

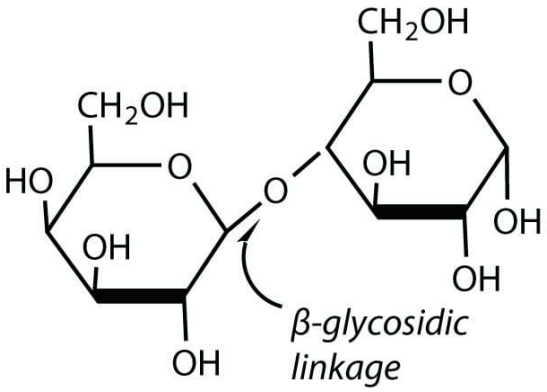
Answers

1.

a.



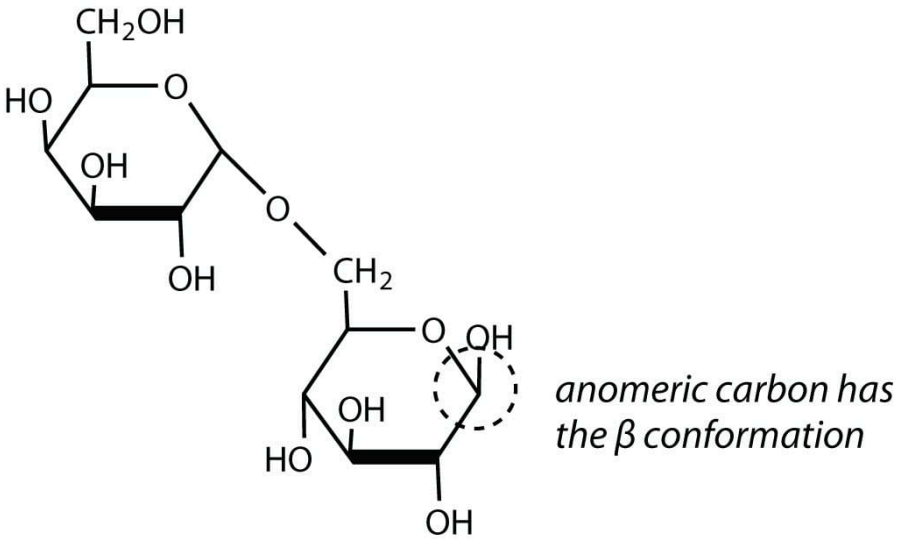
b.



2.

a. α-glycosidic linkage

b.



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12.7 Polysaccharides

Skills to Develop

- 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 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 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.

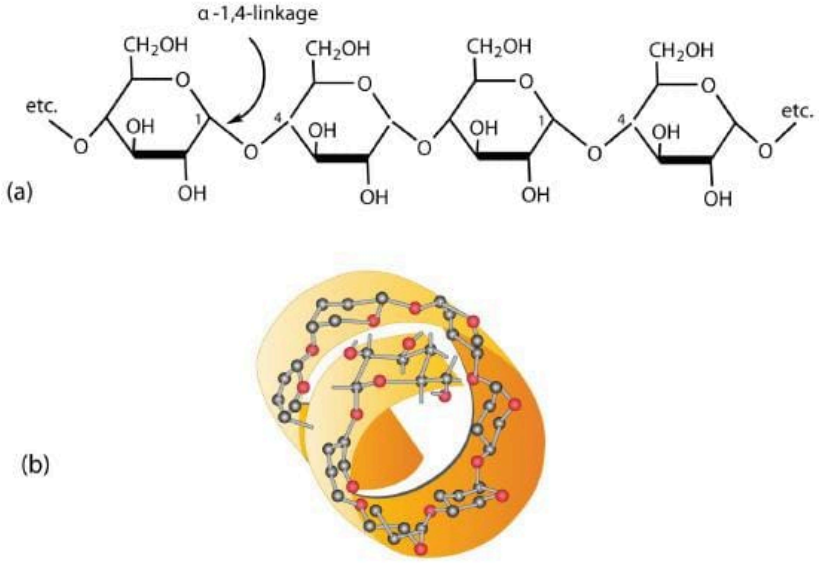


Figure 1*: Amylose. (a) Amylose is a linear chain of α-D-glucose units joined together by α-1,4-glycosidic bonds. (b) Because of hydrogen bonding, amylose acquires a spiral structure that contains six glucose units per turn.*

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 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.

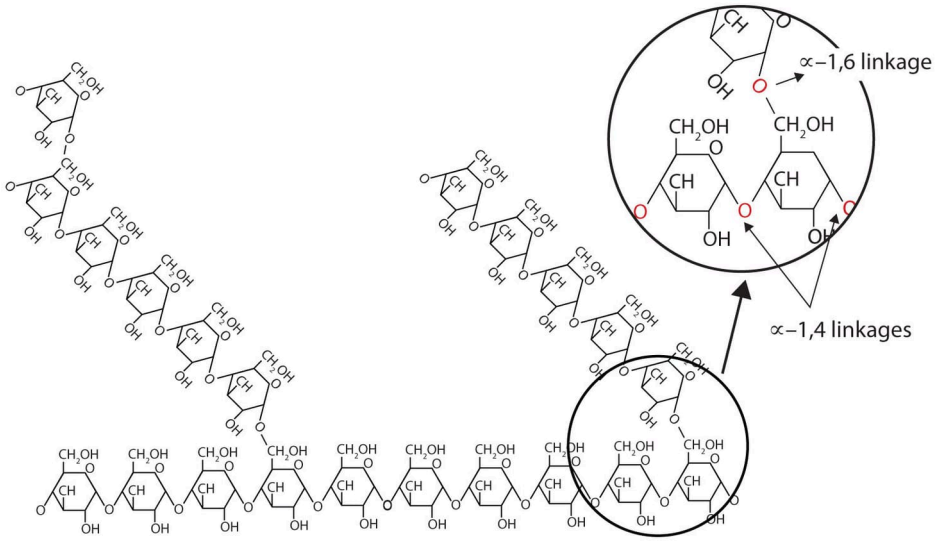


Figure 2: *Representation of the Branching in Amylopectin and Glycogen. Both amylopectin and glycogen contain branch points that are linked through α-1,6-linkages. These branch points occur more often in glycogen.*

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 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 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.

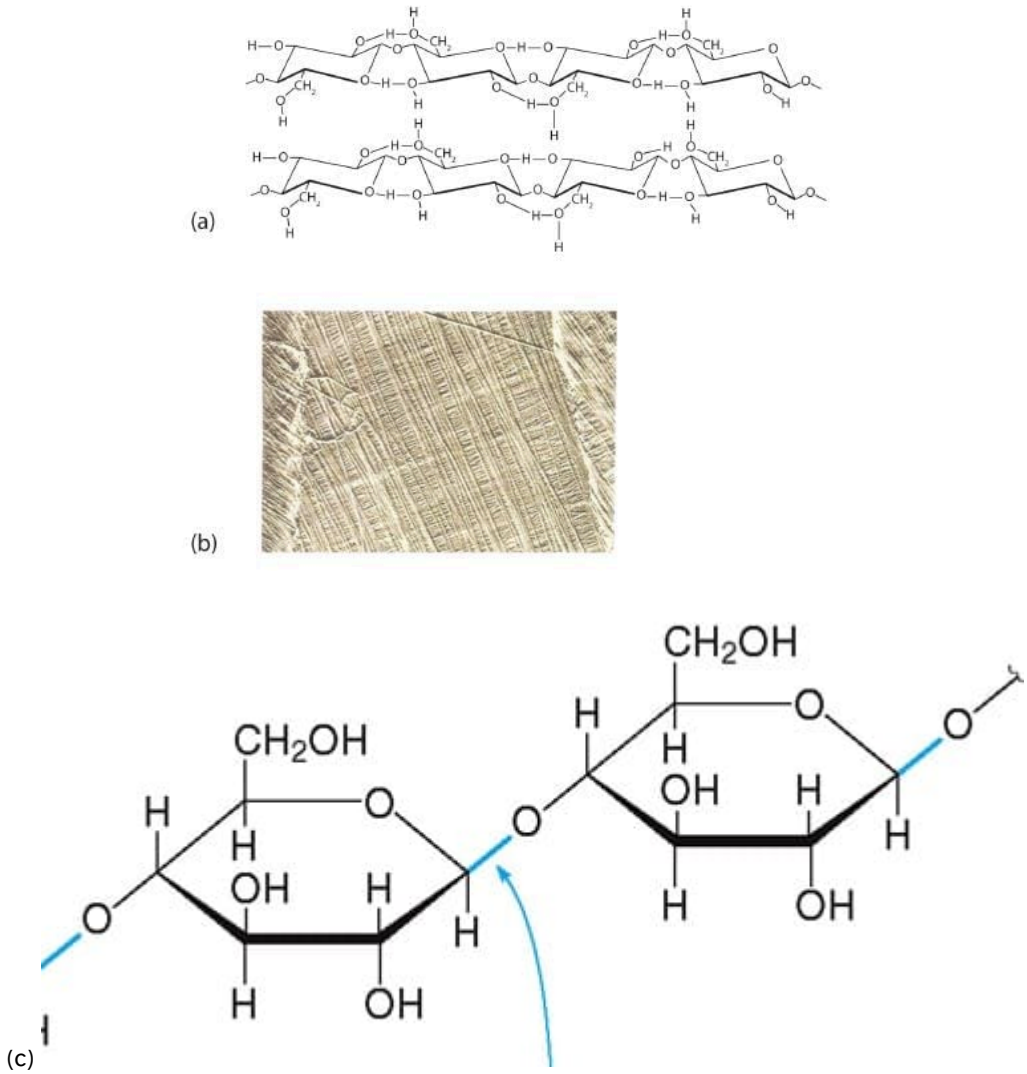


Figure 3: *Cellulose. (a) There is extensive hydrogen bonding in the structure of cellulose. (b) In this electron micrograph of the cell wall of an alga, the wall consists of successive layers of cellulose fibers in parallel arrangement. (c) This last image more clearly shows the beta glycosidic linkages.*

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. 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.



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.

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.

Concept Review Exercises

1. What purposes do starch and cellulose serve in plants?
2. What purpose does glycogen serve in animals?

Answers

1. Starch is the storage form of glucose (energy) in plants, while cellulose is a structural component of the plant cell wall.
2. Glycogen is the storage form of glucose (energy) in animals.

Exercises

1. What monosaccharide is obtained from the hydrolysis of each carbohydrate?

    a. starch
    b. cellulose
    c. glycogen

2. For each carbohydrate listed in Exercise 1, indicate whether it is found in plants or mammals.

3. Which of the following cannot be digested (hydrolyzed into glucose monomers) by humans and why: starch, cellulose & glycogen?

Answers

1. a. glucose
    b. glucose
    c. glucose

2. a. plants; b. plants; c. animals

3. Humans do not produce any enzymes that can digest (hydrolyze) the beta glycosidic linkages in cellulose. (But humans do produce amylase enzymes that can digest the alpha linkages in starch and gylcogen.)

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12.8: Chapter Summary

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

Carbohydrates, a large group of biological compounds containing carbon, hydrogen, and oxygen atoms, include sugars, starch, glycogen, and cellulose. All carbohydrates contain alcohol functional groups, and either an aldehyde or a ketone group (or a functional group that can be converted to an aldehyde or ketone). The simplest carbohydrates are **monosaccharides**. Those with two monosaccharide units are **disaccharides**, and those with many monosaccharide units are **polysaccharides**. Most sugars are either monosaccharides or disaccharides. Cellulose, glycogen, and starch are polysaccharides.

Many carbohydrates exist as **stereoisomers**, in which the three-dimensional spatial arrangement of the atoms in space is the only difference between the isomers. These particular stereoisomers contain at least one **chiral carbon**, a carbon atom that has four different groups bonded to it. A molecule containing a chiral carbon is nonsuperimposable on its mirror image, and two molecules that are nonsuperimposable mirror images of each other are a special type of stereoisomer called **enantiomers**. Enantiomers have the same physical properties, such as melting point, but differ in the direction they rotate polarized light.

A sugar is designated as being a D sugar or an L sugar according to how, in a Fischer projection of the molecule, the hydrogen atom and OH group are attached to the *penultimate* carbon atom, which is the carbon atom immediately before the terminal alcohol carbon atom. If the structure at this carbon atom is the same as that of D-glyceraldehyde (OH to the right), the sugar is a **D sugar**; if the configuration is the same as that of L-glyceraldehyde (OH to the left), the sugar is an **L sugar**.

Monosaccharides of five or more carbons atoms readily form cyclic structures when the carbonyl carbon atom reacts with an OH group on a carbon atom three or four carbon atoms distant. Consequently, glucose in solution exists as an equilibrium mixture of three forms, two of them cyclic (α- and β-) and one open chain. In Haworth projections, the *alpha* form is drawn with the OH group on the "former" carbonyl carbon atom (**anomeric carbon**) pointing downward; the *beta* form, with the OH group pointing upward; these two compounds are stereoisomers and are given the more specific term of **anomers**. Any solid sugar can be all alpha or all beta. Once the sample is dissolved in water, however, the ring opens up into the open-chain structure and then closes to form either the α- or the β-anomer. These interconversions occur back and forth until a dynamic equilibrium mixture is achieved in a process called **mutarotation**.

The carbonyl group present in monosaccharides is easily oxidized by Tollens' or Benedict's reagents (as well as others). Any mono- or disaccharide containing a free anomeric carbon is a **reducing sugar**. The disaccharide *maltose* contains two glucose units joined in an α-1,4-glycosidic linkage. The disaccharide *lactose* contains a galactose unit and a glucose unit joined by a β-1,4-glycosidic linkage. Both maltose and lactose contain a free anomeric carbon that can convert to an aldehyde functional group, so they are reducing sugars; they also undergo mutarotation. Many adults, and some children, have a deficiency of the enzyme lactase (which is needed to break down lactose) and are said to be **lactose intolerant**. A more serious problem is the genetic disease **galactosemia**, which results from the absence of an enzyme needed to convert galactose to glucose.

The disaccharide *sucrose* (table sugar) consists of a glucose unit and a fructose unit joined by a glycosidic linkage. The linkage is designated as an α-1,β-2-glycosidic linkage because it involves the OH group on the first carbon atom of glucose and the OH group on the second carbon atom of fructose. Sucrose is not a reducing sugar because it has no anomeric carbon that can reform a carbonyl group, and it cannot undergo mutarotation because of the restrictions imposed by this linkage.

Starch, the principal carbohydrate of plants, is composed of the polysaccharides **amylose** (10%–30%) and **amylopectin** (70%–90%). When ingested by humans and other animals, starch is hydrolyzed to glucose and becomes the body's energy source. *Glycogen* is the polysaccharide animals use to store excess carbohydrates from their diets. Similar in structure to amylopectin, glycogen is hydrolyzed to glucose whenever an animal needs energy for a metabolic process. The polysaccharide *cellulose* provides structure for plant cells. It is a linear polymer of glucose units joined by β-1,4-glycosidic linkages. It is indigestible in the human body but digestible by many microorganisms, including microorganisms found in the digestive tracts of many herbivores.

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13: 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.

13.0: Introduction to Lipids

13.1: Fatty Acids

13.2: Fats and Oils

13.3: Membranes and Membrane Lipids

13.4: Steroids

13.5: Chapter Summary

13.E: Exercises

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13.0: Introduction to Lipids

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 13.0.1 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.

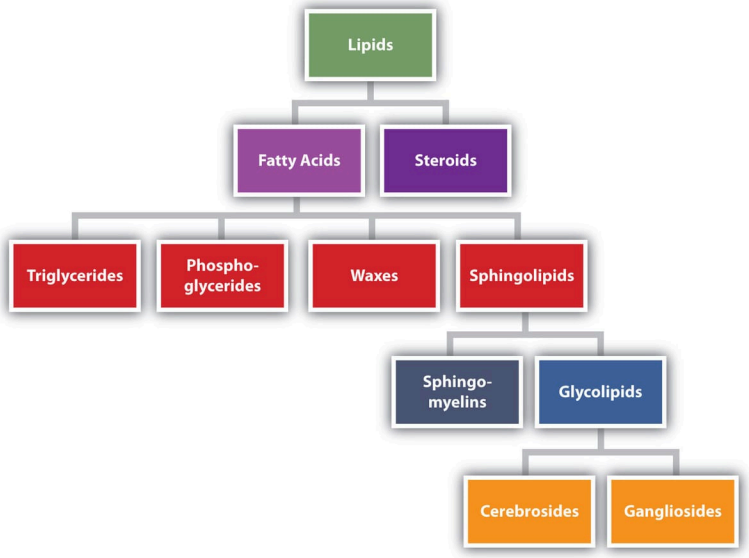


Figure 13.0.1***:*** *Lipid Organization Based on Structural Relationships*

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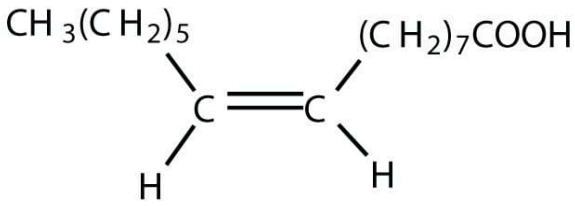
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13.1: Fatty Acids

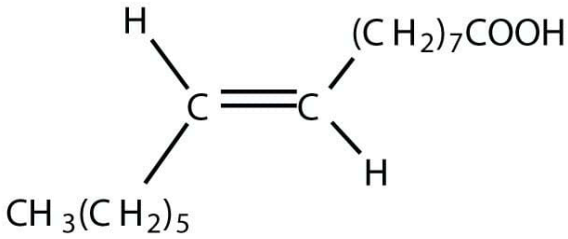
Skills to Develop

- 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 acid



trans fatty acid

Table 13.1.1 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* 13.1.1*: Some Common Fatty Acids Found in Natural Fats

Name	Abbreviated Structural Formula	Condensed Structural
lauric acid	$C_{11}H_{23}COOH$	$CH_3(CH_2)_{10}COO$
myristic acid	$C_{13}H_{27}COOH$	$CH_3(CH_2)_{12}COO$
palmitic acid	$C_{15}H_{31}COOH$	$CH_3(CH_2)_{14}COO$
palmitoleic acid	$C_{15}H_{29}COOH$	$CH_3(CH_2)_5CH=CH(CH_2$
stearic acid	$C_{17}H_{35}COOH$	$CH_3(CH_2)_{16}COO$
oleic acid	$C_{17}H_{33}COOH$	$CH_3(CH_2)_7CH=CH(CH_2$
linoleic acid	$C_{17}H_{31}COOH$	$CH_3(CH_2)_3(CH_2CH=CH)_2($
α-linolenic acid	$C_{17}H_{29}COOH$	$CH_3(CH_2CH=CH)_3(CH_2$
arachidonic acid	$C_{19}H_{31}COOH$	$CH_3(CH_2)_4(CH_2CH=CH)_4($

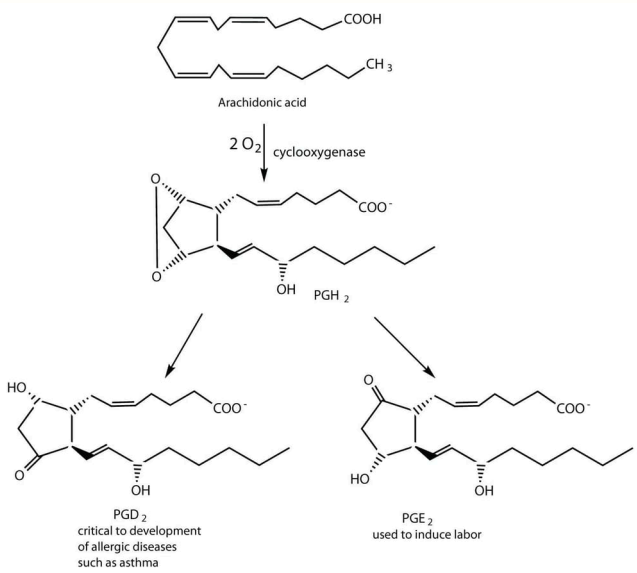
Two polyunsaturated fatty acids—linoleic and α-linolenic acids—are termed essential fatty acids because humans must obtain them from their diets. Both substances are required for normal growth and development, but the human body does not synthesize them. The body uses linoleic acid to synthesize many 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 (part (a) of Figure 13.1.2). Viewed as a whole, however, the saturated fatty acid molecule is relatively straight (part (b) of Figure 13.1.2). 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.

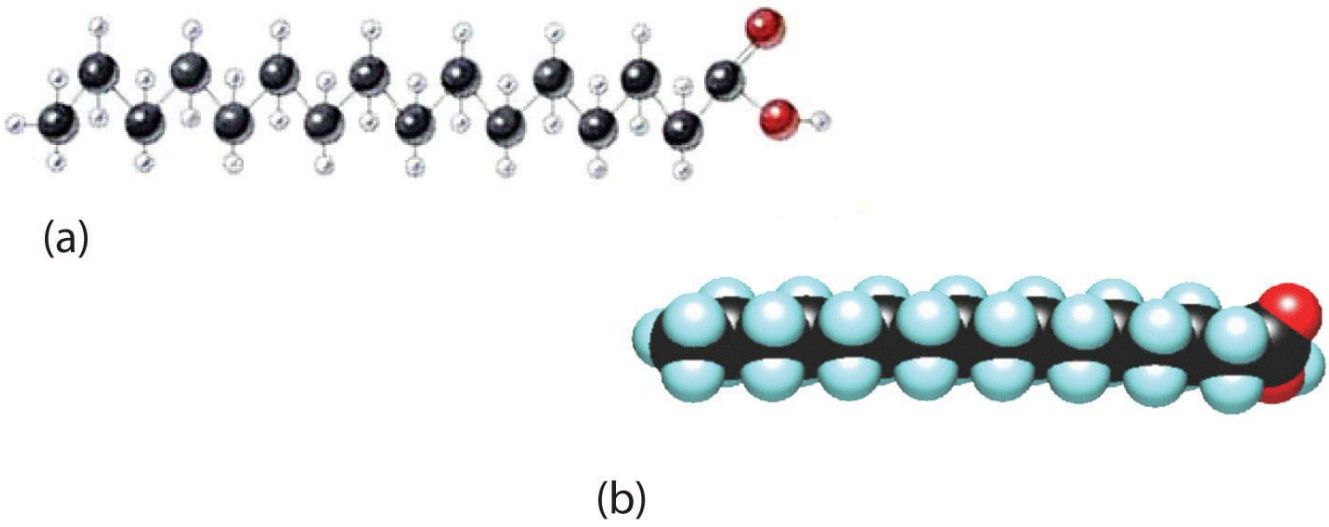
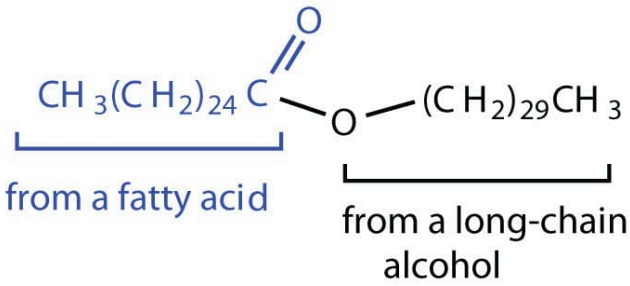


Figure 13.1.2*: The Structure of Saturated Fatty Acids. (a) There is a zigzag pattern formed by the carbon-to-carbon single bonds in the ball-and-stick model of a palmitic acid molecule. (b) A space-filling model of palmitic acid shows the overall straightness of a saturated fatty acid molecule.*

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.



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.

Concept Review Exercises

1. Which fatty acids listed in Table 13.1.1 fall into each category below.

    a. saturated fatty acid
    b. polyunsaturated fatty acid
    c. monounsaturated fatty acid

2. Why do unsaturated fatty acids have lower melting points than saturated fatty acids?

Answers

1. a. saturated: lauric, myristic, palmitic, and stearic acids
    b. polyunsaturated: linoleic, linolenic, and arachidonic acids
    c. monounsaturated: oleic acid

2. Unsaturated fatty acids cannot pack as tightly together as saturated fatty acids due to the presence of the cis double bond that puts a “kink” or bend in the hydrocarbon chain.

Exercises

1. Classify each fatty acid as saturated or unsaturated and indicate the number of carbon atoms in each molecule. (See Table 13.1.1 for structures.)

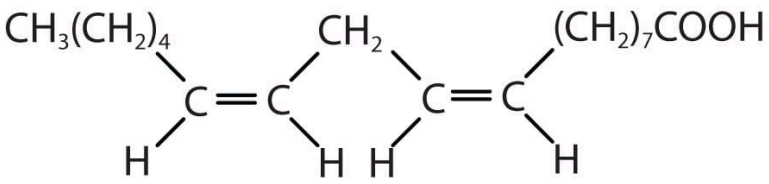
    a. palmitoleic acid
    b. myristic acid
    c. α-linoleic acid

2. Write the line (skeletal) structure for each fatty acid. (See Table 13.1.1 for condensed structures.)

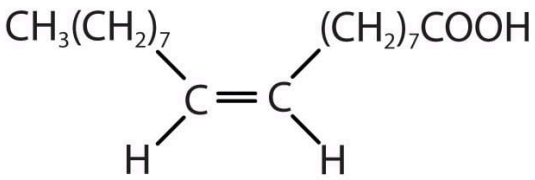
    a. lauric acid
    b. palmitoleic acid
    c. α-linoleic acid

3. Arrange these fatty acids (all contain 18 carbon atoms) in order of increasing melting point. Justify your arrangement.

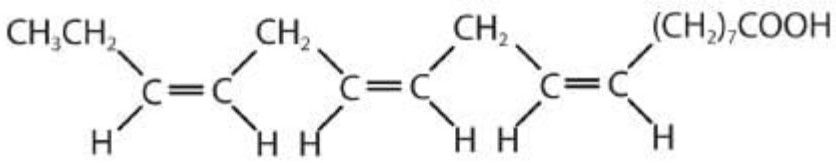
a.



b.



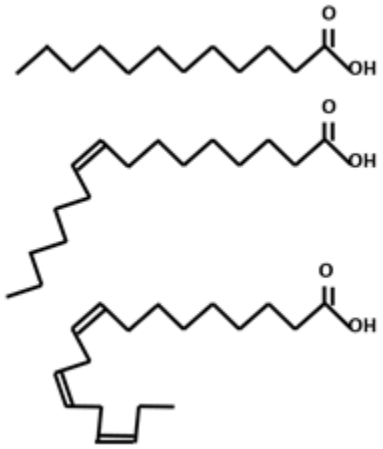
c.



Answers

1. a. unsaturated; 16 carbon atoms
   b. saturated; 14 carbon atoms
   c. unsaturated; 18 carbon atoms

2.



3. c < a < b; They all have 18 carbons, so about the same size. An increase in the number of double bonds will lower the melting point because it is more difficult to closely pack the fatty acids together.

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13.2: Fats and Oils

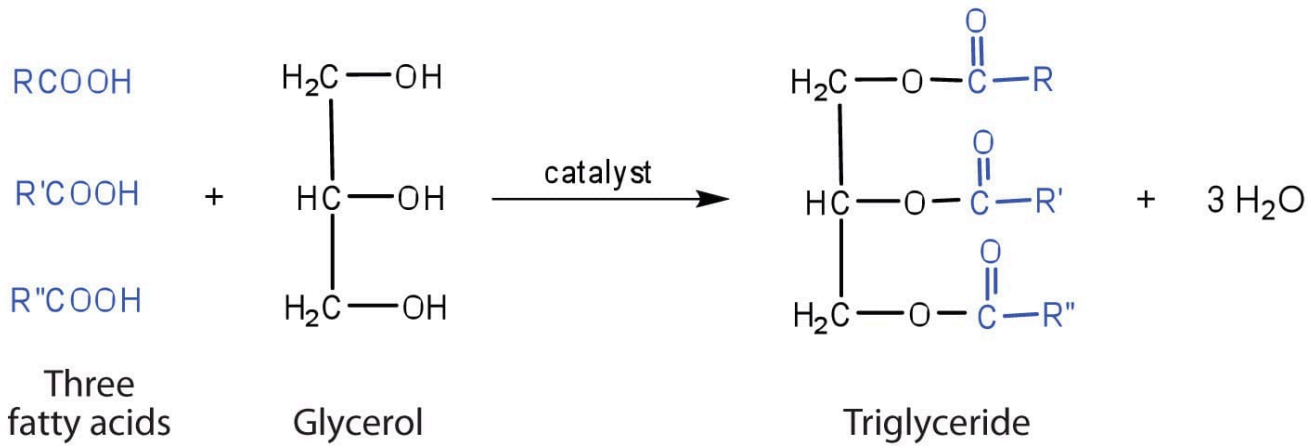
Skills to Develop

- 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.

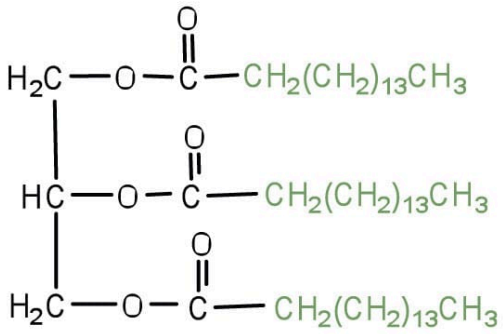
Fats and oils are the most abundant lipids in nature. They provide energy for living organisms, insulate body organs, and transport fat-soluble vitamins through the blood.

Structures of Fats and Oils

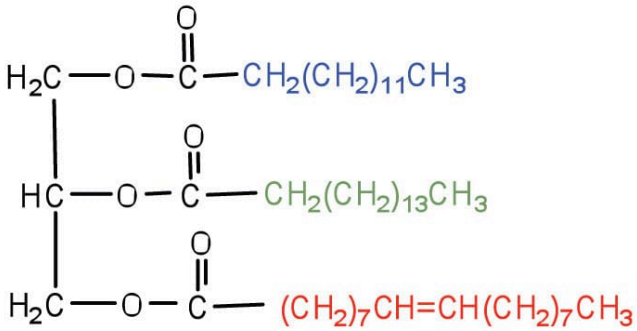
Fats and oils are called triglycerides (or *triacylcylgerols*) because they are esters composed of three fatty acid units joined to *glycerol*, a trihydroxy alcohol:



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 13.2.1 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 13.2.1***:*** *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.**

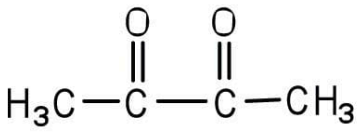
†Coconut oil is highly saturated. It contains an unusually high percentage of the low-melting C_8, C_{10}, and C_{12} saturated fatty acids.

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

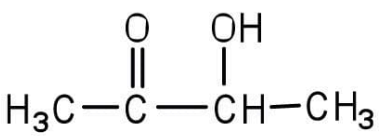
high consumption of saturated fats is a factor, along with the high consumption of cholesterol, in increased risks of heart disease.

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.



Diacetyl

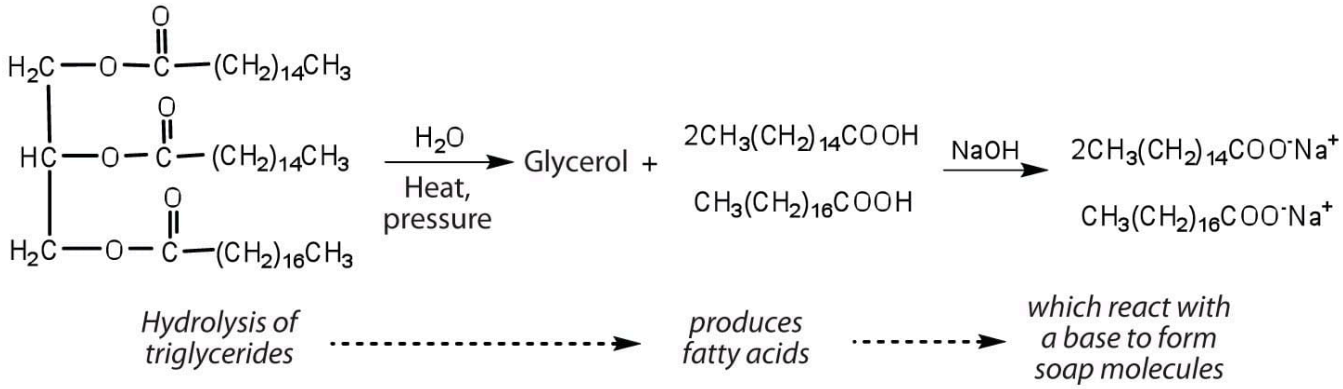


3-hydroxy-2-butanone

Fats and oils are lighter than water, having densities of about 0.8 g/cm^3. They are poor conductors of heat and electricity and therefore serve as excellent insulators for the body, slowing the loss of heat through the skin.

Chemical Reactions of Fats and Oils

Fats and oils can participate in a variety of chemical reactions—for example, because triglycerides are esters, they can be hydrolyzed in the presence of an acid, a base, or specific enzymes known as lipases. The hydrolysis of fats and oils in the presence of a base is used to make soap and is called saponification. Today most soaps are prepared through the hydrolysis of triglycerides (often from tallow, coconut oil, or both) using water under high pressure and temperature [700 lb/in^2 (~50 atm or 5,000 kPa) and 200°C]. Sodium carbonate or sodium hydroxide is then used to convert the fatty acids to their sodium salts (soap molecules):

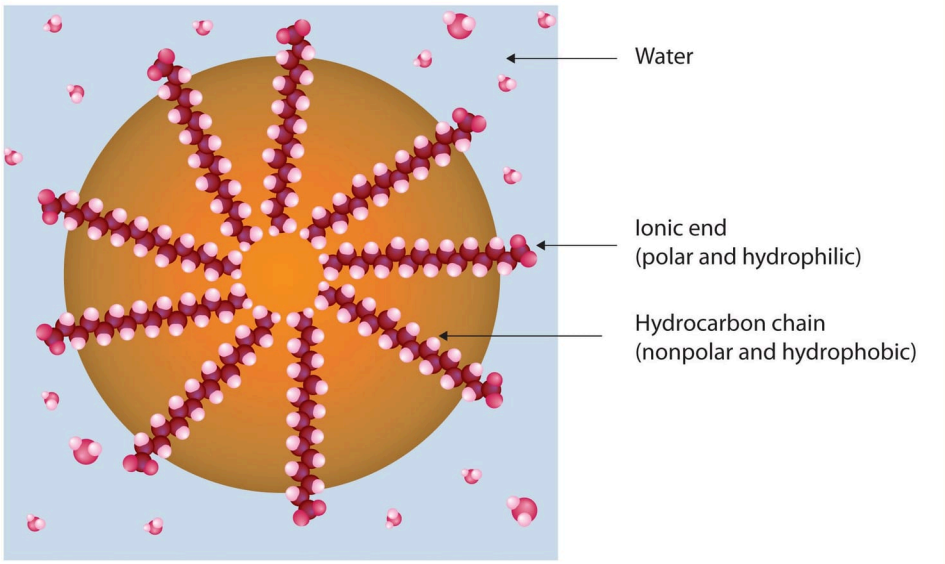


Looking Closer: Soaps

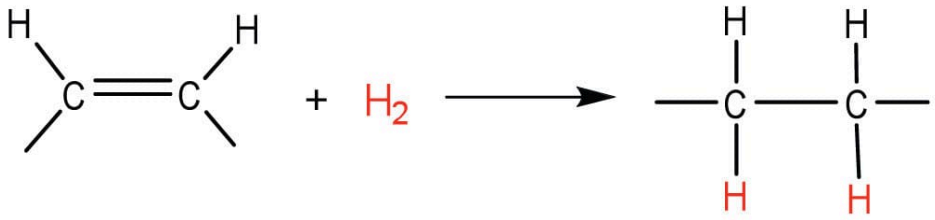
Ordinary soap is a mixture of the sodium salts of various fatty acids, produced in one of the oldest organic syntheses practiced by humans (second only to the fermentation of sugars to produce ethyl alcohol). Both the Phoenicians (600 BCE) and the Romans made soap from animal fat and wood ash. Even so, the widespread production of soap did not begin until the 1700s. Soap was traditionally made by treating molten lard or tallow with a slight excess of alkali in large open vats. The mixture was heated, and steam was bubbled through it. After saponification was completed, the soap was precipitated from the mixture by the addition of sodium chloride (NaCl), removed by filtration, and washed several times with water. It was then dissolved in water and reprecipitated by the addition of more NaCl. The glycerol produced in the reaction was also recovered from the aqueous wash solutions.

Pumice or sand is added to produce scouring soap, while ingredients such as perfumes or dyes are added to produce fragrant, colored soaps. Blowing air through molten soap produces a floating soap. Soft soaps, made with potassium salts, are more expensive but produce a finer lather and are more soluble. They are used in liquid soaps, shampoos, and shaving creams.

Dirt and grime usually adhere to skin, clothing, and other surfaces by combining with body oils, cooking fats, lubricating greases, and similar substances that act like glues. Because these substances are not miscible in water, washing with water alone does little to remove them. Soap removes them, however, because soap molecules have a dual nature. One end, called the *head*, carries an ionic charge (a carboxylate anion) and therefore dissolves in water; the other end, the *tail*, has a hydrocarbon structure and dissolves in oils. The hydrocarbon tails dissolve in the soil; the ionic heads remain in the aqueous phase, and the soap breaks the oil into tiny soap-enclosed droplets called *micelles*, which disperse throughout the solution. The droplets repel each other because of their charged surfaces and do not coalesce. With the oil no longer "gluing" the dirt to the soiled surface (skin, cloth, dish), the soap-enclosed dirt can easily be rinsed away.



The double bonds in fats and oils can undergo hydrogenation and also oxidation. The hydrogenation of vegetable oils to produce semisolid fats is an important process in the food industry. Chemically, it is essentially identical to the catalytic hydrogenation reaction described for alkenes.



In commercial processes, the number of double bonds that are hydrogenated is carefully controlled to produce fats with the desired consistency (soft and pliable). Inexpensive and abundant vegetable oils (canola, corn, soybean) are thus transformed into margarine and cooking fats. In the preparation of margarine, for example, partially hydrogenated oils are mixed with water, salt, and nonfat dry milk, along with flavoring agents, coloring agents, and vitamins A and D, which are added to approximate the look, taste, and nutrition of butter. (Preservatives and antioxidants are also added.) In most commercial peanut butter, the peanut oil has been partially hydrogenated to prevent it from separating out. Consumers could decrease the amount of saturated fat in their diet by using the original unprocessed oils on their foods, but most people would rather spread margarine on their toast than pour oil on it.

Many people have switched from butter to margarine or vegetable shortening because of concerns that saturated animal fats can raise blood cholesterol levels and result in clogged arteries. However, during the hydrogenation of vegetable oils, an isomerization reaction occurs that produces the *trans* fatty acids mentioned in the opening essay. However, studies have shown that *trans* fatty acids also raise cholesterol levels and increase the incidence of heart disease. *Trans* fatty acids do not have the bend in

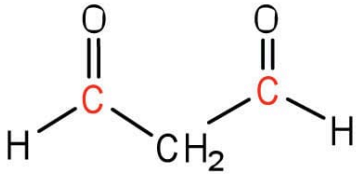
their structures, which occurs in *cis* fatty acids and thus pack closely together in the same way that the saturated fatty acids do. Consumers are now being advised to use polyunsaturated oils and soft or liquid margarine and reduce their total fat consumption to less than 30% of their total calorie intake each day.

Fats and oils that are in contact with moist air at room temperature eventually undergo oxidation and hydrolysis reactions that cause them to turn rancid, acquiring a characteristic disagreeable odor. One cause of the odor is the release of volatile fatty acids by hydrolysis of the ester bonds. Butter, for example, releases foul-smelling butyric, caprylic, and capric acids. Microorganisms present in the air furnish lipases that catalyze this process. Hydrolytic rancidity can easily be prevented by covering the fat or oil and keeping it in a refrigerator.

Another cause of volatile, odorous compounds is the oxidation of the unsaturated fatty acid components, particularly the readily oxidized structural unit



in polyunsaturated fatty acids, such as linoleic and linolenic acids. One particularly offensive product, formed by the oxidative cleavage of both double bonds in this unit, is a compound called *malonaldehyde*.



Malonaldehyde

Rancidity is a major concern of the food industry, which is why food chemists are always seeking new and better antioxidants, substances added in very small amounts (0.001%–0.01%) to prevent oxidation and thus suppress rancidity. Antioxidants are compounds whose affinity for oxygen is greater than that of the lipids in the food; thus they function by preferentially depleting the supply of oxygen absorbed into the product. Because vitamin E has antioxidant properties, it helps reduce damage to lipids in the body, particularly to unsaturated fatty acids found in cell membrane lipids.

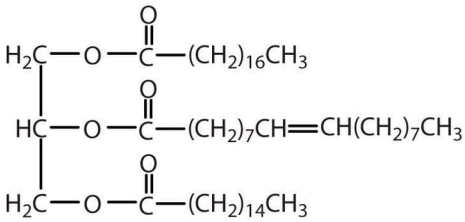
Summary

Fats and oils are composed of molecules known as triglycerides, which are esters composed of three fatty acid units linked to glycerol. An increase in the percentage of shorter-chain fatty acids and/or unsaturated fatty acids lowers the melting point of a fat or oil. The hydrolysis of fats and oils in the presence of a base makes soap and is known as saponification. Double bonds present in unsaturated triglycerides can be hydrogenated to convert oils (liquid) into margarine (solid). The oxidation of fatty acids can form compounds with disagreeable odors. This oxidation can be minimized by the addition of antioxidants.

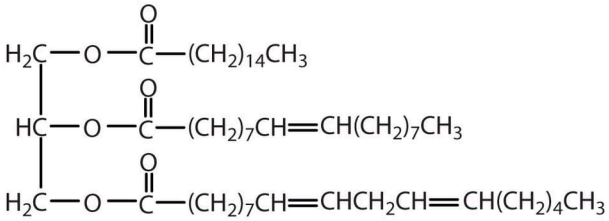
Concept Review Exercises

1. What functions does fat serve in the body?

2. Which of these triglycerides would you expect to find in higher amounts in oils? In fats? Justify your choice.



(a)



(b)

Answers

1. Fats provide energy and long-term energy storage for living organisms. They also provide insulation for body organs and transport fat-soluble vitamins.

2. The triglyceride labeled (a) is expected to be present in higher amounts in fats because it is composed of a greater number of saturated fatty acids. The triglyceride labeled (b) is expected to be present in higher amounts in oils because it is composed of a greater number of unsaturated fatty acids.

Exercises

1. Draw the structure for each compound.

    a. trimyristin (Use table from previous section on Fatty Acids for structure of myristic acid.)
    b. a triglyceride likely to be found in peanut oil (Use tables in this and previous sections for likely fatty acids and structures.)

2. Draw structures to write the reaction for the complete hydrogenation of tripalmitolein (Table from previous section for the condensed structure of palmitoleic acid). Name the product formed.

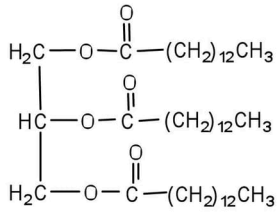
3. Draw structures to write the reaction for the hydrolysis of trilaurin in a basic solution (Table from previous section for the condensed structure of lauric acid).

4. a. What reactions lead to a fat or oil becoming rancid?
    b. How can rancidity be prevented?

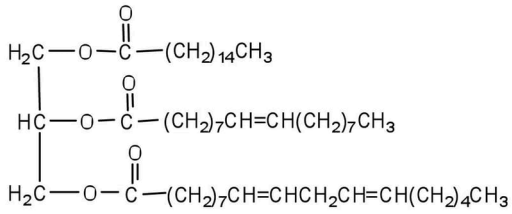
Answers

1.

a.

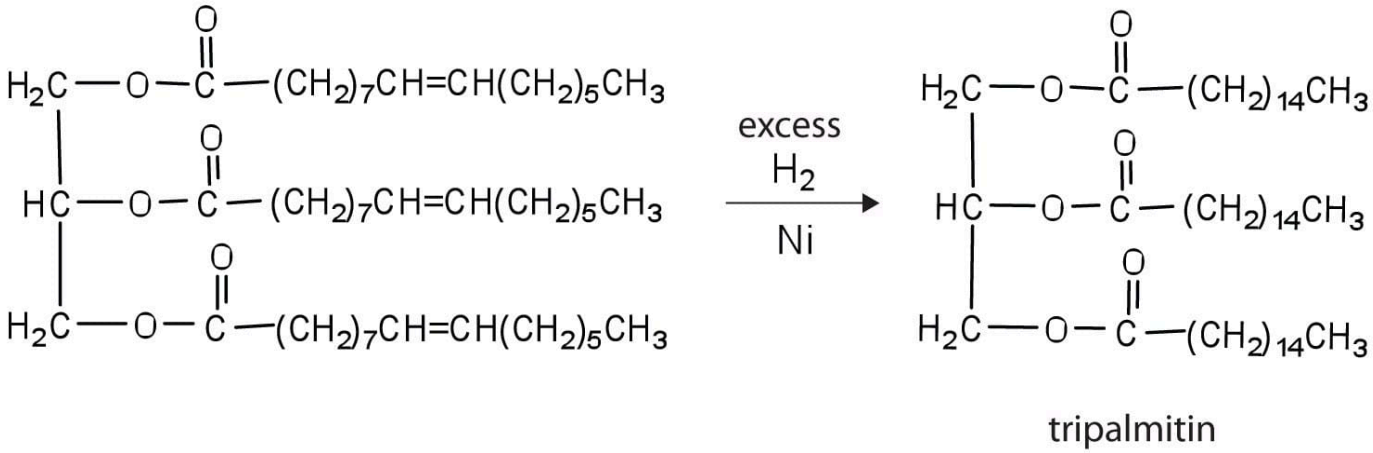


b.



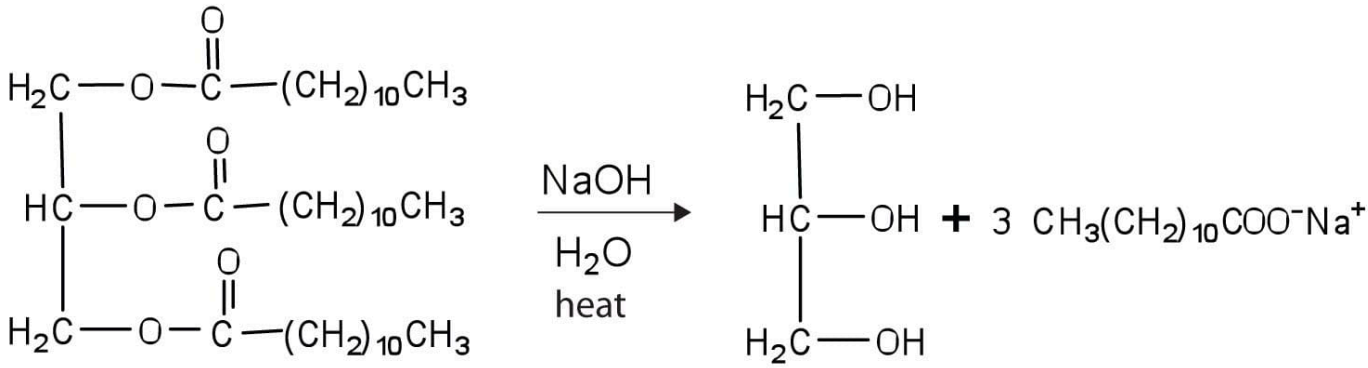
[other answers possible]

2.



tripalmitin

3.



4.

a. Hydrolysis with water or oxidation by O_2
b. Rancidity can be prevented by covering it (to keep out moisture and oxygen) and storing it in a refrigerator. (Cold temperatures slow down reactions.)

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13.3: Membranes and Membrane Lipids

Skills to Develop

- 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 $13.3.1A$) and animal cells (Figure $13.3.1B$) 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.

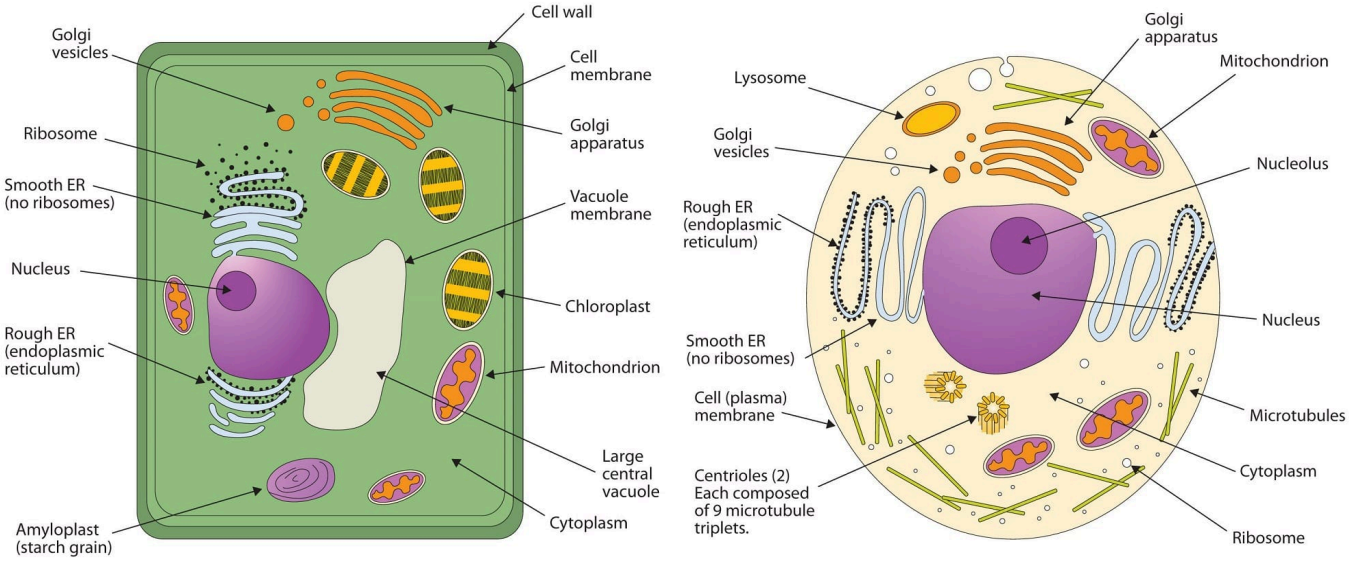


Figure $13.3.1$*: (A) An Idealized Plant Cell. Not all the structures shown here occur in every type of plant cell.* (B) *An Idealized Animal Cell. The structures shown here will seldom all be found in a single animal cell.*

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 $13.3.2$).

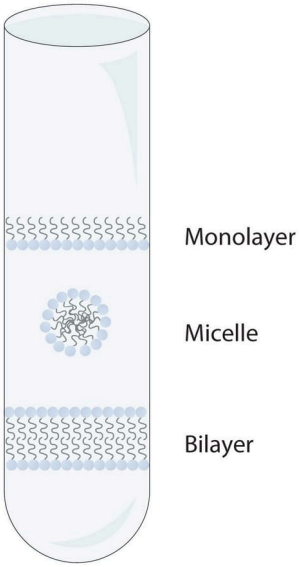


Figure 13.3.2*: Spontaneously Formed Polar Lipid Structures in Water: Monolayer, Micelle, and Bilayer*

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 13.3.3).

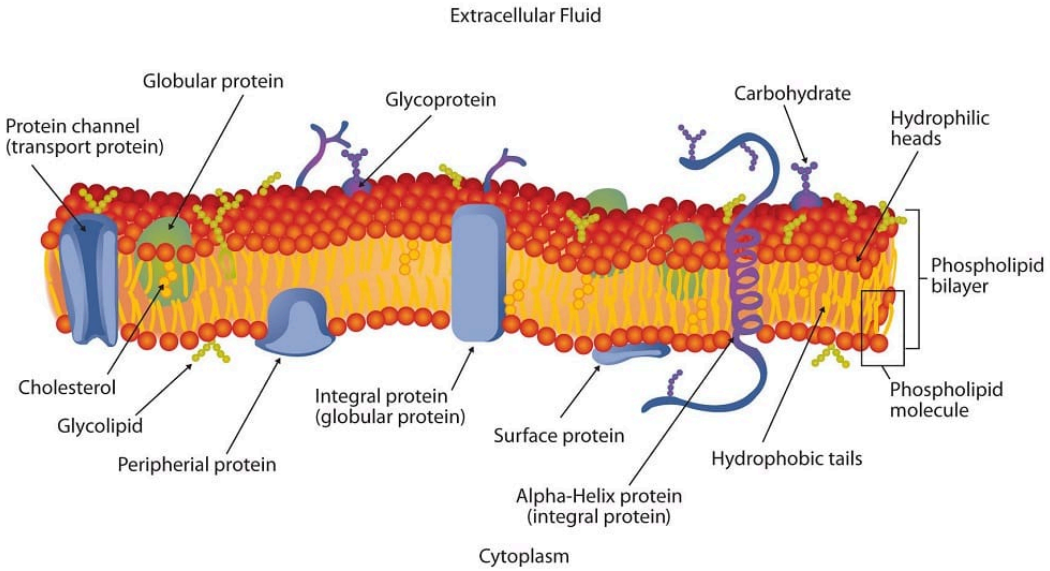


Figure 13.3.3***:*** *Schematic Diagram of a Cell Membrane. The membrane enclosing a typical animal cell is a phospholipid bilayer with embedded cholesterol and protein molecules. Short oligosaccharide chains are attached to the outer surface.*

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 13.3.4.

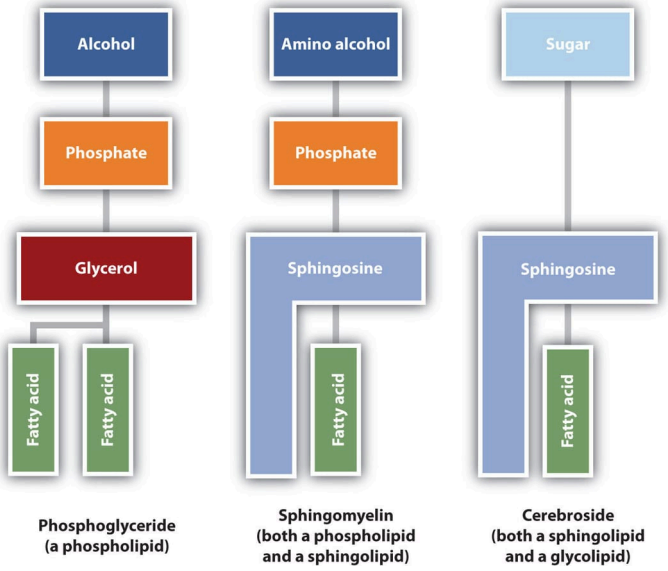


Figure 13.3.4***:*** *Component Structures of Some Important Membrane Lipids*

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 13.3.5) is attached to the third carbon atom of glycerol (part (b) of Figure 13.3.5). Notice that the phosphoglyceride molecule is identical to a triglyceride up to the phosphoric acid unit (part (b) of Figure 13.3.5).

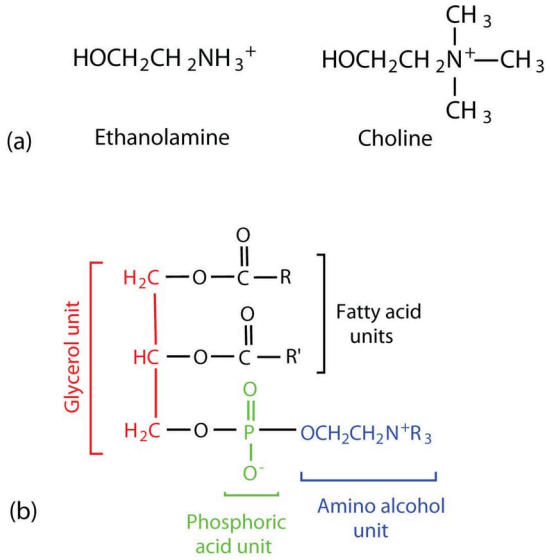
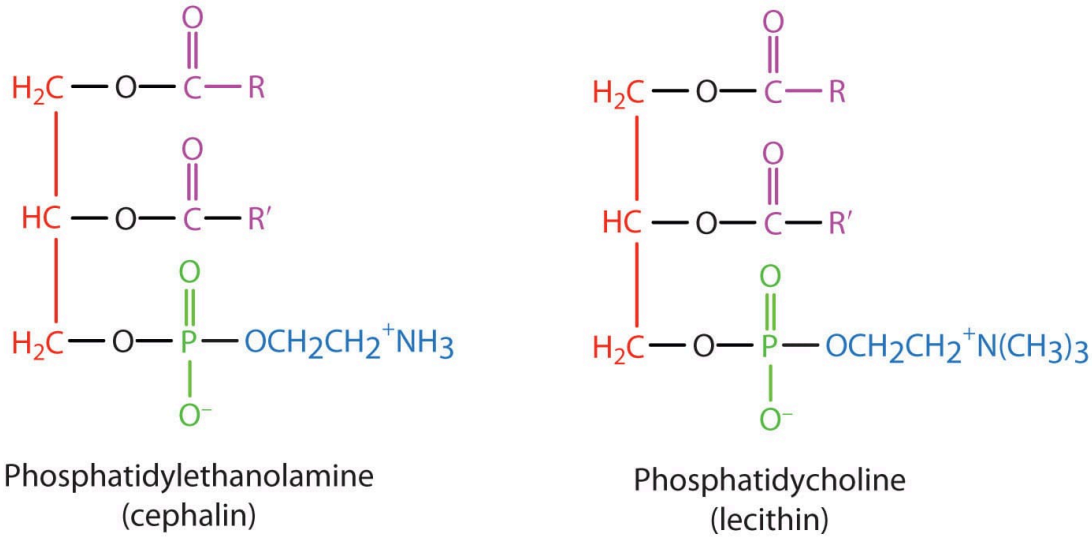


Figure 13.3.5*: Phosphoglycerides. (a) Amino alcohols are commonly found in phosphoglycerides, which are evident in its structural formula (b).*

There are two common types of phosphoglycerides. Phosphoglycerides containing ethanolamine as the amino alcohol are called *phosphatidylethanolamines* or *cephalins*. Cephalins are found in brain tissue and nerves and also have a role in blood clotting. Phosphoglycerides containing choline as the amino alcohol unit are called *phosphatidylcholines* or *lecithins*. Lecithins occur in all living organisms. Like cephalins, they are important constituents of nerve and brain tissue. Egg yolks are especially rich in

lecithins. Commercial-grade lecithins isolated from soybeans are widely used in foods as emulsifying agents. An emulsifying agent is used to stabilize an emulsion—a dispersion of two liquids that do not normally mix, such as oil and water. Many foods are emulsions. Milk is an emulsion of butterfat in water. The emulsifying agent in milk is a protein called *casein*. Mayonnaise is an emulsion of salad oil in water, stabilized by lecithins present in egg yolk.



Sphingomyelins, the simplest sphingolipids, each contain a fatty acid, a phosphoric acid, sphingosine, and choline (Figure 13.3.6). 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.

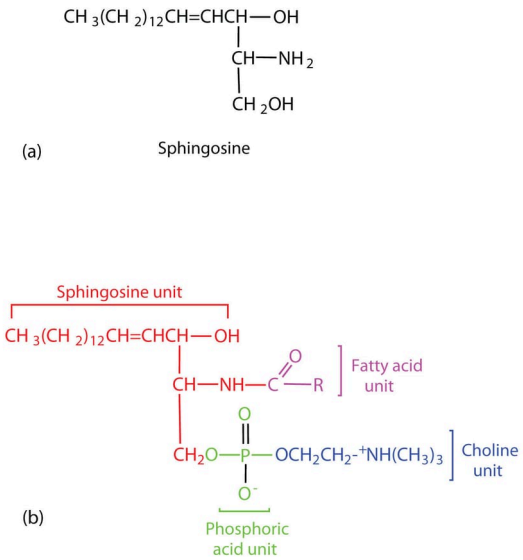


Figure 13.3.6*: Sphingolipids. (a) Sphingosine, an amino alcohol, is found in all sphingolipids. (b) A sphingomyelin is also known as a phospholipid, as evidenced by the phosphoric acid unit in its structure.*

Most animal cells contain sphingolipids called cerebrosides (Figure 13.3.7). 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.

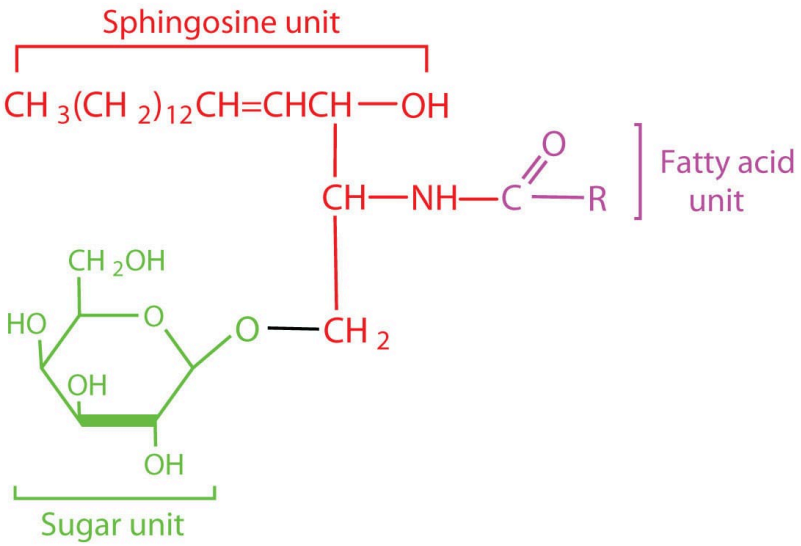


Figure 13.3.7***:*** *Cerebrosides. Cerebrosides are sphingolipids that contain a sugar unit.*

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 13.3.3). 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.

Concept Review Exercises

1. Why is it important that membrane lipids have dual character—part of the molecule is hydrophilic and part of the molecule is hydrophobic?

2. Why do you suppose lecithins (phosphatidylcholines) are often added to processed foods such as hot cocoa mix?

Answers

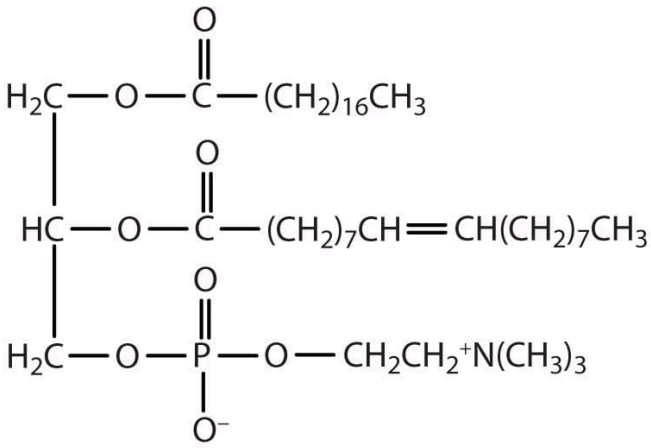
1. The dual character is critical for the formation of the lipid bilayer. The hydrophilic portions of the molecule are in contact with the aqueous environment of the cell, while the hydrophobic portion of the lipids is in the interior of the bilayer and provides a barrier to the passive diffusion of most molecules.

2. Lecithin acts as an emulsifying agent that aids in the mixing of the hot cocoa mix with water and keeps the cocoa mix evenly distributed after stirring.

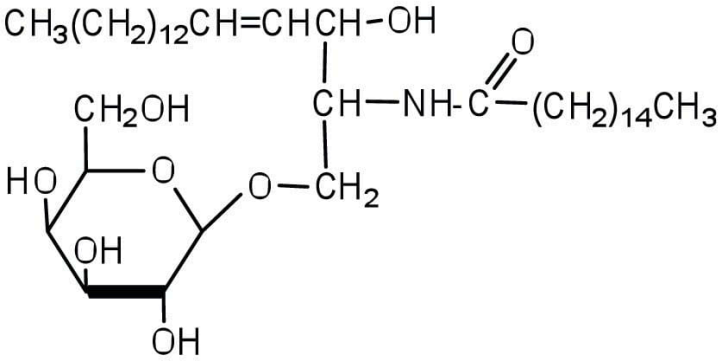
Exercises

1. Which of the following is least likely to be a major part of a lipid bilayer?

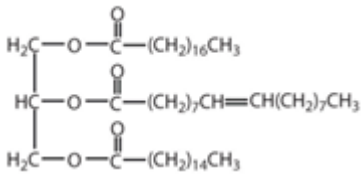
a.



b.



c.

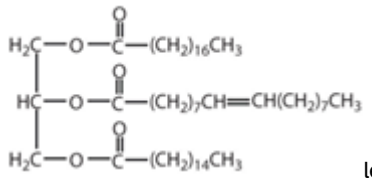


2. a. Distinguish between an integral protein and a peripheral protein.

   b. What is one key function of integral proteins?

Answers

1. The triglyceride (c) is least likely because it does not have a super polar or ionic head.



least likely

The phospholipid (a) has two full charges on one end, in addition to non-polar tails, so it would be great in bilayer. (Most bilayer lipids are phospholipids.)

The glycolipid (b) has no full charges, but the sugar portion is very polar (many OH groups), and it has non-polar tails, so could work.

2.

a. Integral proteins span the lipid bilayer, while peripheral proteins associate with the surfaces of the lipid bilayer.
b. aid in the movement of charged and polar species across the membrane

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13.4: Steroids

Skills to Develop

- To identify the functions of steroids produced in mammals.

All the lipids discussed so far are *saponifiable*, reacting with aqueous alkali to yield simpler components, such as glycerol, fatty acids, amino alcohols, and sugars. Lipid samples extracted from cellular material, however, also contain a small but important fraction that does not react with alkali. The most important nonsaponifiable lipids are the steroids. These compounds include the *bile salts*, *cholesterol* and related compounds, and certain *hormones* (such as cortisone and the sex hormones).

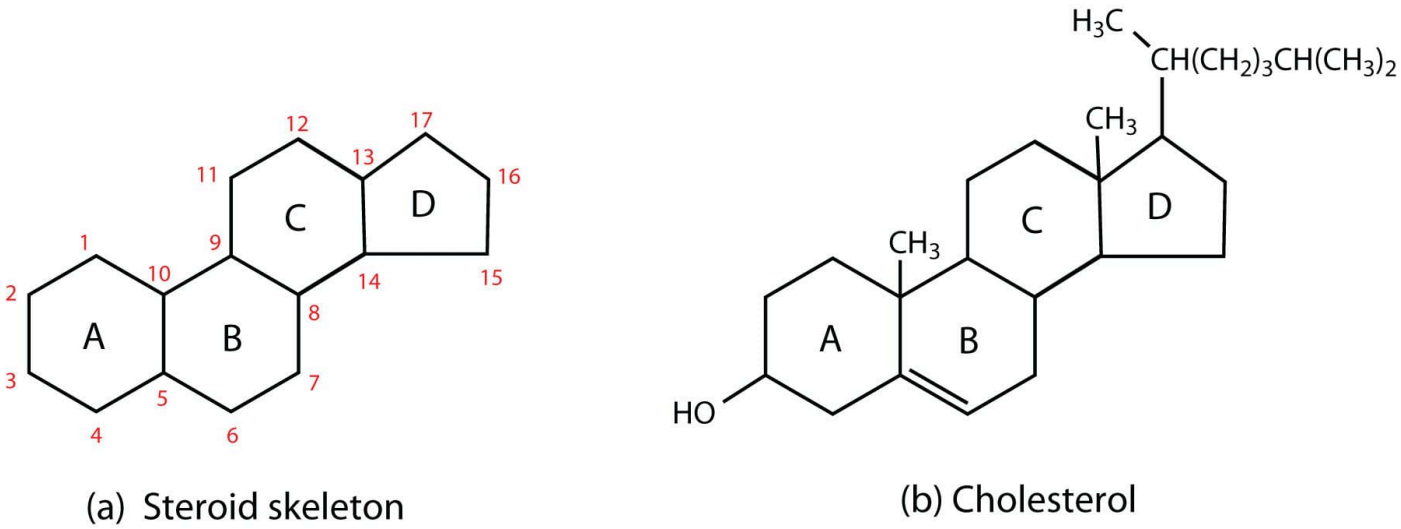


Figure 13.4.1 *Steroids. (a) The four-fused-ring steroid skeleton uses letter designations for each ring and the numbering of the carbon atoms. (b) The cholesterol molecule follows this pattern.*

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 part (a) of Figure 13.4.1. Slight variations in this structure or in the atoms or groups attached to it produce profound differences in biological activity.

Cholesterol

Cholesterol (part (b) of Figure 13.4.1) 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 13.4.2). Indeed, the name *cholesterol* is derived from the Greek *chole*, meaning "bile," and *stereos*, meaning "solid."



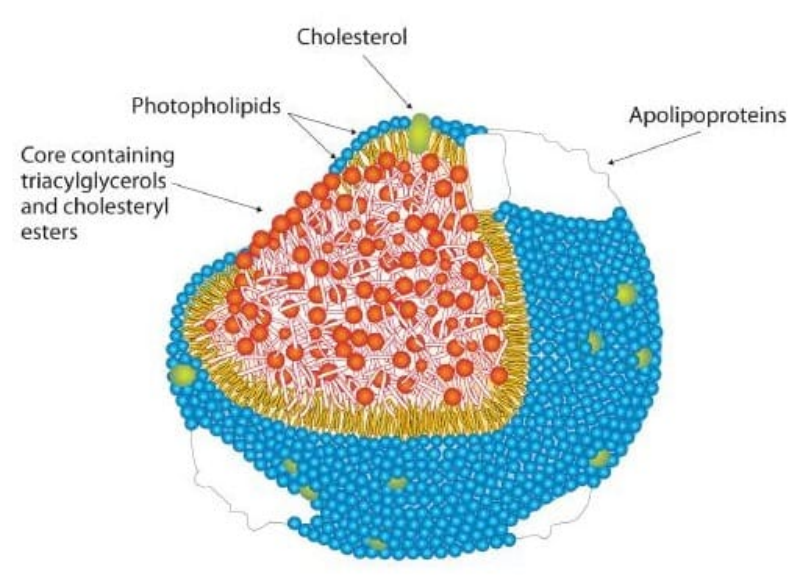
Figure 13.4.2***:*** *Numerous small gallstones made up largely of cholesterol, all removed in one patient. Grid scale 1 mm*

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.

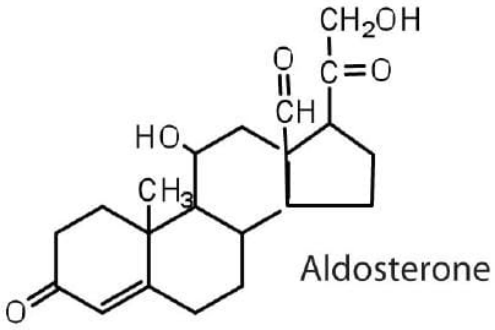
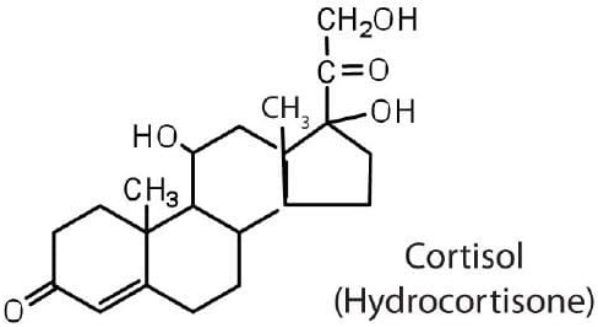
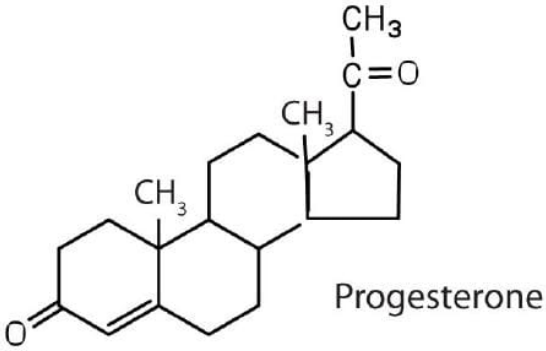
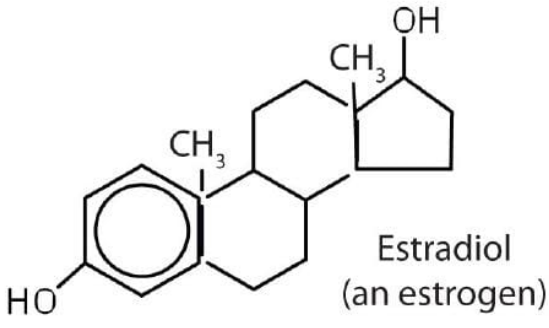
Dietary modifications and increased physical activity can help lower total cholesterol and improve the LDL:HDL ratio. The average American consumes about 600 mg of cholesterol from animal products each day and also synthesizes approximately 1 g of cholesterol each day, mostly in the liver. The amount 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.

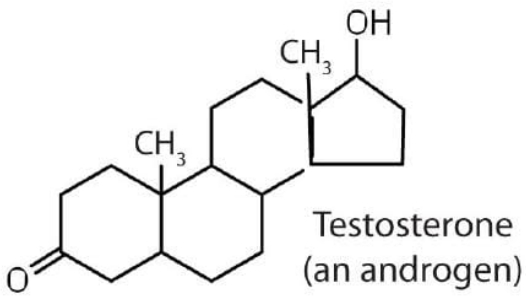
Steroid Hormones

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 13.4.1), 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 13.4.1***:*** *Representative Steroid Hormones and Their Physiological Effects*

Hormone	Effect
 Aldosterone	regulates salt metabolism; stimulates kidneys to retain sodium and excrete potassium
 Cortisol (Hydrocortisone)	stimulates the conversion of proteins to carbohydrates
 Progesterone	regulates the menstrual cycle; maintains pregnancy
 Estradiol (an estrogen)	stimulates female sex characteristics; regulates changes during the menstrual cycle

Hormone	Effect
	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 13.4.3) and an amine such as the amino acid glycine (part (b) of Figure 13.4.3). They are synthesized from cholesterol in the liver, stored in the gallbladder, and then secreted in bile into the small intestine. In the gallbladder, the composition of bile gradually changes as water is absorbed and the other components become more concentrated.

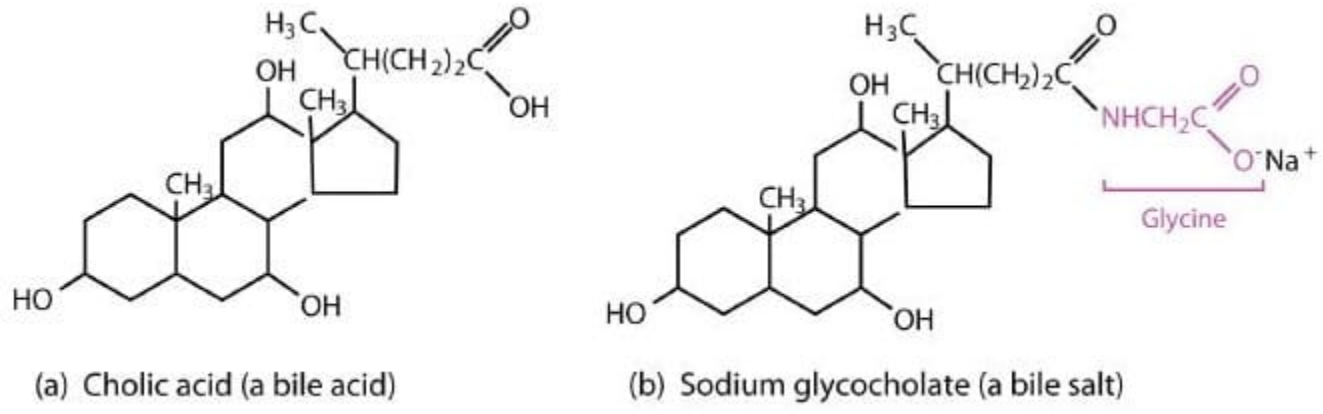


Figure 13.4.3 *Bile Acids. (a) Cholic acid is an example of a bile acid. (b) Sodium glycocholate is a bile salt synthesized from cholic acid and glycine.*

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.

Concept Review Exercises

1. Distinguish between a saponifiable lipid and a nonsaponifiable lipid.

2. Identify a key function for each steroid.

    a. bile salt
    b. cholesterol
    c. steroid hormone

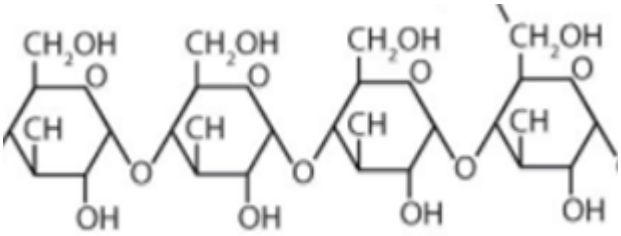
Answers

1. A saponifiable lipid reacts with aqueous alkali to yield simpler components, while a nonsaponifiable lipid does not react with alkali to yield simpler components.

2. a. acts as an emulsifying agent to break down large fat globules and keep these globules suspended in the aqueous digestive environment
    b. a key component of mammalian cell membranes (answers will vary)
    c. chemical messengers

Exercises

1. Would this structure be classified as a steroid?



2. What about a bile salt makes it a good detergent/emulsifier? Why does cholesterol not serve this function very well?

Answers

1. There are four rings, but they are not fused in the same configuration as a steroid skeleton (It is a polysaccharide.)

2. It has an ionic head (full charges of salt end) and a non-polar tail (mostly hydrocarbon fused-ring structure) like a soap. These salts can surround the non-polar lipids and create a soluble micelle with non-polar tails facing the lipids and ionic heads facing out to polar water environment.

Cholesterol only has one polar group (OH with partial charges). The head would have to be more hydrophillic (much more polar or ionic with full charges) to act as a detergent/emulsifier.

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13.5: Chapter 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 triglyceride*s are those containing a higher proportion of saturated fatty acid chains (fewer carbon-to-carbon double bonds); *unsaturated triglyceride*s 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: *micelle*s, *monolayer*s, and *bilayer*s. **Micelles** are aggregations of molecules in which the hydrocarbon tails of the lipids, being hydrophobic, are directed inward (away from the surrounding water), and the hydrophilic heads that are directed outward into the water. **Bilayers** are double layers arranged so that the hydrophobic tails are sandwiched between the two layers of hydrophilic heads, which remain in contact with the water.

Every living cell is enclosed by a *cell membrane* composed of a lipid bilayer. In animal cells, the bilayer consists mainly of phospholipids, glycolipids, and the steroid cholesterol. Embedded in the bilayer are **integral proteins**, and **peripheral proteins** are loosely associated with the surface of the bilayer. Everything between the cell membrane and the membrane of the cell nucleus is called the **cytoplasm**.

Most lipids can be saponified, but some, such as **steroids**, cannot be saponified. The steroid **cholesterol** is found in animal cells but never in plant cells. It is a main component of all cell membranes and a precursor for hormones, vitamin D, and bile salts. Bile salts are the most important constituents of **bile**, which is a yellowish-green liquid secreted by the gallbladder into the small intestine and is needed for the proper digestion of lipids.

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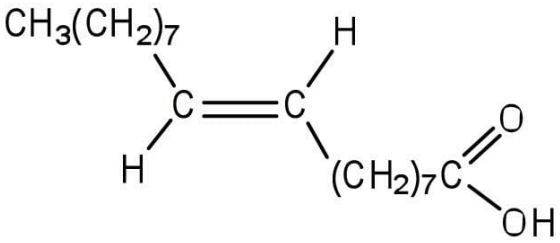
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13.E: Exercises

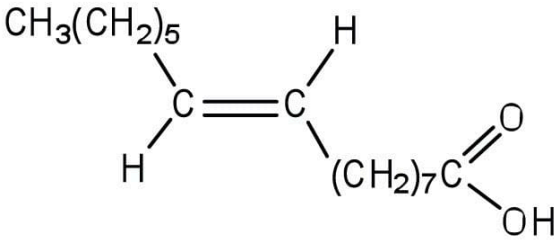
Additional Exercises

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. Draw a typical lecithin molecule that incorporates glycerol, palmitic acid, oleic acid, phosphoric acid, and choline. Circle all the ester bonds.

3. 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

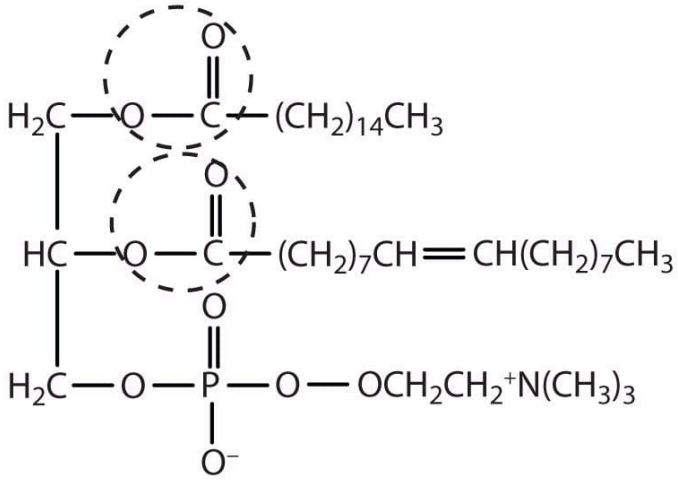
4. How does the structure of cholic acid differ from that of cholesterol? Which compound would you expect to be more polar? Why?

5. a. What fatty acid is the precursor for the prostaglandins? b. Identify three biological effects of prostaglandins.

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.

2. 

3. a. KCl - NO, the ionic compound would not be able to cross the inner non-polar portion of the lipid bilayer.; b. $CH_3CH_2CH_2CH_2CH_2CH_3$ - Yes, this non-polar compound would be able to cross the inner non-polar portion of the lipid bilayer.; c. fructose NO, this relatively large, polar sugar would not be able to cross the inner non-polar portion of the lipid bilayer.

4. Cholic acid is missing the alkene (C=C) but has two additional alcohol (OH) groups and one additional carboxylic acid (COOH) group, compared to cholesterol. The very polar bonds of the hydroxyl and carboxyl groups make cholic acid much more polar overall.

5. a. arachidonic acid; b. induce smooth muscle contraction, lower blood pressure, and contribute to the inflammatory response

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14: 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.

14.1: Properties of Amino Acids

14.2: Reactions of Amino Acids

14.3: Peptides

14.4: Proteins

14.5: Enzymes

14.6 Enzyme Action

14.7: Enzyme Activity

14.8: Enzyme Inhibition

14.9: Enzyme Cofactors and Vitamins

14.10: Chapter Summary

14.E: Exercises

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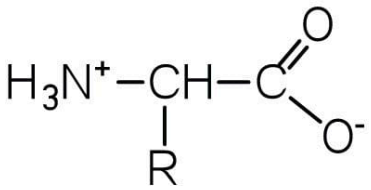
14.1: Properties of Amino Acids

Skills to Develop

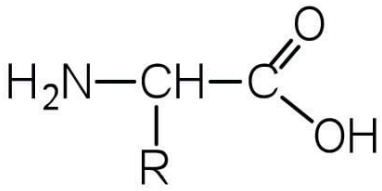
- To recognize amino acids and classify them based on the characteristics of their side chains.

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



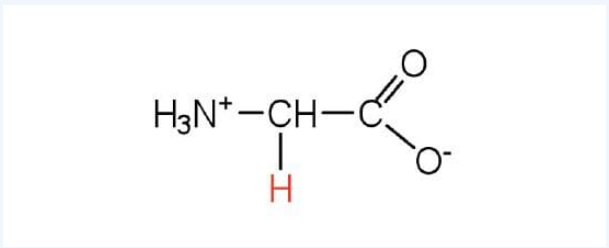
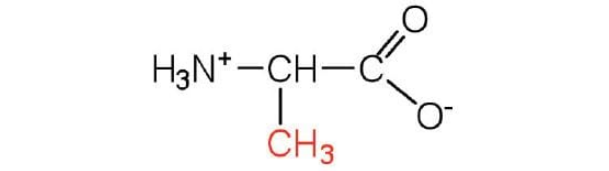
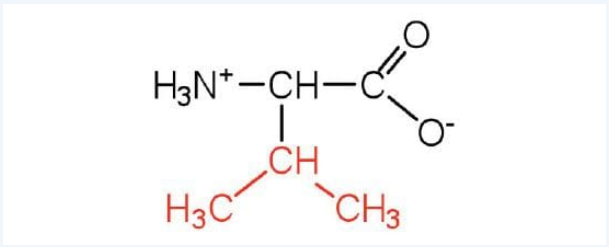
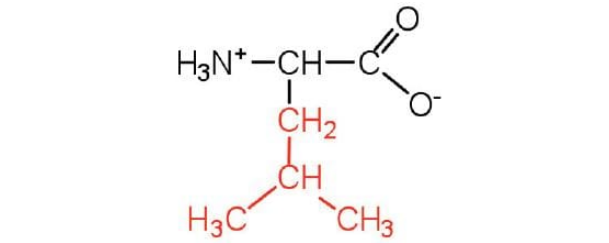
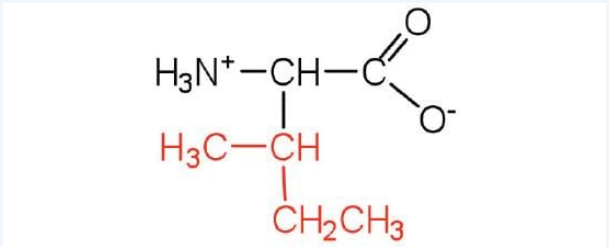
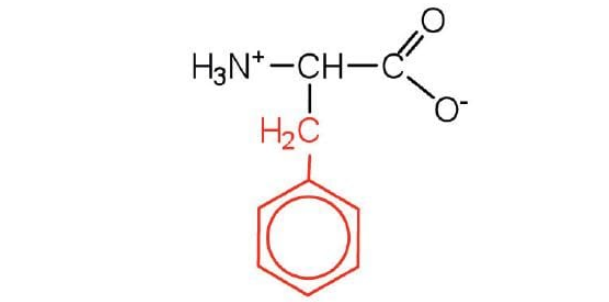
α-Amino acid drawn as an uncharged molecule; not an accurate respresentation of amino acid structure

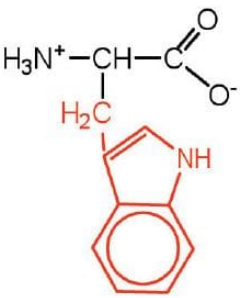
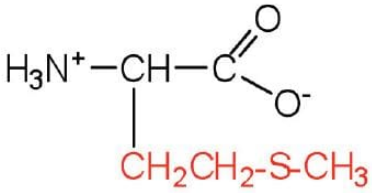
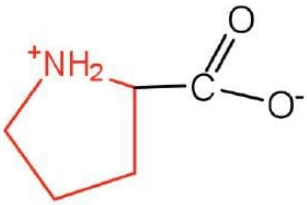
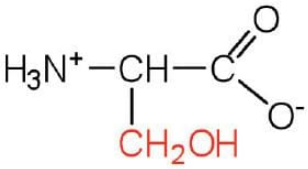
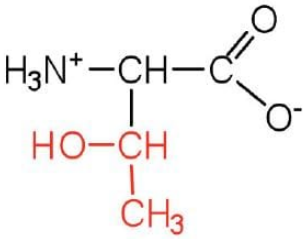
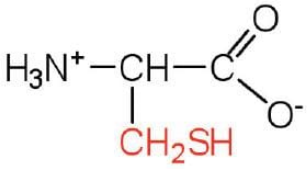
Classification

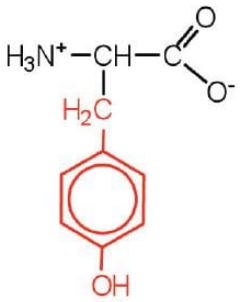
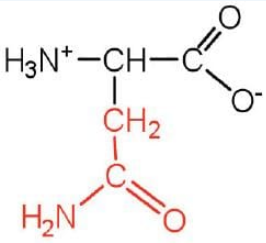
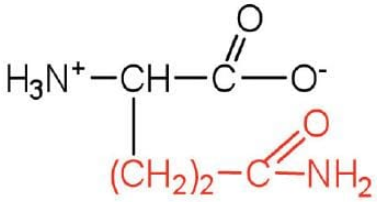
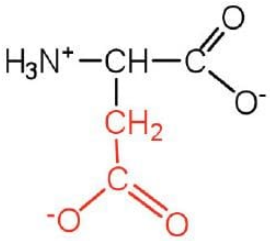
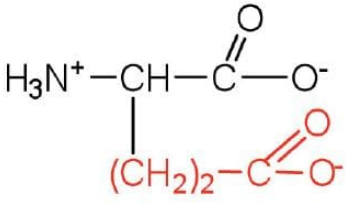
In addition to the amino and carboxyl groups, amino acids have a side chain or R group attached to the α-carbon. Each amino acid has unique characteristics arising from the size, shape, solubility, and ionization properties of its R group. As a result, the side chains of amino acids exert a profound 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 14.1.1.

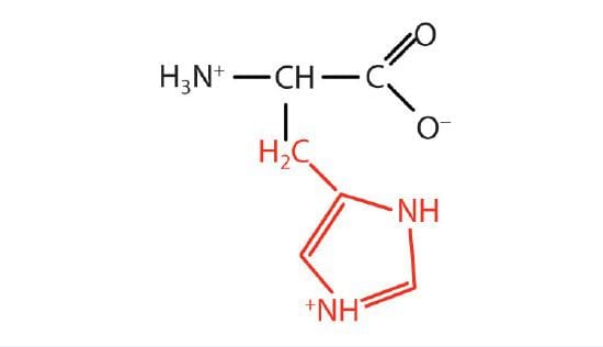
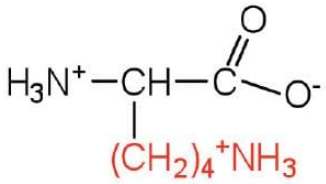
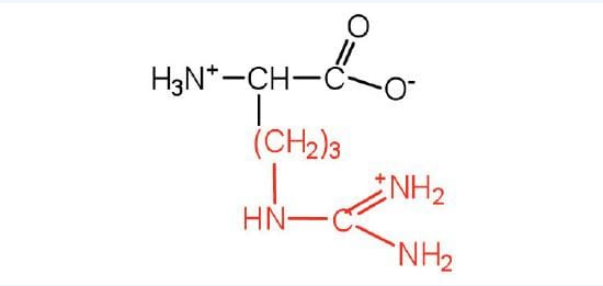
Table 14.1.1: *Common Amino Acids Found in Proteins*

Common Name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
Amino acids with a nonpolar R group				

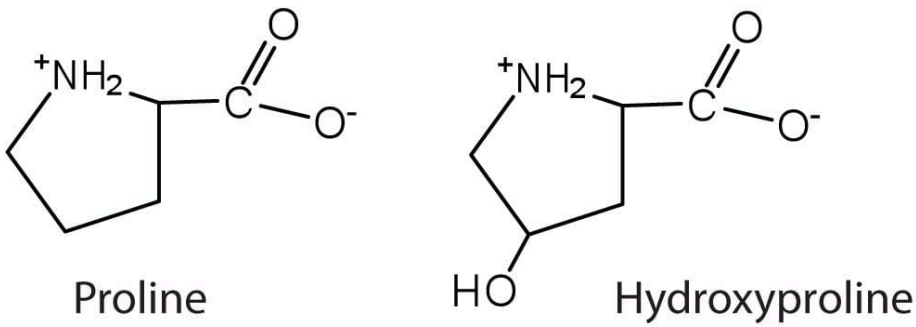
Common Name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
glycine	gly (G)		75	the only amino acid lacking a chiral carbon
alanine	ala (A)		89	—
valine	val (V)		117	a branched-chain amino acid
leucine	leu (L)		131	a branched-chain amino acid
isoleucine	ile (I)		131	an essential amino acid because most animals cannot synthesize branched-chain amino acids
phenylalanine	phe (F)		165	also classified as an aromatic amino acid

Common Name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
tryptophan	trp (W)		204	also classified as an aromatic amino acid
methionine	met (M)		149	side chain functions as a methyl group donor
proline	pro (P)		115	contains a secondary amine group; referred to as an *α-imino acid*
Amino acids with a polar but neutral R group				
serine	ser (S)		105	found at the active site of many enzymes
threonine	thr (T)		119	named for its similarity to the sugar threose
cysteine	cys (C)		121	oxidation of two cysteine molecules yields *cystine*

Common Name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
tyrosine	tyr (Y)		181	also classified as an aromatic amino acid
asparagine	asn (N)		132	the amide of aspartic acid
glutamine	gln (Q)		146	the amide of glutamic acid
Amino acids with a negatively charged R group				
aspartic acid	asp (D)		132	carboxyl groups are ionized at physiological pH; also known as aspartate
glutamic acid	glu (E)		146	carboxyl groups are ionized at physiological pH; also known as glutamate
Amino acids with a positively charged R group				

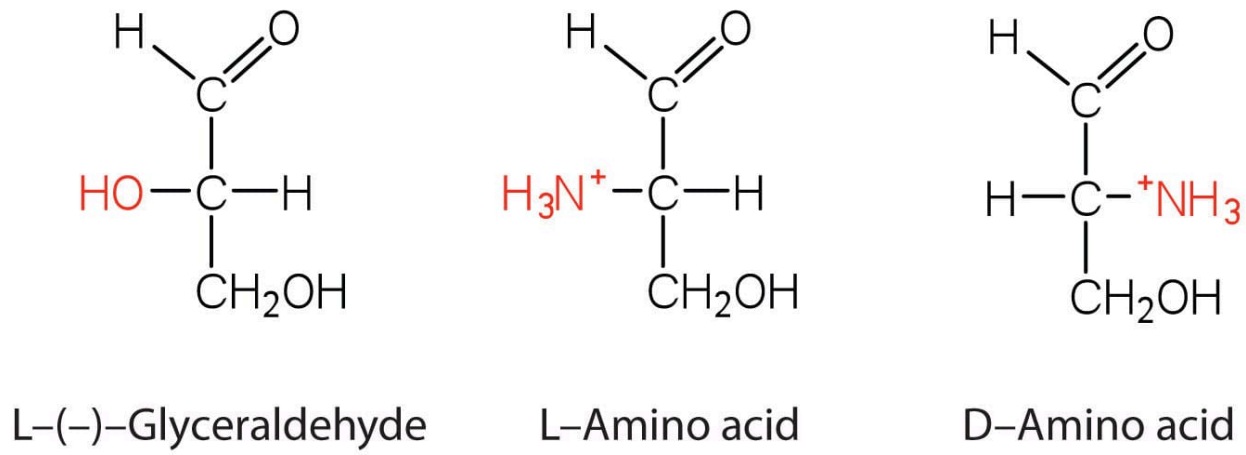
Common Name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
histidine	his (H)		155	the only amino acid whose R group has a pK_a (6.0) near physiological pH
lysine	lys (K)		147	—
arginine	arg (R)		175	almost as strong a base as sodium hydroxide

The first amino acid to be isolated was asparagine in 1806. It was obtained from protein found in asparagus juice (hence the name). Glycine, the major amino acid found in gelatin, was named for its sweet taste (Greek *glykys*, meaning "sweet"). In some cases an amino acid found in a protein is actually a derivative of one of the common 20 amino acids (one such derivative is hydroxyproline). The modification occurs *after* the amino acid has been assembled into a protein.



Configuration

Notice in Table 14.1.1 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 use glyceraldehyde as the reference compound for the assignment of 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 sugar.



We learned that all naturally occurring sugars belong to the D series. It is interesting, therefore, that nearly all known plant and animal proteins are composed entirely of L-amino acids. However, certain bacteria contain D-amino acids in their cell walls, and several antibiotics (e.g., actinomycin D and the gramicidins) contain varying amounts of D-leucine, D-phenylalanine, and D-valine.

Summary

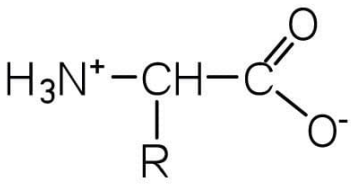
Amino acids can be classified based on the characteristics of their distinctive side chains as nonpolar, polar but uncharged, negatively charged, or positively charged. The amino acids found in proteins are L-amino acids.

Concept Review Exercises

1. What is the general structure of an α-amino acid?
2. Identify the amino acid(s) that fits each description.
    a. also known as aspartate
    b. have a positively charged side group (referred to as basic if the side group is shown with no charge)
    c. does not have a chiral carbon

Answers

1.



2. a. aspartic acid
   b. histidine, lysine & arginine (In Table 14.1.1 above, these basic side chains are shown after accepting H^+, giving them the positive charge.)
   c. glycine

Exercises

1. Write the side chain of each amino acid.

   a. serine
   b. arginine
   c. phenylalanine

2. Draw the structure for each amino acid.

   a. alanine
   b. cysteine
   c. histidine

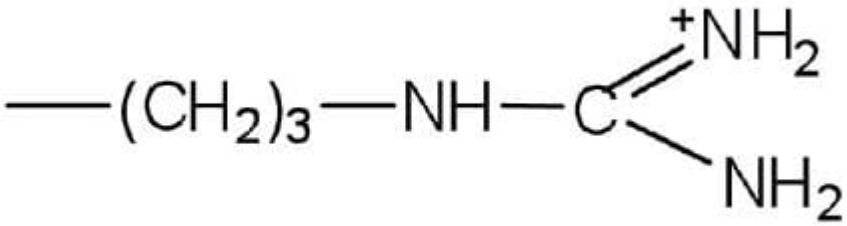
3. Identify an amino acid whose side chain contains a(n)

   a. amide functional group.
   b. alcohol functional group.
   c. carboxyl group.

Answers

1. a. $-CH_2OH$

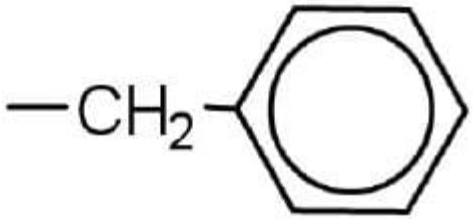
b.



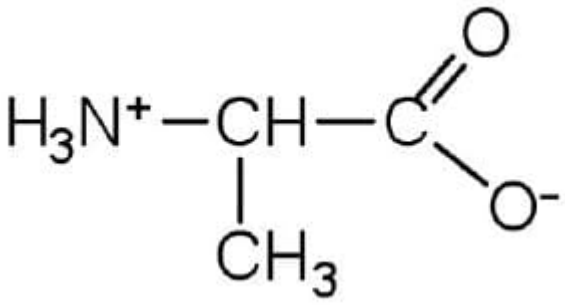
c.

2.

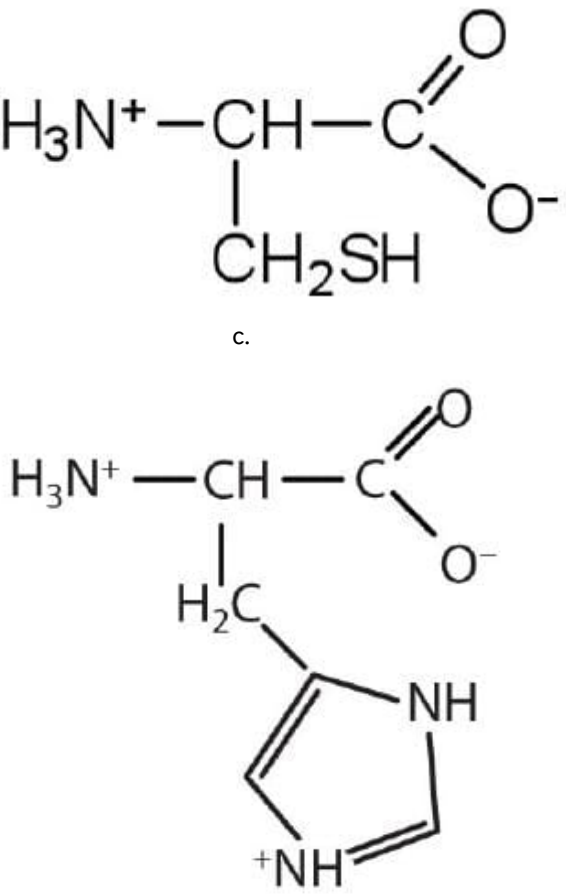
a.



b.



c.



3. a. asparagine or glutamine
   b. serine, threonine, or tyrosine
   c. aspartic acid or glutamic acid

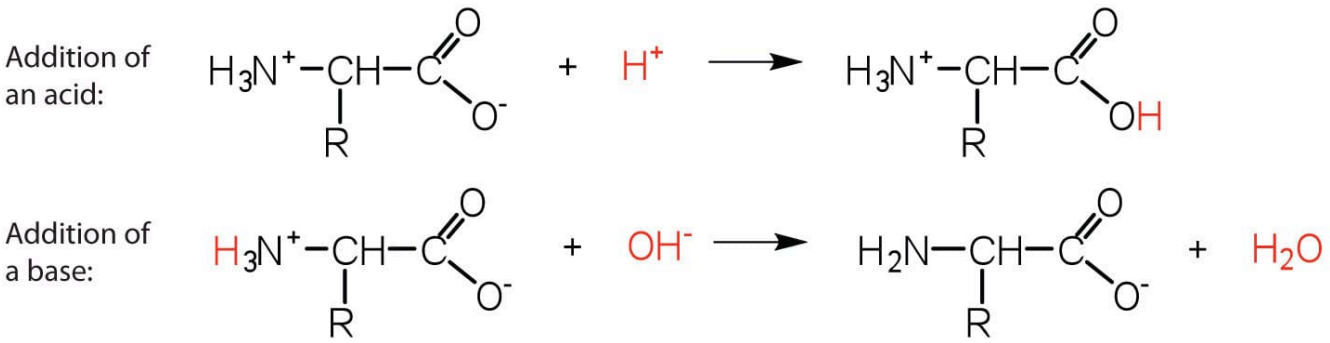
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14.2: Reactions of Amino Acids

Skills to Develop

- 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.

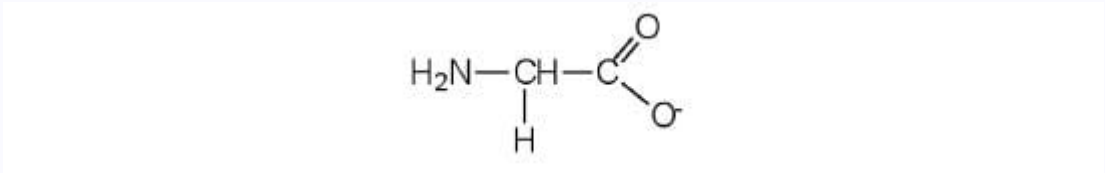


Example 14.2.1

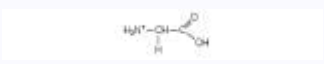
a. Draw the structure for the anion formed when glycine (at neutral pH) reacts with a base.
b. Draw the structure for the cation formed when glycine (at neutral pH) reacts with an acid.

SOLUTION

a. The base removes H^+ from the protonated amine group of $^+H_3N\text{-}CH_2\text{-}CO_2^-$, to become $H_2N\text{-}CH_2\text{-}CO_2^-$.



b. The acid adds H^+ to the carboxylate group of $^+H_3N\text{-}CH_2\text{-}CO_2^-$, to become $^+H_3N\text{-}CH_2\text{-}CO_2H$.



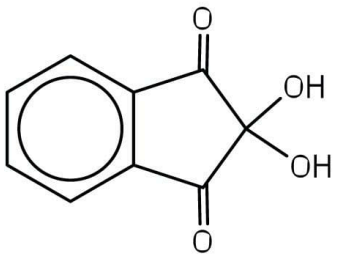
The particular pH at which a given amino acid exists in solution as a zwitterion is called the isoelectric point (pI). At its pI, the positive and negative charges on the amino acid balance, and the molecule as a whole is electrically neutral. The amino acids whose side chains are always neutral have 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 14.2.1).

Table 14.2.1***:*** *ExampIes of Some Representative Amino Acids*

Amino Acid	Classification	pI
alanine	nonpolar	6.0
valine	nonpolar	6.0
serine	polar, uncharged	5.7
threonine	polar, uncharged	6.5
arginine	positively charged (basic)	10.8
histidine	positively charged (basic)	7.6
lysine	positively charged (basic)	9.8
aspartic acid	negatively charged (acidic)	3.0
glutamic acid	negatively charged (acidic)	3.2

Amino acids undergo reactions characteristic of carboxylic acids and amines. The reactivity of these functional groups is particularly important in linking amino acids together to form peptides and proteins, as you will see later in this chapter. Simple chemical tests that are used to detect amino acids take advantage of the reactivity of these functional groups. An example is the ninhydrin test in which the amine functional group of α-amino acids reacts with ninhydrin to form purple-colored compounds. Ninhydrin is used to detect fingerprints because it reacts with amino acids from the proteins in skin cells transferred to the surface by the individual leaving the fingerprint.



Ninhydrin



Summary

Amino acids can act as both an acid and a base due to the presence of the amino and carboxyl functional groups. The pH at which a given amino acid exists in solution as a zwitterion is called the *isoelectric point* (pI).

Concept Review Exercises

1. Define each term.

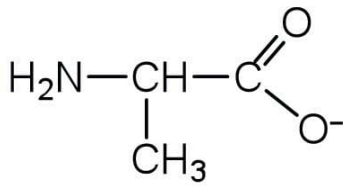
    a. zwitterion
    b. isoelectric point

2. Draw the structure for the anion formed when alanine (at neutral pH) reacts with a base. (See Table 14.1.1 for the structure of alanine.)

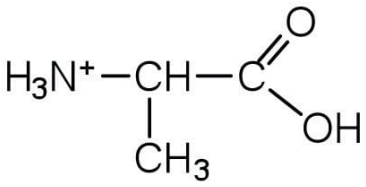
3. Draw the structure for the cation formed when alanine (at neutral pH) reacts with an acid. (See Table 14.1.1 for the structure of alanine.)

Answers

1. a. an electrically neutral compound that contains both negatively and positively charged groups
   b. the pH at which a given amino acid exists in solution as a zwitterion



2.



3.

Exercises

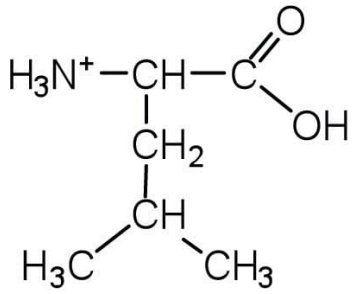
1. Draw the structure of leucine and determine the charge on the molecule in a(n)

    a. acidic solution (pH = 1).
    b. neutral solution (pH = 7).
    c. a basic solution (pH = 11)

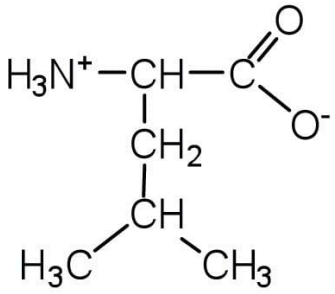
    (See Table 14.1.1 for the structure of leucine.)

Answer

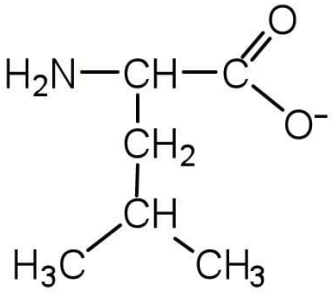
1. a.



b.



c.



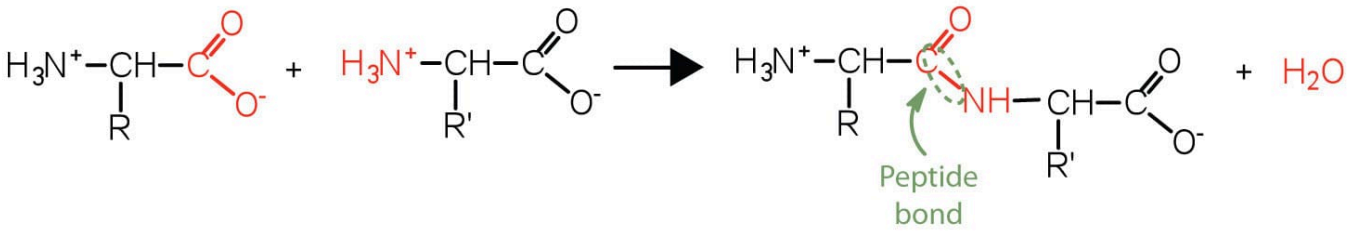
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14.3: Peptides

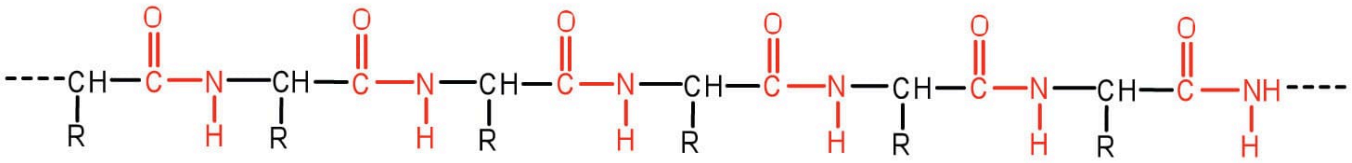
Skills to Develop

- Explain how a peptide is formed from individual amino acids.
- Explain why the sequence of amino acids in a protein is important.

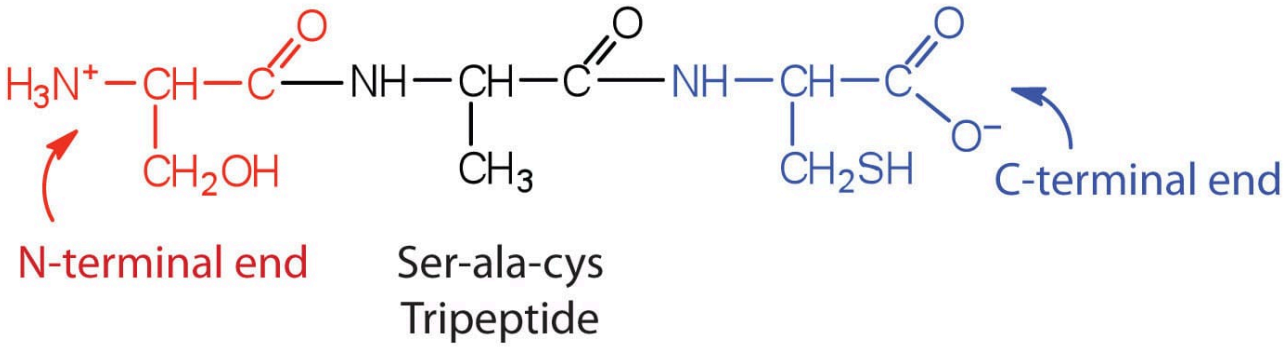
Two or more amino acids can join together into chains called peptides. Previously, we discussed the reaction between ammonia and a carboxylic acid to form an amide. In a similar reaction, the amino group on one amino acid molecule reacts with the carboxyl group on another, releasing a molecule of water 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.

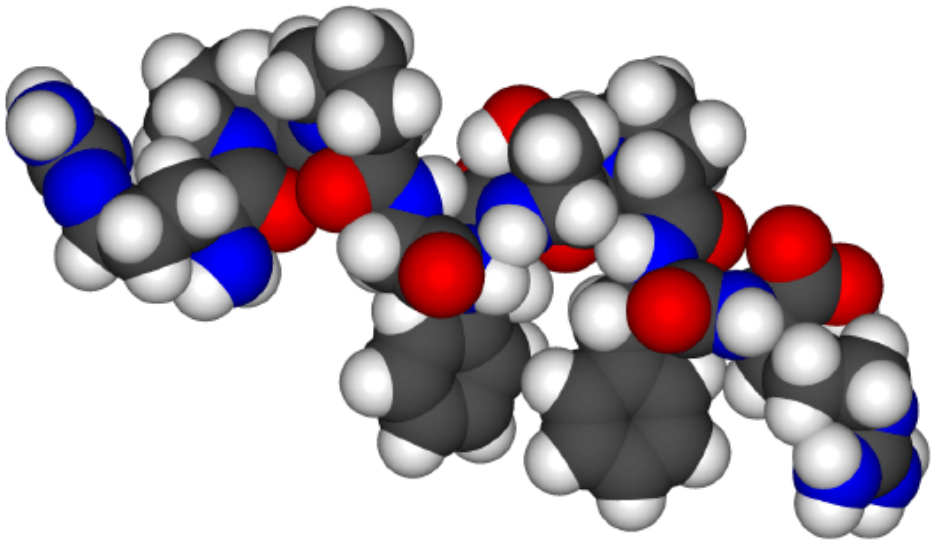


Figure 14.3.1*: Space-filling model of bradykinin. Image used with permission (Public Domain; Fvasconcellos)*

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 14.3.1) 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).

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. (See Table 14.1.1 for the structure of each amino acid.)

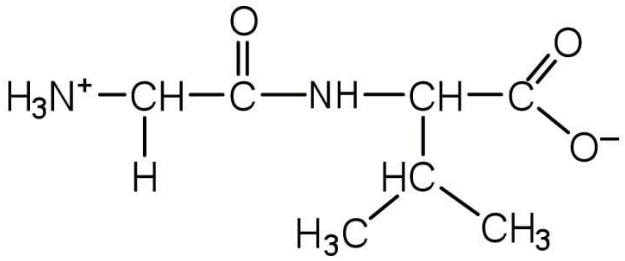
    a. gly-val
    b. val-gly

2. Identify the C- and N-terminal amino acids for the peptide lys-val-phe-gly-arg-cys.

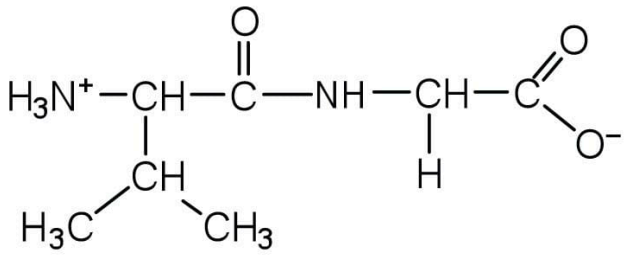
3. It was mentioned in this section that sickle-cell anemia is caused by the change of one amino acid in hemoglobin, valine replacing glutamic acid. Instead of valine, what amino acid would have likely the smallest effect in place of glutamic acid?

Answers

1. a.



b.



2. C-terminal amino acid: cys; N-terminal amino acid: lys

3. Glutamic acid has a negatively charged carboxylate side group, so replacement by aspartic acid (which also has a negatively

charged side group) would likely have the smallest effect. (Valine has a neutral, non-polar side chain so is one of the most different from glutamic acid.)

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14.4: Proteins

Skills to Develop

- 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 14.4.1.

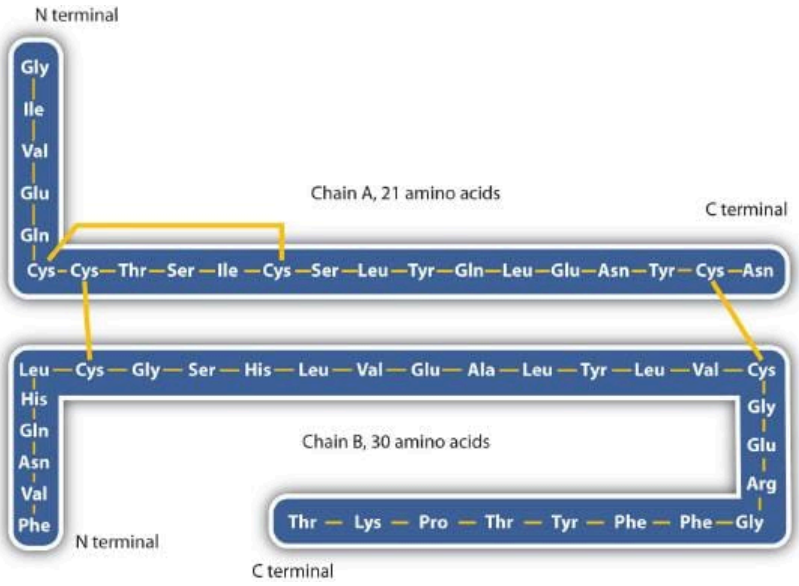


Figure 14.4.1***:*** *Primary Structure of Human Insulin. Human insulin, whose amino acid sequence is shown here, is a hormone that is required for the proper metabolism of glucose.*

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 14.4.2). 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.

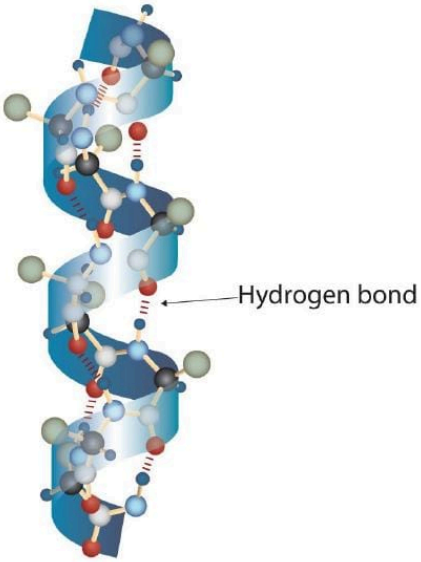


Figure 14.4.2 *A Ball-and-Stick Model of an α-Helix. This ball-and-stick model shows the intrachain hydrogen bonding between carbonyl oxygen atoms and amide hydrogen atoms. Each turn of the helix spans 3.6 amino acids. Note that the side chains (represented as green spheres) point out from the helix.*

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 14.4.3). 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.

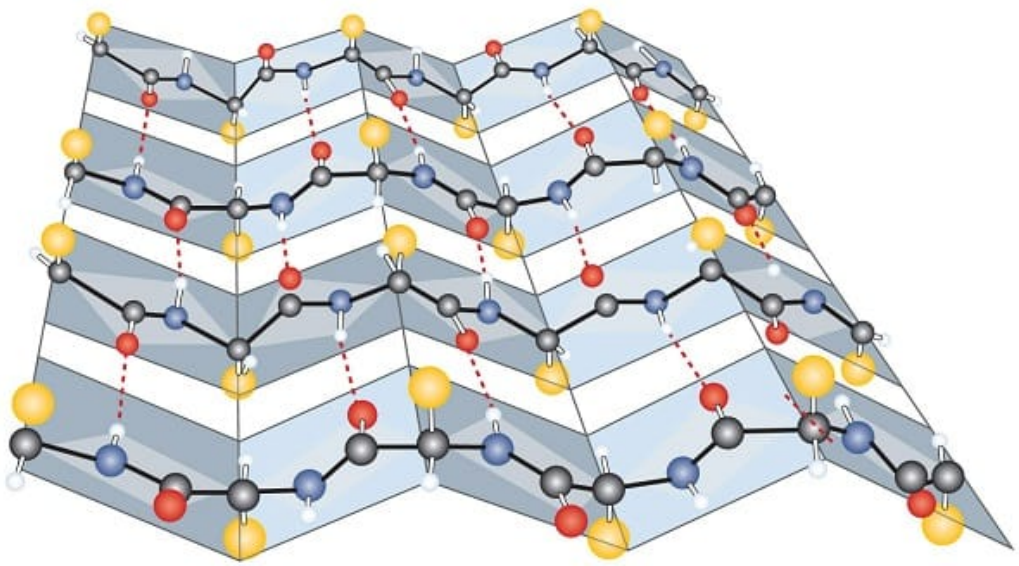


Figure 14.4.3***:*** *A Ball-and-Stick Model of the β-Pleated Sheet Structure in Proteins. The side chains extend above or below the sheet and alternate along the chain. The protein chains are held together by interchain hydrogen bonding.*

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 14.4.4 shows a depiction of the three-dimensional structure of insulin.

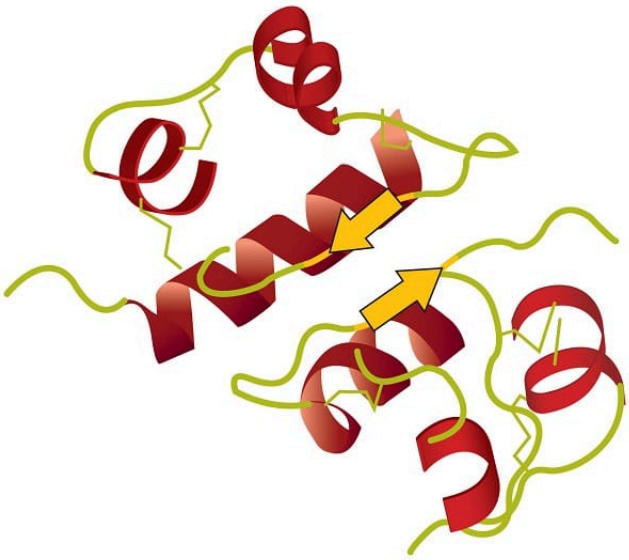


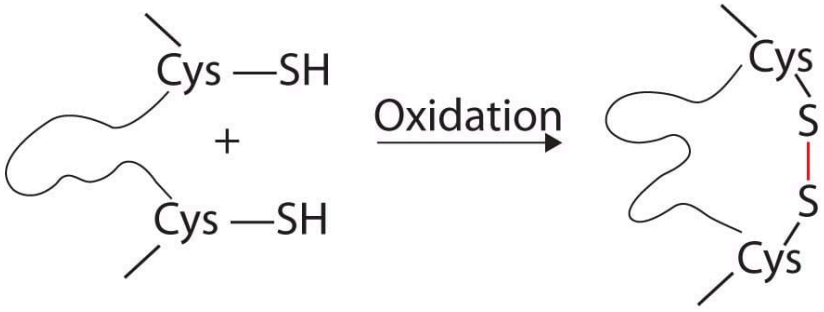
Figure 14.4.4*: A Ribbon Model of the Three-Dimensional Structure of Insulin. The spiral regions represent sections of the polypeptide chain that have an α-helical structure, while the broad arrows represent β-pleated sheet structures.*

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 14.4.5).
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 14.4.5). CORRECTIVE NOTE: At the top of the figure, the dashed line representing a hydrogen-bonoding interaction should go from the hydrogen of water to the oxygen in -CH_2**O**H (not to carbon).

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 14.4.5). Intrachain disulfide linkages are found in many proteins, including insulin (yellow bars in Figure 14.4.1) 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 (shaded parts labeled (d) of Figure 14.4.5). 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.

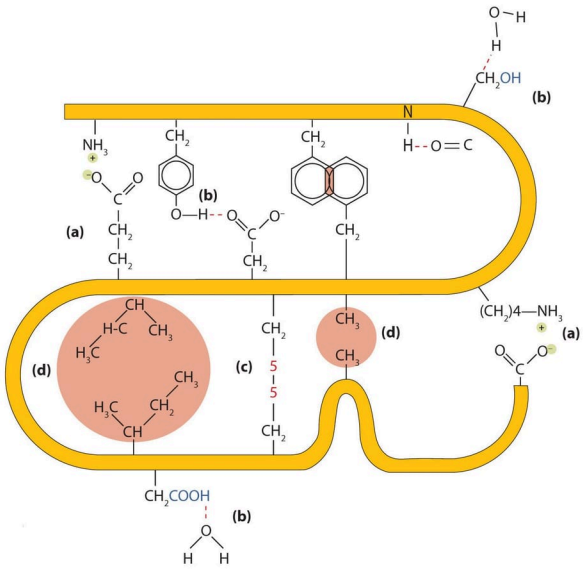


Figure 14.4.5***:*** *Tertiary Protein Structure Interactions. Four interactions stabilize the tertiary structure of a protein: (a) ionic bonding, (b) hydrogen bonding, (c) disulfide linkages, and (d) dispersion forces.*

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 14.4.6). 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 14.4.7.

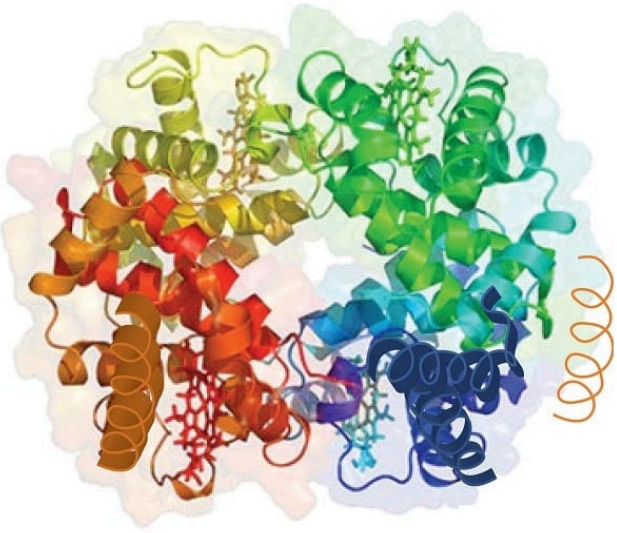


Figure 14.4.6 *The Quaternary Structure of Hemoglobin. Hemoglobin is a protein that transports oxygen throughout the body.*

Source: Image from the RCSB PDB (www.pdb.org) 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).

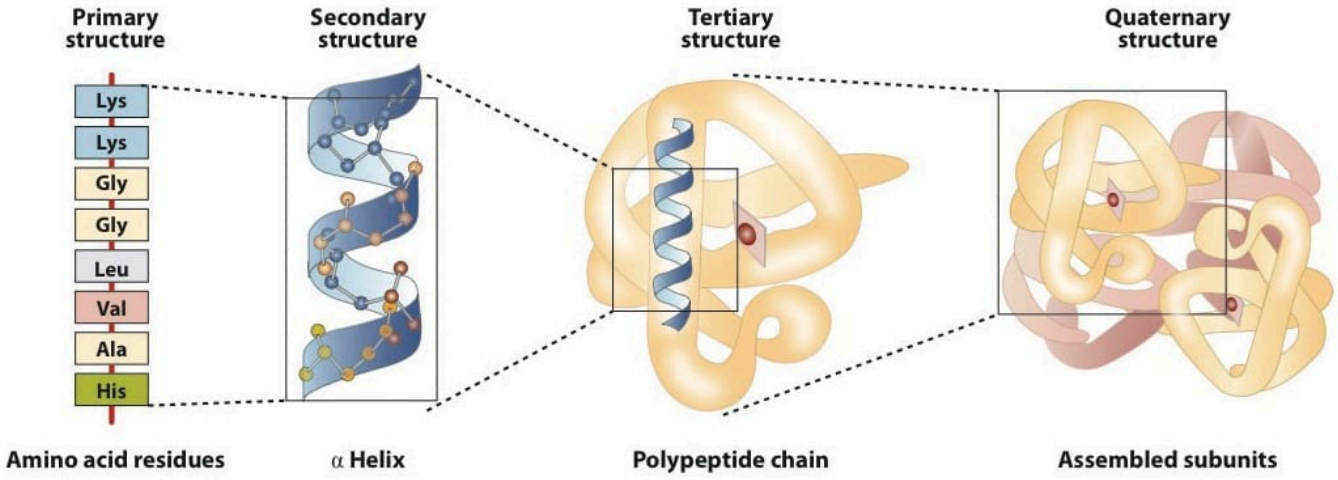


Figure 14.4.7***:*** *Levels of Structure in Proteins*

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 14.4.1).

Figure 14.4.1*: 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 14.4.8). 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.

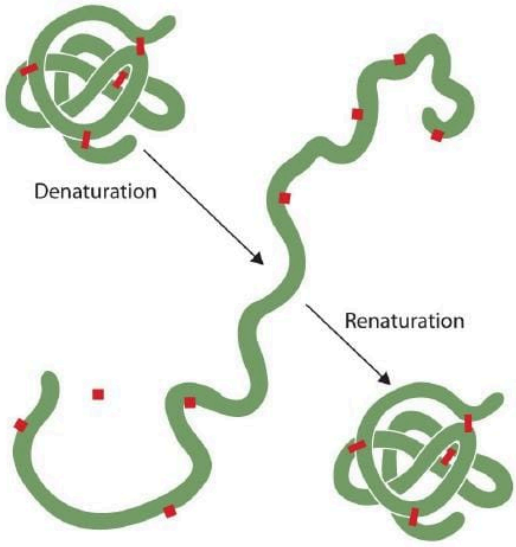


Figure 14.4.8*: Denaturation and Renaturation of a Protein. The denaturation (unfolding) and renaturation (refolding) of a protein is depicted. The red boxes represent stabilizing interactions, such as disulfide linkages, hydrogen bonding, and/or ionic bonds.*

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.

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. hemoglobin in blood
   b. keratin of fingernails
2. 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
3. What level(s) of protein structure is(are) ordinarily disrupted in denaturation? What level(s) is(are) not?
4. Which class of proteins is more easily denatured—fibrous or globular?
5. A particular globular protein is known to function in the aqueous environment of the cytosol of cells. (a) Is a leucine side chain likely to exist in the interior or on the exterior of the folded protein? (b) If one leucine is replaced with a threonine, the protein is less effective but still functional. What amino acid could replace leucine that might have little or no effect? What amino acid could replace leucine that would likely have a greater effect than replacement by threonine?

Answers

1. a. globular (soluble in aqueous blood environment) b. fibrous (insoluble/structural)
2. a. ionic bonding
   b. dispersion forces
   c. dispersion forces

d. disulfide linkage

3. Protein denaturation disrupts the secondary, tertiary, and quaternary levels of structure. Only primary structure is unaffected by denaturation.

4. Globular

5. (a) Leucine is non-polar so it would likely be found on the inside of a globular protein (not outside facing very polar waters). (b) Replacement by another non-polar amino acid, especially one of similar size (like isoleucine) would likely have the smallest impact. If replacement by polar threonine has a negative effect, replacement by one of the charged amino acids (asp, glu, his, lys, arg) might have a greater impact.

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14.5: Enzymes

Skills to Develop

- 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 14.5.1*: 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 14.5.1), with subgroups and secondary subgroups that specify the reaction more precisely.

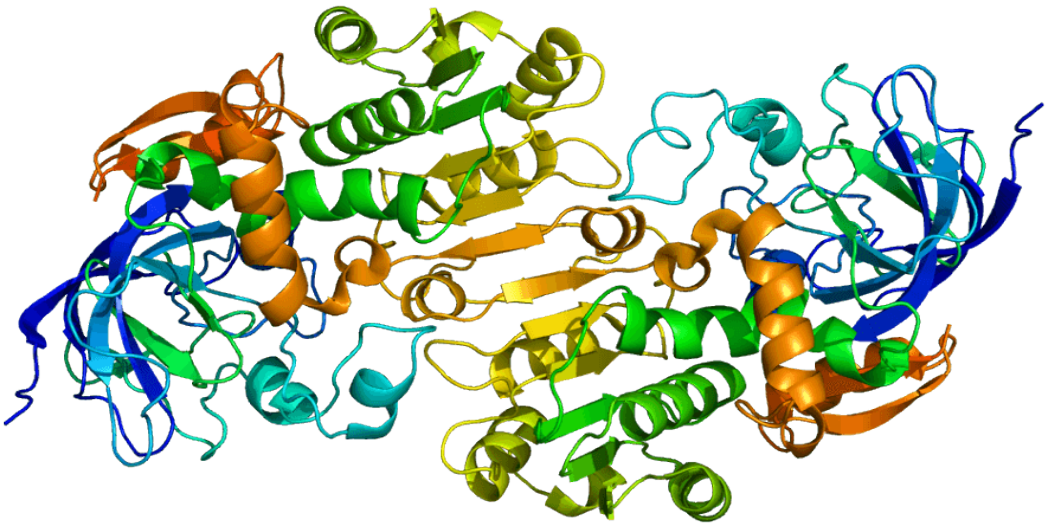
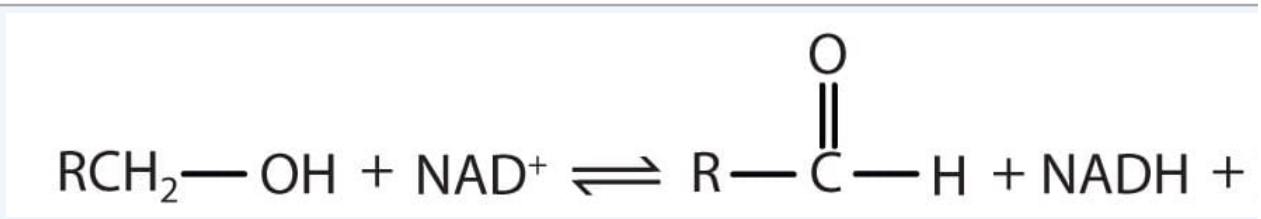


Figure 14.5.1***:*** *Structure of the alcohol dehydrogenase protein. Image used with permission (CC SA-BT 3.0; Emw).*

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 14.5.2 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 14.5.2***:*** *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 dehydr	
Reaction catalyzed:	

Summary

An enzyme is a biological catalyst, a substance that increases the rate of a chemical reaction without being changed or consumed in the reaction. A systematic process is used to name and classify enzymes.

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

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14.6 Enzyme Action

Skills to Develop

- 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:

$$S + E \rightarrow E\text{–}S \tag{1}$$

$$E\text{–}S \rightarrow P + E \tag{2}$$

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 1).

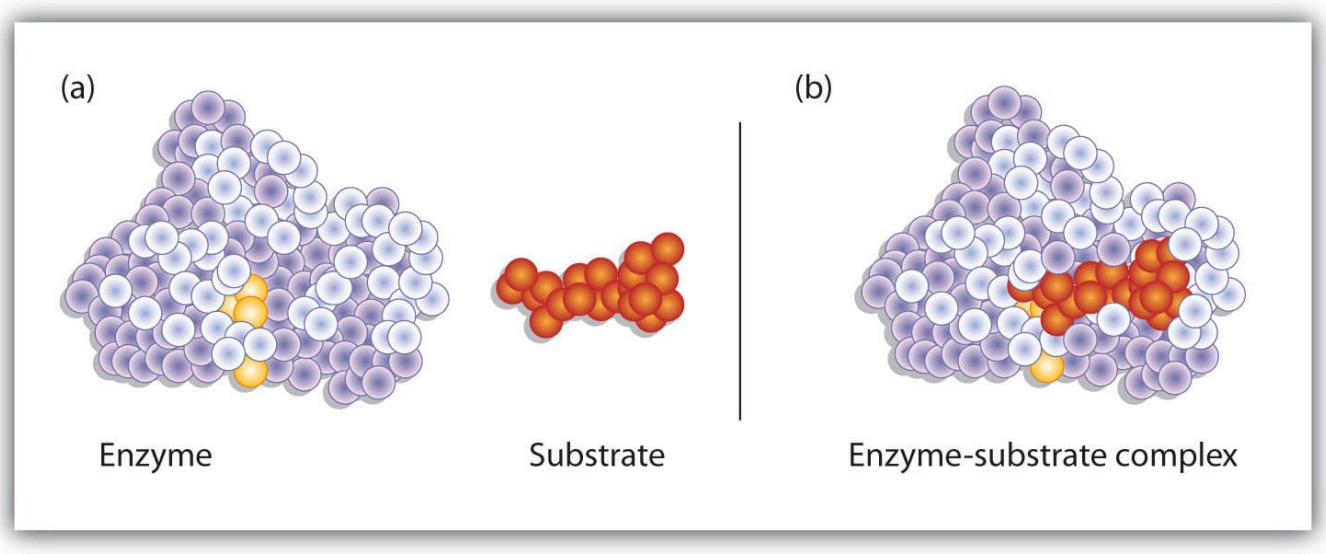


Figure 1: *Substrate Binding to the Active Site of an Enzyme. The enzyme dihydrofolate reductase is shown with one of its substrates: $NADP^+$ (a) unbound and (b) bound. The $NADP^+$ (shown in red) binds to a pocket that is complementary to it in shape and ionic properties.*

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 2). This model portrayed the enzyme as conformationally rigid and able to bond only to substrates that exactly fit the active site.

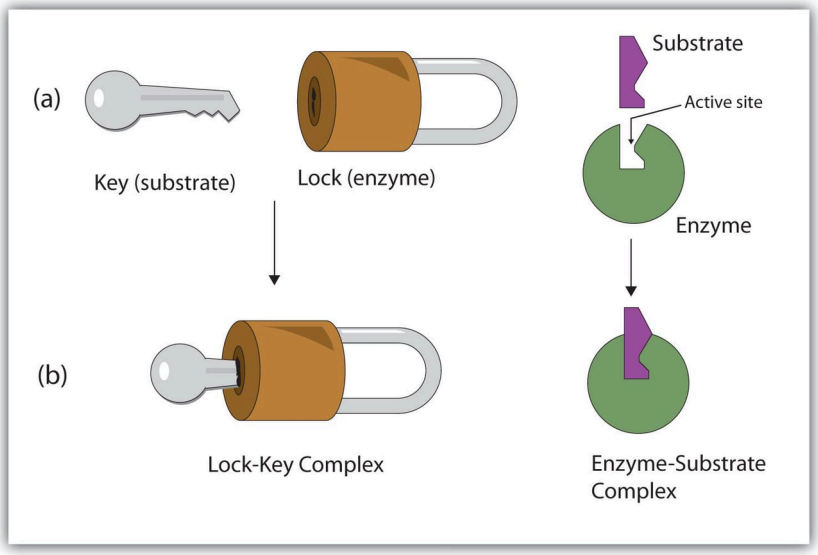


Figure 2: *The Lock-and-Key Model of Enzyme Action. (a) Because the substrate and the active site of the enzyme have complementary structures and bonding groups, they fit together as a key fits a lock. (b) The catalytic reaction occurs while the two are bonded together in the enzyme-substrate complex.*

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 3. After catalysis, the enzyme resumes its original structure.

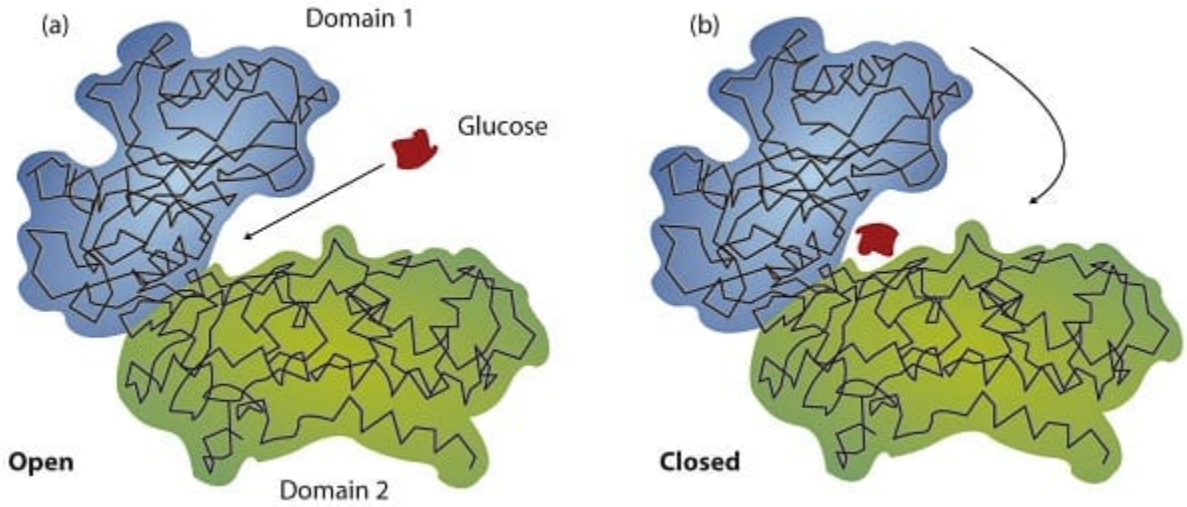


Figure 3: *The Induced-Fit Model of Enzyme Action. (a) The enzyme hexokinase without its substrate (glucose, shown in red) is bound to the active site. (b) The enzyme conformation changes dramatically when the substrate binds to it, resulting in additional interactions between hexokinase and glucose.*

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 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. Any of the polar 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.

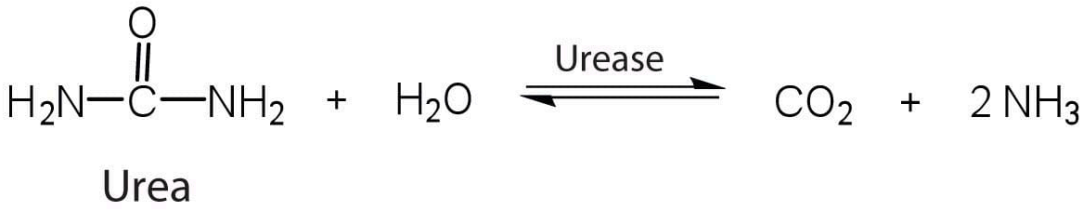
Example 2

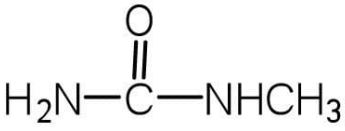
a. What type of interaction would occur between an COO^- group present on a substrate molecule and a functional group in the active site of an enzyme?
b. Suggest an amino acid whose side chain might be in the active site of an enzyme and form the type of interaction you just identified.

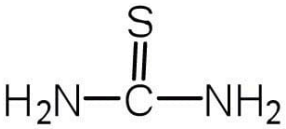
SOLUTION

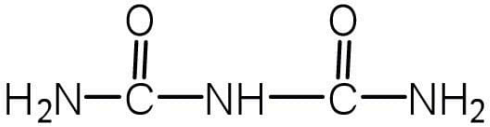
a. Because the carboxyl group has a negative charge, it would likely engage in ion-ion interactions (ionic bonding).
b. Any of the positive amino acid side chains: arginine, histidine & lysine.

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.




Methylurea


Thiourea


Biuret

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.

Concept Review Exercises

1. Distinguish between the lock-and-key model and induced-fit model of enzyme action.

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.

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. 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.

Answers

1. a. hydrogen bonding
   b. ionic bonding
   c. hydrogen bonding
   d. dispersion forces

2.

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).

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14.7: Enzyme Activity

Skills to Develop

- 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 14.7.1). 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).

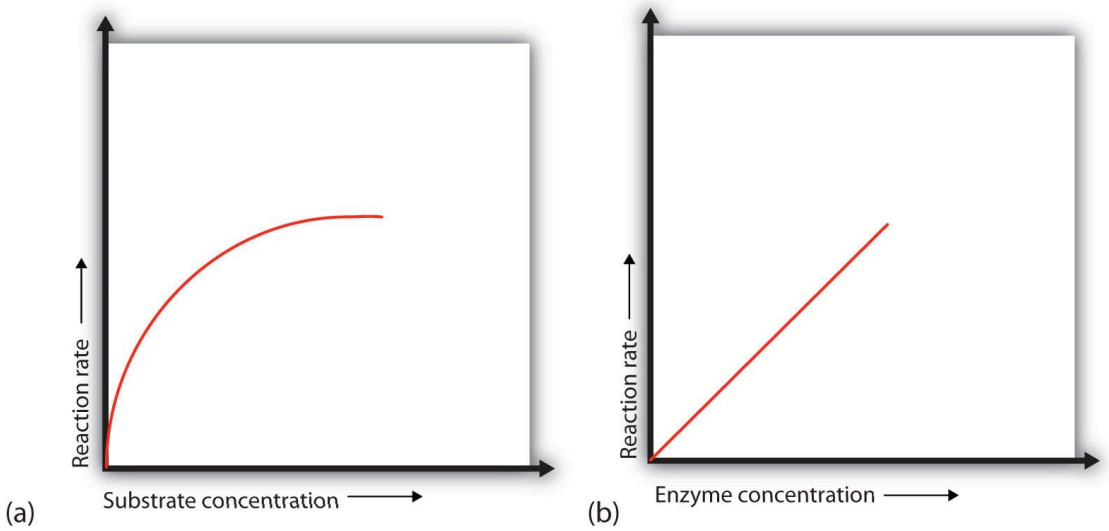


Figure 14.7.1***:*** *Concentration versus Reaction Rate. (a) This graph shows the effect of substrate concentration on the rate of a reaction that is catalyzed by a fixed amount of enzyme. (b) This graph shows the effect of enzyme concentration on the reaction rate at a constant level of substrate.*

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 14.7.1). 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 14.7.2). 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.

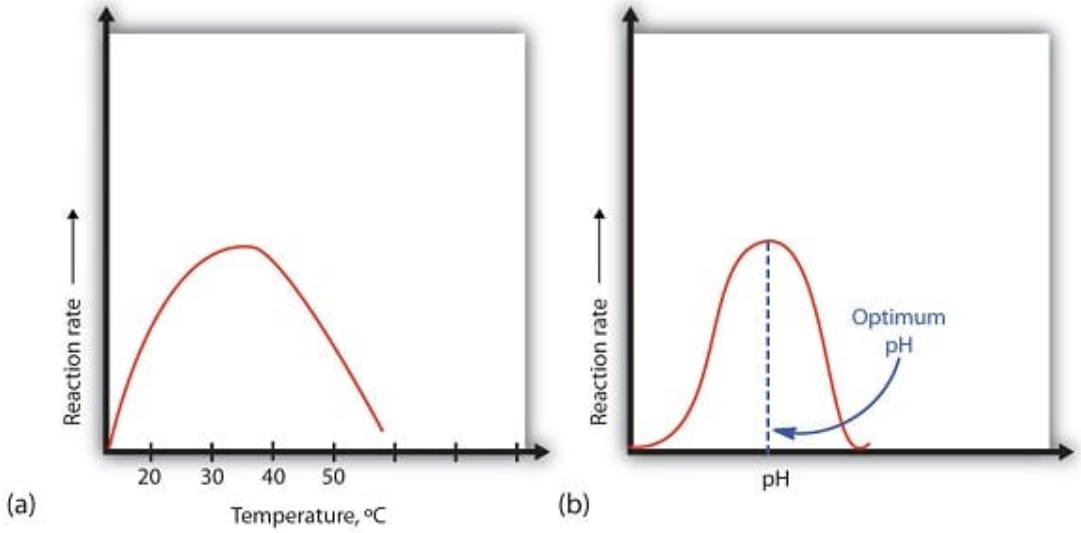


Figure 14.7.2***:*** *Temperature and pH versus Concentration. (a) This graph depicts the effect of temperature on the rate of a reaction that is catalyzed by a fixed amount of enzyme. (b) This graph depicts the effect of pH on the rate of a reaction that is catalyzed by a fixed amount of enzyme.*

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 14.7.2). 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.

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. Milk is often pasteurized, heated to high temperature, to prevent bacterial growth. Based on what you know about enzymes and temperature, explain why pasteurization works.

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.

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.

2. At hight temperatures, the bacterial enzymes denature (unfold) and thus be unable to function (so the bacteria no longer grow and multiply).

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.

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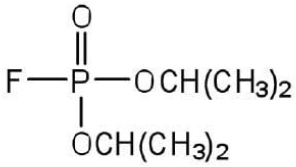
14.8: Enzyme Inhibition

Skills to Develop

- Explain what an enzyme inhibitor is.
- Distinguish between reversible and irreversible inhibitors.
- Distinguish between competitive and noncompetitive inhibitors.

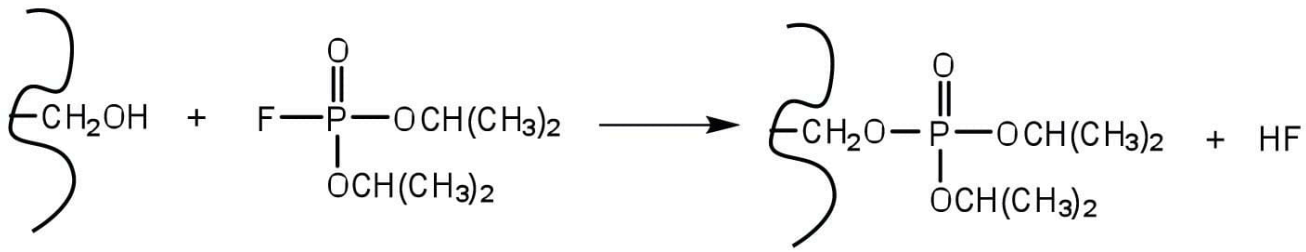
Previously, we noted that enzymes are inactivated at high temperatures and by changes in pH. These are nonspecific factors that would inactivate any enzyme. The activity of enzymes can also be regulated by more specific inhibitors. Many compounds are poisons because they bind covalently to particular enzymes or kinds of enzymes and inactivate them (Table 14.8.1).

Table 14.8.1*: 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)		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 14.8.1). 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.

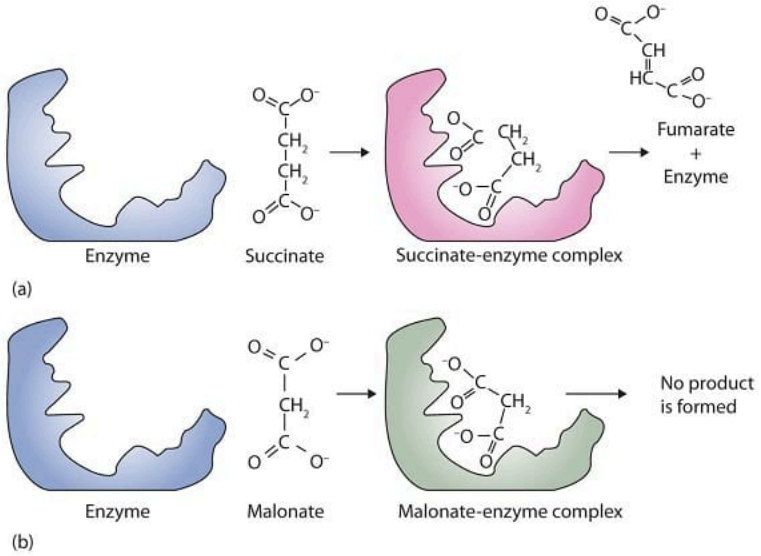


Figure 14.8.1***:*** *Competitive Inhibition. (a) Succinate binds to the enzyme succinate dehydrogenase. A dehydrogenation reaction occurs, and the product—fumarate—is released from the enzyme. (b) Malonate also binds to the active site of succinate dehydrogenase. In this case, however, no subsequent 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.

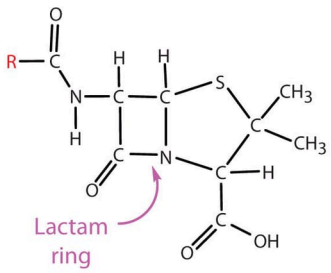
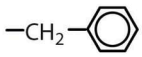
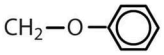
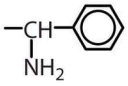
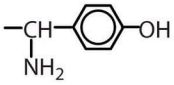
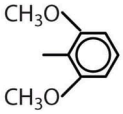
An *antibiotic* is a compound that kills bacteria; it may come from a natural source such as molds or be synthesized with a structure analogous to a naturally occurring antibacterial compound. Antibiotics constitute no well-defined class of chemically related substances, but many of them work by effectively 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.

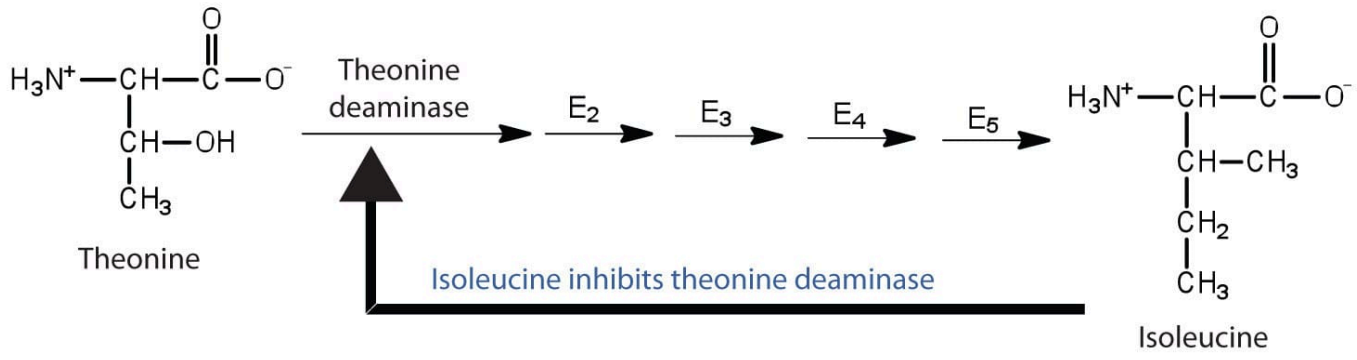


Figure 14.8.2***:*** *Feedback Inhibition of Threonine Deaminase by Isoleucine. Threonine deaminase is the first enzyme in the conversion of threonine to isoleucine. Isoleucine inhibits threonine deaminase through feedback inhibition.*

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 14.8.2).

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.

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. A particular substrate binds to the active site of any enzyme via a hydrophobic London-dispersion interaction. A competitive inhibitor has a non-polar amino acid side chain that can also attach to that active site. Is the inhibitor likely reversible or irreversible?

2. Oxaloacetate ($^-OOCCH_2COCOO^-$) inhibits succinate dehydrogenase. Would you expect oxaloacetate to be a competitive or noncompetitive inhibitor? Explain.

Answer

1. Since London-dispersion forces are relatively weak, the inhibitor is likely reversible (can be released).

2. Oxaloacetate ($^-OOCCH_2COCOO^-$) is similar in size and structure to the succinate substrate ($^-OOCCH_2CH_2COO^-$), so it will also likely fit and attach to the active site of the enzyme, making it a competitive inhibitor.

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14.9: Enzyme Cofactors and Vitamins

Skills to Develop

- 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 14.9.1*: Fat-Soluble Vitamins and Physiological Functions*

Vitamin	Physiological Function
vitamin A (retinol)	formation of vision pigments; differentiation of epithelial cells
vitamin D (cholecalciferol)	increases the body's ability to absorb calcium and phosphorus
vitamin E (tocopherol)	fat-soluble antioxidant
vitamin K (phylloquinone)	formation of prothrombin, a key enzyme in the blood-clotting proce

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 14.9.1 and 14.9.2.

Table 14.9.2***: 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.

Concept Review Exercises

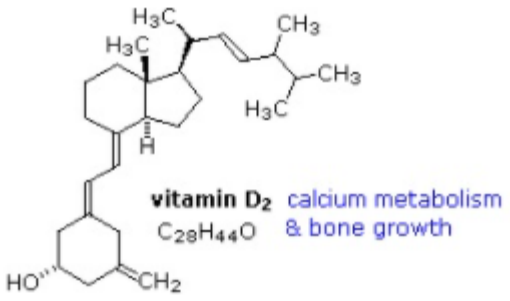
1. What is the difference between a cofactor and a coenzyme?
2. How are vitamins related to coenzymes?

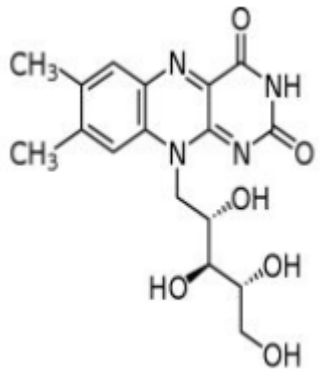
Answers

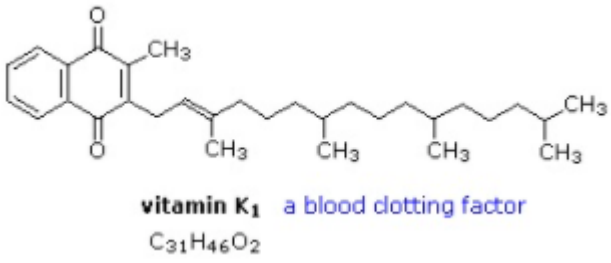
1. A coenzyme is one type of cofactor. Coenzymes are organic molecules required by some enzymes for activity. A cofactor can be either a coenzyme or an inorganic ion.
2. Coenzymes are synthesized from vitamins.

Exercises

1. Identify each vitamin as water soluble or fat soluble.

a. 

b. 

c. 

Answers

1. a. fat soluble (mostly non-polar hydrocarbon)
   b. water soluble (many polar alcohol, amide & amine functional groups)
   c. fat soluble (mostly non-polar hydrocarbon)

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14.10: Chapter 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:

$$E + S \rightarrow E\text{–}S \rightarrow E + P \tag{14.10.1}$$

The original **lock-and-key model** of enzyme and substrate binding pictured a rigid enzyme of unchanging configuration binding to the appropriate substrate. The newer **induced-fit model** describes the enzyme active site as changing its conformation after binding to the substrate.

Most enzymes have maximal activity in a narrow pH range centered on an **optimum pH**. In this pH range, the enzyme is correctly folded, and catalytic groups in the active site have the correct charge (positive, negative, or neutral). For most enzymes, the optimum pH is between 6 and 8.

Substances that interfere with enzyme function are called inhibitors. An **irreversible inhibitor** inactivates enzymes by forming covalent bonds to the enzyme, while a **reversible inhibitor** inactivates an enzyme by a weaker, noncovalent interaction that is easier to disrupt. A **competitive inhibitor** is a reversible inhibitor that is structurally similar to the substrate and binds to the active site. When the inhibitor is bound, the substrate is blocked from the active site and no reaction occurs. Because the binding of such an inhibitor is reversible, a high substrate concentration will overcome the inhibition because it increases the

likelihood of the substrate binding. A **noncompetitive inhibitor** binds reversibly at a site distinct from the active site. Thus, it can bind to either the enzyme or the enzyme-substrate complex. The inhibitor changes the conformation of the active site so that the enzyme cannot function properly. Noncompetitive inhibitors are important in **feedback inhibition**, in which the amount of product produced by a series of reactions is carefully controlled. The final product in a series of reactions acts as a noncompetitive inhibitor of the initial enzyme.

Simple enzymes consist entirely of one or more amino acid chains. Complex enzymes are composed of one or more amino acid chains joined to **cofactors**—inorganic ions or organic **coenzymes**. **Vitamins** are organic compounds that are essential in very small amounts for the maintenance of normal metabolism and generally cannot be synthesized at adequate levels by the body. Vitamins are divided into two broad categories: *fat-soluble* vitamins and *water-soluble* vitamins. Many of the water-soluble vitamins are used for the synthesis of coenzymes.

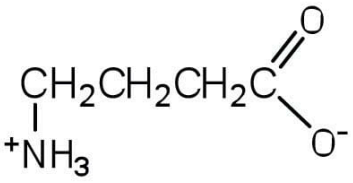
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14.E: Exercises

Additional Exercises

1. Below is 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.

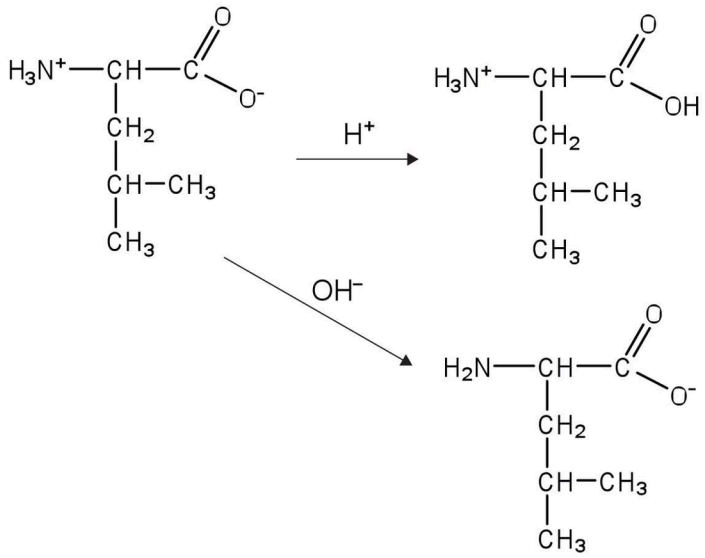


2. Write equations to show how leucine can act as a buffer (that is, how it can neutralize added acid or base).
3. Bradykinin is a peptide hormone composed of nine amino acids that lowers blood pressure. Its primary structure is arg-pro-pro-gly-phe-ser-pro-phe-arg. Would you expect bradykinin to be positively charged, negatively charged, or neutral at a pH of 6.0? Justify your answer.
4. 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.
5. 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)?
6. Which mutations would have more impact on the function of a protein, the substitution of lysine for leucine *or* the substitution of serine for threonine? Explain your reasoning.

Answers

1. This amino acid would not be found in proteins because it is not an α-amino acid (which all have general formula $^{+}H_3NCH(R)CO_2^{-}$, where the amine and carboxyl group are both directly attached to the same alpha carbon).

2. If acid is added, the extra protons react with the negative carboxyl groups of the amino acid. If base is added, it will react with an H+ from the protonated amine group.



3. Bradykinin would be positively charged; all of the amino acids in that chain except for arginine have R groups that do not become either positively or negatively charged. The two arginines have positively charged at neutral pH, so the peptide would have an overall positive two charge.

4. The enzyme is active when the carboxyl group in the R group (CH_2COOH) of aspartic acid does not have the H^+ attached (forming CH_2COO^-); the proton is removed when the solution becomes less acidic, around pH 6 or higher.

5. Normally, reaction rates increase at higher temperatures because the reactants have more energy to overcome the activation energy barrier. With enzymes, however, the activity of enzymes in the body would decrease at higher temperature because the enzymes begin to denature.

6. Substitution of lysine for leucine would have more impact because the change from an amino acid with a nonpolar side chain to one that has a positively charged side chain is more drastic. Both serine and threonine, on the other hand, have polar side chains containing the OH group, so they would behave similarly.

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15: 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.

15.1: Nucleotides

15.2: Nucleic Acid Structure

15.3: Replication and Expression of Genetic Information

15.4: Protein Synthesis and the Genetic Code

15.5: Mutations and Genetic Diseases

15.6: Viruses

15.7: Chapter Summary

15.E: Exercises

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15.1: Nucleotides

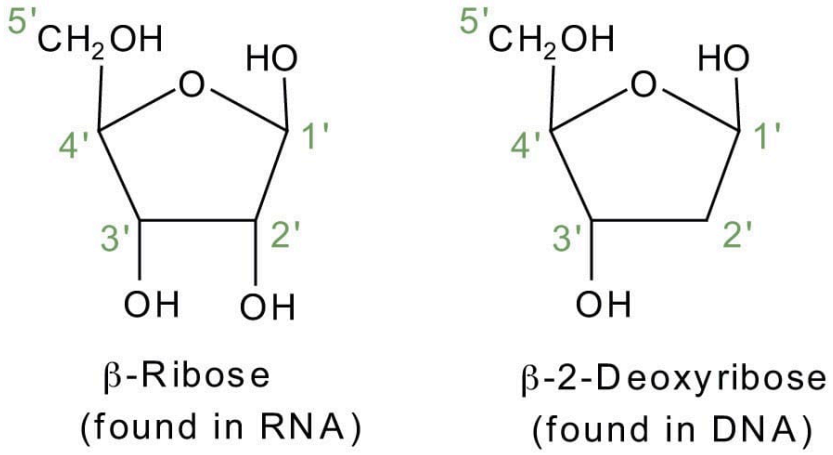
Skills to Develop

- To identify the different molecules that combine to form nucleotides.

The repeating, or monomer, units that are linked together to form nucleic acids are known as nucleotides. The deoxyribonucleic acid (DNA) of a typical mammalian cell contains about 3×10^9 nucleotides. Nucleotides can be further broken down to phosphoric acid (H_3PO_4), a pentose sugar (a sugar with five carbon atoms), and a nitrogenous base (a base containing nitrogen atoms).

$$\text{nucleic acids} \xrightarrow[\text{down into}]{\text{can be broken}} \text{nucleotides} \xrightarrow[\text{down into}]{\text{can be broken}} H_3PO_4 + \text{nitrogen base} + \text{pentose sugar} \tag{15.1.1}$$

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 15.1.1).

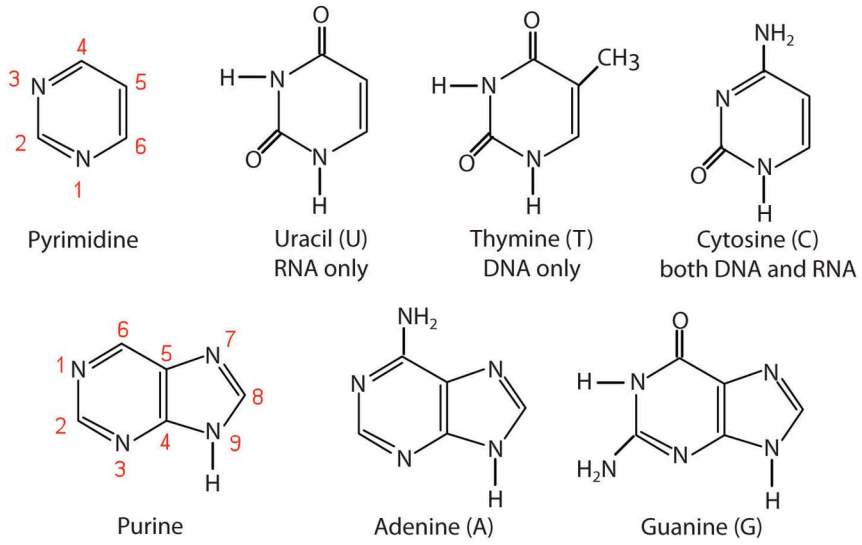


Figure 15.1.1 *The Nitrogenous Bases Found in DNA and RNA*

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 15.1.1 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 15.1.1***:*** *Composition of Nucleotides in DNA and RNA*

Composition	DNA	RNA
purine bases	adenine and guanine	adenine and guanine
pyrimidine bases	cytosine and thymine	cytosine and uracil
pentose sugar	2-deoxyribose	ribose
inorganic acid	phosphoric acid (H_3PO_4)	H_3PO_4

The names and structures of the major ribonucleotides and one of the deoxyribonucleotides are given in Figure 15.1.2.

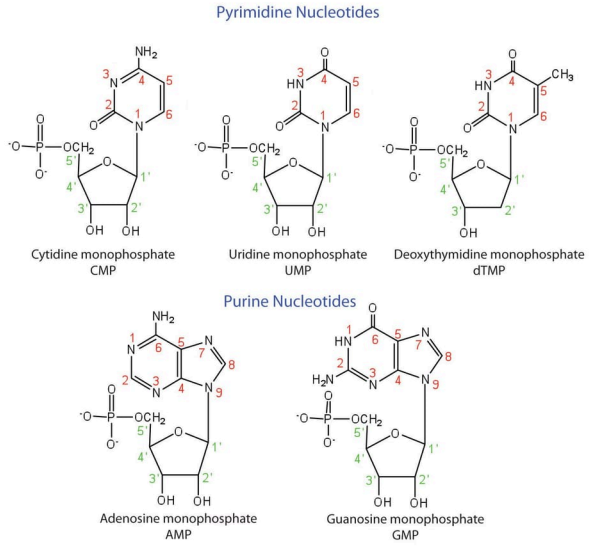


Figure 15.1.2***:*** *The Pyrimidine and Purine Nucleotides*

(SIDE NOTE: Notice that the phosphoric acid group on the structures above is deprotonated --- H^+ has been removed from the oxygens and instead negative charges are shown. Phosphate, PO_4^{3-}, is the deprotonated base form of phosphoric acid, H_3PO_4. It is usually shown this way because physiological pH is 7.4, slightly basic, so inside your cells the groups are more likely to exist in their base form. Because a nucleotide can exist in either the acid or the base forms, the terms "phosphoric acid" and "phosphate" are used interchangeably.)

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 15.1.3, 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.

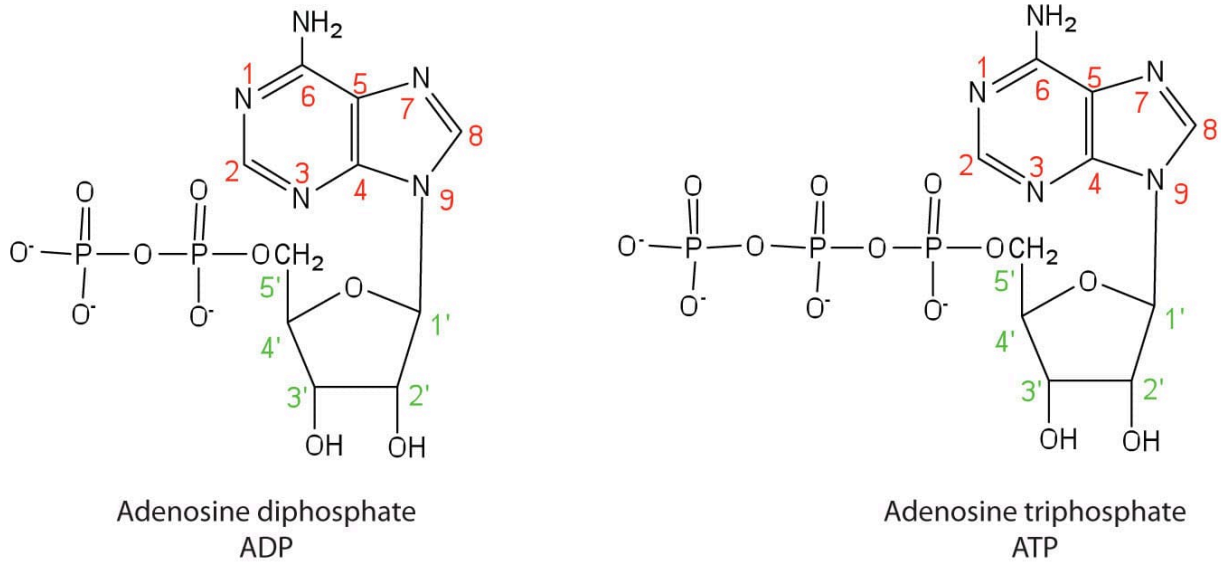


Figure 15.1.3***:*** *Structures of Two Important Adenine-Containing Nucleotides*

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.

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

    (NOTE: Phosphate, PO_4^{3-}, can be listed instead of phosphoric acid, H_3PO_4, above)

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?

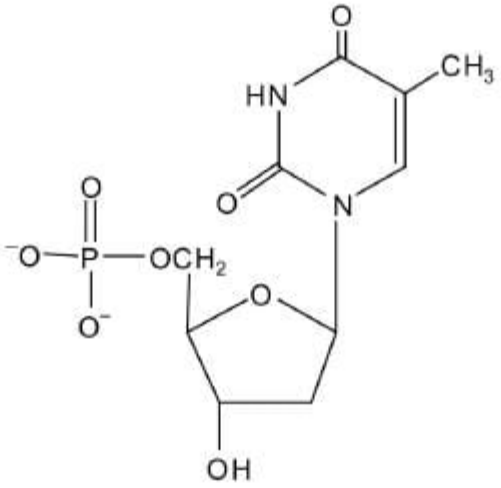
    a. RNA
    b. DNA

2. Identify the major nitrogenous bases in each nucleic acid.

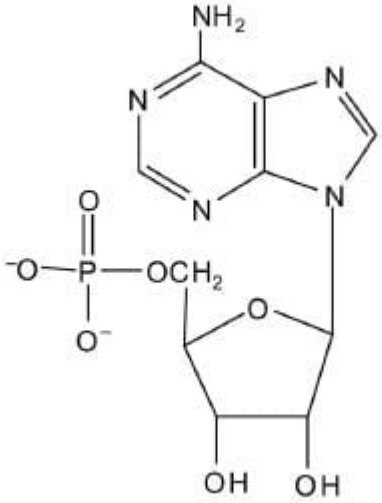
    a. DNA
    b. RNA

3. For each structure, circle the sugar unit and identify the nucleotide as a ribonucleotide or a deoxyribonucleotide.

a.

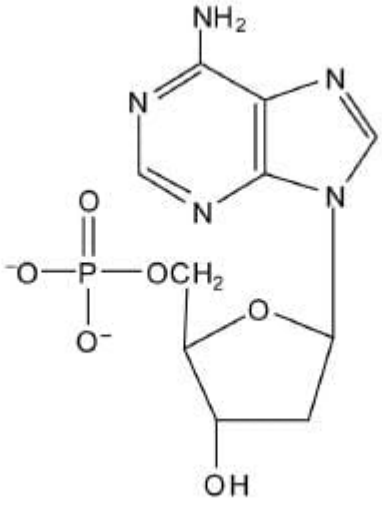


b.

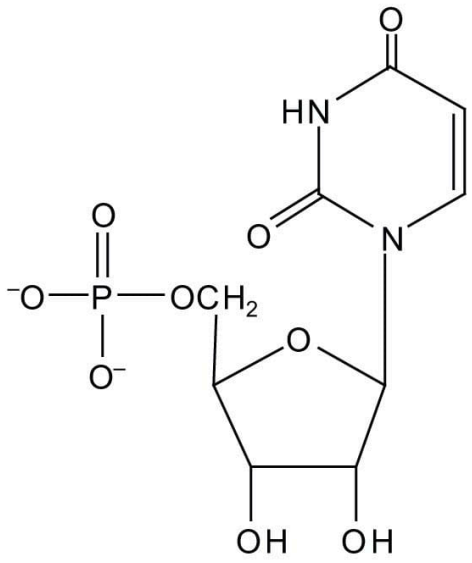


4. For each structure, circle the nitrogenous base and identify it as a purine or pyrimidine.

a.



b.

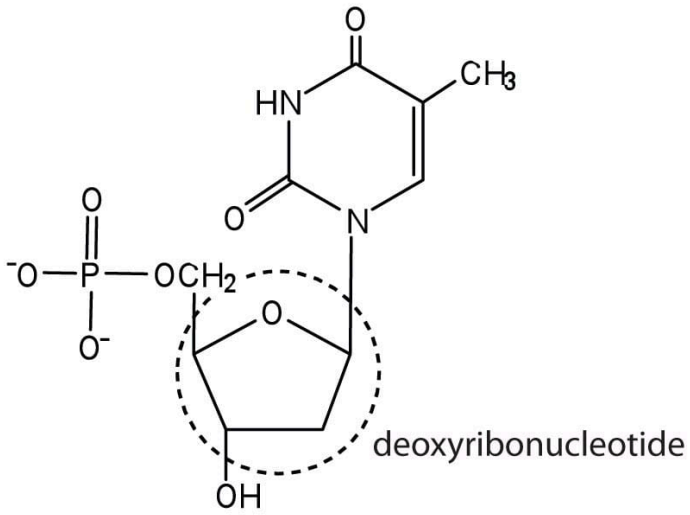


Answers

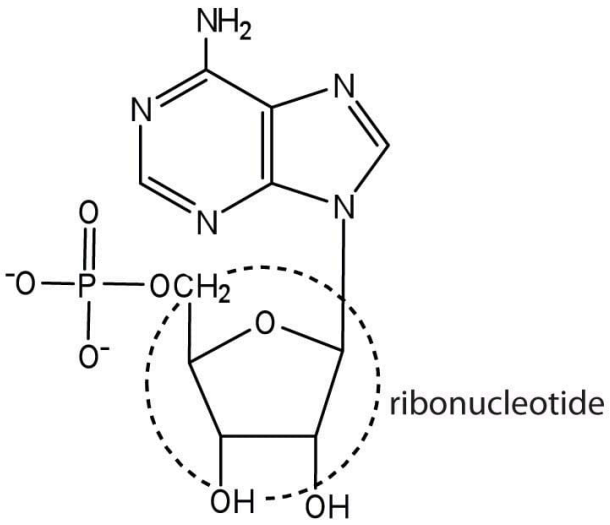
1. a. ribose
   b. deoxyribose

2. a. DNA includes T, C, A & G; b. RNA includes U, C, A & G

3. a.

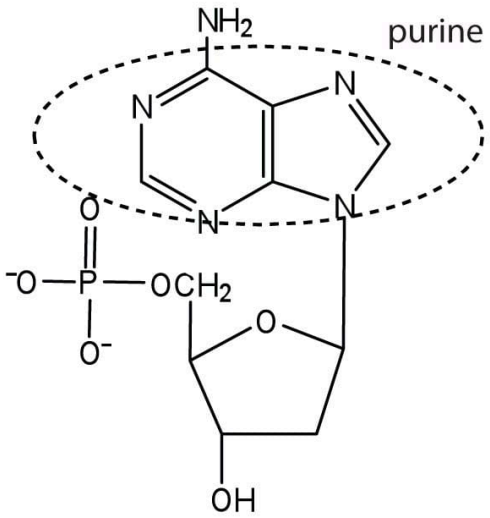


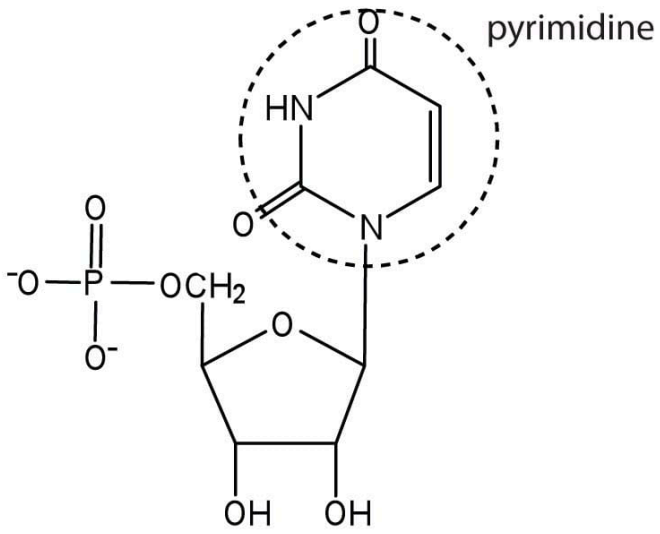
b.


NH2
N
N
N
N
O
-O—P—OCH2
O-
O
ribonucleotide
OH
OH

4.

a.


NH2
purine
N
N
N
N
O
-O—P—OCH2
O-
O
OH



b.

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15.2: 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 15.2.1). 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.

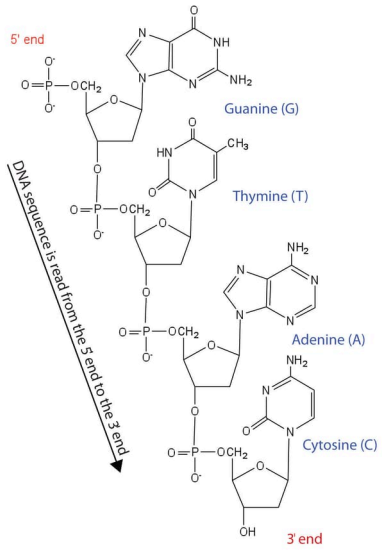


Figure 15.2.1 *Structure of a Segment of DNA. A similar segment of RNA would have OH groups on each C2', and uracil would replace thymine.*

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 15.2.1) 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 15.2.1 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 15.2.2).

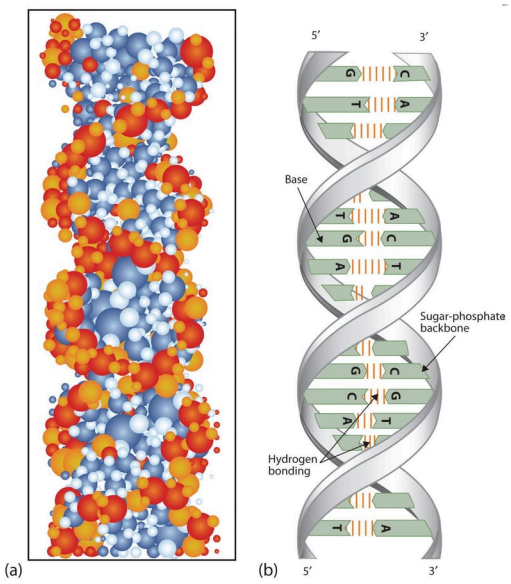


Figure 15.2.2 *DNA Double Helix. (a) This represents a computer-generated model of the DNA double helix. (b) This represents a schematic representation of the double helix, showing the complementary bases.*

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 15.2.3 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).

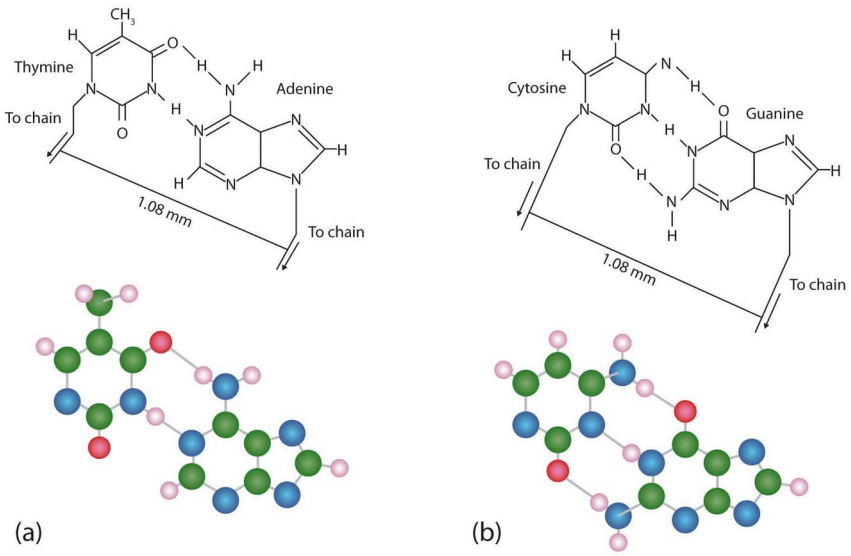


Figure 15.2.3 *Complementary Base Pairing. Complementary bases engage in hydrogen bonding with one another: (a) thymine and adenine; (b) cytosine and guanine.*

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 15.2.4. 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 15.2.3 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.

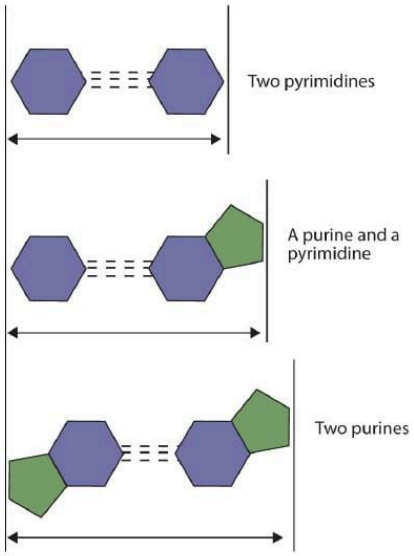


Figure 15.2.4 *Difference in Widths of Possible Base Pairs*

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

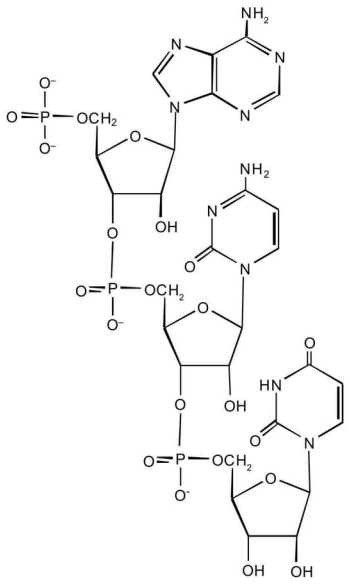
3. The width of the DNA double helix is kept at a constant width, rather than narrowing (if two pyrimidines were across from each other) or widening (if two purines were across from each other).

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. *(Use Figure 19.1.1 as a guide.)*



2. Which nitrogenous base in DNA pairs with each nitrogenous base?

   a. cytosine
   b. adenine

c. guanine
d. thymine

3. Which nitrogenous base in RNA pairs with each nitrogenous base?

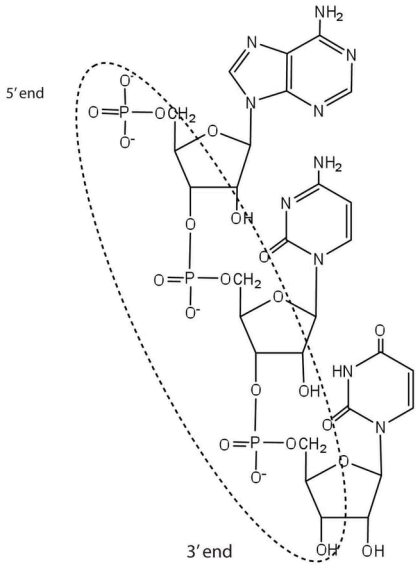
a. cytosine
b. adenine
c. guanine
d. thymine

4. How many hydrogen bonds can form between the two strands in the short DNA segment shown below?

5′ ATGCGACTA 3′ 3′ TACGCTGAT 5′

Answers

1.



c. ACU

2.

a. guanine
b. thymine
c. cytosine
d. adenine

3.

a. guanine
b. uracil
c. cytosine
d. adenine

4. 22 (2 between each AT base pair and 3 between each GC base pair)

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15.3: Replication and Expression of Genetic Information

Skills to Develop

- 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 15.3.1). 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.

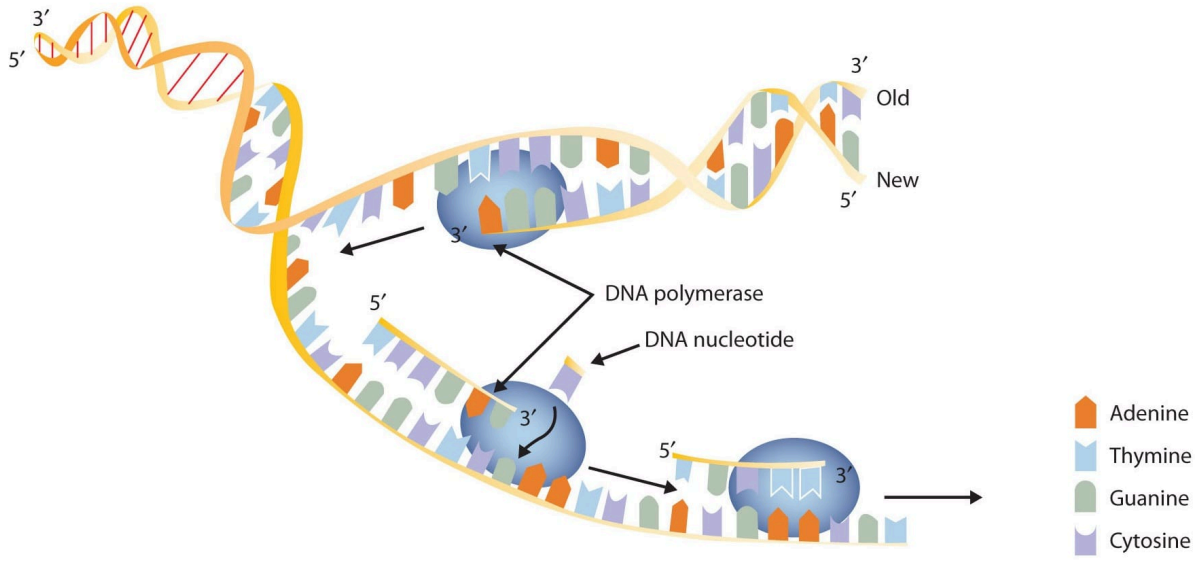


Figure 15.3.1***:*** *A Schematic Diagram of DNA Replication. DNA replication occurs by the sequential unzipping of segments of the double helix. Each new nucleotide is brought into position by DNA polymerase and is added to the growing strand by the formation of a phosphate ester bond. Thus, two double 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 15.3.1

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).

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 15.3.2). 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.

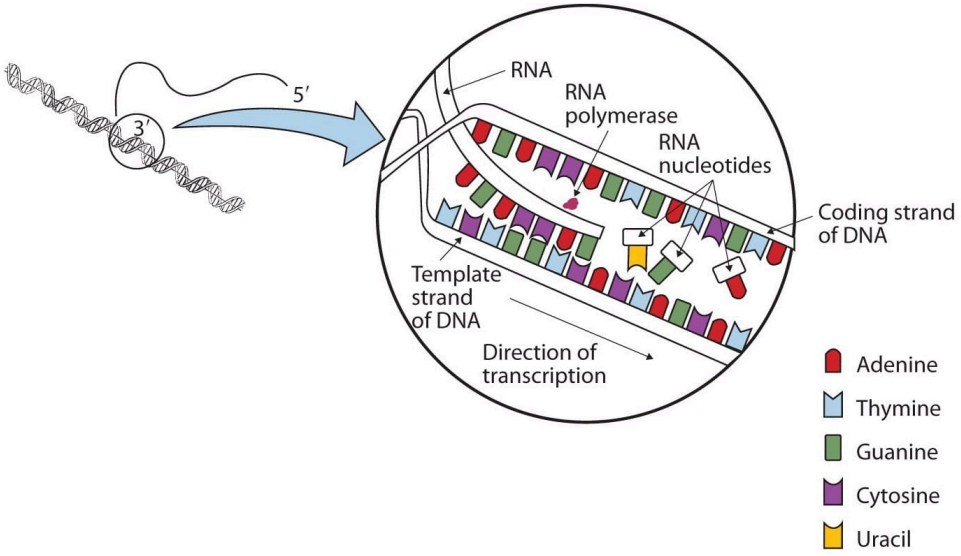


Figure 15.3.2***:*** *A Schematic Diagram of RNA Transcription from a DNA Template. The representation of RNA polymerase is proportionately much smaller than the actual molecule, which encompasses about 50 nucleotides at a time.*

Example 15.3.2

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′).

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 15.3.1). 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 15.3.1*: 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

Type	Function	Approximate Number of Nucleotides	Percentage of Total Cell RNA
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.

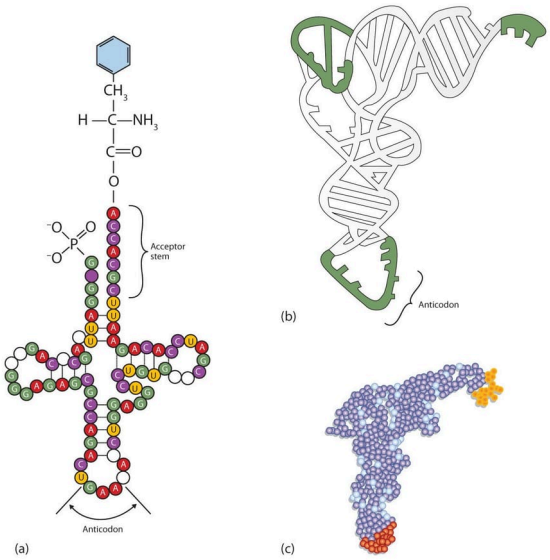


Figure 15.3.3***:*** *Transfer RNA. (a) In the two-dimensional structure of a yeast tRNA molecule for phenylalanine, the amino acid binds to the acceptor stem located at the 3′ end of the tRNA primary sequence. (The nucleotides that are not specifically identified here are slightly altered analogs of 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 15.3.3). 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.

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. 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?

Answers

1. Both processes require a template from which a complementary strand is synthesized.

2.

a. 3′-TACTCGCTGAAACGCCCTAAT-5′

b. 5′-AUGAGCGACUUUGCGGGAUUA-3′

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15.4: Protein Synthesis and the Genetic Code

Skills to Develop

- 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.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

***Video**: NDSU Virtual Cell Animations project animation "Translation". For more information, see http://vcell.ndsu.nodak.edu/animations*

The genetic code can therefore be described as the identification of each group of three nucleotides and its particular amino acid. The sequence of these triplet groups in the mRNA dictates the sequence of the amino acids in the protein. Each individual three-nucleotide coding unit, as we have seen, is called a *codon*.

Protein synthesis is accomplished by orderly interactions between mRNA and the other ribonucleic acids (transfer RNA [tRNA] and ribosomal RNA [rRNA]), the ribosome, and more than 100 enzymes. The mRNA formed in the nucleus during transcription is transported across the nuclear membrane into the cytoplasm to the ribosomes—carrying with it the genetic instructions. The process in which the information encoded in the mRNA is used to direct the sequencing of amino acids and thus ultimately to synthesize a protein is referred to as translation.

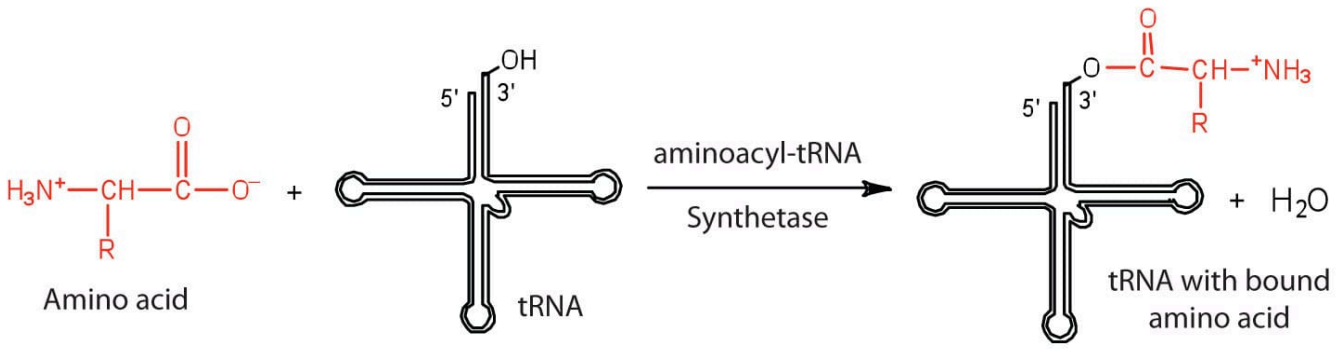


Figure 15.4.1*: Binding of an Amino Acid to Its tRNA*

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 15.4.1). 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 15.4.2 depicts a schematic stepwise representation of this all-important process.

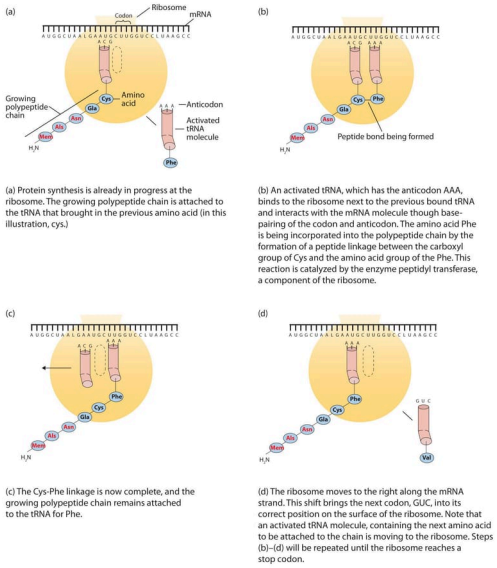


Figure 15.4.2***:*** *The Elongation Steps in Protein Synthesis*

Early experimenters were faced with the task of determining which of the 64 possible codons stood for each of the 20 amino acids. The cracking of the genetic code was the joint accomplishment of several well-known geneticists—notably Har Khorana, Marshall Nirenberg, Philip Leder, and Severo Ochoa—from 1961 to 1964. The genetic dictionary they compiled, summarized in Figure 15.4.3, 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.

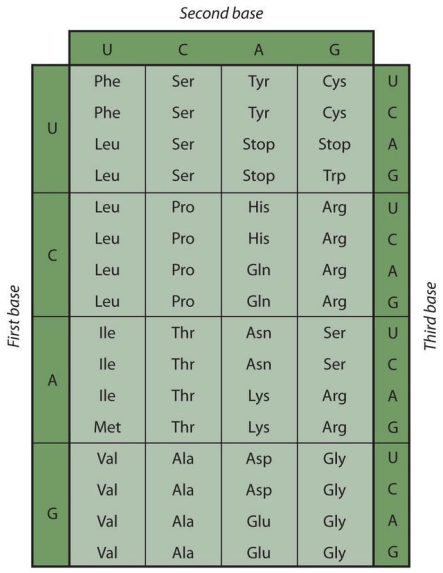


Figure 15.4.3***:*** *The Genetic Code*

Example 15.4.1: Using the Genetic Code

A portion of an mRNA molecule has the sequence 5′-AUGCCACGAGUUGAC-3′. What amino acid sequence does this code for? *(Use Figure 19.4.3 above.)*

SOLUTION

Use Figure 15.4.3 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.

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.

Concept Review Exercises

1. What are the roles of mRNA and tRNA in protein synthesis?
2. How many termination codons are there (and what are they)?
3. What happens when a termination codon is reached during translation?

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. Three (STOP): UAA, UAG, and UGA
3. They are recognized by special proteins called release factors, which signal the end of the translation process. (i.e. It stops adding any more amino acids and releases the completed protein.)

Exercises

1. Use Figure 15.4.3 to identify the amino acids coded for each mRNA molecule in below.

    a. 5′-UUU-3′

    b. 5′-CAU-3′

    c. 5′-AGC-3′

    d. 5′-CCG-3′

2. Use Figure 15.4.3 to determine the amino acid sequence produced from this mRNA sequence: 5′-AUGAGCGACUUUGCGGGAUUA-3′.

Answers

1. a. 3′-AAA-5′ phenyalanine

    b. 3′-GUA-5′ histidine

    c. 3′-UCG-5′ serine

    d. 3′-GGC-5′ proline

4. met-ser-asp-phe-ala-gly-leu

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15.5: Mutations and Genetic Diseases

Skills to Develop

- 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 15.5.1). 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.

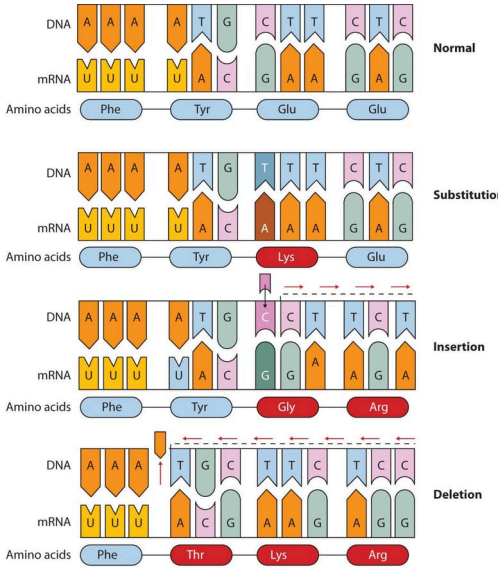


Figure 15.5.1*: Three Types of Point Mutations*

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 15.5.2). 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.

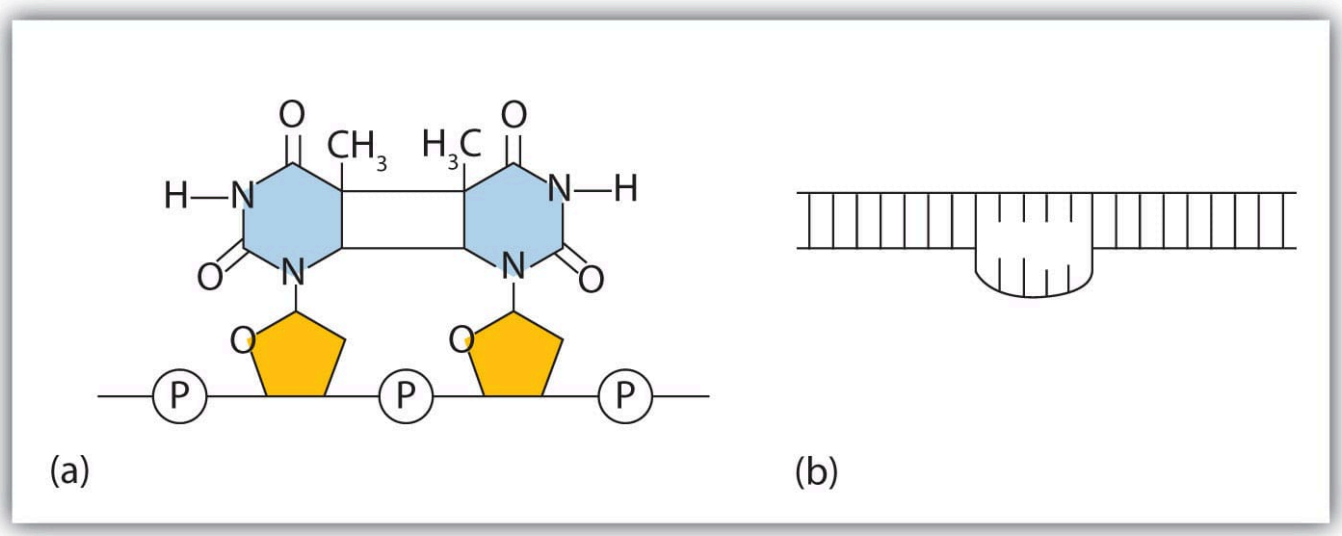


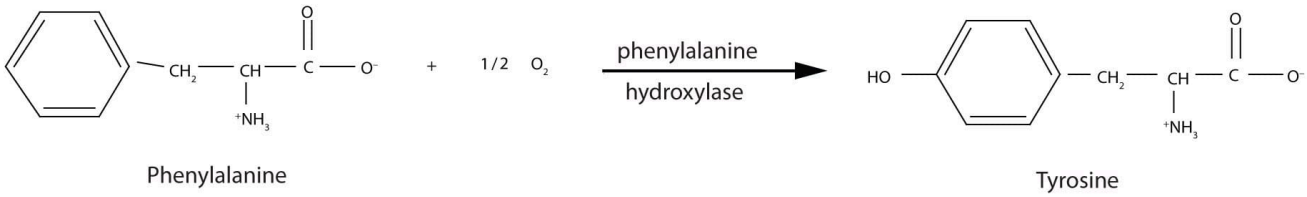
Figure 15.5.2*: An Example of Radiation Damage to DNA. (a) The thymine dimer is formed by the action of UV light. (b) When a defect in the double strand is produced by the thymine dimer, this defect temporarily stops DNA replication, but the dimer can be removed, and the region can be repaired by an 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 15.5.1, 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 15.5.1***:*** *Some Representative Genetic Diseases in Humans and the Protein or Enzyme Responsible*

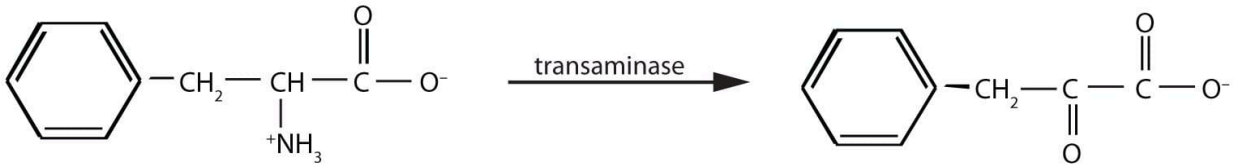
Disease	Responsible Protein or Enzyme
alkaptonuria	homogentisic acid oxidase
galactosemia	galactose 1-phosphate uridyl transferase, galactokinase, or UDP galactose epimerase
Gaucher disease	glucocerebrosidase
gout and Lesch-Nyhan syndrome	hypoxanthine-guanine phosphoribosyl transferase
hemophilia	antihemophilic 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.



Phenylalanine Tyrosine

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.



Phenylalanine Phenylpyruvate

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.

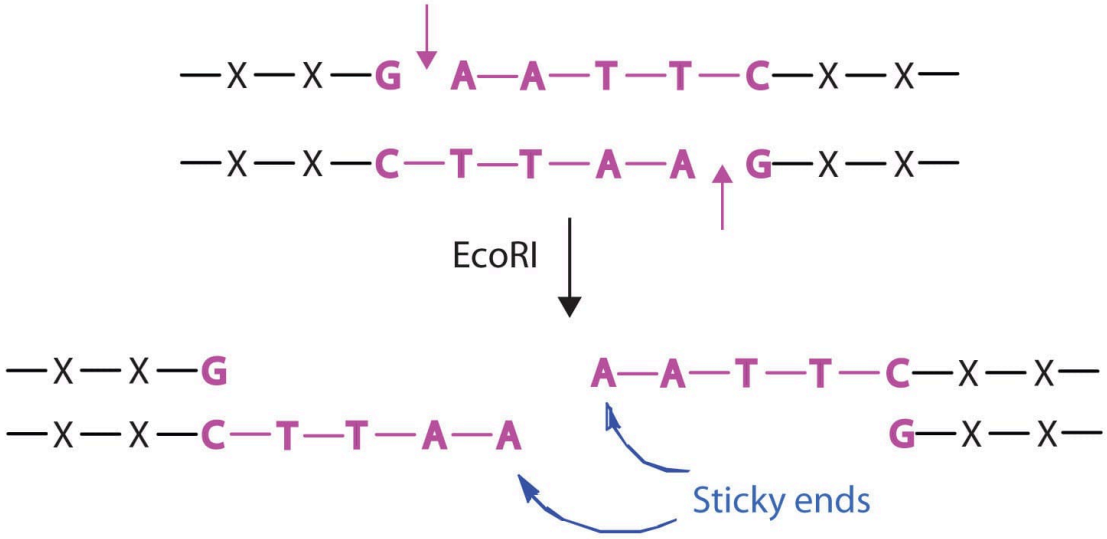
Several genetic diseases are collectively categorized as *lipid-storage diseases*. Lipids are constantly being synthesized and broken down in the body, so if the enzymes that catalyze lipid degradation are missing, the lipids tend to accumulate and cause a variety of medical problems. When a genetic 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

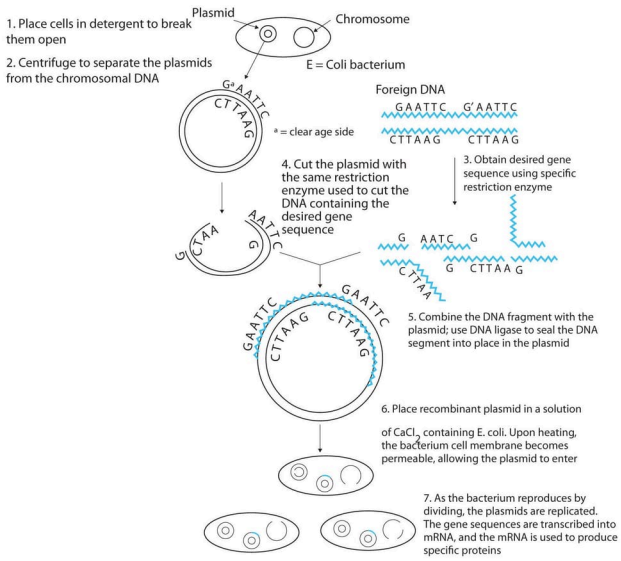
the enormous amount of a cell's DNA, only a minute portion of which contains the gene sequence. Thus, the first task is to obtain smaller pieces of DNA that can be more easily handled. Fortunately, researchers are able to use *restriction enzymes* (also known as restriction endonucleases), discovered 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.

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 15.4.3)?

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 15.4.3)?
3. a. What is a mutagen?
   b. Give two examples of mutagens.

Answers

1. a. substitution
   b. Phenylalanine (UUU) would be replaced with leucine (CUU), but no other amino acids in the protein would change (probably small or moderate affect on protein function).

2. a. deletion; b. All of the amino acids, starting from the mutation, Lys (AAA) --> Tyr (AAC), and continuing on will likely be changed due to this frame shift (likely having catastrophic impact on the protein function).

3. a. a chemical or physical agent that can cause a mutation
   b. UV radiation and gamma radiation (answers will vary)

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15.6: Viruses

Skills to Develop

- 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 15.6.1).

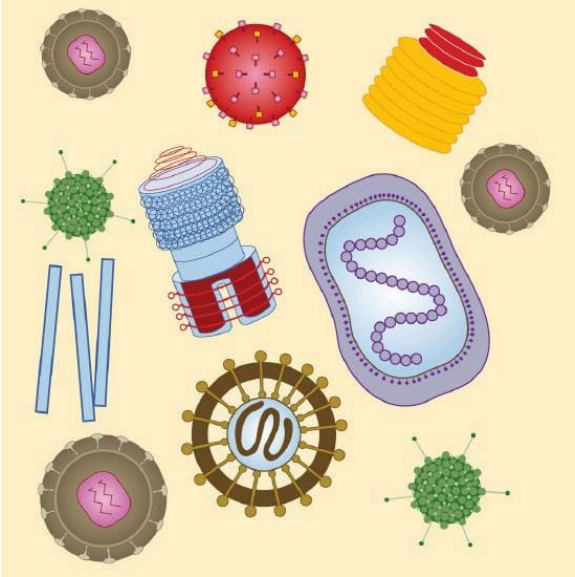


Figure 15.6.1***:*** *Viruses. Viruses come in a variety of shapes that are determined by their protein coats.*

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 15.6.2), 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.

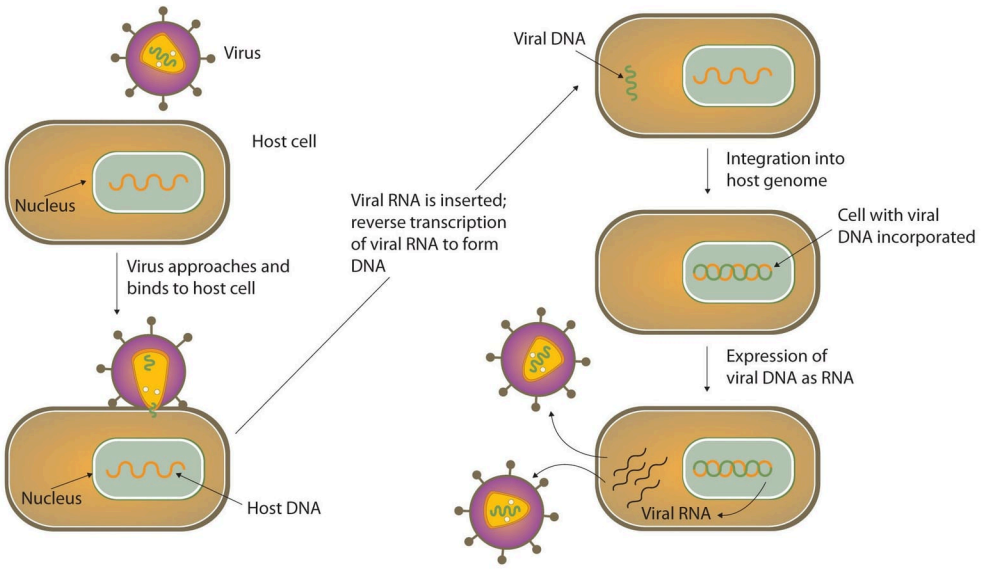
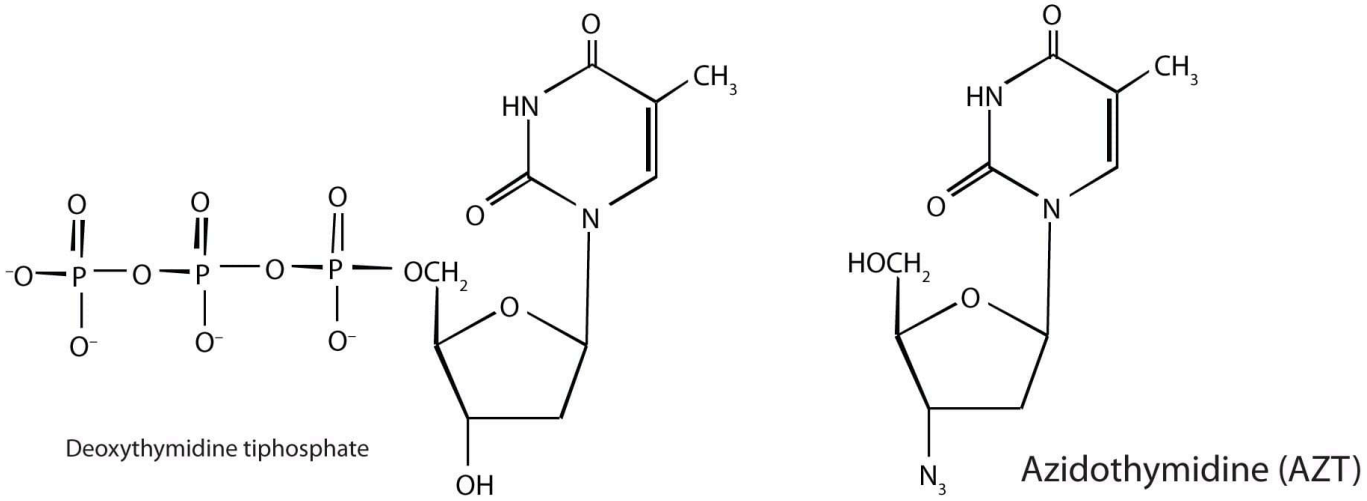
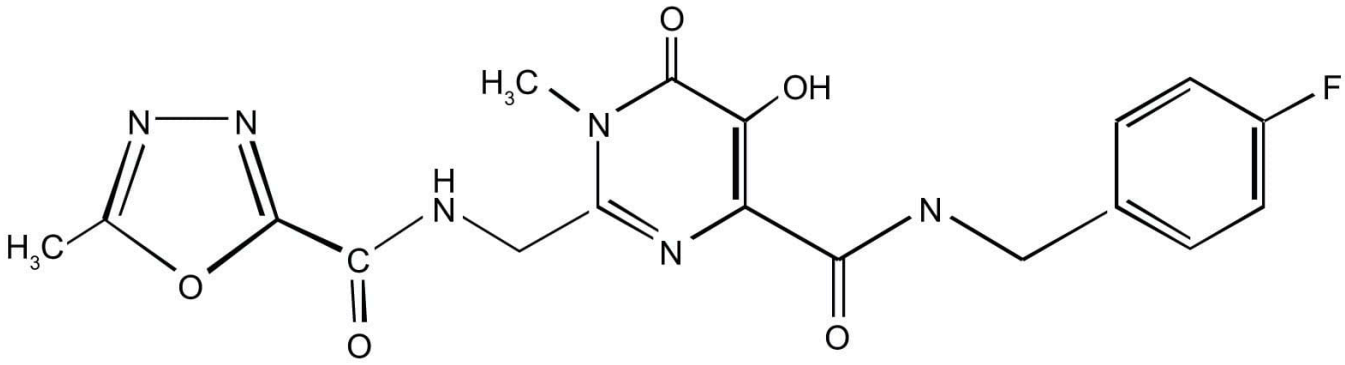


Figure 15.6.2*: Life Cycle of a Retrovirus*

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.



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, http://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).

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.

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.

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15.7: Chapter 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**.

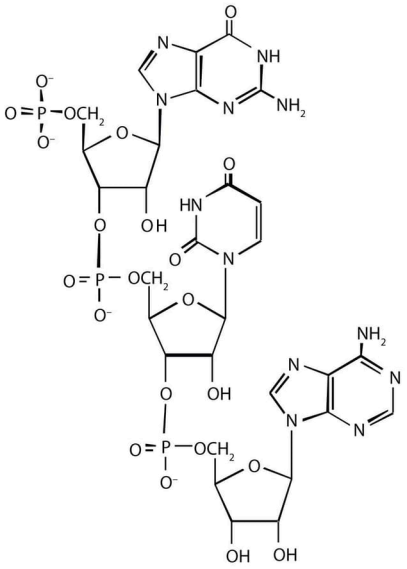
Viruses are infectious agents composed of a tightly packed central core of nucleic acids enclosed by a protective shell of proteins. Viruses contain either DNA or RNA as their genetic material but not both. Some RNA viruses, called **retroviruses**, synthesize DNA in the host cell from their RNA genome. The human immunodeficiency virus (HIV) causes acquired immunodeficiency syndrome (AIDS).

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15.E: Exercises

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. (Use Figure 15.1.1 to identify each base.)

2. 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?

3. 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 part b?

4. A particular DNA coding segment is 5'-ACGTTA**G**CCCCAGCT-3'.

   A) Write the sequence of nucleotides in the corresponding mRNA. B) Determine the amino acid sequence formed from the mRNA in part a during translation.; B) What amino acid sequence results from each of the following mutations? a. deletion of the underlined guanine; b. insertion of thymine immediately after the underlined guanine; c. replacement of the underlined guanine by adenine

Answers

1. a. RNA; the sugar is ribose, rather than deoxyribose; b. 5′-GUA-3′

2. 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.

3. a. Each strand would be replicated, resulting in two double-stranded segments.

(More specifically, the original coding strand, 5′-ATGAGGCATGAGACG-3′, would be paired with a new copy of the template strand, 3′-TACTCCGTACTCTGC-5′.

The original template strand, 3′-TACTCCGTACTCTGC-5′, would be paired with a new copy of the coding strand, 5′-ATGAGGCATGAGACG-3′.)

b. mRNA = 5'-AUGAGGCAUGAGACG-3' c. peptide = met-arg-his-glu-thr

4.

A) mRNA = 5′-ACGUUAGCCCCAGCU-3′; B) Thr-Leu-Ala-Pro-Ala; C) a. Thr-Leu-Pro-Gln-(incomplete triplet codon), b. Thr-Leu-Val-Pro-Ser-(incomplete codon), c. Thr-Leu-Ser-Pro-Ala

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16: 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.

16.0: Introduction to Metabolism

16.1: ATP: the Universal Energy Currency

16.2: Stage I of Catabolism

16.3: Overview of Stage II of Catabolism

16.4: Stage III of Catabolism

16.5: Stage II of Carbohydrate Catabolism

16.6: Stage II of Lipid Catabolism

16.7: Stage II of Protein Catabolism

16.8: Chapter Summary

16.E: Exercises

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16.0: Introduction to 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.

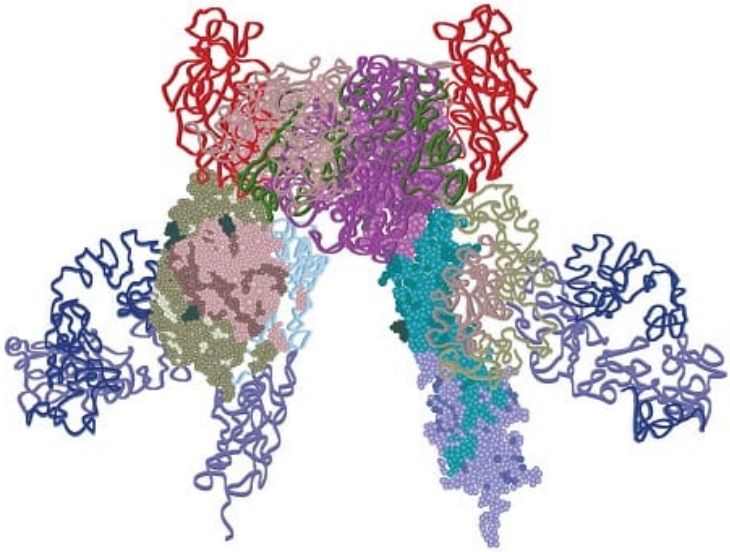


Figure 16.0.1***:*** *Model of the Structure of the Insulin Receptor*

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 (Figure Figure 16.0.2). 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.

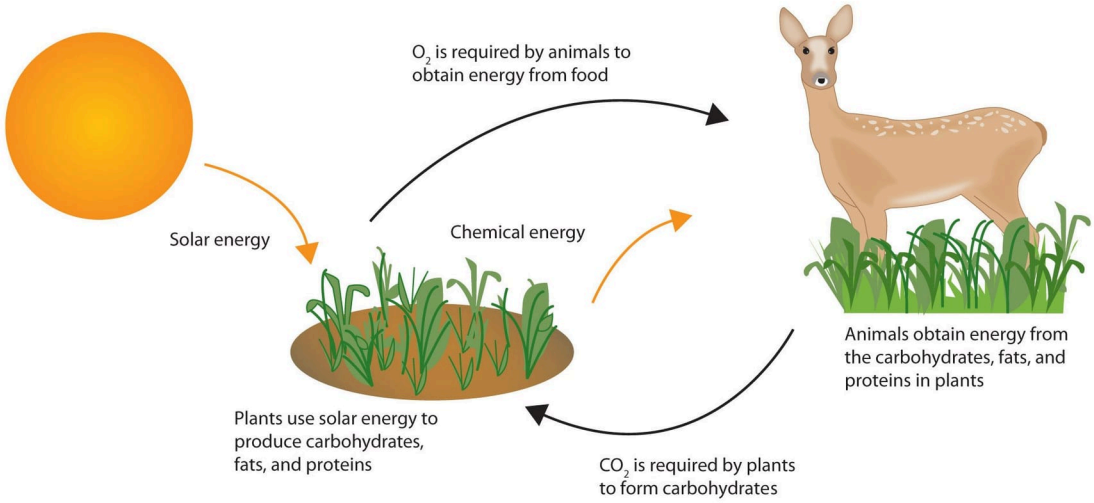


Figure 16.0.2***:*** *Some Energy Transformations in Living Systems*

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.

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**: $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + 670$ kcal
- **Lipid**: $C_{16}H_{32}O_2 + 23O_2 \rightarrow 16CO_2 + 16H_2O + 2{,}385$ kcal

These two equations summarize the biological combustion of a carbohydrate and a lipid by the cell through respiration. Respiration is the collective name for all metabolic processes in which gaseous oxygen is used to oxidize organic matter to carbon dioxide, water, and energy.

Like the combustion of the common fuels we burn in our homes and cars (wood, coal, gasoline), respiration uses oxygen from the air to break down complex organic substances to carbon dioxide and water. But the energy released in the burning of wood is manifested entirely in the form of heat, and excess heat energy is not only useless but also injurious to the living cell. Living organisms instead conserve much of the energy respiration releases by channeling it into a series of stepwise reactions that produce adenosine triphosphate (ATP) or other compounds that ultimately lead to the synthesis of ATP. The remainder of the energy is released as heat and manifested as body temperature.

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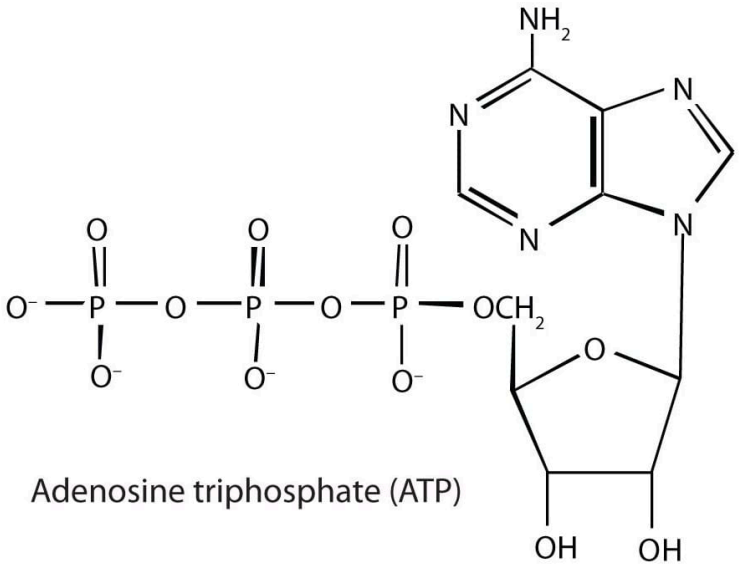
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16.1: ATP: the Universal Energy Currency

Skills to Develop

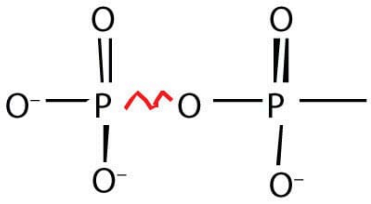
- To describe the importance of ATP as a source of energy in living organisms.

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.



Adenosine triphosphate (ATP)

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).

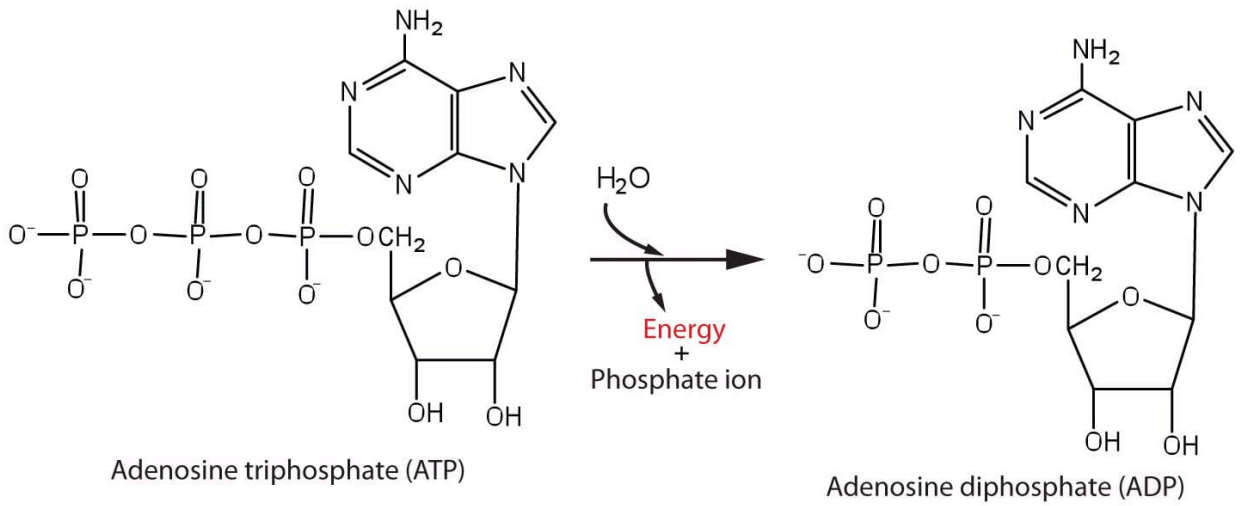


Figure 16.1.1***:*** *Hydrolysis of ATP to Form ADP*

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:

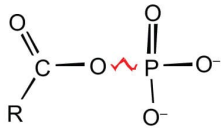
$$ATP + H_2O \rightarrow ADP + P_i + 7.4\ kcal/mol \tag{16.1.1}$$

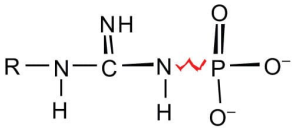
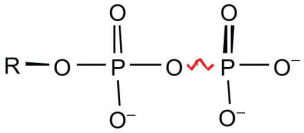
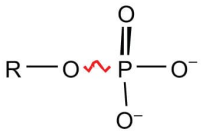
If the hydrolysis of ATP releases energy, its synthesis (from ADP) requires energy. In the cell, ATP is produced by those processes that supply energy to the organism (absorption of radiant energy from the sun in green plants and breakdown of food in animals), and it is hydrolyzed by those processes 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 16.1.1. 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 16.1.1***:*** *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
***PP$_i$ is the pyrophosphate ion.**		

Type	Example	Energy Released (kcal/mol)
guanidine phosphates 	creatine phosphate	−10.3
	arginine phosphate	−9.1
pyrophosphates 	PP_i* → $2P_i$	−7.8
	ATP → AMP + PP_i	−7.7
	ATP → ADP + P_i	−7.5
	ADP → AMP + P_i	−7.5
sugar phosphates 	glucose 1-phosphate	−5.0
	fructose 6-phosphate	−3.8
	AMP → 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.

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

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16.2: Stage I of Catabolism

Skills to Develop

- 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 16.2.1). 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.

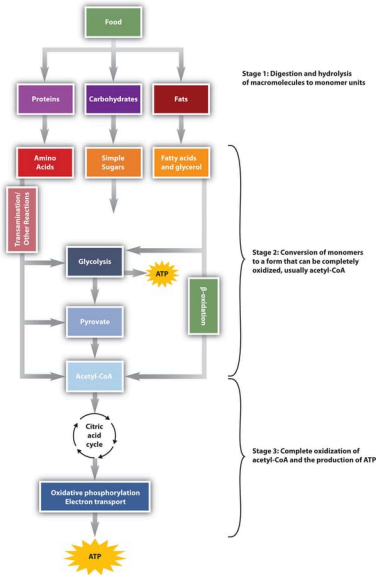


Figure 16.2.1***:*** *Energy Conversions*

The conversion of food into cellular energy (as ATP) occurs in three stages.

Digestion of Carbohydrates

Carbohydrate digestion begins in the mouth (Figure 16.2.2) 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.

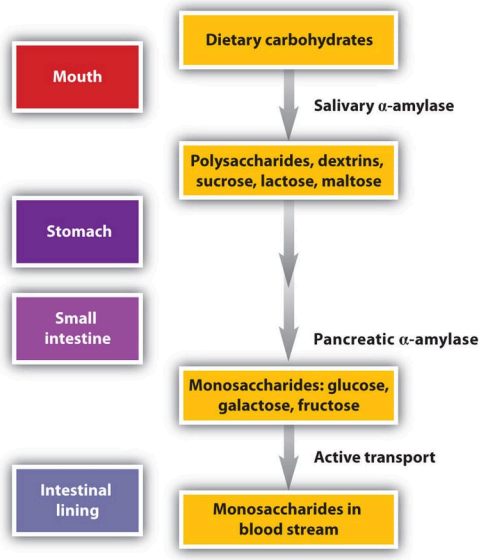


Figure 16.2.2***:*** *The Principal Events and Sites of Carbohydrate Digestion*

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 16.2.3), 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.

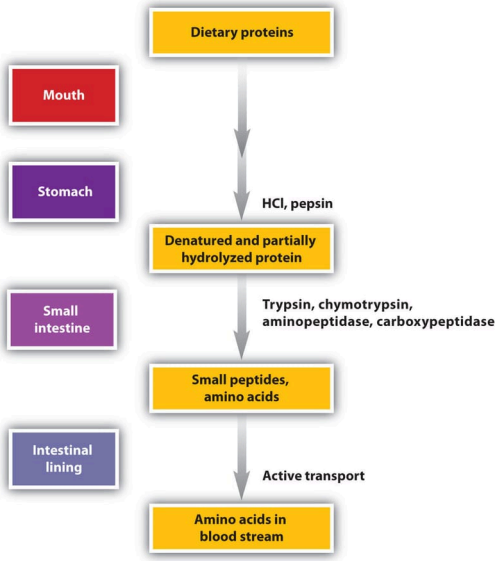


Figure 16.2.3***:*** *The Principal Events and Sites of Protein Digestion*

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 16.2.4): 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.

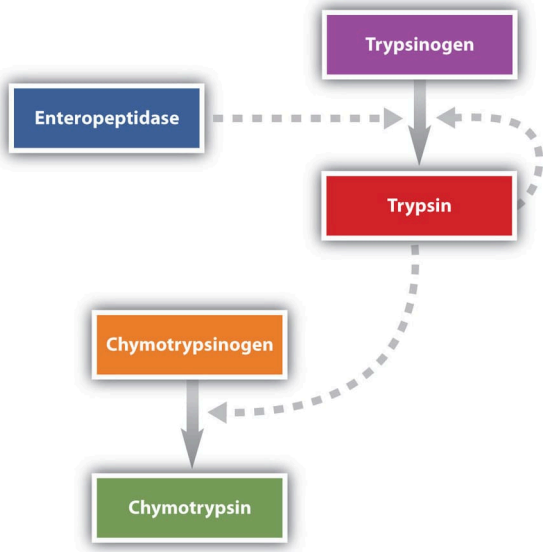


Figure 16.2.4***:*** *Activation of Some Pancreatic Enzymes in the Small Intestine*

Aminopeptidases in the intestinal juice remove amino acids from the N-terminal end of peptides and proteins possessing a free amino group. Figure 16.2.5 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.

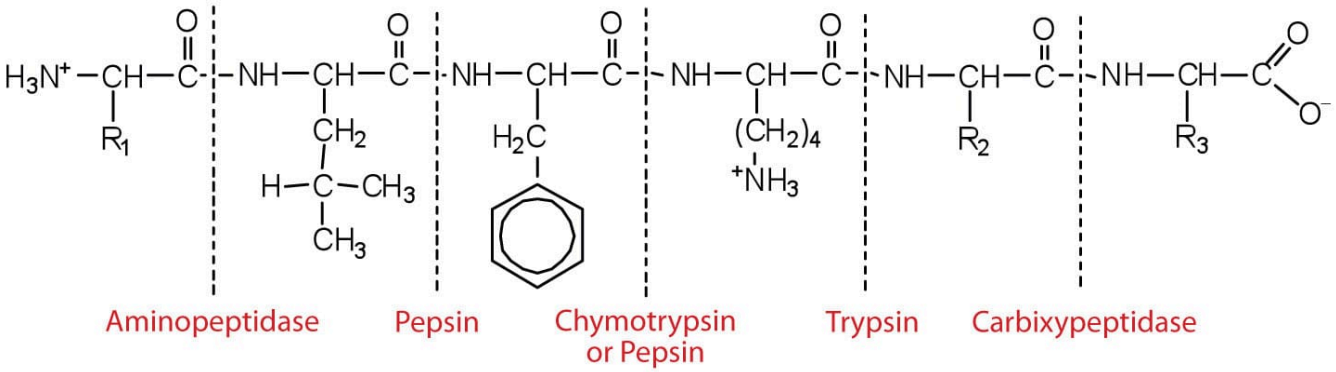


Figure 16.2.5***:*** *Hydrolysis of a Peptide by Several Peptidases*

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 16.2.6). 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.

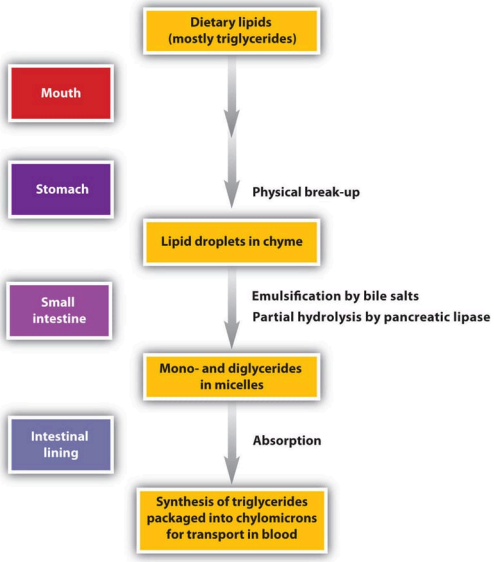
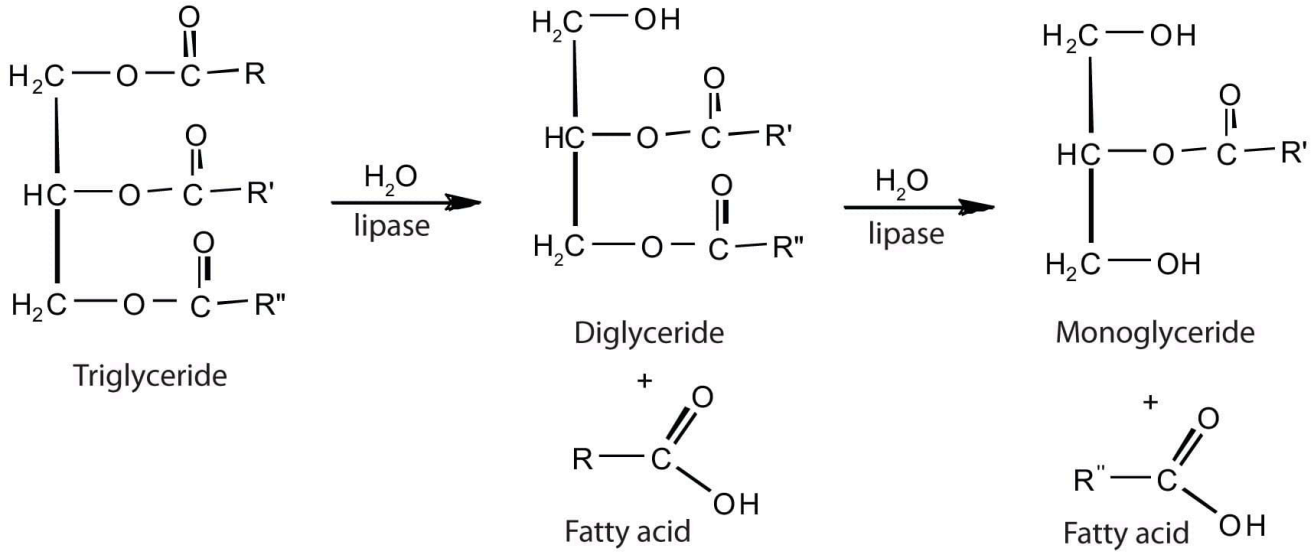


Figure 16.2.6***:*** *The Principal Events and Sites of Lipid (Primarily Triglyceride) Digestion*

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.

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

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16.3: Overview of Stage II of Catabolism

Skills to Develop

- 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.

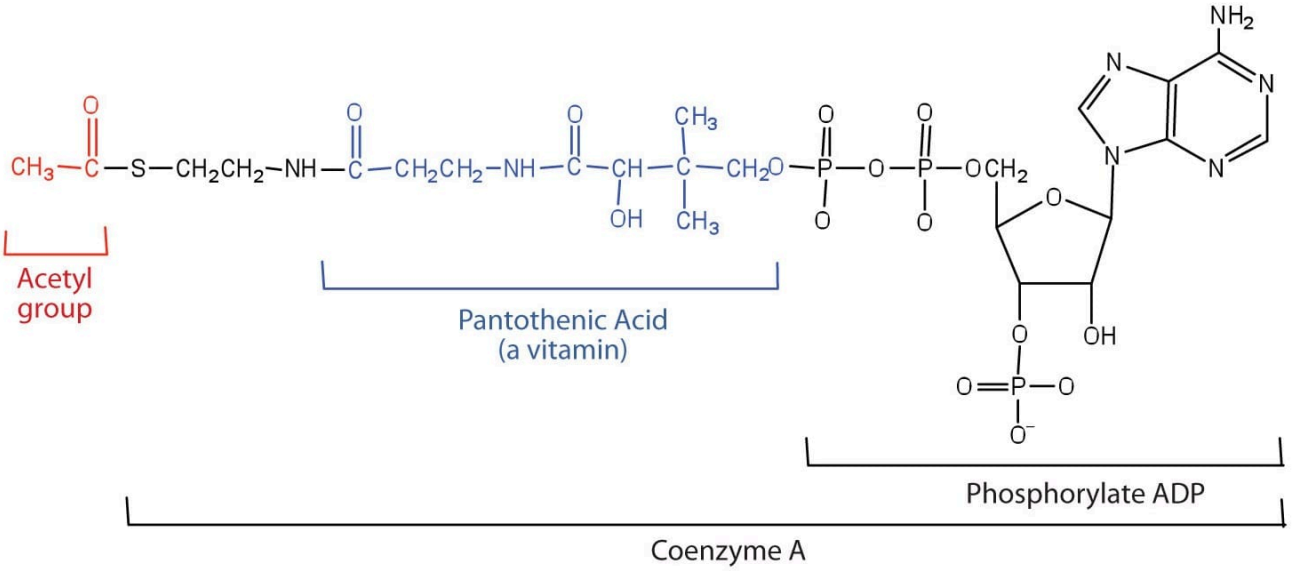


Figure 16.3.1***:*** *The Structure of Acetyl-Coenzyme A (Acetyl-CoA)*

Acetyl-CoA is shown in Figure 16.3.1. 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 16.3.1.

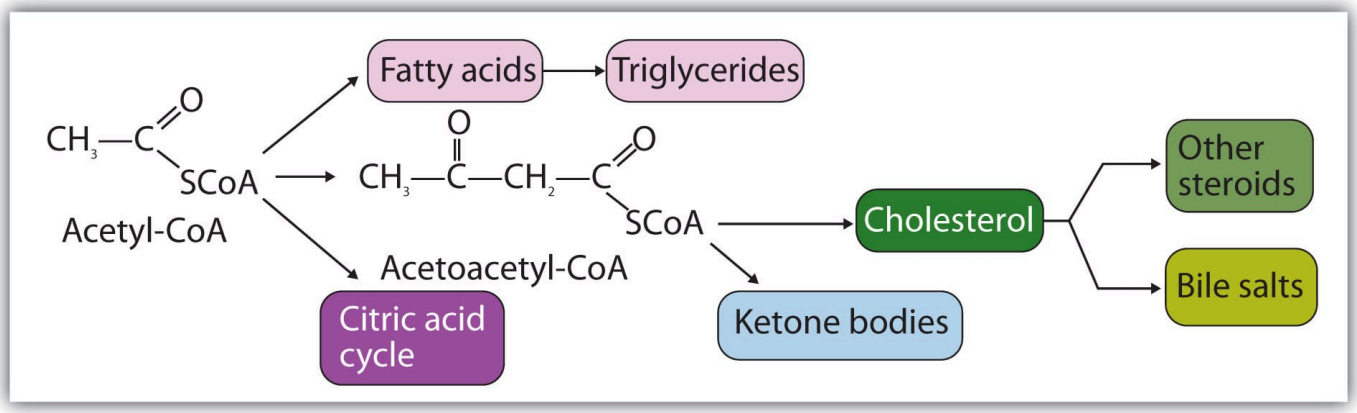


Figure 16.3.2***:*** *Cell Chemistry. Acetyl-CoA plays a variety of roles in cell chemistry.*

Glycolosis

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.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Video: 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 http://vcell.ndsu.edu/animations.

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 16.3.3.

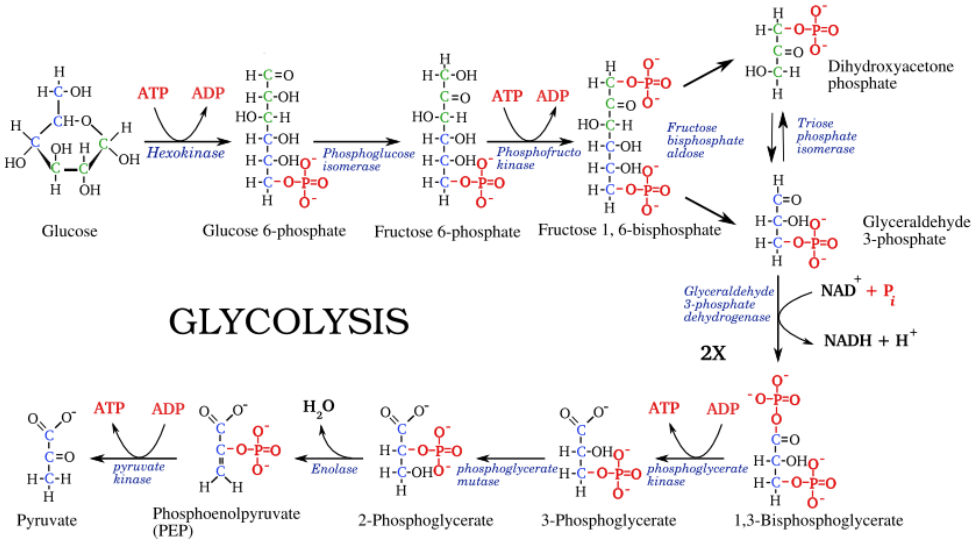


Figure 16.3.3*: Glycolysis pathway. Image used with permission from Wikipedia.*

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.

YouTube Video

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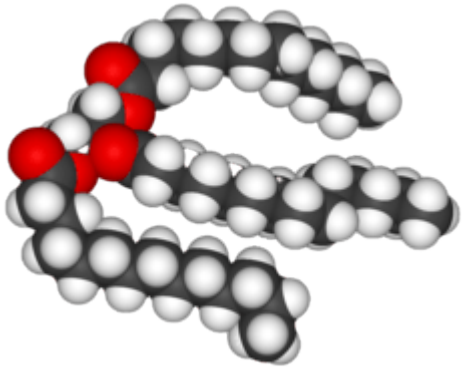
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Video: Fatty acid metabolism / beta oxidation / β-Oxidation

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.



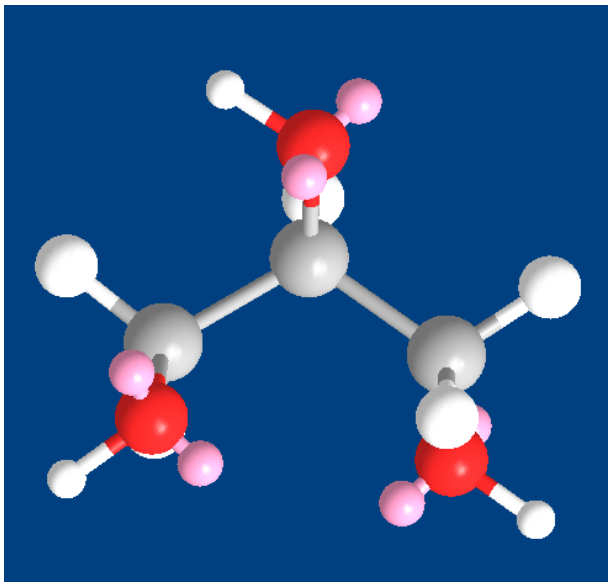


Figure 16.3.4***:*** *Key molecules in beta-oxidation: (left) A triglyceride molecule, (middle) Glycerol, (right) Fatty Acids (unsaturated)*

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.

Beta-Oxidation1.svg

Hydration Step

The trans alkene is then hydrated with the help of Enoyl-CoA hydratase

Beta-Oxidation2.svg

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.

Beta-Oxidation3.svg

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.

Beta-Oxidation4.svg

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.

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

Contributors

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16.4: Stage III of Catabolism

Skills to Develop

- 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 thecitric 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 16.4.1). 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 16.4.1, 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.

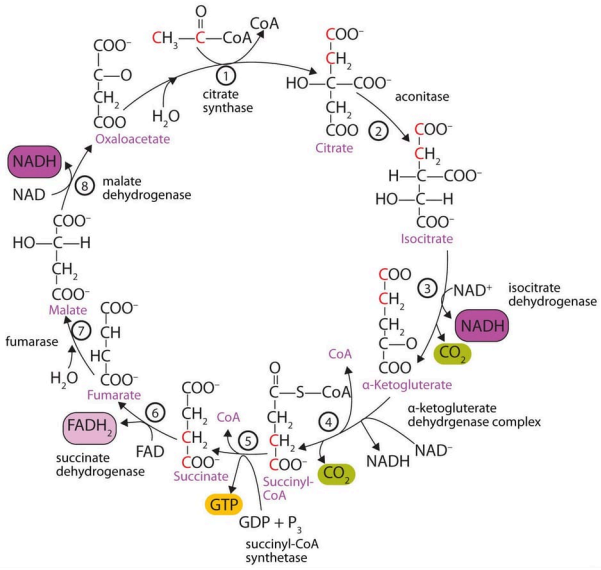


Figure 16.4.1***:*** *Reactions of the Citric Acid Cycle*

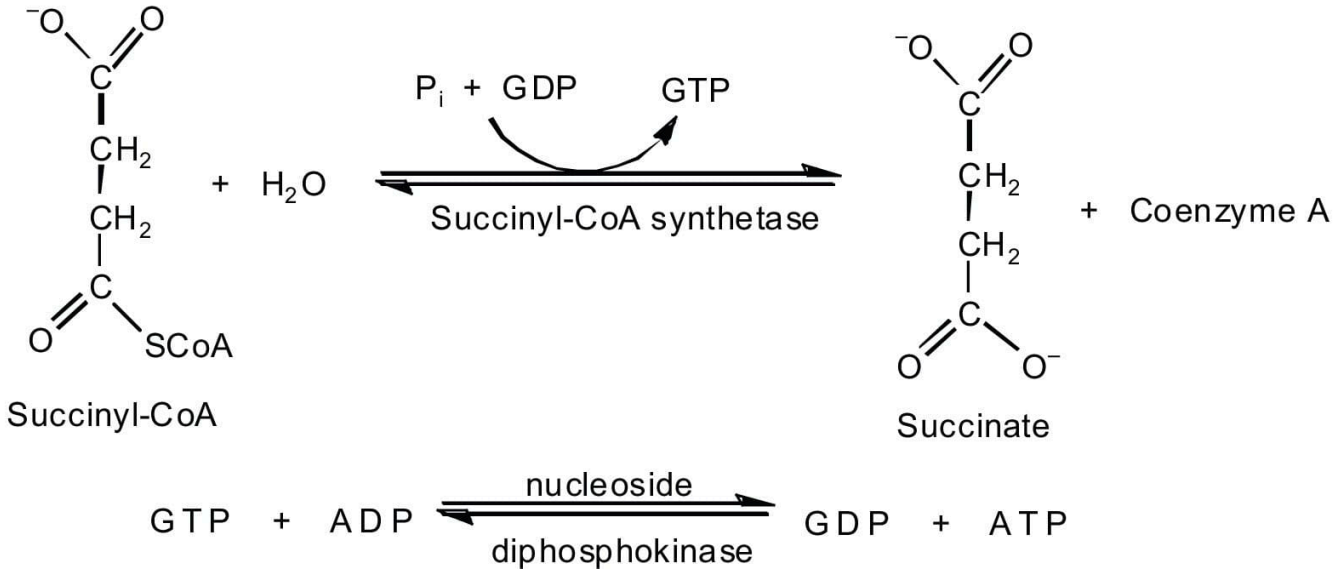
1. In the first step, acetyl-CoA enters the citric acid cycle, and the acetyl group is transferred onto oxaloacetate, yielding citrate. Note that this step releases coenzyme A. The reaction is catalyzed by *citrate synthase*.
2. In the next step, *aconitase* catalyzes the isomerization of citrate to 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.

YouTube Video

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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 http://vcell.ndsu.edu/animations.

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 16.4.2). 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.

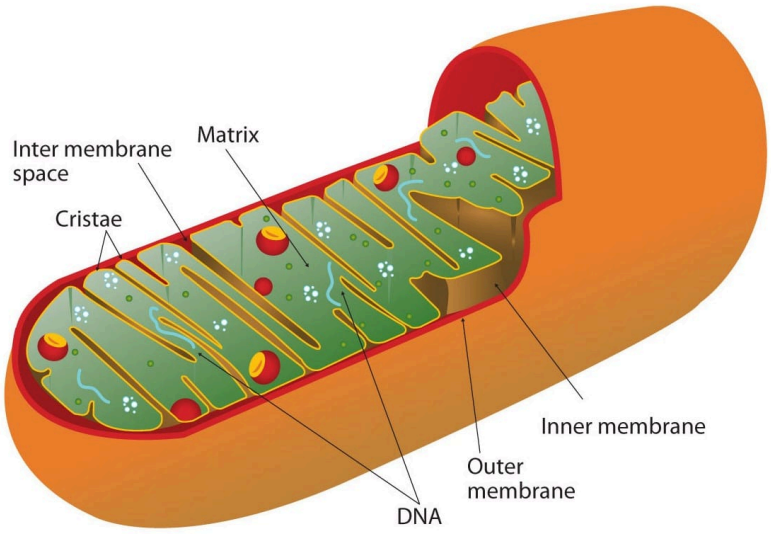


Figure 16.4.2**:** *Respiration*

Cellular respiration occurs in the mitochondria

Figure 16.4.2 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 16.4.3 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.

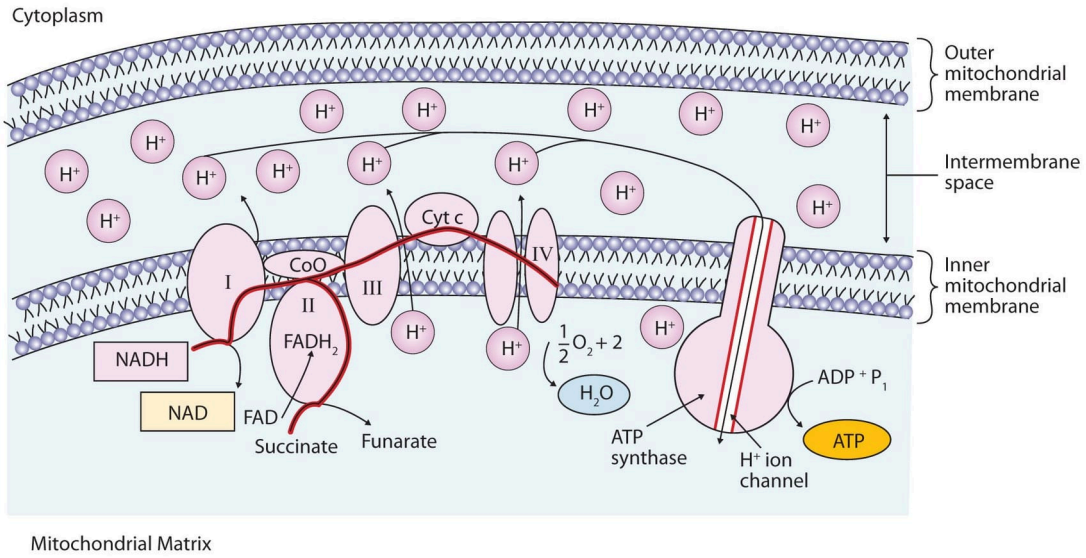
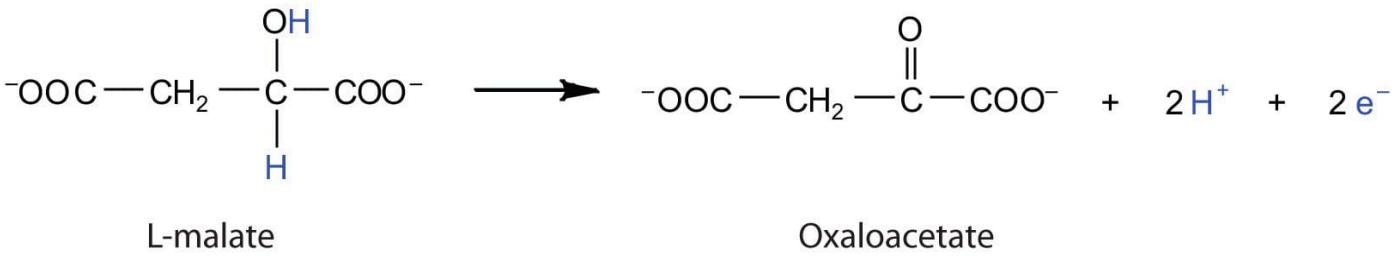


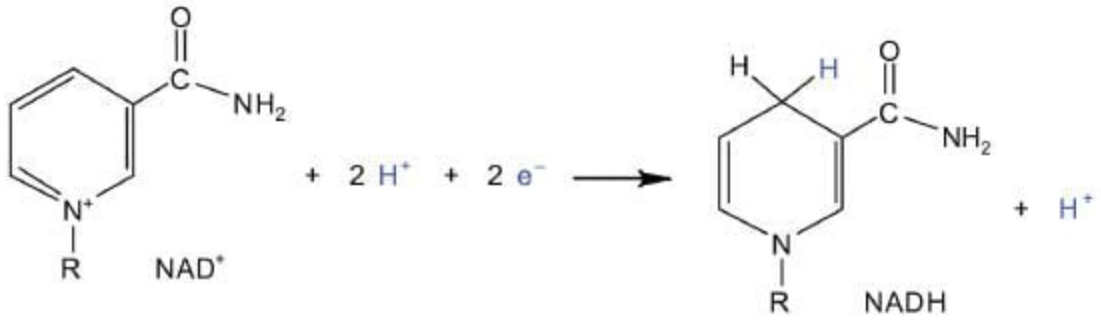
Figure 16.4.3***:*** *The Mitochondrial Electron Transport Chain and ATP Synthase. The red line shows the path of electrons.*

Electrons can enter the electron transport chain through either complex I or II. We will look first at electrons entering at complex I. These electrons come from NADH, which is formed in three reactions of the citric acid cycle. Let's use step 8 as an example, the reaction in which L-malate is oxidized to oxaloacetate and NAD^+ is reduced to NADH. This reaction can be divided into two half reactions:

- *Oxidation half-reaction*:



- *Reduction half-reaction*:

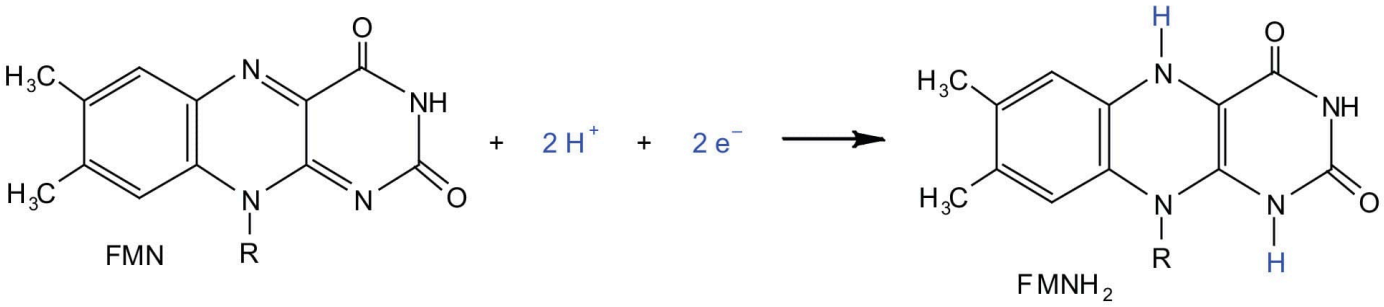


In the oxidation half-reaction, two hydrogen (H^+) ions and two electrons are removed from the substrate. In the reduction half-reaction, the NAD^+ molecule accepts both of those electrons and one of the H^+ ions. The other H^+ ion is transported from the matrix, across the inner mitochondrial membrane, and into the intermembrane space. The NADH diffuses through the matrix and is bound by complex I of the electron transport chain. In the complex, the coenzyme flavin mononucleotide (FMN) accepts both electrons from NADH. By passing the electrons along, NADH is oxidized back to NAD^+ and FMN is reduced to $FMNH_2$ (reduced form of flavin mononucleotide). Again, the reaction can be illustrated by dividing it into its respective half-reactions.

- *Oxidation half-reaction*:



- *Reduction half-reaction*:



Complex I contains several proteins that have iron-sulfur (Fe·S) centers. The electrons that reduced FMN to $FMNH_2$ are now transferred to these proteins. The iron ions in the Fe·S centers are in the Fe(III) form at first, but by accepting an electron, each ion is reduced to the Fe(II) form. Because each Fe·S center can transfer only one electron, two centers are needed to accept the two electrons that will regenerate FMN.

- *Oxidation half-reaction*:

$$FMNH_2 \rightarrow FMN + 2H^+ + 2e^- \tag{16.4.1}$$

- *Reduction half-reaction*:

$$2Fe(III) \cdot S + 2e^- \rightarrow 2Fe(II) \cdot S \tag{16.4.2}$$

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*:

$$FADH_2 \rightarrow FAD + 2H^+ + 2e^- \tag{16.4.3}$$

Reduction half-reaction:

$$2Fe(III) \cdot S + 2e^- \rightarrow 2Fe(II) \cdot S \tag{16.4.4}$$

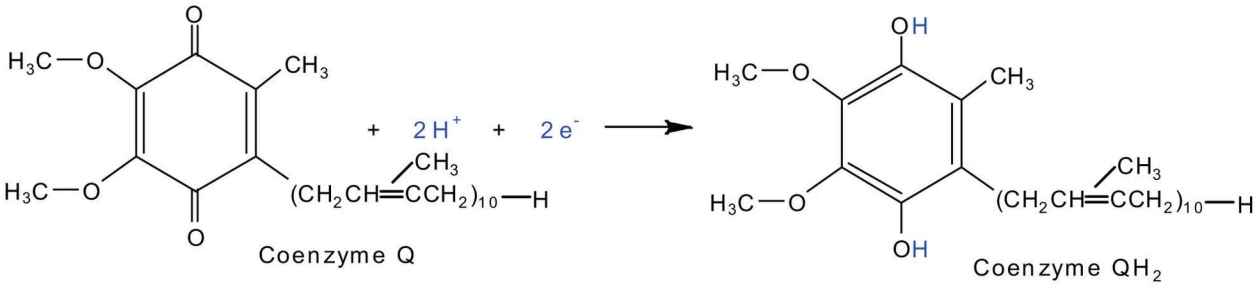
Electrons from complexes I and II are then transferred from the $Fe \cdot S$ protein to coenzyme Q (CoQ), a mobile electron carrier that acts as the electron shuttle between complexes I or II and complex III.

Coenzyme Q is also called ubiquinone because it is ubiquitous in living systems.

- *Oxidation half-reaction*:

$$2Fe(II) \cdot S \rightarrow 2Fe(III) \cdot S + 2e^- \tag{16.4.5}$$

- *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 $16.4.4$). 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*:

$$4Cyt\ a_3\text{–}Fe(II) \rightarrow 4Cyt\ a_3\text{–}Fe(III) + 4e^- \tag{16.4.6}$$

- *Reduction half-reaction*:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

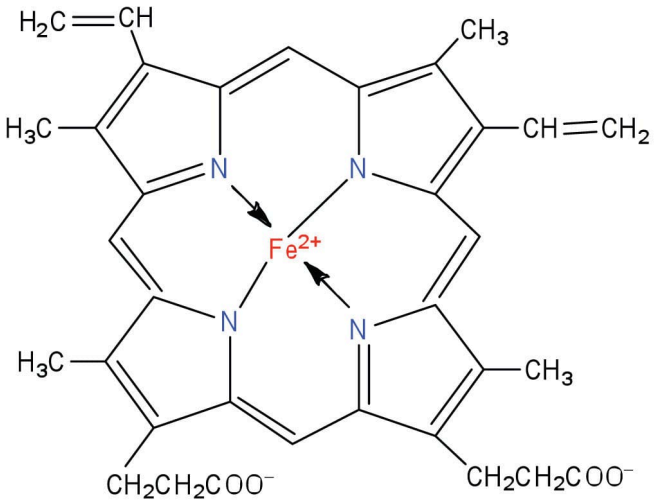


Figure 16.4.4**:** An Iron Porphyrin. Iron porphyrins are present in cytochromes as well as in myoglobin and hemoglobin.

YouTube Video

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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 http://vcell.ndsu.edu/animations

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 16.4.3, 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 16.4.1 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** 16.4.1**:** Maximum Yield of ATP from the Complete Oxidation of 1 Mol of Acetyl-CoA*

Reaction	
Isocitrate → α-ketoglutarate + CO_2	pı
α-ketoglutarate → succinyl-CoA + CO_2	pı
Succinyl-CoA → succinate	p
Succinate → fumarate	pr
Malate → oxaloacetate	pı
1 $FADH_2$ from the citric acid cycle	
3 NADH from the citric acid cycle	yie
Net yield of ATP:	

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.

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.

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.

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16.5: Stage II of Carbohydrate Catabolism

Skills to Develop

- 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 Figure 16.5.1, 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.

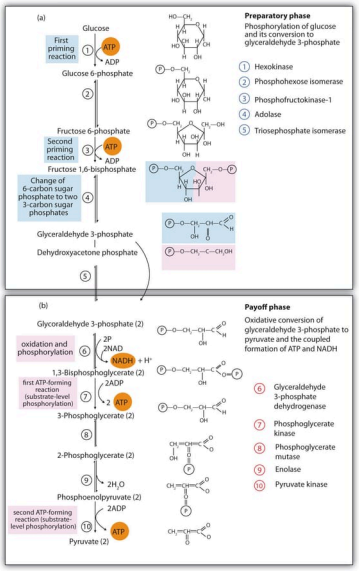


Figure 16.5.1***:*** *Glycolysis*

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.

> 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*.

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*.

Comment: 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.

In the initial step of phase II, 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.

Table 16.5.1: *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

BPG has a high-energy phosphate bond (Table 20.1.1) 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.

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:

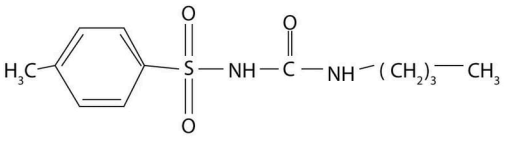
- It is the leading cause of lower limb amputations in the United States.
- It is the leading cause of blindness in adults over age 20.
- It is the leading cause of kidney failure.
- It increases the risk of having a heart attack or stroke by two to four times.

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.

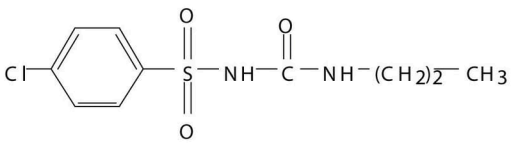
There are two types of diabetes. In immune-mediated diabetes, insufficient amounts of insulin are produced. This type of diabetes develops early in life and is also known as *Type 1 diabetes*, as well as insulin-dependent or juvenile-onset diabetes. Symptoms are rapidly reversed by the administration 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.

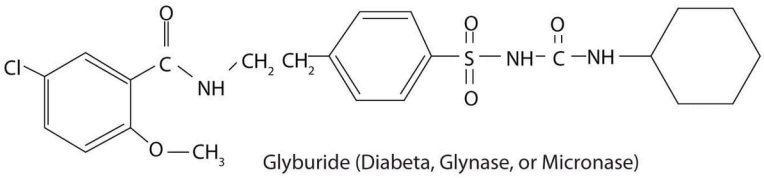


Tolbutamide (Orinase)



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 16.5.2. The conversion to lactate or ethanol under anaerobic conditions allows for the reoxidation of NADH to NAD^+ in the absence of oxygen.

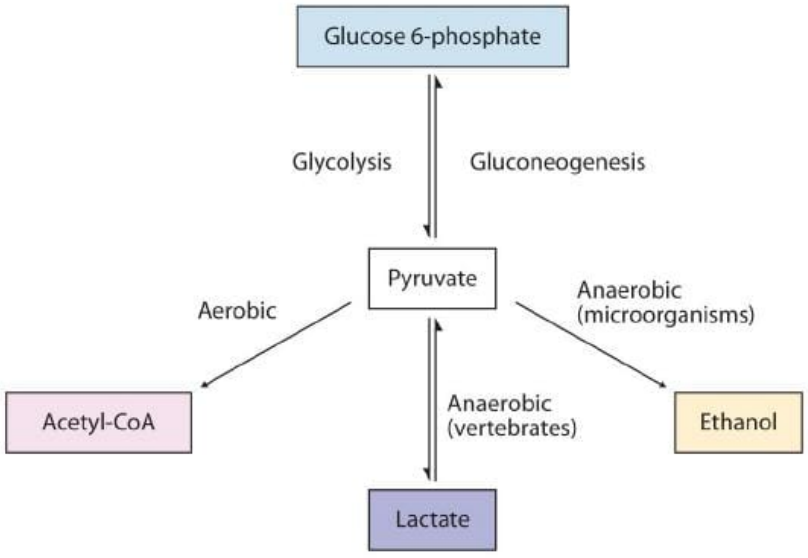


Figure 16.5.2***:*** *Metabolic Fates of Pyruvate*

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:

$$\frac{2 \times 7.4 \text{ kcal}}{670 \text{ kcal}} \times 100 = 2.2\% \tag{16.5.1}$$

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 16.5.1. 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:

$$\frac{38 \times 7.4 \text{ kcal}}{670 \text{ kcal}} \times 100 = 42\% \tag{16.5.2}$$

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.

Concept Review Exercises

1. In glycolysis, how many molecules of pyruvate are produced from one molecule of glucose?

2. In vertebrates, what happens to pyruvate when

a. plenty of oxygen is available?
b. oxygen supplies are limited?

3. In anaerobic glycolysis, how many molecules of ATP are produced from one molecule of glucose?

Answers

1. two

2. a. Pyruvate is completely oxidized to carbon dioxide.
   b. Pyruvate is reduced to lactate, allowing for the reoxidation of NADH to NAD^+.

3. There is a net production of two molecules of ATP.

Exercises

1. Replace each question mark with the correct compound.

   a. $\text{fructose 1,6-bisphosphate} \xrightarrow{\text{aldolase}} ? + ?$
   b. $? + \text{ADP} \xrightarrow{\text{pyruvate kinase}} \text{pyruvate} + \text{ATP}$
   c. $\text{dihydroxyacetone phosphate} \xrightarrow{?} \text{glyceraldehyde 3-phosphate}$
   d. $\text{glucose} + \text{ATP} \xrightarrow{\text{hexokinase}} ? + \text{ADP}$

2. Replace each question mark with the correct compound.

   a. $\text{fructose 6-phosphate} + \text{ATP} \xrightarrow{?} \text{fructose 1,6-bisphosphate} + \text{ADP}$
   b. $? \xrightarrow{\text{phosphoglucose isomerase}} \text{fructose 6-phosphate}$
   c. $\text{glyceraldehyde 3-phosphate} + \text{NAD}^+ + \text{P}_\text{i} \xrightarrow{?} \text{1,3-bisphosphoglycerate} + \text{NADH}$
   d. $\text{3-phosphoglycerate} \xrightarrow{\text{phosphoglyceromutase}} ?$

3. From the reactions in Exercises 1 and 2, select the equation(s) by number and letter in which each type of reaction occurs.

   a. hydrolysis of a high-energy phosphate compound
   b. synthesis of ATP

4. From the reactions in Exercises 1 and 2, select the equation(s) by number and letter in which each type of reaction occurs.

   a. isomerization
   b. oxidation

5. What coenzyme is needed as an oxidizing agent in glycolysis?

6. Calculate

   a. the *total* number of molecules of ATP produced for each molecule of glucose converted to pyruvate in glycolysis.
   b. the number of molecules of ATP hydrolyzed in phase I of glycolysis.
   c. the *net* ATP production from glycolysis alone.

7. How is the NADH produced in glycolysis reoxidized when oxygen supplies are limited in

   a. muscle cells?
   b. yeast?

8. a. Calculate the number of moles of ATP produced by the aerobic oxidation of 1 mol of glucose in a liver cell.

   b. Of the total calculated in Exercise 9a, determine the number of moles of ATP produced in each process.

      a. glycolysis alone

b. the citric acid cycle
c. the electron transport chain and oxidative phosphorylation

Answers

1. a. glyceraldehyde 3-phosphate + dihydroxyacetone phosphate
   b. phosphoenolpyruvate
   c. triose phosphate isomerase
   d. glucose 6-phosphate

3. a. reactions 1b, 1d, and 2a
   b. reaction 1b

5. NAD^+

7. a. Pyruvate is reduced to lactate, and NADH is reoxidized to NAD^+.
   b. Pyruvate is converted to ethanol and carbon dioxide, and NADH is reoxidized to NAD^+.

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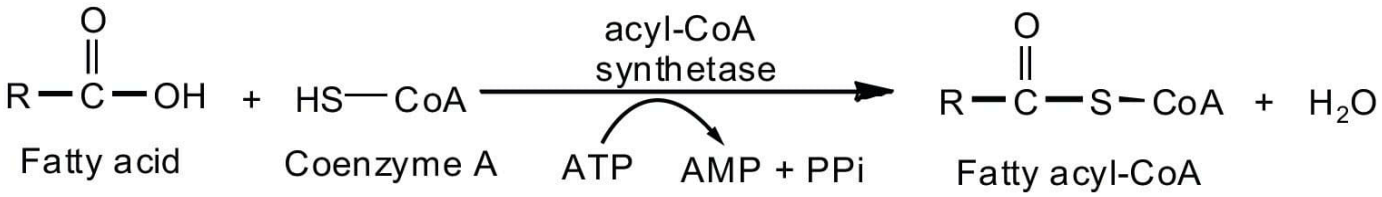
16.6: Stage II of Lipid Catabolism

Skills to Develop

- 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 16.6.1).

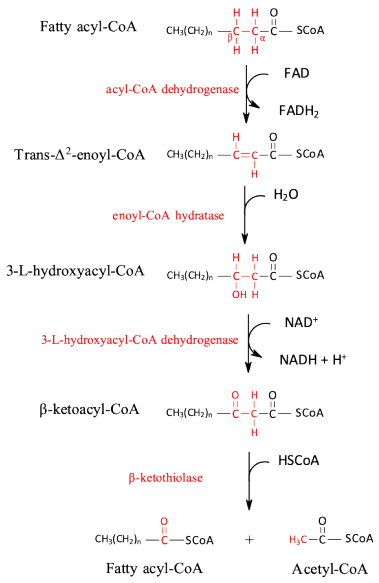


Figure 16.6.1***:*** *Fatty Acid Oxidation. The fatty acyl-CoA formed in the final step becomes the substrate for the first step in the next round of β-oxidation. β-oxidation continues until two acetyl-CoA molecules are produced in the final step.*

The first step in the catabolism of fatty acids is the formation of an alkene in an oxidation reaction catalyzed by *acyl-CoA dehydrogenase*. In this reaction, the coenzyme FAD accepts two hydrogen atoms from the acyl-CoA, one from the α-carbon and one from the β-carbon, forming reduced flavin adenine dinucleotide ($FADH_2$).

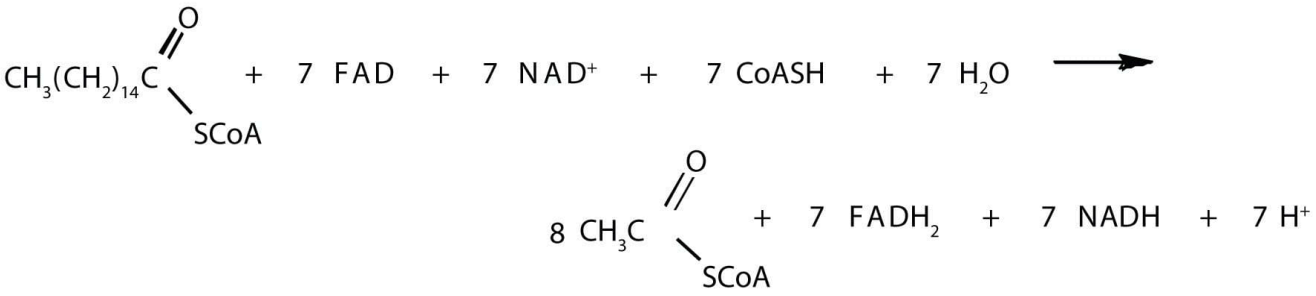
> The $FADH_2$ is reoxidized back to FAD via the electron transport chain that supplies energy to form 1.5–2 molecules of ATP.

Next, the *trans*-alkene is hydrated to form a secondary alcohol in a reaction catalyzed by *enoyl-CoA hydratase*. The enzyme forms only the L-isomer.

The secondary alcohol is then oxidized to a ketone by *β-hydroxyacyl-CoA dehydrogenase*, with NAD^+ acting as the oxidizing agent. The reoxidation of each molecule of NADH to NAD^+ by the electron transport chain furnishes 2.5–3 molecules of ATP.

The final reaction is cleavage of the β-ketoacyl-CoA by a molecule of coenzyme A. The products are acetyl-CoA and a fatty acyl-CoA that has been shortened by two carbon atoms. The reaction is catalyzed by *thiolase*.

The shortened fatty acyl-CoA is then degraded by repetitions of these four steps, each time releasing a molecule of acetyl-CoA. The overall equation for the β-oxidation of palmitoyl-CoA (16 carbon atoms) is as follows:



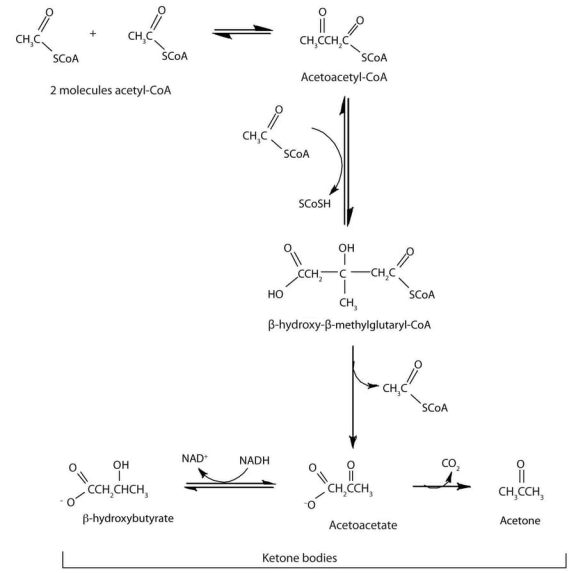
Because each shortened fatty acyl-CoA cycles back to the beginning of the pathway, β-oxidation is sometimes referred to as the fatty acid spiral.

The fate of the acetyl-CoA obtained from fatty acid oxidation depends on the needs of an organism. It may enter the citric acid

cycle and be oxidized to produce energy, it may be used for the formation of water-soluble derivatives known as ketone bodies, or it may serve as the starting material for the synthesis of fatty acids. For more information about the citric acid cycle, see Section 20.4.

Looking Closer: Ketone Bodies

In the liver, most of the acetyl-CoA obtained from fatty acid oxidation is oxidized by the citric acid cycle. However, some of the acetyl-CoA is used to synthesize a group of compounds known as *ketone bodies*: acetoacetate, β-hydroxybutyrate, and acetone. Two acetyl-CoA molecules combine, in a reversal of the final step of β-oxidation, to produce acetoacetyl-CoA. The acetoacetyl-CoA reacts with another molecule of acetyl-CoA and water to form β-hydroxy-β-methylglutaryl-CoA, which is then cleaved to acetoacetate and acetyl-CoA. Most of the acetoacetate is reduced to β-hydroxybutyrate, while a small amount is decarboxylated to carbon dioxide and acetone.



The acetoacetate and β-hydroxybutyrate synthesized by the liver are released into the blood for use as a metabolic fuel (to be converted back to acetyl-CoA) by other tissues, particularly the kidney and the heart. Thus, during prolonged starvation, ketone bodies provide about 70% of the energy requirements of the brain. Under normal conditions, the kidneys excrete about 20 mg of ketone bodies each day, and the blood levels are maintained at about 1 mg of ketone bodies per 100 mL of blood.

In starvation, diabetes mellitus, and certain other physiological conditions in which cells do not receive sufficient amounts of carbohydrate, the rate of fatty acid oxidation increases to provide energy. This leads to an increase in the concentration of acetyl-CoA. The increased acetyl-CoA cannot be oxidized by the citric acid cycle because of a decrease in the concentration of oxaloacetate, which is diverted to glucose synthesis. In response, the rate of ketone body formation in the liver increases further, to a level much higher than can be used by other tissues. The excess ketone bodies accumulate in the blood and the urine, a condition referred to as *ketosis*. When the acetone in the blood reaches the lungs, its volatility causes it to be expelled in the breath. The sweet smell of acetone, a characteristic of ketosis, is frequently noticed on the breath of severely diabetic patients.

Because two of the three kinds of ketone bodies are weak acids, their presence in the blood in excessive amounts overwhelms the blood buffers and causes a marked decrease in blood pH (to 6.9 from a normal value of 7.4). This decrease in pH leads to a serious condition known as *acidosis*. One of the effects of acidosis is a decrease in the ability of hemoglobin to transport oxygen in the blood. In moderate to severe acidosis, breathing becomes labored and very painful. The body also loses fluids and becomes dehydrated as the kidneys attempt to get rid of the acids by eliminating large quantities of water. The lowered oxygen supply and dehydration lead to depression; even mild acidosis leads to lethargy, loss of appetite, and a generally run-down feeling. Untreated patients may go into a coma. At that point, prompt treatment is necessary if the person's life is to be saved.

ATP Yield from Fatty Acid Oxidation

The amount of ATP obtained from fatty acid oxidation depends on the size of the fatty acid being oxidized. For our purposes here. we'll study palmitic acid, a saturated fatty acid with 16 carbon atoms, as a typical fatty acid in the human diet. Calculating its energy yield provides a model for determining the ATP yield of all other fatty acids.

The breakdown by an organism of 1 mol of palmitic acid requires 1 mol of ATP (for activation) and forms 8 mol of acetyl-CoA. Recall from Table 20.4.1 that each mole of acetyl-CoA metabolized by the citric acid cycle yields 10 mol of ATP. The complete degradation of 1 mol of palmitic acid requires the β-oxidation reactions to be repeated seven times. Thus, 7 mol of NADH and 7 mol of $FADH_2$ are produced. Reoxidation of these compounds through respiration yields 2.5–3 and 1.5–2 mol of ATP, respectively. The energy calculations can be summarized as follows:

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:

$$C_{16}H_{32}O_2 + 23O_2 \rightarrow 16CO_2 + 16H_2O + 2,340\ kcal \tag{16.6.1}$$

The percentage of this energy that is conserved by the cell in the form of ATP is as follows:

$$\frac{\text{energy conserved}}{\text{total energy available}} \times 100 = \frac{(129\ \text{ATP})(7.4\ \text{kcal/ATP})}{2,340\ \text{kcal}} \times 100 = 41\% \tag{16.6.2}$$

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 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.

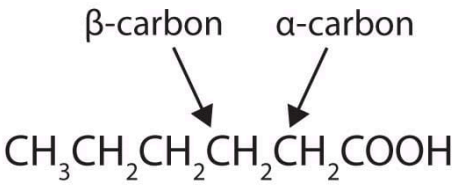
Concept Review Exercises

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.



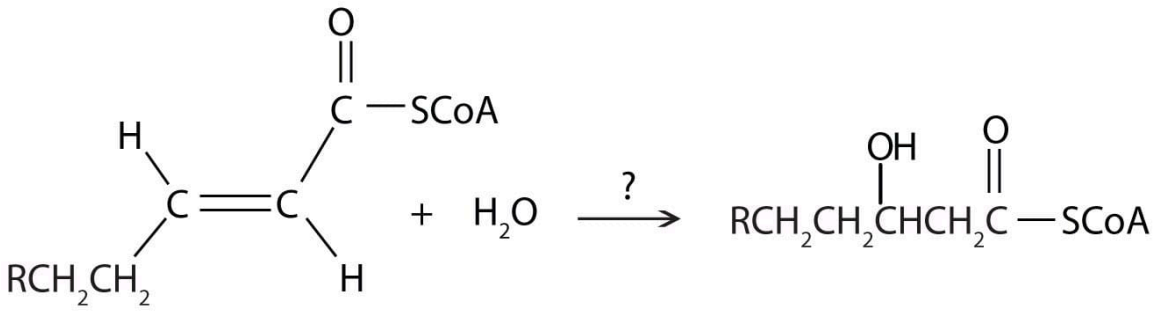
Key Takeaways

- 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.

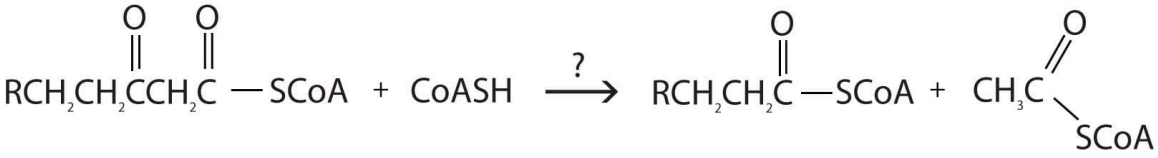
Exercises

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.

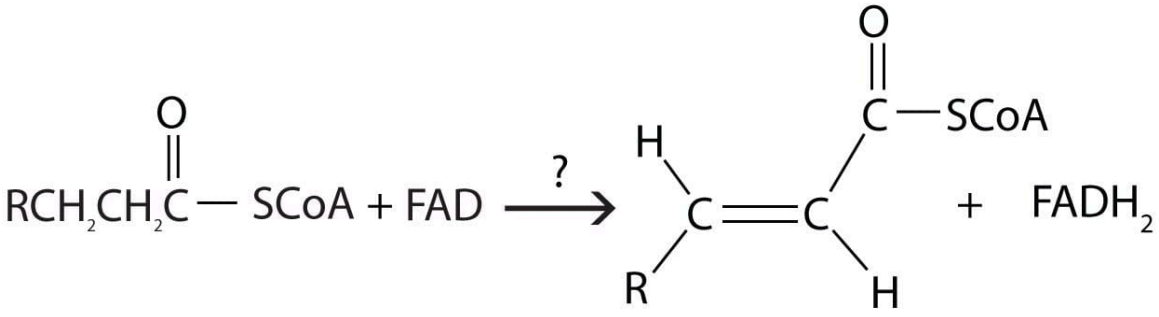
a.



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

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16.7: Stage II of Protein Catabolism

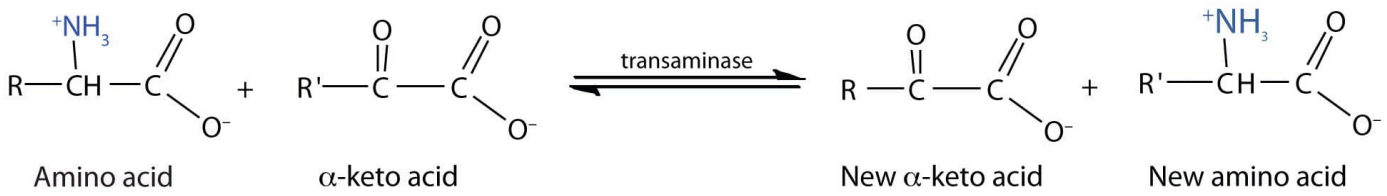
Skills to Develop

- 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.



Alanine and aspartate then undergo a second transamination reaction, transferring their amino groups to α-ketoglutarate and forming glutamate (Figure 16.7.1).

In an α-keto acid, the carbonyl or keto group is located on the carbon atom adjacent to the carboxyl group of the acid.

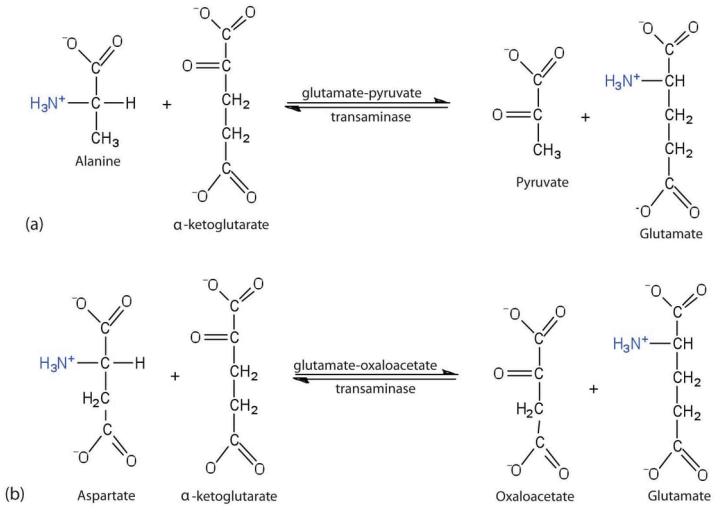
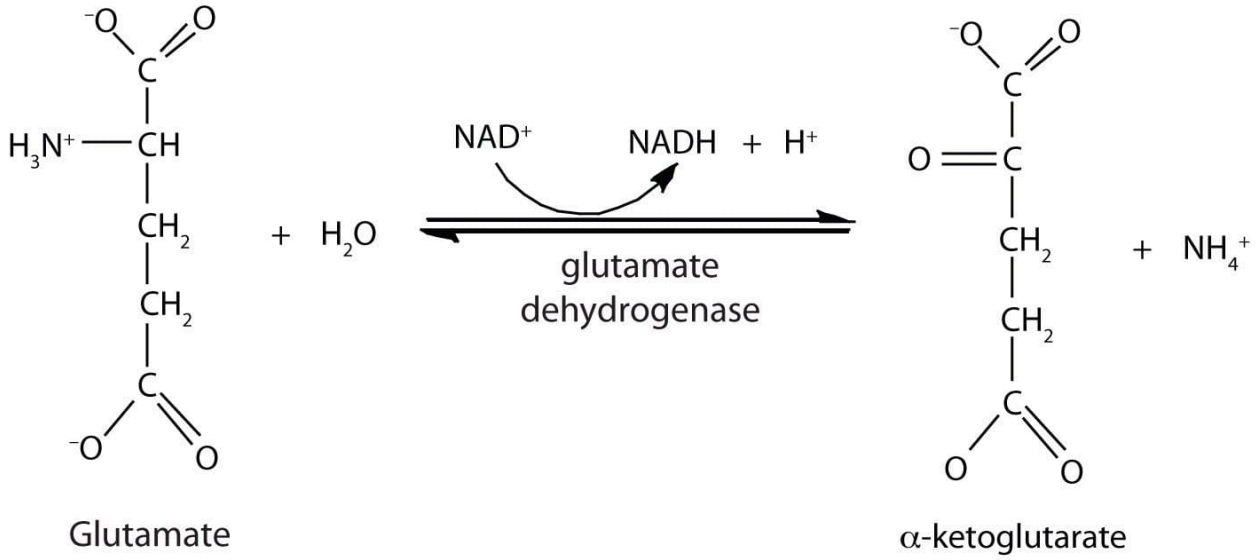


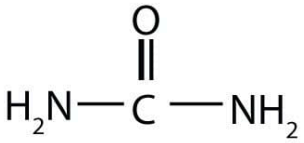
Figure 16.7.1***:*** *Two Transamination Reactions. In both reactions, the final acceptor of the amino group is α-ketoglutarate, and the final product is glutamate.*

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.

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 16.7.2 summarizes the ultimate fates of the carbon skeletons of the 20 amino acids.

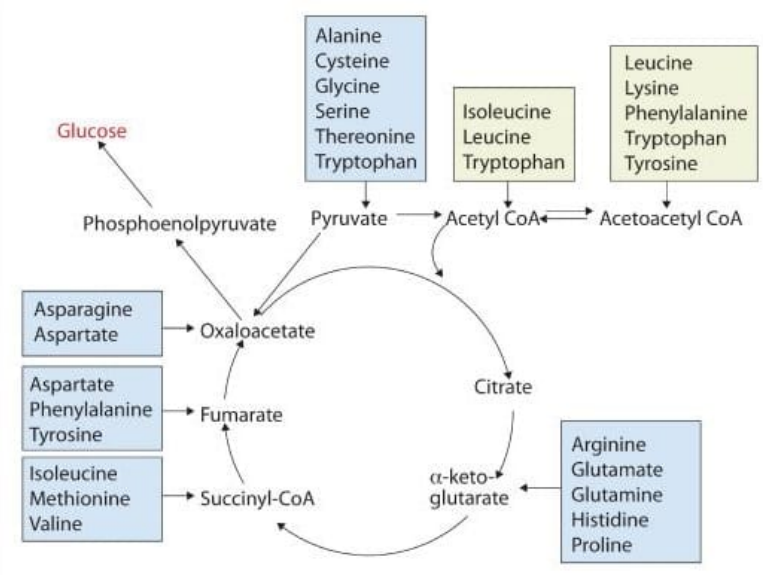


Figure 16.7.2***:*** *Fates of the Carbon Skeletons of Amino Acids*

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. Image used with permission from Wikipedia.

Summary

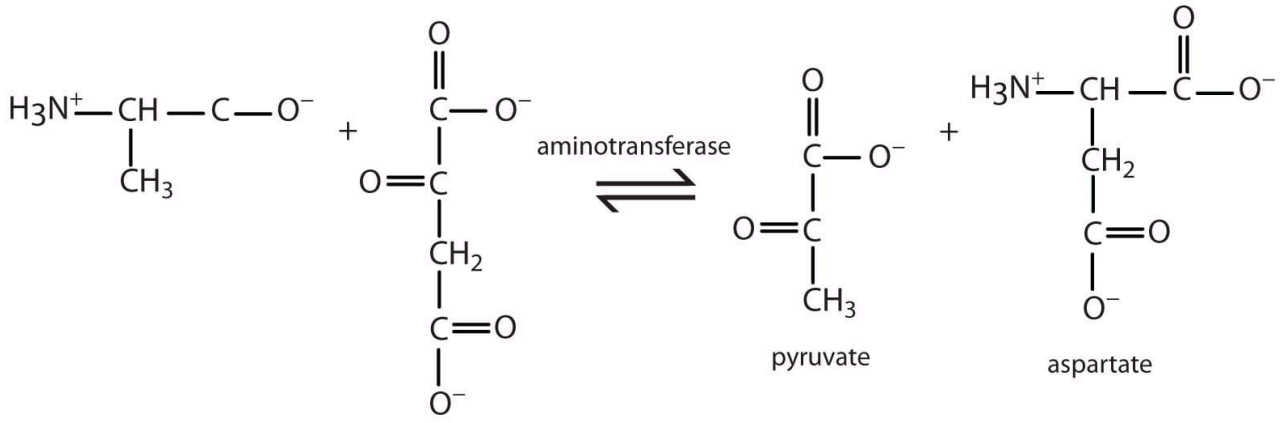
Generally the first step in the breakdown of amino acids is the removal of the amino group, usually through a reaction known as transamination. The carbon skeletons of the amino acids undergo further reactions to form compounds that can either be used for the synthesis of glucose or the synthesis of ketone bodies.

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

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16.8: Chapter 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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16.E: 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. $\text{fructose 1,6-bisphosphate} \xrightarrow{\text{aldolase}} ? + ?$
    b. $? + \text{ADP} \xrightarrow{\text{pyruvate kinase}} \text{pyruvate} + \text{ATP}$
    c. $\text{dihydroxyacetone phosphate} \xrightarrow{?} \text{glyceraldehyde 3-phosphate}$
    d. $\text{glucose} + \text{ATP} \xrightarrow{\text{hexokinase}} ? + \text{ADP}$
2. Replace each question mark with the correct compound.
    a. $\text{fructose 6-phosphate} + \text{ATP} \xrightarrow{?} \text{fructose 1,6-bisphosphate} + \text{ADP}$
    b. $? \xrightarrow{\text{phosphoglucose isomerase}} \text{fructose 6-phosphate}$
    c. $\text{glyceraldehyde 3-phosphate} + \text{NAD}^+ + \text{P}_\text{i} \xrightarrow{?} \text{1,3-bisphosphoglycerate} + \text{NADH}$
    d. $\text{3-phosphoglycerate} \xrightarrow{\text{phosphoglyceromutase}} ?$
3. From the reactions in Exercises 1 and 2, select the equation(s) by number and letter in which each type of reaction occurs.
    a. hydrolysis of a high-energy phosphate compound
    b. synthesis of ATP
4. From the reactions in Exercises 1 and 2, select the equation(s) by number and letter in which each type of reaction occurs.
    a. isomerization
    b. oxidation
5. What coenzyme is needed as an oxidizing agent in glycolysis?
6. Calculate

a. the *total* number of molecules of ATP produced for each molecule of glucose converted to pyruvate in glycolysis.
b. the number of molecules of ATP hydrolyzed in phase I of glycolysis.
c. the *net* ATP production from glycolysis alone.

7. How is the NADH produced in glycolysis reoxidized when oxygen supplies are limited in

a. muscle cells?
b. yeast?

8. a. Calculate the number of moles of ATP produced by the aerobic oxidation of 1 mol of glucose in a liver cell.
b. Of the total calculated in Exercise 9a, determine the number of moles of ATP produced in each process.
    a. glycolysis alone
    b. the citric acid cycle
    c. the electron transport chain and oxidative phosphorylation

Answers

1. a. glyceraldehyde 3-phosphate + dihydroxyacetone phosphate
b. phosphoenolpyruvate
c. triose phosphate isomerase
d. glucose 6-phosphate
3. a. reactions 1b, 1d, and 2a
b. reaction 1b

5. NAD^+

7. a. Pyruvate is reduced to lactate, and NADH is reoxidized to NAD^+.
b. Pyruvate is converted to ethanol and carbon dioxide, and NADH is reoxidized to NAD^+.

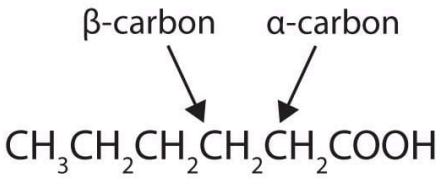
20.6: Stage II of Lipid Catabolism

• Concept Review Exercises

1. How are fatty acids activated prior to being transported into the mitochondria and oxidized?
2. Draw the structure of hexanoic (caproic) acid and identify the α-carbon and the β-carbon.

Answers

1. They react with CoA to form fatty acyl-CoA molecules.

2. 

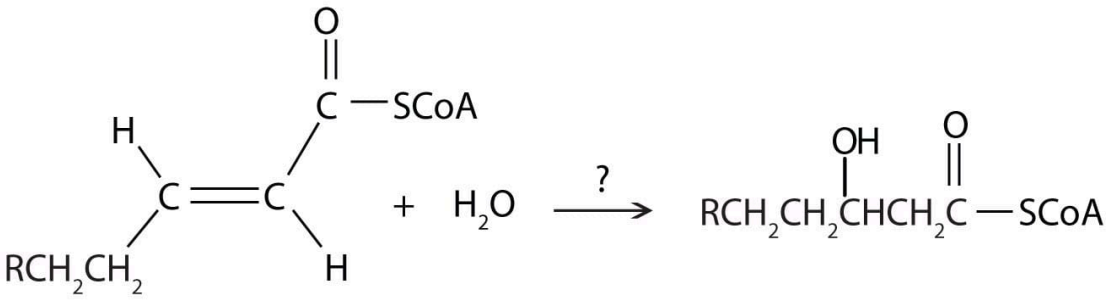
Key Takeaways

- Fatty acids, obtained from the breakdown of triglycerides and other lipids, are oxidized through a series of reactions known as β-oxidation.
- In each round of β-oxidation, 1 molecule of acetyl-CoA, 1 molecule of NADH, and 1 molecule of $FADH_2$ are produced.
- The acetyl-CoA, NADH, and $FADH_2$ are used in the citric acid cycle, the electron transport chain, and oxidative phosphorylation to produce ATP.

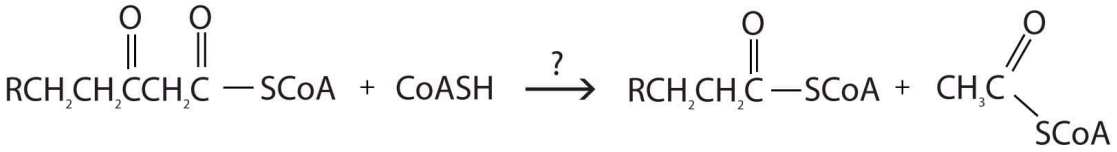
Exercises

1. For each reaction found in β-oxidation, identify the enzyme that catalyzes the reaction and classify the reaction as oxidation-reduction, hydration, or cleavage.

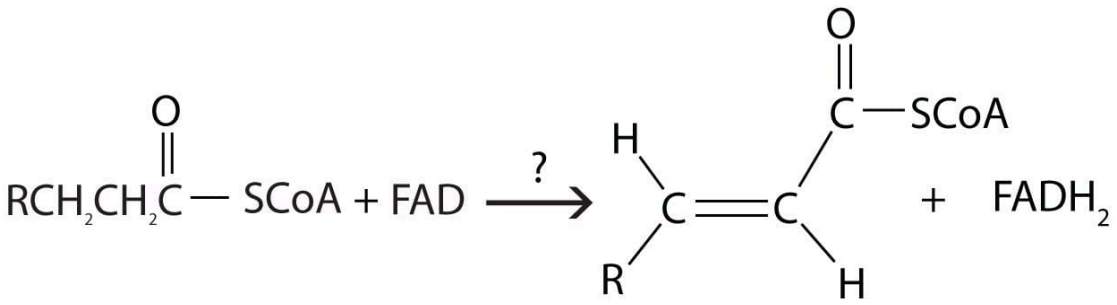
a.



b.



c.



2. What are the products of β-oxidation?
3. How many rounds of β-oxidation are necessary to metabolize lauric acid (a saturated fatty acid with 12 carbon atoms)?
4. How many rounds of β-oxidation are necessary to metabolize arachidic acid (a saturated fatty acid with 20 carbon atoms)?
5. When myristic acid (a saturated fatty acid with 14 carbon atoms) is completely oxidized by β-oxidation, how many molecules of each are formed?
   a. acetyl-CoA
   b. $FADH_2$
   c. NADH
6. When stearic acid (a saturated fatty acid with 18 carbon atoms) is completely oxidized by β-oxidation, how many molecules of each are formed?
   a. acetyl-CoA
   b. $FADH_2$
   c. NADH
7. What is the net yield of ATP from the complete oxidation, in a liver cell, of one molecule of myristic acid?
8. What is the net yield of ATP from the complete oxidation, in a liver cell, of one molecule of stearic acid?

Answers

1. a. enoyl-CoA hydratase; hydration
   b. thiolase; cleavage
   c. acyl-CoA dehydrogenase; oxidation-reduction
3. five rounds
5. a. 7 molecules

b. 6 molecules
c. 6 molecules

7. 112 molecules

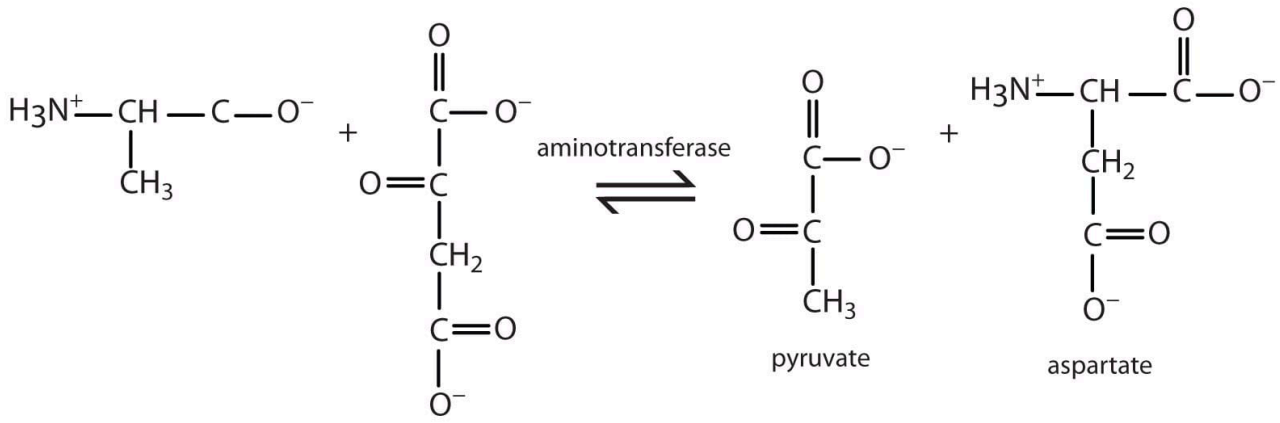
20.7: Stage II of Protein Catabolism

Concept Review Exercises

1. a. Write the equation for the transamination reaction between alanine and oxaloacetate.
   b. Name the two products that are formed.
2. What is the purpose of oxidative deamination?

Answers

1. a.



   b. pyruvate and aspartate

2. Oxidative deamination provides a reaction in which the amino group [as the ammonium (NH_4^+) ion] is removed from a molecule, not simply transferred from one molecule to another. Most of the NH_4^+ ion is converted to urea and excreted from the body.

Exercises

1. Write the equation for the transamination reaction between valine and pyruvate.
2. Write the equation for the transamination reaction between phenylalanine and oxaloacetate.
3. What products are formed in the oxidative deamination of glutamate?
4. Determine if each amino acid is glucogenic, ketogenic, or both.
   a. phenylalanine
   b. leucine
   c. serine
5. Determine if each amino acid is glucogenic, ketogenic, or both.
   a. asparagine
   b. tyrosine
   c. valine

Answers



1.

3. α-ketoglutarate, NADH, and NH_4^+

5. a. glucogenic
   b. both
   c. glucogenic

Additional Exercises

1. Hydrolysis of which compound—arginine phosphate or glucose 6-phosphate—would provide enough energy for the phosphorylation of ATP? Why?

2. If a cracker, which is rich in starch, is chewed for a long time, it begins to develop a sweet, sugary taste. Why?

3. Indicate where each enzymes would cleave the short peptide ala-ser-met-val-phe-gly-cys-lys-asp-leu.

   a. aminopeptidase
   b. chymotrypsin

4. Indicate where each enzymes would cleave the short peptide ala-ser-met-val-phe-gly-cys-lys-asp-leu.

   a. trypsin
   b. carboxypeptidase

5. If the methyl carbon atom of acetyl-CoA is labeled, where does the label appear after the acetyl-CoA goes through one round of the citric acid cycle?

6. If the carbonyl carbon atom of acetyl-CoA is labeled, where does the label appear after the acetyl-CoA goes through one round of the citric acid cycle?

7. The average adult consumes about 65 g of fructose daily (either as the free sugar or from the breakdown of sucrose). In the liver, fructose is first phosphorylated to fructose 1-phosphate, which is then split into dihydroxyacetone phosphate and glyceraldehyde. Glyceraldehyde is then phosphorylated to glyceraldehyde 3-phosphate, with ATP as the phosphate group donor. Write the equations (using structural formulas) for these three steps. Indicate the type of enzyme that catalyzes each step.

8. What critical role is played by both BPG and PEP in glycolysis?

9. How is the NADH produced in glycolysis reoxidized when oxygen supplies are abundant?

10. When a triglyceride is hydrolyzed to form three fatty acids and glycerol, the glycerol can be converted to glycerol 3-phosphate and then oxidized to form dihydroxyacetone phosphate, an intermediate of glycolysis. (In this reaction, NAD^+ is reduced to NADH.) If you assume that there is sufficient oxygen to completely oxidize the pyruvate formed from dihydroxyacetone phosphate, what is the maximum amount of ATP formed from the complete oxidation of 1 mol of glycerol?

11. How is the $FADH_2$ from β-oxidation converted back to FAD?

12. If 1 mol of alanine is converted to pyruvate in a muscle cell (through transamination) and the pyruvate is then metabolized via the citric acid cycle, the electron transport chain, and oxidative phosphorylation, how many moles of ATP are produced?

13. If the essential amino acid leucine (2-amino-4-methylpentanoic acid) is lacking in the diet, an α-keto acid can substitute for it. Give the structure of the α-keto acid and the probable reaction used to form leucine from this α-keto acid.

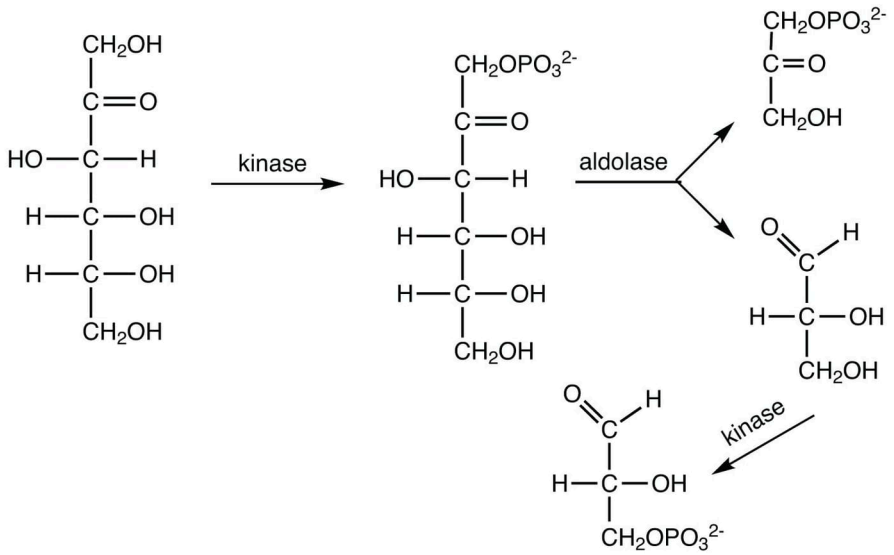
Answers

1. The hydrolysis of arginine phosphate releases more energy than is needed for the synthesis of ATP, while hydrolysis of glucose 6-phosphate does not.

3. a. The enzyme will cleave off amino acids one at a time beginning with alanine (the N-terminal end).
   b. following phenylalanine

5. Half of the label will be on the second carbon atom of oxaloacetate, while the other half will be on the third carbon atom.

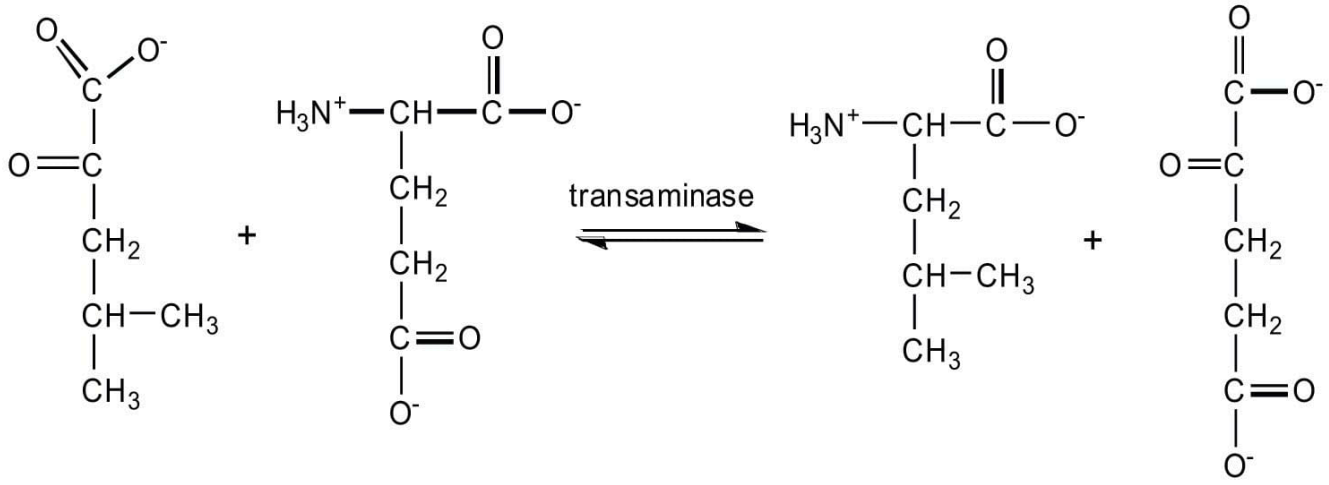
7.



9. When oxygen is abundant, NADH is reoxidized through the reactions of the electron transport chain.

11. $FADH_2$ is reoxidized back to FAD via the electron transport chain.

13.



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17: 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.

17.1: Radioactivity

17.2: Half-Life

17.3: Units of Radioactivity

17.4: Uses of Radioactive Isotopes

17.5: Nuclear Energy

17.6: Chapter Summary

17.E: Exercises

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17.1: Radioactivity

Skills to Develop

- 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:

$$^{12}_{6}\mathrm{C} \tag{17.1.1}$$

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}H and ^{3}H, are given their own names: deuterium (D) and tritium (T), respectively. Another way of expressing a particular isotope is to list the mass number after the element name, like carbon-12 or hydrogen-3.

Atomic theory in the 19th century presumed that nuclei had fixed compositions. But in 1896, the French scientist Henri Becquerel found that a uranium compound placed near a photographic plate made an image on the plate, even if the compound was wrapped in black cloth. He reasoned that the uranium compound was emitting some kind of radiation that passed through the cloth to expose the photographic plate. Further investigations showed that the radiation was a combination of particles and electromagnetic rays, with its ultimate source as the atomic nucleus. These emanations were ultimately called, collectively, radioactivity.

There are three main forms of radioactive emissions. The first is called an alpha particle,which is symbolized by the Greek letter α. An alpha particle is composed of two protons and two neutrons, and so 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:

$$^{235}_{92}\mathrm{U} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{231}_{90}\mathrm{Th} \tag{17.1.2}$$

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 17.1.1: Radon-222

Write the nuclear equation that represents the radioactive decay of radon-222 by alpha particle emission and identify the daughter isotope.

SOLUTION

Radon has an atomic number of 86, so the parent isotope is represented as $^{222}_{86}\mathrm{Rn}$. We represent the alpha particle as $^{4}_{2}\mathrm{He}$ and use subtraction (222 – 4 = 218 and 86 – 2 = 84) to identify the daughter isotope as an isotope of polonium, $^{218}_{84}\mathrm{Po}$:

$$^{222}_{86}\mathrm{Rn} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{218}_{84}\mathrm{Po}$$

Exercise 17.1.1: Polonium-209

Write the nuclear equation that represents the radioactive decay of polonium-209 by alpha particle emission and identify the daughter isotope.

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 $^{0}_{-1}\mathrm{e}$ 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:

$$^{14}_{6}\mathrm{C} \rightarrow {}^{14}_{7}\mathrm{N} + {}^{0}_{-1}\mathrm{e} \tag{17.1.3}$$

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:

$$^{222}_{86}\mathrm{Rn} \rightarrow {}^{218}_{84}\mathrm{Po} + {}^{4}_{2}\mathrm{He} + \gamma \tag{17.1.4}$$

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 17.1.2: Boron-12

Write the nuclear equation that represents the radioactive decay of boron-12 by beta particle emission and identify the daughter isotope. A gamma ray is emitted simultaneously with the beta particle.

SOLUTION

The parent isotope is $^{12}_{5}\mathrm{B}$ while one of the products is an electron, $^{0}_{-1}\mathrm{e}$. 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:

$$^{12}_{5}\mathrm{B} \rightarrow {}^{12}_{6}\mathrm{C} + {}^{0}_{-1}\mathrm{e} + \gamma \tag{17.1.5}$$

The daughter isotope is $^{12}_{6}\mathrm{C}$.

Exercise 17.1.2: Iodine-131

Write the nuclear equation that represents the radioactive decay of iodine-131 by beta particle emission and identify the daughter isotope. A gamma ray is emitted simultaneously with the beta particle.

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 17.1.1 summarizes the properties of the three main types of radioactive emissions.

Table 17.1.1***:*** *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

$$^{235}_{92}\mathrm{U} \rightarrow {}^{139}_{56}\mathrm{Ba} + {}^{94}_{36}\mathrm{Kr} + 2{}^{1}_{0}\mathrm{n} \tag{17.1.6}$$

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.

Contributors

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17.2: Half-Life

Skills to Develop

- 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 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 17.2.1.

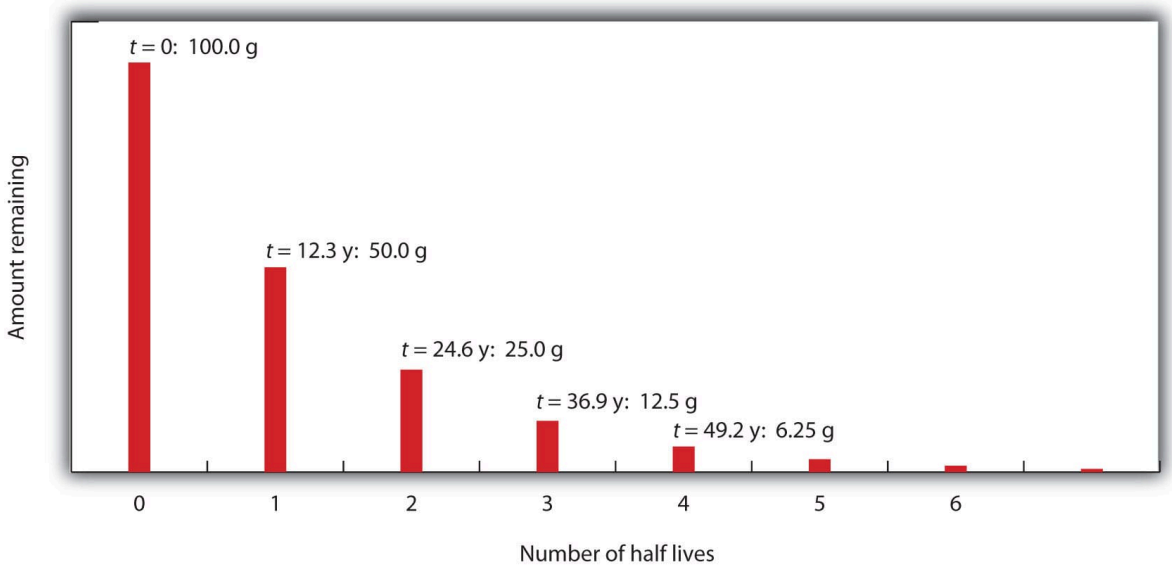


Figure 17.2.1*: Radioactive Decay. During each successive half-life, half of the initial amount will radioactively decay.*

We can determine the amount of a radioactive isotope remaining after a given number half-lives by using the following expression:

$$\text{amount remaining} = \text{initial amount} \times \left(\frac{1}{2}\right)^{n} \tag{17.2.1}$$

where *n* is the number of half-lives. This expression works even if the number of half-lives is not a whole number.

Example 17.2.1: Fluorine-20

The half-life of ^{20}F is 11.0 s. If a sample initially contains 5.000 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 using the previous equation, $n = 4$. Substituting and solving results in the following:

$$\text{amount remaining} = 5.00\ \text{g} \times \left(\frac{1}{2}\right)^4$$

$$\text{amount remaining} = 5.00\ \text{g} \times \frac{1}{16}$$

$$\text{amount remaining} = 0.313\ \text{g}$$

Less than one-third of a gram of ^{20}F remains.

Exercise 17.2.1: Titanium-44

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?

Half-lives of isotopes range from fractions of a microsecond to billions of years. Table 17.2.1 lists the half-lives of some isotopes.

Table 17.2.1*: 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 17.2.2: Iodine-125

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).

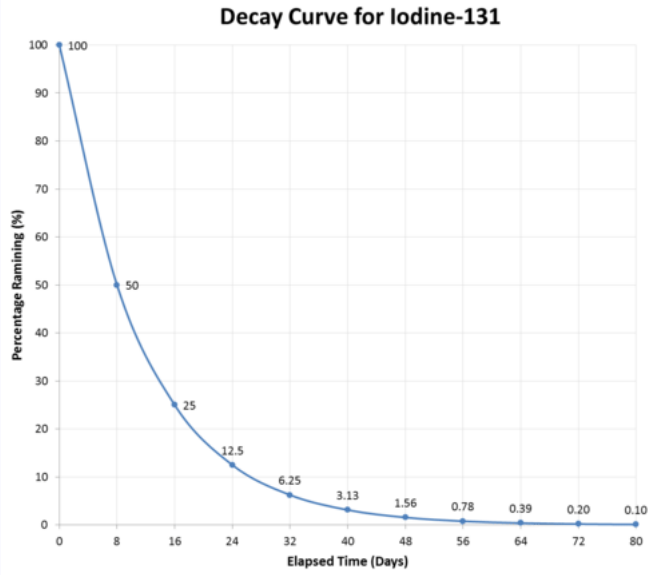
Equation 17.2.1 can be used to calculate the amount of radioactivity remaining after a given time:

$$N_t = N_0 \times (0.5)^{\text{number of half-lives}}$$

where N_t = activity at time t and N_0 = initial activity at time $t = 0$.

If we have an initial activity of $42,000 \text{ cpm}$, 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 I-125. The activity decreases by one-half during each succeeding half-life.

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.

Contributors

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17.3: Units of Radioactivity

Skills to Develop

- To express amounts of radioactivity in a variety of units.

In Section 11.2, 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 in the early 1900s.

Example 17.3.1

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:

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 17.3.1

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?

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

$$\text{rem} = \text{rad} \times \text{factor}$$

where *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, the 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 17.3.1 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* 17.3.1*: 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 17.3.2 lists the potential threats to health at various amounts of exposure over short periods of time (hours or days).

Table 17.3.2*: Effects of Short-Term Exposure to Radioactivity and Radiation*

Exposure (rem)	Effect
1 (over a full year)	no detectable effect
~20	increased risk of some cancers
~100	damage to bone marrow and other tissues; possible internal bleeding; decrease in white blood cell count
200–300	visible "burns" on skin, nausea, vomiting, and fatigue
>300	loss of white blood cells; hair loss
~600	death

One of the simplest ways of detecting radioactivity is by using a piece of photographic film embedded in a badge or a pen. On a regular basis, the film is developed and checked for exposure. A comparison of the exposure level of the film with a set of standard exposures indicates the amount of radiation a person was exposed to.



Figure 17.3.1*: 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 17.3.1). 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.

Contributors

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17.4: Uses of Radioactive Isotopes

Skills to Develop

- 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 17.4.1) 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.

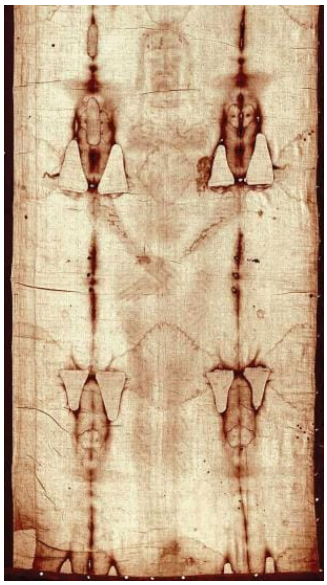


Figure 17.4.1***:*** *Shroud of Turin. In 1989, several groups of scientists used carbon-14 dating to demonstrate that the age of the Shroud of Turin was only 600–700 y. Many people still cling to a different notion, despite the scientific evidence.*

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 cobalt-60 or cesium-137. 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 17.4.2). 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.

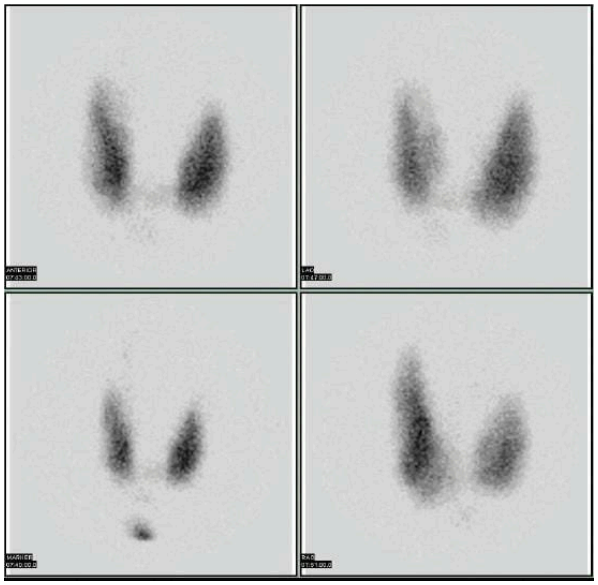


Figure 17.4.2***:*** *Medical Diagnostics. Radioactive iodine can be used to image the thyroid gland for diagnostic purposes. Source:*

Scan courtesy of Myo Han, http://en.wikipedia.org/wiki/File:Thyroid_scan.jpg.

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 17.4.1 lists several radioactive isotopes and their medical uses.

Table 17.4.1*: 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 17.4.3: *(left) Combined apparatus for positron emission tomography (PET) and X-ray computer tomography (CT), Siemens Biograph (right) Whole-body PET scan using* ^{18}*F-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.

Contributors

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17.5: Nuclear Energy

Skills to Develop

- 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:

$$\underset{235.0439}{^{235}\mathrm{U}} \rightarrow \underset{138.9088}{^{139}\mathrm{Ba}} + \underset{93.9343}{^{94}\mathrm{Kr}} + \underset{2\times1.0087}{2\,^{1}\mathrm{n}} \tag{17.5.1}$$

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:

$$E = mc^2 \tag{17.5.2}$$

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:

$$E = (-0.0001834\ kg)(3.00 \times 10^8\ m/s)^2 = -1.65 \times 10^{13}\ J = -1.65 \times 10^{10}\ kJ \tag{17.5.3}$$

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:

$$^{235}\mathrm{U} + {}^{1}\mathrm{n} \rightarrow {}^{139}\mathrm{Ba} + {}^{94}\mathrm{Kr} + 3\,{}^{1}\mathrm{n} + \text{energy}$$

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.

Note

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 17.5.1: Plutonium-239

Plutonium-239 can absorb a neutron and undergo a fission reaction to produce an atom of gold-204 and an atom of phosphorus-31. Write the balanced nuclear equation for the process and determine the number of neutrons given off as part of the reaction.

SOLUTION

Using the data given, we can write the following initial equation:

$$^{1}_{0}\text{n} + {}^{239}_{94}\text{Pu} \rightarrow {}^{204}_{79}\text{Au} + {}^{31}_{15}\text{P} + ?{}^{1}_{0}\text{n}$$

In balanced nuclear equations, the sums of the subscripts on each sides of the equation are the same, as are the sums of the superscripts. The subscripts are already balanced: 0 + 94 = 94 and 79 + 15 = 94. The superscripts on the left equal 240 (1 + 239) but equal 235 (204 + 31) on the right. We need five more mass number units on the right. Five neutrons should be the products of the process for the mass numbers to balance. (Because the atomic number of a neutron is zero, including five neutrons on the right does not change the overall sum of the subscripts.) Thus, the balanced nuclear equation is as follows:

$$^{1}_{0}\text{n} + {}^{239}_{94}\text{Pu} \rightarrow {}^{204}_{79}\text{Au} + {}^{31}_{15}\text{P} + 5{}^{1}_{0}\text{n}$$

We predict that the overall process will give off five neutrons.

Exercise 17.5.1

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.

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 17.5.1 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.

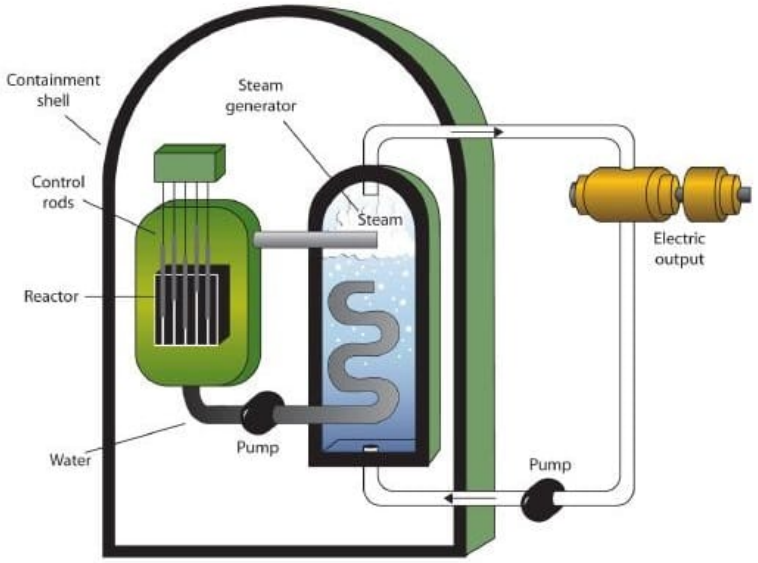


Figure 17.5.1*: A Diagram of a Nuclear Power Plant for Generating Electricity. The two main components of the power plant are the nuclear reactor itself and the steam-driven turbine and electricity generator.*

Notice that the fission of uranium produces two more free neutrons than were present to begin with. These neutrons can themselves stimulate other uranium nuclei to undergo fission, releasing yet more energy and even more neutrons, which can in turn induce even more uranium fission. A single neutron can thus begin a process that grows exponentially in a phenomenon called a chain reaction:

$$1 \rightarrow 2 \rightarrow 4 \rightarrow 8 \rightarrow 16 \rightarrow 32 \rightarrow 64 \rightarrow 128 \rightarrow 256 \rightarrow 512 \rightarrow 1{,}024 \rightarrow 2{,}048 \rightarrow 4{,}096 \rightarrow 8{,}192 \rightarrow 16{,}384 \rightarrow \ldots$$

Because energy is produced with each fission event, energy is also produced exponentially and in an uncontrolled fashion. The

quick production of energy creates an explosion. This is the mechanism behind the atomic bomb.

The first controlled chain reaction was achieved on December 2, 1942, in an experiment supervised by Enrico Fermi in a laboratory underneath the football stadium at the University of Chicago.

Although fairly simple in theory, an atomic bomb is difficult to produce, in part because uranium-235, the isotope that undergoes fission, makes up only 0.7% of natural uranium; the rest is mostly uranium-238, which does not undergo fission. (Remember that the radioactive process that a nucleus undergoes is characteristic of the isotope.) To make uranium useful for nuclear reactors, the uranium in uranium-235 must be *enriched* to about 3%. Enrichment of uranium is a laborious and costly series of physical and chemical separations. To be useful in an atomic bomb, the uranium in uranium-235 must be enriched to 70% or more. At lesser concentrations, the chain reaction cannot sustain itself, so no explosion is produced.

Fusion is another nuclear process that can be used to produce energy. In this process, smaller nuclei are combined to make larger nuclei, with an accompanying release of energy. One example is the hydrogen fusion, which makes helium. While the steps of the process are complicated, the net reaction is:

$$4\,{}^{1}\mathrm{H} \rightarrow {}^{4}\mathrm{He} + 2.58 \times 10^{12}\ J \tag{17.5.4}$$

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.

Contributors

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17.6: Chapter Summary

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

Some atoms have unstable nuclei that emit particles and high-energy electromagnetic radiation to form new elements that are more stable. This emission of particles and electromagnetic radiation is called **radioactivity**. There are three main types of spontaneous radioactive emission: **alpha particles**, which are equivalent to helium nuclei; **beta particles**, which are electrons; and **gamma radiation**, which is high-energy electromagnetic radiation. Another type of radioactive process is **spontaneous fission**, in which large nuclei spontaneously break apart into smaller nuclei and, often, neutrons. In all forms of radioactivity, new elements are formed from the radioactive reactants.

Radioactive isotopes decay at different rates. The rate of an isotope's decay is expressed as a **half-life**, which is the amount of time required for half of the original material to decay. The length of its half-life is a characteristic of the particular isotope and can range from less than microseconds to billions of years.

Amounts of radioactivity are measured in several different ways. A **becquerel** is equal to one radioactive decay per second. A **curie** represents 3.7×10^{10} decays per second. Other units describe the amount of energy absorbed by body tissues. One **rad** is equivalent to 0.01 joule of energy absorbed per gram of tissue. Different tissues react differently to different types of radioactivity. The **rem** unit takes into account not only the energy absorbed by the tissues, but also includes a numerical multiplication factor to account for the type of radioactivity and the type of tissue. The average annual radiation exposure of a person is less than 360 millirem, over 80% of which is from natural sources. Radioactivity can be detected using photographic film or other devices such as **Geiger counters**.

Radioactive isotopes have many useful applications. They can be used as **tracers** to follow the journey of a substance through a system, like an underground waterway or a metabolic pathway. Radioactive isotopes can be used to date objects, since the amount of parent and daughter isotopes can sometimes be measured very accurately. Radioactive emission can be used to sterilize food for a longer edible lifetime. There are also a number of diagnostic and therapeutic medical applications for radioactive isotopes.

Radioactive processes occur with simultaneous changes in energy. This **nuclear energy** can be used to generate power for human use. **Nuclear reactors** use the energy released by fission of large isotopes to generate electricity. When carefully controlled, fission can produce a **chain reaction** that facilitates the continuous production of energy. If not carefully controlled, a very quick production of energy can result, as in an **atomic bomb**. Natural uranium does not contain enough of the proper isotope of uranium to work in a nuclear reactor, so it must first be **enriched** in uranium-235. Forcing small nuclei together to make larger nuclei, a process called **fusion**, also gives off energy; however, scientists have yet to achieve a controlled fusion process.

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17.E: 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: $^{14}_{6}\mathrm{C} \rightarrow {}_{7}{}^{14}\mathrm{N} + {}^{0}_{-1}\mathrm{e}$ (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. $^{244}_{94}\mathrm{Pu} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{240}_{92}\mathrm{U}$; the daughter isotope is $^{240}_{92}\mathrm{U}$, an atom of uranium.

10. $^{212}_{87}\mathrm{Fr} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{208}_{85}\mathrm{At}$; the daughter isotope is $^{208}_{85}\mathrm{At}$, an atom of astatine.

11. $^{121}_{50}\mathrm{Sn} \rightarrow {}^{0}_{-1}\mathrm{e} + {}^{121}_{51}\mathrm{Sb}$; the daughter isotope is $^{121}_{51}\mathrm{Sb}$, an atom of antimony.

12. $^{99}_{43}\mathrm{Tc} \rightarrow {}^{0}_{-1}\mathrm{e} + {}^{99}_{44}\mathrm{Mo}$; the daughter isotope is $^{99}_{44}\mathrm{Mo}$, an atom of antimony.

13. 0.512 MeV

14. 3.16×10^{-14} J

15. Beta particles; shielding of the appropriate thickness can protect against both alpha and beta particles.

16. Gamma rays; can be shielded by thick, dense material such as lead (Pb). Alpha particles has low energy; can shielded by a piece of paper.

17. Nuclear fission is when large nuclei break down into smaller nuclei.

18. A nucleus must be very large. Examples are Th-232 and U-235.

11.2 Half-Life

Concept Review Exercises

1. Define *half-life*.
2. Describe a way to determine the amount of radioactive isotope remaining after a given number of half-lives.

Answers

1. Half-life is the amount of time needed for half of a radioactive material to decay.
2. take half of the initial amount for each half-life of time elapsed

Exercises

1. Do all isotopes have a half-life? Explain.

2. Which is more radioactive—an isotope with a long half-life or an isotope with a short half-life?

3. What percent of a sample remains after one half-life? Three half-lives?

4. The half-life of polonium-218 is 3.0 min. How much of a 0.540 mg sample would remain after 9.0 minutes have passed?

5. The half-life of protactinium-234 is 6.69 hours. If a 0.812 mg sample of Pa-239 decays for 40.14 hours, what mass of the isotope remains?

6. How long does it take for 1.00 g of ^{103}Pd to decay to 0.125 g if its half-life is 17.0 d?

7. How long does it take for 2.00 g of ^{94}Nb to decay to 0.0625 g if its half-life is 20,000 y?

8. It took 75 y for 10.0 g of a radioactive isotope to decay to 1.25 g. What is the half-life of this isotope?

9. It took 49.2 s for 3.000 g of a radioactive isotope to decay to 0.1875 g. What is the half-life of this isotope?

Answers

1. Only radioactive isotopes have half-lives.

2. An isotope with a shorter half-life decay more rapidly is more radioactive.

3. 1 half-life: 50%; 3 half-lives: 12.5%

4. 9.0 min = 3 half-lives (make 3 arrows): 0.540 mg --> 0.270 mg --> 0.135 mg --> 0.0675 mg

5. 0.0127 mg

6. 51.0 d

7. 100 000 y

8. 25 y

9. 12.3 s

11.3 Units of Radioactivity

Concept Review Exercise

1. What units are used to quantify radioactivity?

Answer

1. the curie, the becquerel, the rad, the gray, the sievert, and the rem

Exercises

1. Define *rad*.
2. Define *rem*.
3. How does a becquerel differ from a curie?
4. How is the curie defined?
5. A sample of radon gas has an activity of 140.0 mCi. If the half-life of radon is 1,500 y, how long before the activity of the sample is 8.75 mCi?
6. A sample of curium has an activity of 1,600 Bq. If the half-life of curium is 24.0 s, how long before its activity is 25.0 Bq?
7. If a radioactive sample has an activity of 65 μCi, how many disintegrations per second are occurring?
8. If a radioactive sample has an activity of 7.55×10^5 Bq, how many disintegrations per second are occurring?
9. Describe how a radiation exposure in rems is determined.
10. Which contributes more to the rems of exposure—alpha or beta particles? Why?
11. Use Table 11.3.2 to determine which sources of radiation exposure are inescapable and which can be avoided. What percentage of radiation is unavoidable?
12. What percentage of the approximate annual radiation exposure comes from radioactive atoms that are in the body naturally?
13. Explain how a film badge works to detect radiation.
14. Explain how a Geiger counter works to detect radiation.

Answers

1. Known as the radiation absorbed dose, a rad is the absorption of 0.01 J/g of tissue.

2. Known as roentgen equivalent man, a rem is an absorption of one rad times a factor. The factor is variable depending on the type of emission and the type of irradiated tissue.

3. A becquerel is smaller and equals 1 decay per second. A curie is 3.7×10^{10} Bq.

4. A curie is defined as 3.7×10^{10} decays per second.

5. 6000 y

6. 144 s

7. 2.41×10^6 disintegrations per second

8. 7.55×10^5 disintegrations per second

9. The radiation exposure is determined by the number of rads times the quality factor of the radiation.

10. Alpha contributes more than beta because of its bigger size and electrical charge.

11. At least 16% (terrestrial and cosmic sources) of radioactivity is unavoidable; the rest depends on what else a person is exposed to.

12. About 11% come from radioactive atoms that are in the body naturally.

13. A film badge uses film, which is exposed as it is subjected to radiation.

14. The Geiger counter consists of a tube with electrodes and is filled with an inert (argon) gas. Radiation entering the tube ionizes the gas, and the ions are attracted to the electrodes and produce an electric pulse (clicking sound).

11.4 Uses of Radioactive Isotopes

Concept Review Exercise

1. Describe some of the different ways that amounts of radioactivity are applied in society.

Answer

1. Radioactive isotopes are used in dating, as tracers, and in medicine as diagnostic and treatment tools.

Exercises

1. Define *tracer* is and give an example of how tracers work.
2. Name two isotopes that have been used as tracers.
3. Explain how radioactive dating works.
4. Name an isotope that has been used in radioactive dating.
5. The current disintegration rate for carbon-14 is 14.0 Bq. A sample of burnt wood discovered in an archaeological excavation is found to have a carbon-14 decay rate of 3.5 Bq. If the half-life of carbon-14 is 5,700 y, approximately how old is the wood sample?
6. A small asteroid crashes to Earth. After chemical analysis, it is found to contain 1 g of technetium-99 to every 3 g of ruthenium-99, its daughter isotope. If the half-life of technetium-99 is 210,000 y, approximately how old is the asteroid?
7. What do you think are some of the positive aspects of irradiation of food?
8. What do you think are some of the negative aspects of irradiation of food?
9. Describe how iodine-131 is used to both diagnose and treat thyroid problems.
10. List at least five organs that can be imaged using radioactive isotopes.

11. Which radioactive emissions can be used therapeutically?

12. Which isotope is used in therapeutics primarily for its gamma ray emissions?

13. What volume of a radioisotope should be given if a patient needs 125 mCi of a solution which contains 45 mCi in 5.0 mL?

14. Sodium-24 is used to treat leukemia. A 36-kg patient is prescribed 145 μCi/kg and it is supplied to the hospital in a vial containing 250 μCi/mL. What volume should be given to the patient?

15. Lead-212 is one of the radioisotopes used in the treatment of breast cancer. A patient needs a 15 μCi dose and it is supplied as a solution with a concentration of 2.5 μCi/mL. What volume does the patient need? Given the half-life of lead is 10.6 hours, what will be the radioactivity of the sample after approximately four days?

Answers

1. A tracer follows the path of a chemical or a physical process. One of the uses of a tracer is following the path of water underground (answers will vary).

2. Tritium (^{3}H) and Carbon-14 (^{14}C) (answers will vary)

3. Radioactive dating works by comparing the amounts of parent and daughter isotopes and calculating back to how long ago all of the material was just the parent isotope.

4. Carbon-14 (^{14}C) and Uranium-235 (^{235}U) (answers will vary)

5. about 11,400 y

6. about 420,000 y

7. increased shelf life (answers will vary)

8. reduction in the food's vitamin content and cost

9. Iodine-131 is preferentially absorbed by the thyroid gland and can be used to measure the gland’s activity or destroy bad cells in the gland.

10. brain, bone, heart, thyroid, lung (answers will vary)

11. gamma rays, beta particles, or alpha particles

12. cobalt-60

13. 125mCi x (5.0mL/45mCi)=14mL

14. 36kg x (145μCi/kg) x (1mL/250μCi)=21mL

15. Volume given: 15μCi x (1mL/2.5μCi) = 6.0mL

Elapsed time in hours: 4 days x (24 hr/day) = 96 hr

Number of half-lives: 96 hrs/10.6 hours = 9

Radioactivity remaining after 9 half-lives: 0.029 μCi

11.5 Nuclear Energy

Concept Review Exercises

1. How is nuclear energy produced?

2. What is the difference between fission and fusion?

Answers

1. Nuclear energy is produced by carefully controlling the speed of a fission reaction.
2. In fission, large nuclei break down into small ones; in fusion, small nuclei combine to make larger ones. In both cases, a lot of energy is emitted.

Exercises

1. In the spontaneous fission of uranium-233, the following reaction occurs:

   $^{233}U + {}^{1}n \rightarrow {}^{142}Ce + {}^{82}Se + 10{}^{1}n$

   For every mole of ^{233}U that decays, 0.1355 g of mass is lost. How much energy is given off per mole of ^{233}U reacted?
2. In the spontaneous fission of plutonium-241, the following reaction occurs:

   $^{241}Pu + {}^{1}n \rightarrow {}^{104}Ru + {}^{124}Sn + 14{}^{1}n$

   For every mole of ^{241}Pu that decays, 0.1326 g of mass is lost. How much energy is given off per mole of ^{241}Pu reacted?
3. The two rarer isotopes of hydrogen—deuterium and tritium—can also be fused to make helium by the following reaction:

   $^{2}H + {}^{3}H \rightarrow {}^{4}He + {}^{1}n$

   In the course of this reaction, 0.01888 g of mass is lost. How much energy is emitted in the reaction of 1 mol of deuterium and tritium?
4. A process called *helium burning* is thought to occur inside older stars, forming carbon:

   $3{}^{4}He \rightarrow {}^{12}C$

   If the reaction proceeds with 0.00781 g of mass lost on a molar basis, how much energy is given off?
5. Briefly describe how a nuclear reactor generates electricity.
6. Briefly describe the difference between how a nuclear reactor works and how a nuclear bomb works.
7. What is a chain reaction?
8. Why must uranium be enriched to supply nuclear energy?

Answers

1. 1.22×10^{13} J

2. 1.19×10^{13} J

3. 1.70×10^{12} J

4. 7.03×10^{11} J

5. A nuclear reactor generates heat, which is used to generate steam that turns a turbine to generate electricity.

6. Both nuclear reactor and nuclear bomb are powered by fission reaction however, in a nuclear reactor, the fission is monitored and controlled to occur continuously for a much longer time. In a nuclear bomb, the reaction is uncontrolled to explode in one

event.

7. A chain reaction is an ever-expanding series of processes that, if left unchecked, can cause a runaway reaction and possibly an explosion.

8. Natural uranium ores contain only 0.7% U-235. Most nuclear reactors require enriched U-235 for their fuel.

11.6: Chapter Summary

Additional Exercises

1. Given that many elements are metals, suggest why it would be unsafe to have radioactive materials in contact with acids.

2. Many alpha-emitting radioactive substances are relatively safe to handle, but inhaling radioactive dust can be very dangerous. Why?

3. Uranium can be separated from its daughter isotope thorium by dissolving a sample in acid and adding sodium iodide, which precipitates thorium(III) iodide:

   $Th^{3+}(aq) + 3I^{-}(aq) \rightarrow ThI_3(s)$

   If 0.567 g of Th^{3+} were dissolved in solution, how many milliliters of 0.500 M NaI(aq) would have to be added to precipitate all the thorium?

4. Thorium oxide can be dissolved in an acidic solution:

   $ThO_2(s) + 4H^{+} \rightarrow Th^{4+}(aq) + 2H_2O(\ell)$

   How many milliliters of 1.55 M HCl(aq) are needed to dissolve 10.65 g of ThO_2?

5. Radioactive strontium is dangerous because it can chemically replace calcium in the human body. The bones are particularly susceptible to radiation damage. Write the nuclear equation for the beta emission of strontium-90.

6. Write the nuclear equation for the beta emission of iodine-131, the isotope used to diagnose and treat thyroid problems.

7. A common uranium compound is uranyl nitrate hexahydrate [$UO_2(NO_3)_2\_6H_2O$]. What is the formula mass of this compound?

8. Plutonium forms three oxides: PuO, PuO_2, and Pu_2O_3. What are the formula masses of these three compounds?

9. A banana contains 600 mg of potassium, 0.0117% of which is radioactive potassium-40. If 1 g of potassium-40 has an activity of 2.626×10^5 Bq, what is the activity of a banana?

10. Smoke detectors typically contain about 0.25 mg of americium-241 as part of the smoke detection mechanism. If the activity of 1 g of americium-241 is 1.26×10^{11} Bq, what is the activity of americium-241 in the smoke detector?

11. Uranium hexafluoride (UF_6) reacts with water to make uranyl fluoride (UO_2F_2) and hydrogen fluoride (HF). Balance the following chemical equation:

    $UF_6 + H_2O \rightarrow UO_2F_2 + HF$

12. The cyclopentadienyl anion ($C_5H_5^{-}$) is an organic ion that can make ionic compounds with positive ions of radioactive elements, such as Np^{3+}. Balance the following chemical equation:

    $NpCl_3 + Be(C_5H_5)_2 \rightarrow Np(C_5H_5)_3 + BeCl_2$

Answers

1. Acids can dissolve metals, making aqueous solutions.

2. Alpha rays are dangerous only when the alpha emitter is in direct contact with tissue cells inside the body.

3. 14.7 mL

4. 104 mL

5. $^{90}_{38}\mathrm{Sr} \rightarrow {}^{0}_{-1}\mathrm{e} + {}^{90}_{39}\mathrm{Y}$

6. $^{131}_{53}\mathrm{I} \rightarrow {}^{0}_{-1}\mathrm{e} + {}^{131}_{54}\mathrm{Xe}$

7. 502 g/mol

8. PuO = 260.06 g/mol; PuO_2 = 276.06 g/mol; Pu_2O_3 = 536.12 g/mol

9. about 18 Bq

10. 3.15 x 10^7 Bq

11. $UF_6 + 2H_2O \rightarrow UO_2F_2 + 4HF$

12. $2NpCl_3 + 3Be(C_5H_5)_2 \rightarrow 2Np(C_5H_5)_3 + 3BeCl_2$

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11: Organic Chemistry - Functional Groups and Properties

Organic chemistry is the study of the chemistry of carbon compounds. Why focus on carbon? Carbon has properties that give its chemistry unparalleled complexity. It forms four covalent bonds, which give it great flexibility in bonding. It makes fairly strong bonds with itself (a characteristic called *catenation*), allowing for the formation of large molecules; it also forms fairly strong bonds with other elements, allowing for the possibility of a wide variety of substances. No other element demonstrates the versatility of carbon when it comes to making compounds. So an entire field of chemistry is devoted to the study of the compounds and reactivity of one element.

Because of the potential for complexity, chemists have defined a rather rigorous system to describe the chemistry of carbon. We will introduce some of that system in this chapter. Should you continue your study of chemistry beyond this text, you will find a much larger world of organic chemistry than we can cover in a single chapter.

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INDEX

E

equilibrium
7.7: Equilibrium

equilibrium constant
7.7: Equilibrium

H

heat
7.2: Heat

S

specific heat
7.2: Heat

steroids
13.4: Steroids

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GLOSSARY

S

Sample Word 1 | Sample Definition 1

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    - InfoPage - *Undeclared*
    - InfoTitle - *CC BY-NC-SA 4.0*
    - Table of Contents - *Undeclared*
    - Licensing - *Undeclared*
  - 1: Chemistry, Matter, and Measurement - *CC BY-NC-SA 4.0*
    - 1.1: What Is Chemistry? - *CC BY-NC-SA 4.0*
    - 1.2: The Classification of Matter - *CC BY-NC-SA 4.0*
    - 1.3: Measurements - *CC BY-NC-SA 4.0*
    - 1.4: Expressing Numbers: Scientific Notation - *CC BY-NC-SA 4.0*
    - 1.5: Expressing Numbers: Significant Figures - *CC BY-NC-SA 4.0*
    - 1.6: The International System of Units - *CC BY-NC-SA 4.0*
    - 1.7: Converting Units - *CC BY-NC-SA 4.0*
    - 1.8: Chapter Summary - *CC BY-NC-SA 4.0*
    - 1.E: Exercises - *CC BY-NC-SA 4.0*
  - 2: Elements, Atoms, and the Periodic Table - *CC BY-NC-SA 4.0*
    - 2.1: The Elements - *CC BY-NC-SA 4.0*
    - 2.2: Atomic Theory - *CC BY-NC-SA 4.0*
    - 2.3: The Structure of Atoms - *CC BY-NC-SA 4.0*
    - 2.4: Nuclei of Atoms - *CC BY-NC-SA 4.0*
    - 2.5: Atomic Masses - *CC BY-NC-SA 4.0*
    - 2.6: Arrangements of Electrons - *CC BY-NC-SA 4.0*
    - 2.7: The Periodic Table - *CC BY-NC-SA 4.0*
    - 2.8: Chapter Summary - *CC BY-NC-SA 4.0*
    - 2.E: Exercises - *CC BY-NC-SA 4.0*
  - 3: Ionic Bonding and Simple Ionic Compounds - *CC BY-NC-SA 4.0*
    - 3.1: Two Types of Bonding - *CC BY-NC-SA 4.0*
    - 3.2: Ions - *CC BY-NC-SA 4.0*
    - 3.3: Formulas for Ionic Compounds - *CC BY-NC-SA 4.0*
    - 3.4: Ionic Nomenclature - *CC BY-NC-SA 4.0*
    - 3.5: Formula Mass - *CC BY-NC-SA 4.0*
    - 3.6: Chapter Summary - *CC BY-NC-SA 4.0*
    - 3.E: Exercises - *CC BY-NC-SA 4.0*
  - 4: Covalent Bonding and Simple Molecular Compounds - *CC BY-NC-SA 4.0*
    - 4.1: Covalent Bonds - *CC BY-NC-SA 4.0*
    - 4.2: Multiple Covalent Bonds - *CC BY-NC-SA 4.0*
    - 4.3: Covalent Compounds: Formulas and Names - *CC BY-NC-SA 4.0*
    - 4.4: Characteristics of Covalent Bonds - *CC BY-NC-SA 4.0*
    - 4.5: Characteristics of Molecules - *CC BY-NC-SA 4.0*
    - 4.6: Organic Chemistry - *CC BY-NC-SA 4.0*
    - 4.7: Chapter Summary - *CC BY-NC-SA 4.0*
    - 4.E: Exercise - *CC BY-NC-SA 4.0*
  - 5: Introduction to Chemical Reactions - *CC BY-NC-SA 4.0*
    - 5.1: The Law of Conservation of Matter - *CC BY-NC-SA 4.0*
    - 5.2: Chemical Equations - *CC BY-NC-SA 4.0*
    - 5.3: Quantitative Relationships Based on Chemical Equations - *CC BY-NC-SA 4.0*
    - 5.4: Some Types of Chemical Reactions - *CC BY-NC-SA 4.0*
    - 5.5: Oxidation-Reduction (Redox) Reactions - *CC BY-NC-SA 4.0*
    - 5.6: Redox Reactions in Organic Chemistry and Biochemistry - *CC BY-NC-SA 4.0*
    - 5.7: Chapter Summary - *CC BY-NC-SA 4.0*
    - 5.E: Exercises - *CC BY-NC-SA 4.0*
  - 6: Quantities in Chemical Reactions - *CC BY-NC-SA 4.0*

- 6.1: The Mole - *CC BY-NC-SA 4.0*
- 6.2: Atomic and Molar Masses - *CC BY-NC-SA 4.0*
- 6.3: Mole-Mass Conversions - *CC BY-NC-SA 4.0*
- 6.4: Mole-Mole Relationships in Chemical Reactions - *CC BY-NC-SA 4.0*
- 6.5: Mole-Mass and Mass-Mass Problems - *CC BY-NC-SA 4.0*
- 6.6: Chapter Summary - *CC BY-NC-SA 4.0*
- 6.E: Exercise - *CC BY-NC-SA 4.0*

◦ 7: Energy and Chemical Processes - *CC BY-NC-SA 4.0*
- 7.1: Energy and Its Units - *CC BY-NC-SA 4.0*
- 7.2: Heat - *CC BY-NC-SA 4.0*
- 7.3: Phase Changes - *CC BY-NC-SA 4.0*
- 7.4: Bond Energies and Chemical Reactions - *CC BY-NC-SA 4.0*
- 7.5: The Energy of Biochemical Reactions - *CC BY-NC-SA 4.0*
- 7.6: Energetics and Kinetics - *CC BY-NC-SA 4.0*
- 7.7: Equilibrium - *CC BY-NC-SA 4.0*
- 7.8: Chapter Summary - *CC BY-NC-SA 4.0*
- 7.E: Exercises - *CC BY-NC-SA 4.0*

◦ 8: Solids, Liquids, and Gases - *CC BY-NC-SA 4.0*
- 8.1: Intermolecular Interactions - *CC BY-NC-SA 4.0*
- 8.2: Solids and Liquids - *CC BY-NC-SA 4.0*
- 8.3 Gases and Pressure - *CC BY-NC-SA 4.0*
- 8.4: Gas Laws - *CC BY-NC-SA 4.0*
- 8.5: Chapter Summary - *CC BY-NC-SA 4.0*
- 8.E: Exercises - *CC BY-NC-SA 4.0*

◦ 9: Solutions - *CC BY-NC-SA 4.0*
- 9.1: Solutions - *CC BY-NC-SA 4.0*
- 9.2: Concentration - *CC BY-NC-SA 4.0*
- 9.3: The Dissolution Process - *CC BY-NC-SA 4.0*
- 9.4: Properties of Solutions - *CC BY-NC-SA 4.0*
- 9.5: Chapter Summary - *CC BY-NC-SA 4.0*
- 9.E: Exercises - *CC BY-NC-SA 4.0*

◦ 10: Acids and Bases - *CC BY-NC-SA 4.0*
- 10.1: Arrhenius Definition of Acids and Bases - *CC BY-NC-SA 4.0*
- 10.2 Brønsted-Lowry Definition of Acids and Bases - *CC BY-NC-SA 4.0*
- 10.3: Water - Both an Acid and a Base - *CC BY-NC-SA 4.0*
- 10.4: The Strengths of Acids and Bases - *CC BY-NC-SA 4.0*
- 10.5: Buffers - *CC BY-NC-SA 4.0*
- 10.6: Chapter Summary - *CC BY-NC-SA 4.0*
- 10.E: Exercises - *CC BY-NC-SA 4.0*

◦ 11: Organic Chemistry - *CC BY-NC-SA 4.0*
- 11.1: Organic Chemistry - *CC BY-NC-SA 4.0*
- 11.2: Alkanes - *CC BY-NC-SA 4.0*
- 11.3: Condensed Structural and Line-Angle Formulas - *CC BY-NC-SA 4.0*
- 11.4: Cycloalkanes - *CC BY-NC-SA 4.0*
- 11.5: Alkenes - *CC BY-NC-SA 4.0*
- 11.6: IUPAC Nomenclature - *CC BY-NC-SA 4.0*
- 11.7: Organic Compounds with Functional Groups - *CC BY-NC-SA 4.0*
- 11.8: Physical Properties of Organic Compounds - *CC BY-NC-SA 4.0*
- 11.9: Chemical Properties: Carboxylic Acids - *CC BY-NC-SA 4.0*
- 11.10: Chemical Properties: Amines as Bases - *CC BY-NC-SA 4.0*
- 11.E: Organic Chemistry (Exercises) - *CC BY-NC-SA 4.0*
- 11.S: Organic Chemistry (Summary) - *CC BY-NC-SA 4.0*

◦ 11: Organic Chemistry - Functional Groups and Properties - *CC BY-NC-SA 4.0*

◦ 12: Carbohydrates - *CC BY-NC-SA 4.0*
- 12.1: Carbohydrates - *CC BY-NC-SA 4.0*
- 12.2: Classes of Monosaccharides - *CC BY-NC-SA 4.0*
- 12.3: Important Hexoses - *CC BY-NC-SA 4.0*
- 12.4: Cyclic Structures of Monosaccharides - *CC BY-NC-SA 4.0*
- 12.5 Properties of Monosaccharides - *CC BY-NC-SA 4.0*
- 12.6 Disaccharides - *CC BY-NC-SA 4.0*
- 12.7 Polysaccharides - *CC BY-NC-SA 4.0*
- 12.8: Chapter Summary - *CC BY-NC-SA 4.0*

◦ 13: Lipids - *CC BY-NC-SA 4.0*
- 13.0: Introduction to Lipids - *CC BY-NC-SA 4.0*
- 13.1: Fatty Acids - *CC BY-NC-SA 4.0*
- 13.2: Fats and Oils - *CC BY-NC-SA 4.0*
- 13.3: Membranes and Membrane Lipids - *CC BY-NC-SA 4.0*
- 13.4: Steroids - *CC BY-NC-SA 4.0*
- 13.5: Chapter Summary - *CC BY-NC-SA 4.0*
- 13.E: Exercises - *CC BY-NC-SA 4.0*

◦ 14: Amino Acids, Proteins, and Enzymes - *CC BY-NC-SA 4.0*
- 14.1: Properties of Amino Acids - *CC BY-NC-SA 4.0*
- 14.2: Reactions of Amino Acids - *CC BY-NC-SA 4.0*
- 14.3: Peptides - *CC BY-NC-SA 4.0*
- 14.4: Proteins - *CC BY-NC-SA 4.0*
- 14.5: Enzymes - *CC BY-NC-SA 4.0*
- 14.6 Enzyme Action - *CC BY-NC-SA 4.0*
- 14.7: Enzyme Activity - *CC BY-NC-SA 4.0*
- 14.8: Enzyme Inhibition - *CC BY-NC-SA 4.0*
- 14.9: Enzyme Cofactors and Vitamins - *CC BY-NC-SA 4.0*
- 14.10: Chapter Summary - *CC BY-NC-SA 4.0*
- 14.E: Exercises - *CC BY-NC-SA 4.0*

◦ 15: Nucleic Acids - *CC BY-NC-SA 4.0*
- 15.1: Nucleotides - *CC BY-NC-SA 4.0*
- 15.2: Nucleic Acid Structure - *CC BY-NC-SA 4.0*
- 15.3: Replication and Expression of Genetic Information - *CC BY-NC-SA 4.0*
- 15.4: Protein Synthesis and the Genetic Code -

CC BY-NC-SA 4.0
- 15.5: Mutations and Genetic Diseases - *CC BY-NC-SA 4.0*
- 15.6: Viruses - *CC BY-NC-SA 4.0*
- 15.7: Chapter Summary - *CC BY-NC-SA 4.0*
- 15.E: Exercises - *CC BY-NC-SA 4.0*

◦ 16: Energy Metabolism - *CC BY-NC-SA 4.0*
- 16.0: Introduction to Metabolism - *CC BY-NC-SA 4.0*
- 16.1: ATP: the Universal Energy Currency - *CC BY-NC-SA 4.0*
- 16.2: Stage I of Catabolism - *CC BY-NC-SA 4.0*
- 16.3: Overview of Stage II of Catabolism - *CC BY-NC-SA 4.0*
- 16.4: Stage III of Catabolism - *CC BY-NC-SA 4.0*
- 16.5: Stage II of Carbohydrate Catabolism - *CC BY-NC-SA 4.0*
- 16.6: Stage II of Lipid Catabolism - *CC BY-NC-SA 4.0*
- 16.7: Stage II of Protein Catabolism - *CC BY-NC-SA 4.0*
- 16.8: Chapter Summary - *CC BY-NC-SA 4.0*
- 16.E: Exercises - *CC BY-NC-SA 4.0*

◦ 17: Nuclear Chemistry - *CC BY-NC-SA 4.0*
- 17.1: Radioactivity - *CC BY-NC-SA 4.0*
- 17.2: Half-Life - *CC BY-NC-SA 4.0*
- 17.3: Units of Radioactivity - *CC BY-NC-SA 4.0*
- 17.4: Uses of Radioactive Isotopes - *CC BY-NC-SA 4.0*
- 17.5: Nuclear Energy - *CC BY-NC-SA 4.0*
- 17.6: Chapter Summary - *CC BY-NC-SA 4.0*
- 17.E: Exercises - *CC BY-NC-SA 4.0*

◦ Back Matter - *CC BY-NC-SA 4.0*
- Index - *Undeclared*
- Glossary - *Undeclared*
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