

FOUNDATIONS OF ORGANIC CHEMISTRY



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MUIH Organic Chemistry

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TABLE OF CONTENTS

MUIH Organic Chemistry

Licensing

1: Matter and Solutions

- 1.1: What is Chemistry?
- 1.2: The Classification of Matter
- 1.3: Solutions
- 1.4: The Dissolution Process
- 1.5: Intermolecular Forces
- 1.S: Chemistry and Matter (Summary)

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

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

4: Covalent Bonding and Simple Molecular Compounds

- 4.1: Covalent Bonds
- 4.2: Covalent Compounds- Formulas and Names
- 4.3: Multiple Covalent Bonds
- 4.4: Polar Covalent Bonds and Electronegativity
- 4.5: Characteristics of Molecules
- 4.6: Intermolecular Forces
- 4.7: Naming Binary Molecular Compounds
- 4.S: Covalent Bonding and Simple Molecular Compounds (Summary)

5: Classification and Balancing of Chemical Reactions

- 5.1: Chemical Equations
- 5.2: Balancing Chemical Equations
- 5.3: Acids, Bases, and Neutralization Reactions
- 5.4: Redox Reactions
- 5.5: Recognizing Redox Reactions
- 5.6: Net Ionic Equations

- 5.7: Le Chatelier's Principle
- 5.S: Introduction to Chemical Reactions (Summary)

6: Organic Chemistry of Hydrocarbons

- 6.1: Introduction to Organic Chemistry
- 6.2: Condensed Structural and Line-Angle Formulas
- 6.3: Structures and Names of Alkanes
- 6.4: Branched-Chain Alkanes
- 6.5: Cycloalkanes
- 6.6: IUPAC Nomenclature
- 6.7: Alkenes- Structure and Nomenclature
- 6.8: Alkenes- Cis-Trans Isomerization
- 6.9: Alkynes
- 6.10: Aromatic Compounds
- 6.11: Aromatic Compounds- Structure and Nomenclature
- 6.12: Physical Properties of Hydrocarbons
- 6.13: Chapter Summary
- 6.E: Unsaturated and Aromatic Hydrocarbons (Exercises)

7: Organic Compounds of Oxygen

- 7.1: Prelude to Organic Compounds of Oxygen
- 7.2: Organic Compounds with Functional Groups
- 7.3: Alcohols - Nomenclature and Classification
- 7.4: Physical Properties of Alcohols
- 7.5: Phenols
- 7.6: Ethers
- 7.7: Aldehydes and Ketones- Structure and Names
- 7.8: Properties of Aldehydes and Ketones
- 7.S: Organic Compounds of Oxygen (Summary)

8: Acids and Bases

- 8.1: Brønsted-Lowry Definition of Acids and Bases
- 8.2: Water is both an Acid and a Base
- 8.3: The Strengths of Acids and Bases
- 8.4: pH and K_w
- 8.5: Buffers
- 8.6: Chapter Summary

9: Organic Acids and Bases and Some of Their Derivatives

- 9.1: Prelude to Organic Acids and Bases and Some of Their Derivatives
- 9.2: Carboxylic Acids - Structures and Names
- 9.3: The Formation of Carboxylic Acids
- 9.4: Physical Properties of Carboxylic Acids
- 9.5: Chemical Properties of Carboxylic Acids- Ionization and Neutralization
- 9.6: Esters - Structures and Names
- 9.7: Physical Properties of Esters
- 9.8: Preparation of Esters
- 9.9: Hydrolysis of Esters
- 9.S: Organic Acids and Bases and Some of Their Derivatives (Summary)

10: Functional Group Reactions

- 10.1: Oxidation-Reduction (Redox) Reactions
- 10.2: Redox Reactions in Organic Chemistry
- 10.3: Reactions that Form Alcohols
- 10.4: Reactions of Alcohols
- 10.5: The Formation of Carboxylic Acids
- 10.6: Properties of Esters
- 10.7: Hydrolysis of Esters
- 10.8: Hydrolysis of Amides
- 10.9: Summary

11: Carbohydrates

- 11.1: Prelude to Carbohydrates
- 11.2: Carbohydrates
- 11.3: Classes of Monosaccharides
- 11.4: Important Hexoses
- 11.5: Cyclic Structures of Monosaccharides
- 11.6: Properties of Monosaccharides
- 11.7: Disaccharides
- 11.8: Polysaccharides
- 11.S: Carbohydrates (Summary)

12: Lipids

- 12.1: Prelude to Lipids
- 12.2: Fatty Acids
- 12.3: Fats and Oils
- 12.4: Membranes and Membrane Lipids
- 12.5: Steroids
- 12.S: Lipids (Summary)

13: Proteins and Enzymes

- 13.1: Properties of Amino Acids
- 13.2: Reactions of Amino Acids
- 13.3: Organic Sulfur Compounds
- 13.4: Amines - Structures and Names
- 13.5: Physical Properties of Amines
- 13.6: Amines as Bases
- 13.7: Amides- Structures and Names
- 13.8: Physical Properties of Amides
- 13.9: Formation of Amides
- 13.10: Chemical Properties of Amides- Hydrolysis
- 13.11: Peptides
- 13.12: Proteins
- 13.13: Enzymes
- 13.14: Enzymatic Catalysis
- 13.15: Enzyme Activity
- 13.16: Enzyme Regulation
- 13.17: Enzyme Cofactors and Vitamins
- 13.18: Chapter Summary

14: Nucleic Acids

- [14.1: Nucleotides](#)
- [14.2: Nucleic Acid Structure](#)
- [14.3: Chapter Summary](#)

15: Flow of Genetic Information

- [15.1: Replication and Expression of Genetic Information](#)
- [15.2: Translation](#)
- [15.3: Mutations and Genetic Diseases](#)

16: Energy Metabolism

- [16.1: Prelude to Energy Metabolism](#)
- [16.2: ATP- the Universal Energy Currency](#)
- [16.3: Stage I of Catabolism](#)
- [16.4: Overview of Stage II of Catabolism](#)
- [16.5: Stage III of Catabolism](#)
- [16.6: Stage II of Carbohydrate Catabolism](#)
- [16.7: Stage II of Lipid Catabolism](#)
- [16.8: Stage II of Protein Catabolism](#)
- [16.S: Energy Metabolism \(Summary\)](#)

[Index](#)

[Glossary](#)

[Detailed Licensing](#)

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CHAPTER OVERVIEW

1: Matter and Solutions

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 knowledge of chemical principles is essential for other sciences. You might be surprised at the extent to which chemistry pervades your life.

[1.1: What is Chemistry?](#)

[1.2: The Classification of Matter](#)

[1.3: Solutions](#)

[1.4: The Dissolution Process](#)

[1.5: Intermolecular Forces](#)

[1.S: Chemistry and Matter \(Summary\)](#)

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1.1: What is Chemistry?

Learning Objectives

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

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

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

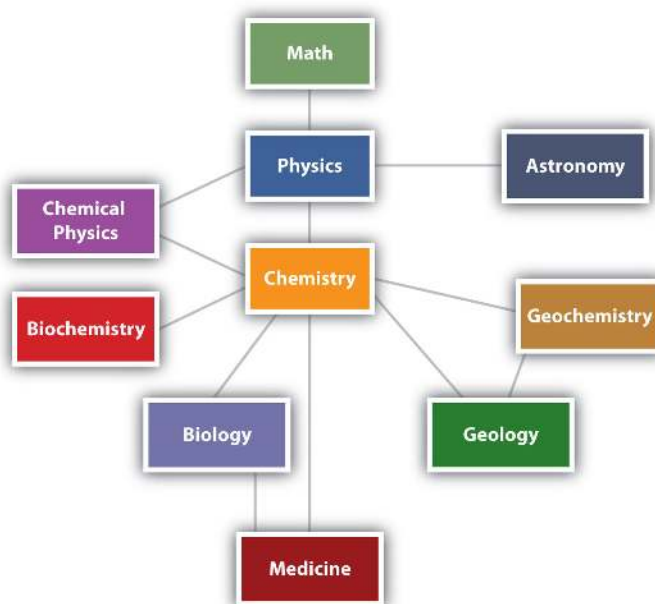


Figure 1.1.1: The Relationships between Some of the Major Branches of Science. Chemistry lies more or less in the middle, which emphasizes its importance to many branches of science.

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

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

Alchemy

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

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

symbols to represent substances, some of which are shown in the accompanying figure. This was not done to better communicate ideas, as chemists do today, but to maintain the secrecy of alchemical knowledge, keeping others from sharing in it.

↺	⊖	⊙	⊕	▽	⊖	⊕	SM	♂	♀	♂	♀	☾	♂	♂	▽
⊖	♂	♂	♂	⊕	⊕	⊕	⊖	⊖	☾	☾	♀	♂	♂	♂	▽
⊕	♂	♀	⊖	⊙	⊙	⊙	⊕	♂	☾	♀	PC	♀	♂	♂	⊖
▽	♀	♂	⊕	⊙	⊙	⊙	⊕	♀	♂						
SM	☾	♀	▽		♂		♂	♂	♀						
	♀	☾	♂					☾	♂						
			♀					♂	♂						
		☾						♀							
	☾							☾							

Esprits acides.	Terre absorbante.	Q Cuivre.	♂ Soufre minéral. [Principe.
Acide du sel marin.	^{SN} Substances métalliques.	♂ Fer.	♂ Principe huileux ou Soufre
Acide nitreux.	☿ Mercure.	♂ Plomb.	♂ Esprit de vinaigre.
Acide vitriolique.	☿ Règle d'Antimoine.	♂ Etain.	▽ Eau.
Sel alcali fixe.	☿ Or.	♂ Zinc.	☉ Sel
Sel alcali volatil.	☿ Argent.	♂ Pierre Calaminaire.	▽ Esprit de vin et Esprits ar-

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

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

✓ Exercise 1.1.1

Which fields of study are branches of science? Explain.

- a. sculpture
- b. astronomy

Answer a

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

Answer b

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

? Exercise 1.1.2

Which fields of study are branches of science?

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

Answer

a, b and c only

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

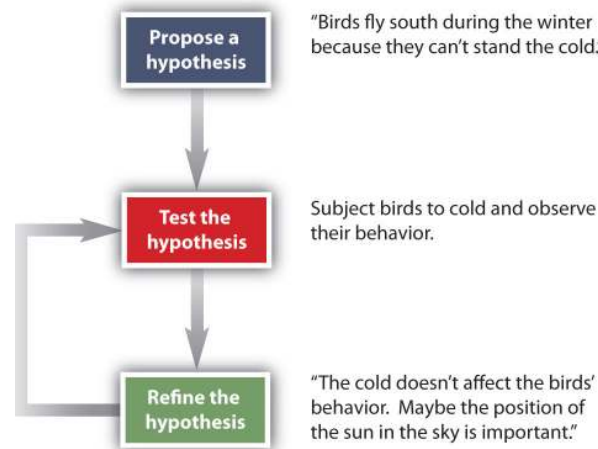


Figure 1.1.2: The General Steps of the Scientific Method. After an observation is made or a question is identified, a hypothesis is made and experiments are designed to test the hypothesis.

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

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

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

1.1.3Exercise

Define science and chemistry.

Answer

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

1.1.4Exercise

Name the steps of the scientific method.

Answer

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

Key Takeaways

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

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1.2: The Classification of Matter

Learning Objectives

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

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

Physical and Chemical Properties

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



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

Elements and Compounds

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

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

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

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

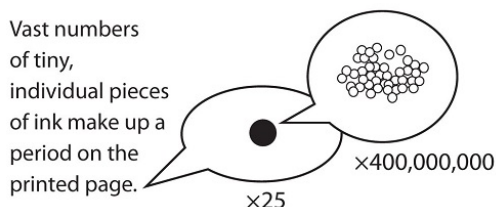


Figure 1.2.2: How Many Particles Are Needed for a Period in a Sentence? Although we do not notice it from a macroscopic perspective, matter is composed of microscopic particles so tiny that billions of them are needed to make a speck we can see with the naked eye. The $\times 25$ and $\times 400,000,000$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

Mixtures

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

✓ Example 1.2.1

How would a chemist categorize each example of matter?

- saltwater
- soil
- water
- oxygen

Answer a

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

Answer b

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

Answer c

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

Answer d

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

? Exercise 1.2.2

How would a chemist categorize each example of matter?

- breakfast coffee
- hydrogen
- an egg

Answer a

homogeneous mixture or solution

Answer b

element

Answer c

heterogeneous mixture

Phases or Physical States of Matter

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

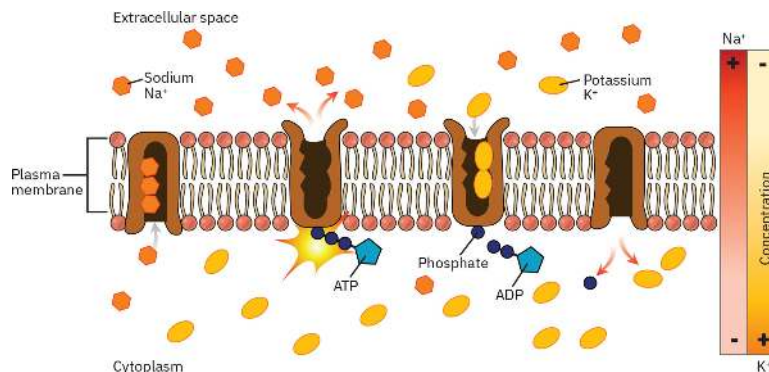


Figure 1.2.3: The three most common states or phases of matter are solid, liquid, and gas. (CC BY-4.0; OpenStax)

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

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



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

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

Table 1.2.1: Phase Changes

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

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

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

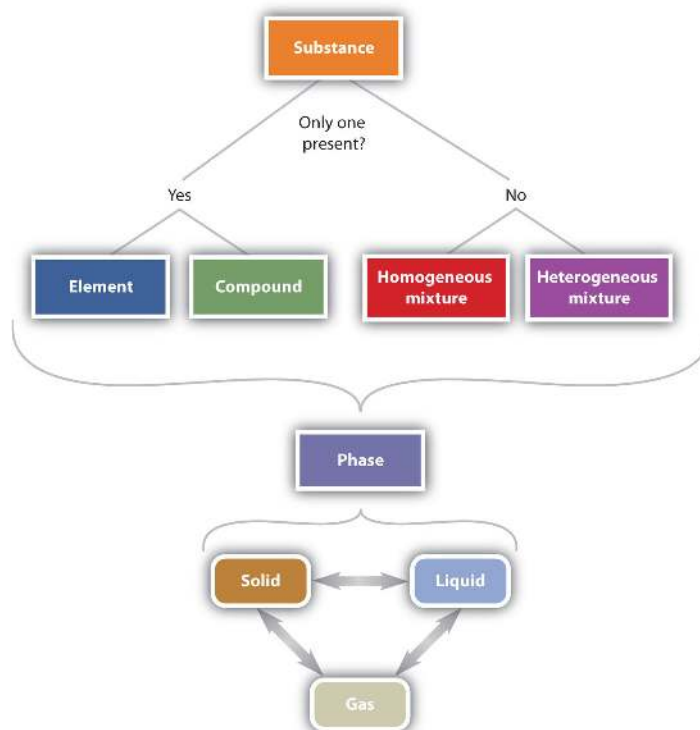


Figure 1.2.6: The Classification of Matter. Matter can be classified in a variety of ways, depending on its properties.

This table starts with a substance. If there is only one present, it can either be an element or a compound. If there is more than one present, it can either be a homogeneous mixture or a heterogeneous mixture. From these choices, the substance can be in a certain phase. It can either be solid, liquid, or gas, and each phase can go from one to another.

Concept Review Exercises

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

Answers

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

Key Takeaways

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

? Exercise 1.2.3

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

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

Answer

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

? Exercise 1.2.4

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

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

Answer

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

? Exercise 1.2.5

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

Answer

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

? Exercise 1.2.6

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

Answer

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

? Exercise 1.2.7

Give two examples of a heterogeneous mixture.

Answer

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

? Exercise 1.2.8

Give two examples of a homogeneous mixture.

Answer

vinegar and rubbing alcohol (answers will vary)

? Exercise 1.2.9

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

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

Answer

1. element
2. heterogeneous mixture
3. compound

? Exercise 1.2.10

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

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

Answer

1. compound
2. element
3. heterogeneous mixture

? Exercise 1.2.11

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

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

Answer

1. heterogeneous mixture
2. solution
3. compound

? Exercise 1.2.12

What word describes each phase change?

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

Answer

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

? Exercise 1.2.13

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

Answer

1. freezing
2. condensation
3. deposition

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1.3: Solutions

Learning Objectives

- To understand what causes solutions to form.

A solution is another name for a homogeneous mixture. A *mixture* is 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 1.3.1 lists some common types of solutions, with examples of each.

Table 1.3.1: Types of Solutions

Solvent Phase	Solute Phase	Example
gas	gas	air
liquid	gas	carbonated beverages
liquid	liquid	ethanol ($\text{C}_2\text{H}_5\text{OH}$) in H_2O (alcoholic beverages)
liquid	solid	saltwater
solid	gas	H_2 gas absorbed by Pd metal
solid	liquid	$\text{Hg}(\ell)$ in dental fillings
solid	solid	steel alloys

What causes a solution to form? The simple answer is that the solvent and the solute must have similar intermolecular interactions. When this is the case, the individual particles of solvent and solute can easily mix so intimately that each particle of solute is surrounded by particles of solvent, forming a solution. However, if two substances have very different intermolecular interactions, large amounts of energy are required to force their individual particles to mix intimately, so a solution does not form. Thus two alkanes like *n*-heptane, C_7H_{16} , and *n*-hexane, C_6H_{14} , are completely miscible in all proportions. The C_7H_{16} and C_6H_{14} molecules are so similar (recall Section 4.6) that there are only negligible differences in intermolecular forces.

For a similar reason, methanol, CH_3OH , is completely miscible with water. In this case both molecules are polar and can form hydrogen bonds among themselves, and so there are strong intermolecular attractions within each liquid. However, CH_3OH dipoles can align with H_2O dipoles, and CH_3OH molecules can hydrogen bond to H_2O molecules, and so the attractions among unlike molecules in the solution are similar to those among like molecules in each pure liquid.

This process leads to a simple rule of thumb: *like dissolves like*. Solvents that are very polar will dissolve solutes that are very polar or even ionic. Solvents that are nonpolar will dissolve nonpolar solutes. Thus water, being polar, is a good solvent for ionic compounds and polar solutes like ethanol ($\text{C}_2\text{H}_5\text{OH}$). However, water does not dissolve nonpolar solutes, such as many oils and greases (Figure 1.3.1).



Figure 1.3.1: 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 1.3.1

Water is considered a polar solvent. Which substances should dissolve in water?

1. methanol (CH_3OH)
2. sodium sulfate (Na_2SO_4)
3. octane (C_8H_{18})

Solution

Because water is polar, substances that are polar or ionic will dissolve in it.

1. Because of the OH group in methanol, we expect its molecules to be polar. Thus, we expect it to be soluble in water. As both water and methanol are liquids, the word *miscible* can be used in place of *soluble*.
2. Sodium sulfate is an ionic compound, so we expect it to be soluble in water.
3. Like other hydrocarbons, octane is nonpolar, so we expect that it would not be soluble in water.

? Exercise 1.3.1

Toluene ($C_6H_5CH_3$) is widely used in industry as a nonpolar solvent. Which substances should dissolve in toluene?

- a. water (H_2O)
- b. sodium sulfate (Na_2SO_4)
- c. octane (C_8H_{18})

Answer

Octane only.

✓ Example 1.3.2

Predict which of the following compounds will be most soluble in water:

- a. CH_3CH_2OH
Ethanol
- b. $CH_3CH_2CH_2CH_2CH_2CH_2OH$
Hexanol

Solution

Since ethanol contains an **OH** group, it can hydrogen bond to water. Although the same is true of hexanol, the OH group is found only at one end of a fairly large molecule. The rest of the molecule can be expected to behave much as though it were a nonpolar alkane. This substance should thus be much less soluble than the first. Experimentally we find that ethanol is completely miscible with water, while only 0.6 g hexanol dissolves in 100 g water.

1.3.2Exercise

Would I_2 be more soluble in CCl_4 or H_2O ?

Answer

I_2 is nonpolar. Of the two solvents, CCl_4 is nonpolar and H_2O is polar, so I_2 would be expected to be more soluble in CCl_4 .

Key Takeaway

- Solutions form because a solute and a solvent experience similar intermolecular interactions.

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1.4: The Dissolution Process

Learning Objectives

- To describe the dissolution process at the molecular level

The Dissolution Process

What occurs at the molecular level to cause a solute to dissolve in a solvent? The answer depends in part on the solute, but there are some similarities common to all solutes.

Recall the rule that *like dissolves like*. This means that substances must have similar intermolecular forces to form solutions. When a soluble solute is introduced into a solvent, the particles of solute can interact with the particles of solvent. In the case of a solid or liquid solute, the interactions between the solute particles and the solvent particles are so strong that the individual solute particles separate from each other and, surrounded by solvent molecules, enter the solution. (Gaseous solutes already have their constituent particles separated, but the concept of being surrounded by solvent particles still applies.) This process is called **solvation** and is illustrated in Figure 1.4.1. When the solvent is water, the word **hydration**, rather than solvation, is used.

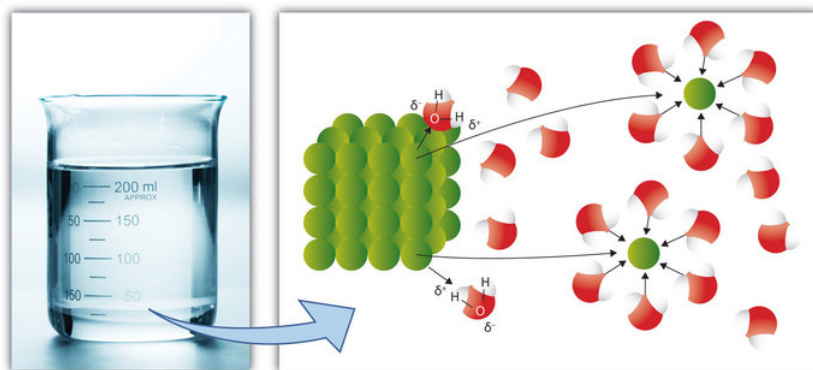


Figure 1.4.1: Solvation. When a solute dissolves, the individual particles of solute become surrounded by solvent particles. Eventually the particle detaches from the remaining solute, surrounded by solvent molecules in solution. Source: Photo © Thinkstock

Ionic Compounds and Covalent Compounds as Solutes

In the case of molecular solutes like glucose, the solute particles are individual molecules. However, if the solute is ionic, the individual ions separate from each other and become surrounded by solvent particles. That is, the cations and anions of an ionic solute separate when the solute dissolves. This process is referred to as **dissociation** (Figure 1.4.1).

The dissociation of soluble ionic compounds gives solutions of these compounds an interesting property: they conduct electricity. Because of this property, soluble ionic compounds are referred to as electrolytes. Many ionic compounds dissociate completely and are therefore called **strong electrolytes**. Sodium chloride is an example of a strong electrolyte. Some compounds dissolve but dissociate only partially, and solutions of such solutes may conduct electricity only weakly. These solutes are called **weak electrolytes**. Acetic acid (CH_3COOH), the compound in vinegar, is a weak electrolyte. Solutes that dissolve into individual neutral molecules without dissociation do not impart additional electrical conductivity to their solutions and are called nonelectrolytes. Table sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) is an example of a nonelectrolyte.

The term electrolyte is used in medicine to mean any of the important ions that are dissolved in aqueous solution in the body. Important physiological electrolytes include Na^+ , K^+ , Ca^{2+} , Mg^{2+} , and Cl^- .

✓ Example 1.4.1

The following substances all dissolve to some extent in water. Classify each as an electrolyte or a nonelectrolyte.

- potassium chloride (KCl)
- fructose ($\text{C}_6\text{H}_{12}\text{O}_6$)

3. isopropyl alcohol [$\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$]
4. magnesium hydroxide [$\text{Mg}(\text{OH})_2$]

Solution

Each substance can be classified as an ionic solute or a nonionic solute. Ionic solutes are electrolytes, and nonionic solutes are nonelectrolytes.

1. Potassium chloride is an ionic compound; therefore, when it dissolves, its ions separate, making it an electrolyte.
2. Fructose is a sugar similar to glucose. (In fact, it has the same molecular formula as glucose.) Because it is a molecular compound, we expect it to be a nonelectrolyte.
3. Isopropyl alcohol is an organic molecule containing the alcohol functional group. The bonding in the compound is all covalent, so when isopropyl alcohol dissolves, it separates into individual molecules but not ions. Thus, it is a nonelectrolyte.
4. Magnesium hydroxide is an ionic compound, so when it dissolves it dissociates. Thus, magnesium hydroxide is an electrolyte.

? Exercise 1.4.1

The following substances all dissolve to some extent in water. Classify each as an electrolyte or a nonelectrolyte.

- a. acetone (CH_3COCH_3)
- b. iron(III) nitrate [$\text{Fe}(\text{NO}_3)_3$]
- c. elemental bromine (Br_2)
- d. sodium hydroxide (NaOH)

Answer

- a. nonelectrolyte
- b. electrolyte
- c. nonelectrolyte
- d. electrolyte

Electrolytes in Body Fluids

Our body fluids are solutions of electrolytes and many other things. The combination of blood and the circulatory system is the *river of life*, because it coordinates all the life functions. When the heart stops pumping in a heart attack, the life ends quickly. Getting the heart restarted as soon as one can is crucial in order to maintain life.

The primary electrolytes required in the body fluid are cations (of calcium, potassium, sodium, and magnesium) and anions (of chloride, carbonates, aminoacetates, phosphates, and iodide). These are nutritionally called **macrominerals**.

Electrolyte balance is crucial to many body functions. Here's some extreme examples of what can happen with an imbalance of electrolytes: elevated potassium levels may result in cardiac arrhythmias; decreased extracellular potassium produces paralysis; excessive extracellular sodium causes fluid retention; and decreased plasma calcium and magnesium can produce muscle spasms of the extremities.

When a patient is dehydrated, a carefully prepared (commercially available) electrolyte solution is required to maintain health and well being. In terms of child health, oral electrolyte is given when a child is dehydrated due to diarrhea. The use of oral electrolyte maintenance solutions, which is responsible for saving millions of lives worldwide over the last 25 years, is one of the most important medical advances in protecting the health of children in the century, explains Juilus G.K. Goepp, MD, assistant director of the Pediatric Emergency Department of the Children's Center at Johns Hopkins Hospital. If a parent provides an oral electrolyte maintenance solution at the very start of the illness, dehydration can be prevented. The functionality of electrolyte solutions is related to their properties, and interest in electrolyte solutions goes far beyond chemistry.

Sports drinks are designed to rehydrate the body after excessive fluid depletion. Electrolytes in particular promote normal rehydration to prevent fatigue during physical exertion. Are they a good choice for achieving the recommended fluid intake? Are

they performance and endurance enhancers like they claim? Who should drink them?

Typically, eight ounces of a sports drink provides between fifty and eighty calories and 14 to 17 grams of carbohydrate, mostly in the form of simple sugars. Sodium and potassium are the most commonly included electrolytes in sports drinks, with the levels of these in sports drinks being highly variable. The American College of Sports Medicine says a sports drink should contain 125 milligrams of sodium per 8 ounces as it is helpful in replenishing some of the sodium lost in sweat and promotes fluid uptake in the small intestine, improving hydration.

Gatorade

In the summer of 1965, the assistant football coach of the University of Florida Gators requested scientists affiliated with the university study why the withering heat of Florida caused so many heat-related illnesses in football players and provide a solution to increase athletic performance and recovery post-training or game. The discovery was that inadequate replenishment of fluids, carbohydrates, and electrolytes was the reason for the “wilting” of their football players. Based on their research, the scientists concocted a drink for the football players containing water, carbohydrates, and electrolytes and called it “Gatorade.” In the next football season the Gators were nine and two and won the Orange Bowl. The Gators’ success launched the sports-drink industry, which is now a multibillion-dollar industry that is still dominated by Gatorade.



University of Florida football player Chip Hinton testing Gatorade in 1965, pictured next to the leader of its team of inventors, [Robert Cade](#).

Key Takeaway

- When a solute dissolves, its individual particles are surrounded by solvent molecules and are separated from each other.

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1.5: Intermolecular Forces

Learning Objectives

- Describe the types of intermolecular forces possible between atoms or molecules in condensed phases (dispersion forces, dipole-dipole attractions, and hydrogen bonding)
- Identify the types of intermolecular forces experienced by specific molecules based on their structures
- Explain the relation between the intermolecular forces present within a substance and the temperatures associated with changes in its physical state

As was the case for gaseous substances, the kinetic molecular theory may be used to explain the behavior of solids and liquids. In the following description, the term *particle* will be used to refer to an atom, molecule, or ion. Note that we will use the popular phrase “intermolecular attraction” to refer to attractive forces between the particles of a substance, regardless of whether these particles are molecules, atoms, or ions.

Consider these two aspects of the molecular-level environments in solid, liquid, and gaseous matter:

- Particles in a solid are tightly packed together and often arranged in a regular pattern; in a liquid, they are close together with no regular arrangement; in a gas, they are far apart with no regular arrangement.
- Particles in a solid vibrate about fixed positions and do not generally move in relation to one another; in a liquid, they move past each other but remain in essentially constant contact; in a gas, they move independently of one another except when they collide.

The differences in the properties of a solid, liquid, or gas reflect the strengths of the attractive forces between the atoms, molecules, or ions that make up each phase. The phase in which a substance exists depends on the relative extents of its intermolecular forces (IMFs) and the kinetic energies (KE) of its molecules. IMFs are the various forces of attraction that may exist between the atoms and molecules of a substance due to electrostatic phenomena, as will be detailed in this module. These forces serve to hold particles close together, whereas the particles’ KE provides the energy required to overcome the attractive forces and thus increase the distance between particles. Figure 1.5.1 illustrates how changes in physical state may be induced by changing the temperature, hence, the average KE, of a given substance.

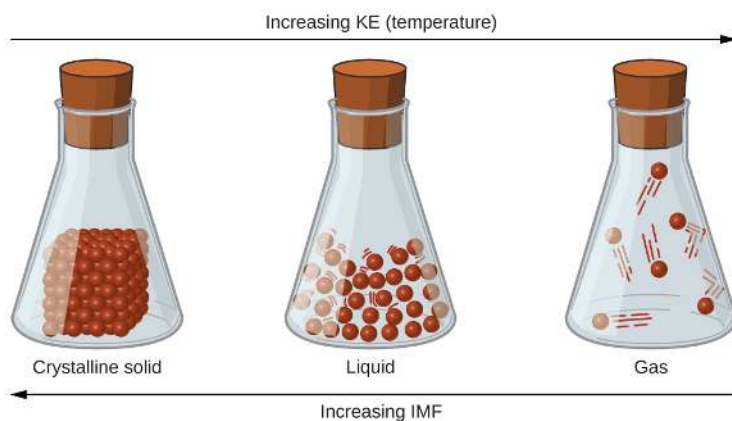
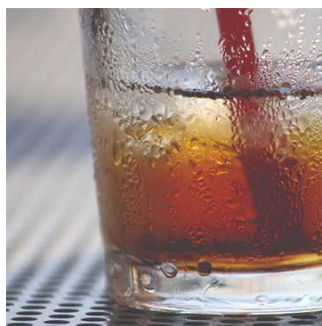


Figure 1.5.1: Transitions between solid, liquid, and gaseous

states of a substance occur when conditions of temperature or pressure favor the associated changes in intermolecular forces. (Note: The space between particles in the gas phase is much greater than shown.) Three sealed flasks are labeled, “Crystalline solid,” “Liquid,” and “Gas,” from left to right. The first flask holds a cube composed of small spheres sitting on the bottom while the second flask shows a lot of small spheres in the bottom that are spaced a small distance apart from one another and have lines around them to indicate motion. The third flask shows a few spheres spread far from one another with larger lines to indicate motion. There is a right-facing arrow that spans the top of all three flasks. The arrow is labeled, “Increasing K E (temperature).” There is a left-facing arrow that spans the bottom of all three flasks. The arrow is labeled, “Increasing I M F.”

As an example of the processes depicted in this figure, consider a sample of water. When gaseous water is cooled sufficiently, the attractions between H_2O molecules will be capable of holding them together when they come into contact with each other; the gas condenses, forming liquid H_2O . For example, liquid water forms on the outside of a cold glass as the water vapor in the air is cooled by the cold glass, as seen in Figure 1.5.2.



(a)



(b)

Figure 1.5.2: Condensation forms when water

vapor in the air is cooled enough to form liquid water, such as (a) on the outside of a cold beverage glass or (b) in the form of fog. (credit a: modification of work by Jenny Downing; credit b: modification of work by Cory Zanker) Image a shows a brown colored beverage in a glass with condensation on the outside. Image b shows a body of water with fog hovering above the surface of the water.

We can also liquefy many gases by compressing them, if the temperature is not too high. The increased pressure brings the molecules of a gas closer together, such that the attractions between the molecules become strong relative to their KE. Consequently, they form liquids. Butane, C_4H_{10} , is the fuel used in disposable lighters and is a gas at standard temperature and pressure. Inside the lighter's fuel compartment, the butane is compressed to a pressure that results in its condensation to the liquid state, as shown in Figure 1.5.3.



Figure 1.5.3: Gaseous butane is compressed within the storage compartment of a disposable lighter, resulting in its condensation to the liquid state. (credit: modification of work by "Sam-Cat"/Flickr)

Finally, if the temperature of a liquid becomes sufficiently low, or the pressure on the liquid becomes sufficiently high, the molecules of the liquid no longer have enough KE to overcome the IMF between them, and a solid forms. A more thorough discussion of these and other changes of state, or phase transitions, is provided in a later module of this chapter.

1.5.1: Forces between Molecules

Under appropriate conditions, the attractions between all gas molecules will cause them to form liquids or solids. This is due to intermolecular forces, not *intramolecular* forces. *Intramolecular* forces are those *within* the molecule that keep the molecule together, for example, the bonds between the atoms. *Intermolecular* forces are the attractions *between* molecules, which determine many of the physical properties of a substance. Figure 1.5.4 illustrates these different molecular forces. The strengths of these attractive forces vary widely, though usually the IMFs between small molecules are weak compared to the intramolecular forces that bond atoms together within a molecule. For example, to overcome the IMFs in one mole of liquid HCl and convert it into

gaseous HCl requires only about 17 kilojoules. However, to break the covalent bonds between the hydrogen and chlorine atoms in one mole of HCl requires about 25 times more energy—430 kilojoules.

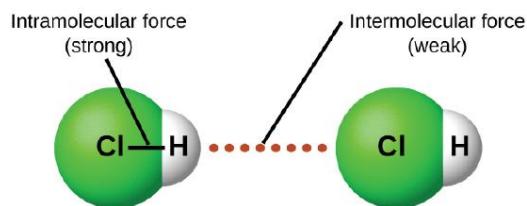


Figure 1.5.4: Intramolecular forces keep a molecule intact. Intermolecular forces hold multiple molecules together and determine many of a substance's properties. An image is shown in which two molecules composed of a green sphere labeled "Cl" connected on the right to a white sphere labeled "H" are near one another with a dotted line labeled "Intermolecular force (weak)" drawn between them. A line connects the two spheres in each molecule and the line is labeled "Intramolecular force (strong)."

All of the attractive forces between neutral atoms and molecules are known as van der Waals forces, although they are usually referred to more informally as intermolecular attraction. We will consider the various types of IMFs in the next three sections of this module.

1.5.2: Dispersion Forces

One of the three van der Waals forces is present in all condensed phases, regardless of the nature of the atoms or molecules composing the substance. This attractive force is called the London dispersion force in honor of German-born American physicist Fritz London who, in 1928, first explained it. This force is often referred to as simply the dispersion force. Because the electrons of an atom or molecule are in constant motion (or, alternatively, the electron's location is subject to quantum-mechanical variability), at any moment in time, an atom or molecule can develop a temporary, instantaneous dipole if its electrons are distributed asymmetrically. The presence of this dipole can, in turn, distort the electrons of a neighboring atom or molecule, producing an induced dipole. These two rapidly fluctuating, temporary dipoles thus result in a relatively weak electrostatic attraction between the species—a so-called dispersion force like that illustrated in Figure 1.5.5.

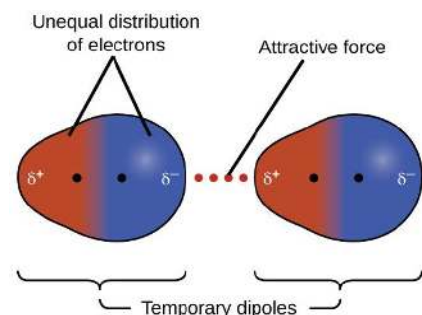


Figure 1.5.5: Dispersion forces result from the formation of temporary dipoles, as illustrated here for two nonpolar diatomic molecules. Two pairs of molecules are shown where each molecule has one larger blue side labeled "delta sign, negative sign" and a smaller red side labeled "delta sign, positive sign." Toward the middle of the both molecules, but still on each distinct side, is a black dot. Between the two images is a dotted line labeled, "Attractive force." In the first image, the red and blue sides are labeled, "Unequal distribution of electrons." Below both images are brackets. The brackets are labeled, "Temporary dipoles."

Dispersion forces that develop between atoms in different molecules can attract the two molecules to each other. The forces are relatively weak, however, and become significant only when the molecules are very close. Larger and heavier atoms and molecules exhibit stronger dispersion forces than do smaller and lighter atoms and molecules. F_2 and Cl_2 are gases at room temperature (reflecting weaker attractive forces); Br_2 is a liquid, and I_2 is a solid (reflecting stronger attractive forces). Trends in observed melting and boiling points for the halogens clearly demonstrate this effect, as seen in Table 1.5.1.

Table 1.5.1: Melting and Boiling Points of the Halogens

Halogen	Molar Mass	Atomic Radius	Melting Point	Boiling Point
fluorine, F_2	38 g/mol	72 pm	53 K	85 K
chlorine, Cl_2	71 g/mol	99 pm	172 K	238 K

Halogen	Molar Mass	Atomic Radius	Melting Point	Boiling Point
bromine, Br ₂	160 g/mol	114 pm	266 K	332 K
iodine, I ₂	254 g/mol	133 pm	387 K	457 K
astatine, At ₂	420 g/mol	150 pm	575 K	610 K

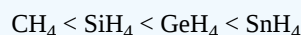
The increase in melting and boiling points with increasing atomic/molecular size may be rationalized by considering how the strength of dispersion forces is affected by the electronic structure of the atoms or molecules in the substance. In a larger atom, the valence electrons are, on average, farther from the nuclei than in a smaller atom. Thus, they are less tightly held and can more easily form the temporary dipoles that produce the attraction. The measure of how easy or difficult it is for another electrostatic charge (for example, a nearby ion or polar molecule) to distort a molecule's charge distribution (its electron cloud) is known as polarizability. A molecule that has a charge cloud that is easily distorted is said to be very polarizable and will have large dispersion forces; one with a charge cloud that is difficult to distort is not very polarizable and will have small dispersion forces.

✓ Example 1.5.1: London Forces and Their Effects

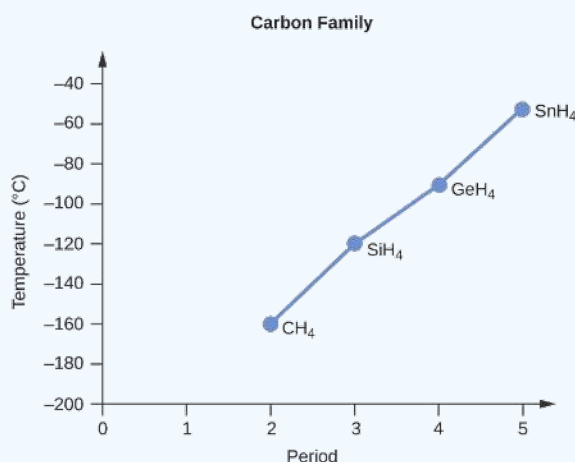
Order the following compounds of a group 14 element and hydrogen from lowest to highest boiling point: CH₄, SiH₄, GeH₄, and SnH₄. Explain your reasoning.

Solution

Applying the skills acquired in the chapter on chemical bonding and molecular geometry, all of these compounds are predicted to be nonpolar, so they may experience only dispersion forces: the smaller the molecule, the less polarizable and the weaker the dispersion forces; the larger the molecule, the larger the dispersion forces. The molar masses of CH₄, SiH₄, GeH₄, and SnH₄ are approximately 16 g/mol, 32 g/mol, 77 g/mol, and 123 g/mol, respectively. Therefore, CH₄ is expected to have the lowest boiling point and SnH₄ the highest boiling point. The ordering from lowest to highest boiling point is expected to be



A graph of the actual boiling points of these compounds versus the period of the group 14 elements shows this prediction to be correct:



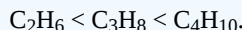
A line graph, titled "Carbon Family," is shown where the y-axis is labeled "Temperature, (degree sign C)" and has values of "negative 200" to "negative 40" from bottom to top in increments of 20. The x-axis is labeled "Period" and has values of "0" to "5" in increments of 1. The first point on the graph is labeled "C H subscript 4" and is at point "2, negative 160." The second point on the graph is labeled "S i H subscript 4" and is at point "3, negative 120" while the third point on the graph is labeled "G e H subscript 4" and is at point "4, negative 100." The fourth point on the graph is labeled "S n H subscript 4" and is at point "5, negative 60."

? Exercise 1.5.1

Order the following hydrocarbons from lowest to highest boiling point: C_2H_6 , C_3H_8 , and C_4H_{10} .

Answer

All of these compounds are nonpolar and only have London dispersion forces: the larger the molecule, the larger the dispersion forces and the higher the boiling point. The ordering from lowest to highest boiling point is therefore



The shapes of molecules also affect the magnitudes of the dispersion forces between them. For example, boiling points for the isomers *n*-pentane, isopentane, and neopentane (shown in Figure 1.5.6) are 36 °C, 27 °C, and 9.5 °C, respectively. Even though these compounds are composed of molecules with the same chemical formula, C_5H_{12} , the difference in boiling points suggests that dispersion forces in the liquid phase are different, being greatest for *n*-pentane and least for neopentane. The elongated shape of *n*-pentane provides a greater surface area available for contact between molecules, resulting in correspondingly stronger dispersion forces. The more compact shape of isopentane offers a smaller surface area available for intermolecular contact and, therefore, weaker dispersion forces. Neopentane molecules are the most compact of the three, offering the least available surface area for intermolecular contact and, hence, the weakest dispersion forces. This behavior is analogous to the connections that may be formed between strips of VELCRO brand fasteners: the greater the area of the strip's contact, the stronger the connection.

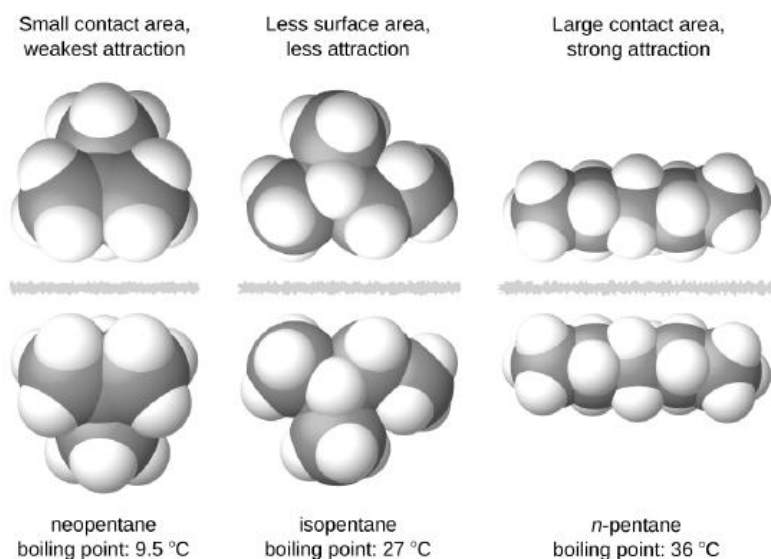
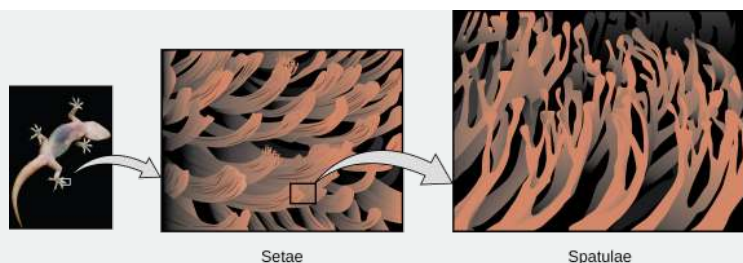


Figure 1.5.6: The strength of the dispersion forces

increases with the contact area between molecules, as demonstrated by the boiling points of these pentane isomers. Three images of molecules are shown. The first shows a cluster of large, gray spheres each bonded together and to several smaller, white spheres. There is a gray, jagged line and then the mirror image of the first cluster of spheres is shown. Above these two clusters is the label, "Small contact area, weakest attraction," and below is the label, "neopentane boiling point: 9.5 degrees C." The second shows a chain of three gray spheres bonded by the middle sphere to a fourth gray sphere. Each gray sphere is bonded to several smaller, white spheres. There is a jagged, gray line and then the mirror image of the first chain appears. Above these two chains is the label, "Less surface area, less attraction," and below is the label, "isopentane boiling point: 27 degrees C." The third image shows a chain of five gray spheres bonded together and to several smaller, white spheres. There is a jagged gray line and then the mirror image of the first chain appears. Above these chains is the label, "Large contact area, strong attraction," and below is the label, "*n*-pentane boiling point 36 degrees C."

📌 Applications: Geckos and Intermolecular Forces

Geckos have an amazing ability to adhere to most surfaces. They can quickly run up smooth walls and across ceilings that have no toe-holds, and they do this without having suction cups or a sticky substance on their toes. And while a gecko can lift its feet easily as it walks along a surface, if you attempt to pick it up, it sticks to the surface. How are geckos (as well as spiders and some other insects) able to do this? Although this phenomenon has been investigated for hundreds of years, scientists only recently uncovered the details of the process that allows geckos' feet to behave this way.



Setae

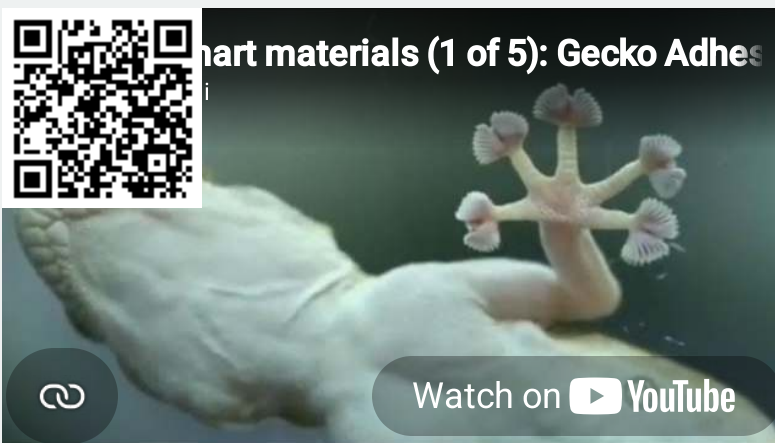
Spatulae

Figure 1.5.7: Geckos' toes contain large numbers of

tiny hairs (setae), which branch into many triangular tips (spatulae). Geckos adhere to surfaces because of van der Waals attractions between the surface and a gecko's millions of spatulae. By changing how the spatulae contact the surface, geckos can turn their stickiness "on" and "off." (credit photo: modification of work by "JC*+A"/Flickr) Three figures are shown. The first is a photo of the bottom of a gecko's foot. The second is bigger version which shows the setae. The third is a bigger version of the setae and shows the spatulae.

Geckos' toes are covered with hundreds of thousands of tiny hairs known as *setae*, with each seta, in turn, branching into hundreds of tiny, flat, triangular tips called *spatulae*. The huge numbers of spatulae on its setae provide a gecko, shown in Figure 1.5.7, with a large total surface area for sticking to a surface. In 2000, Kellar Autumn, who leads a multi-institutional gecko research team, found that geckos adhered equally well to both polar silicon dioxide and nonpolar gallium arsenide. This proved that geckos stick to surfaces because of dispersion forces—weak intermolecular attractions arising from temporary, synchronized charge distributions between adjacent molecules. Although dispersion forces are very weak, the total attraction over millions of spatulae is large enough to support many times the gecko's weight.

In 2014, two scientists developed a model to explain how geckos can rapidly transition from "sticky" to "non-sticky." Alex Greaney and Congcong Hu at Oregon State University described how geckos can achieve this by changing the angle between their spatulae and the surface. Geckos' feet, which are normally nonsticky, become sticky when a small shear force is applied. By curling and uncurling their toes, geckos can alternate between sticking and unsticking from a surface, and thus easily move across it. Further investigations may eventually lead to the development of better adhesives and other applications.



Watch this video to learn more about Kellar Autumn's research that determined that van der Waals forces are responsible for a gecko's ability to cling and climb.

1.5.3: Dipole-Dipole Attractions

Recall from the chapter on chemical bonding and molecular geometry that *polar* molecules have a partial positive charge on one side and a partial negative charge on the other side of the molecule—a separation of charge called a *dipole*. Consider a polar molecule such as hydrogen chloride, HCl. In the HCl molecule, the more electronegative Cl atom bears the partial negative charge, whereas the less electronegative H atom bears the partial positive charge. An attractive force between HCl molecules results from the attraction between the positive end of one HCl molecule and the negative end of another. This attractive force is called a dipole-dipole attraction—the electrostatic force between the partially positive end of one polar molecule and the partially negative end of another, as illustrated in Figure 1.5.8.

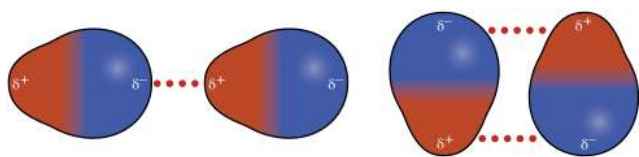


Figure 1.5.8: This image shows two arrangements of polar molecules,

such as HCl, that allow an attraction between the partial negative end of one molecule and the partial positive end of another. Two pairs of molecules are shown where each molecule has one larger blue side labeled “delta sign, negative sign” and a smaller red side labeled “delta sign, positive sign”. In the first pair, the red sides of the two molecules both face to the left and the blue side to the right. A horizontal dotted line lies in between the two. In the second pair, the molecules face up and down, with the red and blue ends aligning. A horizontal dotted line lies between the red and blue ends facing upward and another lies between the red and blue ends facing downward.

The effect of a dipole-dipole attraction is apparent when we compare the properties of HCl molecules to nonpolar F_2 molecules. Both HCl and F_2 consist of the same number of atoms and have approximately the same molecular mass. At a temperature of 150 K, molecules of both substances would have the same average KE. However, the dipole-dipole attractions between HCl molecules are sufficient to cause them to “stick together” to form a liquid, whereas the relatively weaker dispersion forces between nonpolar F_2 molecules are not, and so this substance is gaseous at this temperature. The higher normal boiling point of HCl (188 K) compared to F_2 (85 K) is a reflection of the greater strength of dipole-dipole attractions between HCl molecules, compared to the attractions between nonpolar F_2 molecules. We will often use values such as boiling or freezing points, or enthalpies of vaporization or fusion, as indicators of the relative strengths of IMFs of attraction present within different substances.

✓ Example 1.5.2: Dipole-Dipole Forces and Their Effects

Predict which will have the higher boiling point: N_2 or CO. Explain your reasoning.

Solution

CO and N_2 are both diatomic molecules with masses of about 28 amu, so they experience similar London dispersion forces. Because CO is a polar molecule, it experiences dipole-dipole attractions. Because N_2 is nonpolar, its molecules cannot exhibit dipole-dipole attractions. The dipole-dipole attractions between CO molecules are comparably stronger than the dispersion forces between nonpolar N_2 molecules, so CO is expected to have the higher boiling point.

A common method for preparing oxygen is the decomposition

? Exercise 1.5.2

Predict which will have the higher boiling point: ICl or Br_2 . Explain your reasoning.

Answer

ICl. ICl and Br_2 have similar masses (~160 amu) and therefore experience similar London dispersion forces. ICl is polar and thus also exhibits dipole-dipole attractions; Br_2 is nonpolar and does not. The relatively stronger dipole-dipole attractions require more energy to overcome, so ICl will have the higher boiling point.

1.5.4: Hydrogen Bonding

Nitrosyl fluoride (ONF, molecular mass 49 amu) is a gas at room temperature. Water (H_2O , molecular mass 18 amu) is a liquid, even though it has a lower molecular mass. We clearly cannot attribute this difference between the two compounds to dispersion forces. Both molecules have about the same shape and ONF is the heavier and larger molecule. It is, therefore, expected to experience more significant dispersion forces. Additionally, we cannot attribute this difference in boiling points to differences in the dipole moments of the molecules. Both molecules are polar and exhibit comparable dipole moments. The large difference between the boiling points is due to a particularly strong dipole-dipole attraction that may occur when a molecule contains a hydrogen atom bonded to a fluorine, oxygen, or nitrogen atom (the three most electronegative elements). The very large difference in electronegativity between the H atom (2.1) and the atom to which it is bonded (4.0 for an F atom, 3.5 for an O atom, or 3.0 for a N atom), combined with the very small size of a H atom and the relatively small sizes of F, O, or N atoms, leads to *highly concentrated partial charges* with these atoms. Molecules with F-H, O-H, or N-H moieties are very strongly attracted to similar

moieties in nearby molecules, a particularly strong type of dipole-dipole attraction called hydrogen bonding. Examples of hydrogen bonds include $\text{HF} \cdots \text{HF}$, $\text{H}_2\text{O} \cdots \text{HOH}$, and $\text{H}_3\text{N} \cdots \text{HNH}_2$, in which the hydrogen bonds are denoted by dots. Figure 1.5.9 illustrates hydrogen bonding between water molecules.

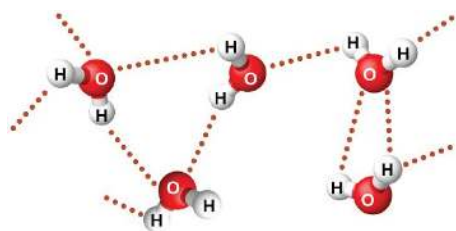


Figure 1.5.9: Water molecules participate in multiple hydrogen-bonding interactions with nearby water molecules. Five water molecules are shown near one another, but not touching. A dotted line lies between many of the hydrogen atoms on one molecule and the oxygen atom on another molecule.

Despite use of the word “bond,” keep in mind that hydrogen bonds are *intermolecular* attractive forces, not *intramolecular* attractive forces (covalent bonds). Hydrogen bonds are much weaker than covalent bonds, only about 5 to 10% as strong, but are generally much stronger than other dipole-dipole attractions and dispersion forces.

Hydrogen bonds have a pronounced effect on the properties of condensed phases (liquids and solids). For example, consider the trends in boiling points for the binary hydrides of group 15 (NH_3 , PH_3 , AsH_3 , and SbH_3), group 16 (H_2O , H_2S , H_2Se , and H_2Te), and group 17 (HF , HCl , HBr , and HI). The boiling points of the heaviest three hydrides for each group are plotted in Figure 1.5.10. As we progress down any of these groups, the polarities of the molecules decrease slightly, whereas the sizes of the molecules increase substantially. The effect of increasingly stronger dispersion forces dominates that of increasingly weaker dipole-dipole attractions, and the boiling points are observed to increase steadily. For the group 15, 16, and 17 hydrides, the boiling points for each class of compounds increase with increasing molecular mass for elements in periods 3, 4, and 5.

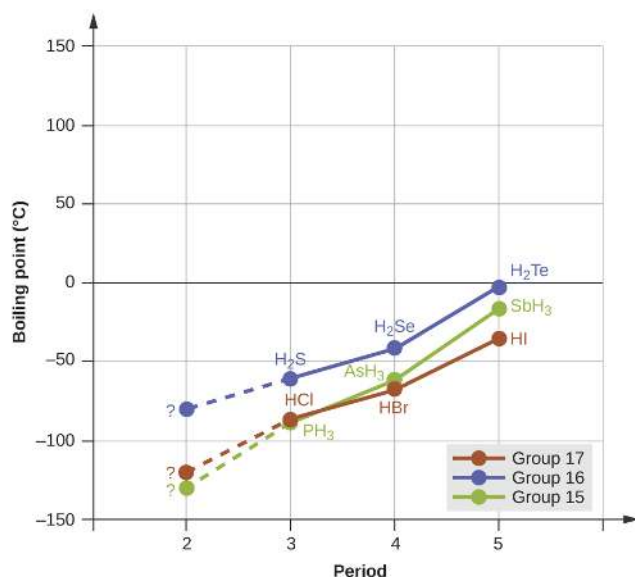


Figure 1.5.10: In comparison to periods 3–5, the binary hydrides of period 2 elements in groups 17, 16 and 15 (F, O and N, respectively) exhibit anomalously high boiling points due to hydrogen bonding. A line graph is shown where the y-axis is labeled “Boiling point (, degree sign, C)” and has values of “ negative 150” to “150” from bottom to top in increments of 50. The x-axis is labeled “Period” and has values of “0” to “5” in increments of 1. Three lines are shown on the graph and are labeled in the legend. The red line is labeled as “halogen family,” the blue is “oxygen family” and the green is “nitrogen family.” The first point on the red line is labeled “question mark” and is at point “2, negative 120”. The second point on the line is labeled “H C I” and is at point “3, negative 80” while the third point on the line is labeled “H B r” and is at point “4, negative 60”. The fourth point on the line is labeled “H I” and is at point “5, negative 40.” The first point on the green line is labeled “question mark” and is at point “2, negative 125.” The second point on the line is labeled “P H, subscript 3” and is at point “3, negative 80” while the third point on the line is labeled “A s H, subscript 3” and is at point “4, negative 55.” The fourth point on the line is labeled “S b H, subscript 3” and is at point “5, negative 10.” The first point on the blue line is labeled “question mark” and is at point “2, negative 80.” The second point on the line is labeled “H, subscript 2, S” and is at point “3, negative 55” while the third point on the line is labeled “H, subscript 2, S e” and is at point “4, negative 45.” The fourth point on the line is labeled “H, subscript 2, T e” and is at point “5, negative 3.”

If we use this trend to predict the boiling points for the lightest hydride for each group, we would expect NH_3 to boil at about -120°C , H_2O to boil at about -80°C , and HF to boil at about -110°C . However, when we measure the boiling points for these compounds, we find that they are dramatically higher than the trends would predict, as shown in Figure 1.5.10. The stark contrast between our naïve predictions and reality provides compelling evidence for the strength of hydrogen bonding.

✓ Example 1.5.3: Effect of Hydrogen Bonding on Boiling Points

Consider the compounds dimethylether (CH_3OCH_3), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), and propane ($\text{CH}_3\text{CH}_2\text{CH}_3$). Their boiling points, not necessarily in order, are -42.1°C , -24.8°C , and 78.4°C . Match each compound with its boiling point. Explain your reasoning.

Solution

The VSEPR-predicted shapes of CH_3OCH_3 , $\text{CH}_3\text{CH}_2\text{OH}$, and $\text{CH}_3\text{CH}_2\text{CH}_3$ are similar, as are their molar masses (46 g/mol, 46 g/mol, and 44 g/mol, respectively), so they will exhibit similar dispersion forces. Since $\text{CH}_3\text{CH}_2\text{CH}_3$ is nonpolar, it may exhibit *only* dispersion forces. Because CH_3OCH_3 is polar, it will also experience dipole-dipole attractions. Finally, $\text{CH}_3\text{CH}_2\text{OH}$ has an $-\text{OH}$ group, and so it will experience the uniquely strong dipole-dipole attraction known as hydrogen bonding. So the ordering in terms of strength of IMFs, and thus boiling points, is $\text{CH}_3\text{CH}_2\text{CH}_3 < \text{CH}_3\text{OCH}_3 < \text{CH}_3\text{CH}_2\text{OH}$. The boiling point of propane is -42.1°C , the boiling point of dimethylether is -24.8°C , and the boiling point of ethanol is 78.5°C .

? Exercise 1.5.3

Ethane (CH_3CH_3) has a melting point of -183°C and a boiling point of -89°C . Predict the melting and boiling points for methylamine (CH_3NH_2). Explain your reasoning.

Answer

The melting point and boiling point for methylamine are predicted to be significantly greater than those of ethane. CH_3CH_3 and CH_3NH_2 are similar in size and mass, but methylamine possesses an $-\text{NH}$ group and therefore may exhibit hydrogen bonding. This greatly increases its IMFs, and therefore its melting and boiling points. It is difficult to predict values, but the known values are a melting point of -93°C and a boiling point of -6°C .

1.5.5: Hydrogen Bonding and DNA

Deoxyribonucleic acid (DNA) is found in every living organism and contains the genetic information that determines the organism's characteristics, provides the blueprint for making the proteins necessary for life, and serves as a template to pass this information on to the organism's offspring. A DNA molecule consists of two (anti-)parallel chains of repeating nucleotides, which form its well-known double helical structure, as shown in Figure 1.5.10.

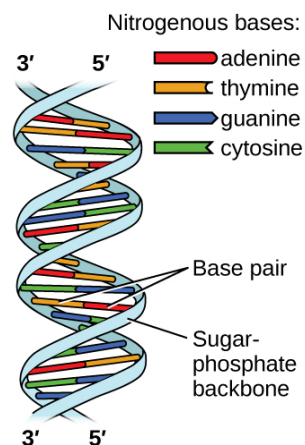


Figure 1.5.11: Two separate DNA molecules form a double-stranded helix in which the molecules are held together via hydrogen bonding. (credit: modification of work by Jerome Walker, Dennis Myts) Two images are shown. The first lies on the left side of the page and shows a helical structure like a twisted ladder where the rungs of the ladder, labeled “Base pair” are red, yellow, green and blue paired bars. The red and yellow bars, which are always paired together, are labeled in the

legend, which is titled “Nitrogenous bases” as “adenine” and “thymine,” respectively. The blue and green bars, which are always paired together, are labeled in the legend as “guanine” and “cytosine,” respectively. At the top of the helical structure, the left-hand side rail, or “Sugar, dash, phosphate backbone,” is labeled as “3, prime” while the right is labeled as “5, prime.” These labels are reversed at the bottom of the helix. To the right of the page is a large Lewis structure. The top left corner of this structure, labeled “5, prime,” shows a phosphorus atom single bonded to three oxygen atoms, one of which has a superscripted negative charge, and double bonded to a fourth oxygen atom. One of the single bonded oxygen atoms is single bonded to the left corner of a five-membered ring with an oxygen atom at its top point and which is single bonded to an oxygen atom on the bottom left. This oxygen atom is single bonded to a phosphorus atom that is single bonded to two other hydrogen atoms and double bonded to a fourth oxygen atom. The lower left of these oxygen atoms is single bonded to another oxygen atom that is single bonded to a five-membered ring with an oxygen in the upper bonding site. The bottom left of this ring has a hydroxyl group attached to it while the upper right carbon is single bonded to a nitrogen atom that is part of a five-membered ring bonded to a six-membered ring. Both of these rings have points of unsaturation and nitrogen atoms bonded into their structures. On the right side of the six-membered ring are two single bonded amine groups and a double bonded oxygen. Three separate dotted lines extend from these sites to corresponding sites on a second six-membered ring. This ring has points of unsaturation and a nitrogen atom in the bottom right bonding position that is single bonded to a five-membered ring on the right side of the image. This ring is single bonded to a carbon that is single bonded to an oxygen that is single bonded to a phosphorus. The phosphorus is single bonded to two other oxygen atoms and double bonded to a fourth oxygen atom. This group is labeled “5, prime.” The five-membered ring is also bonded on the top side to an oxygen that is bonded to a phosphorus single bonded to two other oxygen atoms and double bonded to a fourth oxygen atom. The upper left oxygen of this group is single bonded to a carbon that is single bonded to a five-membered ring with an oxygen in the bottom bonding position. This ring has a hydroxyl group on its upper right side that is labeled “3, prime” and is bonded on the left side to a nitrogen that is a member of a five-membered ring. This ring is bonded to a six-membered ring and both have points of unsaturation. This ring has a nitrogen on the left side, as well as an amine group, that have two dotted lines leading from them to an oxygen and amine group on a six membered ring. These dotted lines are labeled “Hydrogen bonds.” The six membered ring also has a double bonded oxygen on its lower side and a nitrogen atom on its left side that is single bonded to a five-membered ring. This ring connects to the two phosphate groups mentioned at the start of this to form a large circle. The name “guanine” is written below the lower left side of this image while the name “cytosine” is written on the lower right. The name “thymine” is written above the right side of the image and “adenine” is written on the top right. Three sections are indicated below the images where the left is labeled “Sugar, dash, phosphate backbone,” the middle is labeled “Bases” and the right is labeled “Sugar, dash, phosphate backbone.”

Each nucleotide contains a (deoxyribose) sugar bound to a phosphate group on one side, and one of four nitrogenous bases on the other. Two of the bases, cytosine (C) and thymine (T), are single-ringed structures known as pyrimidines. The other two, adenine (A) and guanine (G), are double-ringed structures called purines. These bases form complementary base pairs consisting of one purine and one pyrimidine, with adenine pairing with thymine, and cytosine with guanine. Each base pair is held together by hydrogen bonding. A and T share two hydrogen bonds, C and G share three, and both pairings have a similar shape and structure

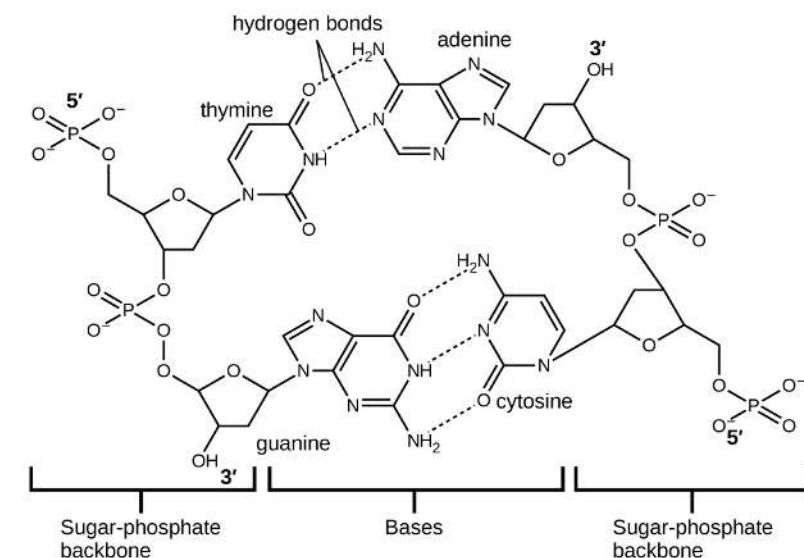


Figure 1.5.12: The geometries of the base

molecules result in maximum hydrogen bonding between adenine and thymine (AT) and between guanine and cytosine (GC), so-called “complementary base pairs.” A large Lewis structure is shown. The top left corner of this structure, labeled “5, prime,” shows a phosphorus atom single bonded to three oxygen atoms, one of which has a superscripted negative charge, and double bonded to a fourth oxygen atom. One of the single bonded oxygen atoms is single bonded to the left corner of a five-membered

ring with an oxygen atom at its top point and which is single bonded to an oxygen atom on the bottom left. This oxygen atom is single bonded to a phosphorus atom that is single bonded to two other hydrogen atoms and double bonded to a fourth oxygen atom. The lower left of these oxygen atoms is single bonded to another oxygen atom that is single bonded to a five-membered ring with an oxygen in the upper bonding site. The bottom left of this ring has a hydroxyl group attached to it while the upper right carbon is single bonded to a nitrogen atom that is part of a five-membered ring bonded to a six-membered ring. Both of these rings have points of unsaturation and nitrogen atoms bonded into their structures. On the right side of the six-membered ring are two single bonded amine groups and a double bonded oxygen. Three separate dotted lines extend from these sites to corresponding sites on a second six-membered ring. This ring has points of unsaturation and a nitrogen atom in the bottom right bonding position that is single bonded to a five-membered ring on the right side of the image. This ring is single bonded to a carbon that is single bonded to an oxygen that is single bonded to a phosphorus. The phosphorus is single bonded to two other oxygen atoms and double bonded to a fourth oxygen atom. This group is labeled “5, prime.” The five-membered ring is also bonded on the top side to an oxygen that is bonded to a phosphorus single bonded to two other oxygen atoms and double bonded to a fourth oxygen atom. The upper left oxygen of this group is single bonded to a carbon that is single bonded to a five-membered ring with an oxygen in the bottom bonding position. This ring has a hydroxyl group on its upper right side that is labeled “3, prime” and is bonded on the left side to a nitrogen that is a member of a five-membered ring. This ring is bonded to a six-membered ring and both have points of unsaturation. This ring has a nitrogen on the left side, as well as an amine group, that have two dotted lines leading from them to an oxygen and amine group on a six membered ring. These dotted lines are labeled “Hydrogen bonds.” The six membered ring also has a double bonded oxygen on its lower side and a nitrogen atom on its left side that is single bonded to a five-membered ring. This ring connects to the two phosphate groups mentioned at the start of this to form a large circle. The name “guanine” is written below the lower left side of this image while the name “cytosine” is written on the lower right. The name “thymine” is written above the right side of the image and “adenine” is written on the top right. Three sections are indicated below the images where the left is labeled “Sugar, dash, phosphate backbone,” the middle is labeled “Bases” and the right is labeled “Sugar, dash, phosphate backbone.”

The cumulative effect of millions of hydrogen bonds effectively holds the two strands of DNA together. Importantly, the two strands of DNA can relatively easily “unzip” down the middle since hydrogen bonds are relatively weak compared to the covalent bonds that hold the atoms of the individual DNA molecules together. This allows both strands to function as a template for replication.

Summary

The physical properties of condensed matter (liquids and solids) can be explained in terms of the kinetic molecular theory. In a liquid, intermolecular attractive forces hold the molecules in contact, although they still have sufficient kinetic energy to move past each other. Intermolecular attractive forces, collectively referred to as van der Waals forces, are responsible for the behavior of liquids and solids and are electrostatic in nature. Dipole-dipole attractions result from the electrostatic attraction of the partial negative end of one dipolar molecule for the partial positive end of another. The temporary dipole that results from the motion of the electrons in an atom can induce a dipole in an adjacent atom and give rise to the London dispersion force. London forces increase with increasing molecular size. Hydrogen bonds are a special type of dipole-dipole attraction that results when hydrogen is bonded to one of the three most electronegative elements: F, O, or N.

Glossary

dipole-dipole attraction

intermolecular attraction between two permanent dipoles

dispersion force

(also, London dispersion force) attraction between two rapidly fluctuating, temporary dipoles; significant only when particles are very close together

hydrogen bonding

occurs when exceptionally strong dipoles attract; bonding that exists when hydrogen is bonded to one of the three most electronegative elements: F, O, or N

induced dipole

temporary dipole formed when the electrons of an atom or molecule are distorted by the instantaneous dipole of a neighboring atom or molecule

instantaneous dipole

temporary dipole that occurs for a brief moment in time when the electrons of an atom or molecule are distributed asymmetrically

intermolecular force

noncovalent attractive force between atoms, molecules, and/or ions

polarizability

measure of the ability of a charge to distort a molecule's charge distribution (electron cloud)

van der Waals force

attractive or repulsive force between molecules, including dipole-dipole, dipole-induced dipole, and London dispersion forces; does not include forces due to covalent or ionic bonding, or the attraction between ions and molecules

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1.S: Chemistry and Matter (Summary)

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.

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CHAPTER OVERVIEW

2: Elements, Atoms, and the Periodic Table

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

[2.1: 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.S: Elements, Atoms, and the Periodic Table \(Summary\)](#)

Template:HideTOC

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

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2.1: The Elements

Learning Objectives

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

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



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

Abundance

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

Table 2.1.1: Elemental Composition of Earth

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

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

On the planet Earth, however, the situation is rather different. Oxygen makes up 46.1% of the mass of Earth's crust (the relatively thin layer of rock forming Earth's surface), mostly in combination with other elements, while silicon makes up 28.2%. Hydrogen, the most abundant element in the universe, makes up only 0.14% of Earth's crust. Table 2.1.1 lists the relative abundances of

elements on Earth as a whole and in Earth's crust. Table 2.1.2 lists the relative abundances of elements in the human body. If you compare Table 2.1.1 and Table 2.1.2, you will find disparities between the percentage of each element in the human body and on Earth. Oxygen has the highest percentage in both cases, but carbon, the element with the second highest percentage in the body, is relatively rare on Earth and does not even appear as a separate entry in Table 2.1.1; carbon is part of the 0.174% representing "other" elements. How does the human body concentrate so many apparently rare elements?

Table 2.1.2: Elemental Composition of a Human Body

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

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

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

LOOKING CLOSER: PHOSPHOROUS, THE CHEMICAL BOTTLENECK

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

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

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

Names and Symbols

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

Today, new elements are usually named after famous scientists.

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

Table 2.1.3: Element Names and Symbols

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

*The symbol comes from the Latin name of element.

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

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

✓ Example 2.1.1

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

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

Answer a

Br

Answer b

B

Answer c

C

Answer d

Ca

Answer e

Au

? Exercise 2.1.1

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

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

Answer a

Mn

Answer b

Mg

Answer c

Ne

Answer d

N

Answer e

Ag

✓ Example 2.1.2

What element is represented by each chemical symbol?

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

Answer a

sodium

Answer b

mercury

Answer c

phosphorus

Answer d

potassium

Answer e

iodine

? Exercise 2.1.2

What element is represented by each chemical symbol?

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

Answer a

lead

Answer b

tin

Answer c

uranium

Answer d

oxygen

Answer e

fluorine

Concept Review Exercises

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

Answers

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

Key Takeaways

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

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2.2: Atomic Theory

Learning Objectives

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

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

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

The modern atomic theory, proposed about 1803 by the English chemist John Dalton (Figure 2.2.1), is a fundamental concept that states that all elements are composed of atoms. Previously, we defined an atom as the smallest part of an element that maintains the identity of that element. Individual atoms are extremely small; even the largest atom has an approximate diameter of only 5.4×10^{-10} m. With that size, it takes over 18 million of these atoms, lined up side by side, to equal the width of your little finger (about 1 cm).

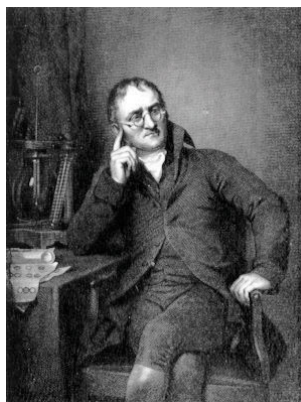


Figure 2.2.1 John Dalton was an English scientist who enunciated the modern atomic theory.

Most elements in their pure form exist as **individual atoms**. For example, a macroscopic chunk of iron (Fe) metal is composed, microscopically, of individual atoms. Some elements, however, exist as groups of atoms called molecules. Several important elements exist as two-atom combinations and are called **diatomic molecules**. In representing a diatomic molecule, we use the symbol of the element and include the **subscript "2"** to indicate that two atoms of that element are joined together. The elements that exist as diatomic molecules are hydrogen (H₂), nitrogen (N₂), fluorine (F₂), oxygen (O₂), iodine (I₂), chlorine (Cl₂) and bromine (Br₂). A few other elements can exist as 3-atom molecules like ozone (O₃) and 4-atom molecules like phosphorus (P₄). The most common form of the element sulfur is composed of molecules that consist of eight atoms of sulfur; its molecular formula is S₈ (Figure 2.2.2).

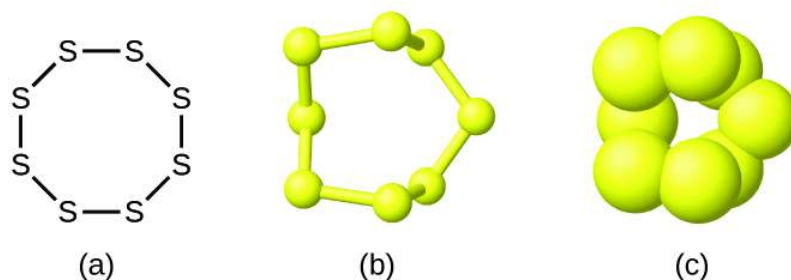


Figure 2.2.2: A molecule of sulfur is composed of eight sulfur atoms and is therefore written as S₈. It can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. Sulfur atoms are represented by yellow spheres.

It is important to note that a subscript following a symbol and a number in front of a symbol do not represent the same thing; for example, H_2 and 2H represent distinctly different species. H_2 is a molecular formula; it represents a diatomic molecule of hydrogen, consisting of two atoms of the element that are chemically bonded together. The expression 2H , on the other hand, indicates two separate hydrogen atoms that are **not** combined as a unit. The expression 2H_2 represents two molecules of diatomic hydrogen (Figure 2.2.3).

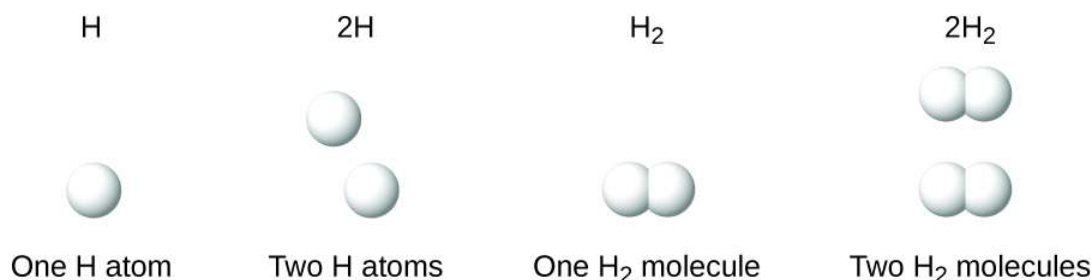


Figure 2.2.3: The symbols H , 2H , H_2 , and 2H_2 represent very different entities.

✓ Example 2.2.1

Write the chemical formula of the following elements:

- oxygen
- carbon
- potassium

Solution

Memorizing the diatomic molecules is worthwhile for our future endeavors. A mnemonic device to help in the memorization of the diatomic elements is as follows: **Have No Fear Of Ice Cold Beer**. (hydrogen, nitrogen, fluorine, oxygen, iodine, chlorine and bromine).

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

Exercise 2.2.1

Write the chemical formula of the following elements:

- hydrogen
- nitrogen
- neon

Answer a

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

Answer b

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

Answer c

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

📌 Looking Closer: Atomic Theory

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

150 years or so before Dalton, natural philosophy had been maturing into modern science, and the scientific method was being used to study nature. So when Dalton announced a modern atomic theory, he was proposing a fundamental theory to describe many previous observations of the natural world; he was not just participating in a philosophical discussion.

Concept Review Exercises

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

Answers

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

Key Takeaways

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

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2.3: The Structure of Atoms

Learning Objectives

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

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

Subatomic Particles

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

Finally, additional experiments pointed to the existence of a third particle. Evidence produced in 1932 established the existence of the neutron, a particle with about the same mass as a proton but with no electrical charge, it is *neutral*. We understand now that all atoms can be broken down into subatomic particles: protons, neutrons, and electrons. Table 2.3.1 lists some of their important characteristics and the symbols used to represent each particle.

Table 2.3.1: Properties of the Subatomic Particles

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

The Nucleus

How are these subatomic particles arranged? Between 1909 and 1911, Ernest Rutherford, a Cambridge physicist, and his associates Hans Geiger and Ernest Marsden performed experiments that provided strong evidence concerning the internal structure of an atom. They took a very thin metal foil, such as gold or platinum, and aimed a beam of positively charged particles (called alpha particles, which are combinations of two protons and two neutrons) from a radioactive source toward the foil. Surrounding the foil was a detector—either a scintillator (a material that glows when hit by such particles) or some unexposed film (which is exposed where the particles hit it). The detector allowed the scientists to determine the distribution of the alpha particles after they interacted with the foil. Figure 2.3.1 shows a diagram of the experimental setup.

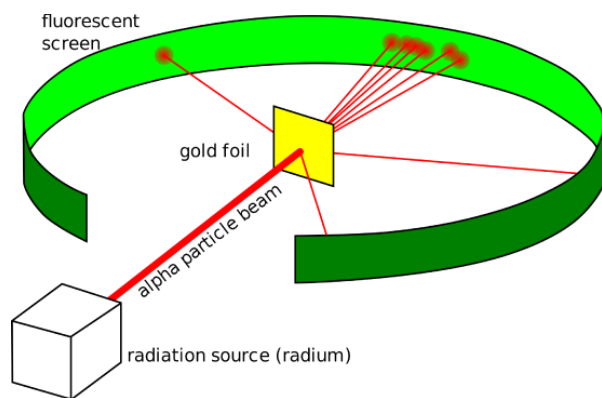


Figure 2.3.1: The Geiger-Marsden Experimental Setup. Experiments

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

Rutherford proposed the following model to explain these experimental results. Protons and neutrons are concentrated in a central region he called the nucleus (plural, *nuclei*) of the atom. Electrons are outside the nucleus and orbit about it because they are attracted to the positive charge in the nucleus. Most of the mass of an atom is in the nucleus, while the orbiting electrons account for an atom’s size. As a result, an atom consists largely of empty space. Rutherford called his description the “planetary model” of the atom. Figure 2.3.2 shows how this model explains the experimental results.

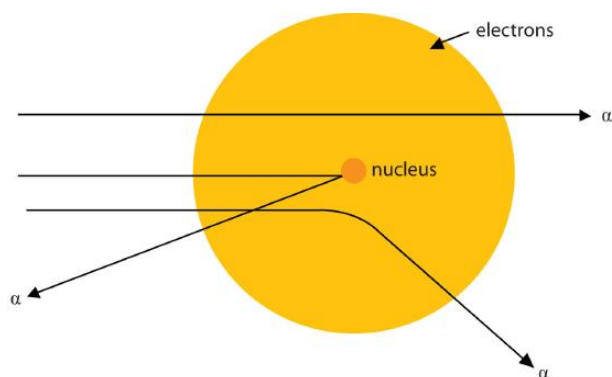


Figure 2.3.2: Rutherford’s Metal Foil Experiments. Rutherford

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

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

Rutherford’s model is essentially the same model that we use today to describe atoms but with one important modification. The planetary model suggests that electrons occupy certain specific, circular orbits about the nucleus. We know now that this model is overly simplistic. A better description is that electrons form fuzzy clouds around nuclei. Figure 2.3.3 shows a more modern version of our understanding of atomic structure.

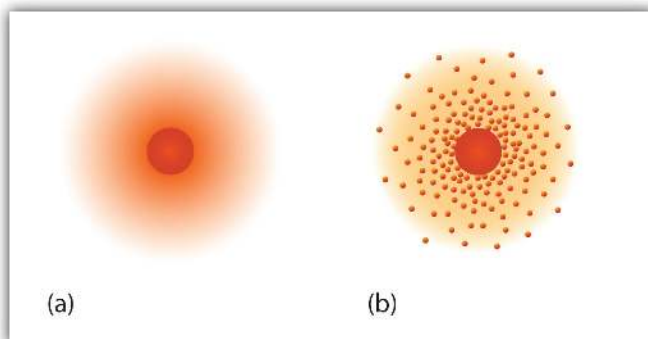


Figure 2.3.3: A Modern Depiction of Atomic Structure. A more

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

Concept Review Exercises

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

Answers

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

Key Takeaways

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

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2.4: Nuclei of Atoms

Learning Objectives

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

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

Atomic Number

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

For example, hydrogen has the atomic number 1; all hydrogen atoms have 1 proton in their nuclei. Helium has the atomic number 2; all helium atoms have 2 protons in their nuclei. There is no such thing as a hydrogen atom with 2 protons in its nucleus; a nucleus with 2 protons would be a helium atom. The atomic number *defines* an element. Table 2.4.1 lists some common elements and their atomic numbers. Based on its **atomic number**, you can determine the **number of protons in the nucleus** of an atom. The largest atoms have over 100 protons in their nuclei.

✓ Example 2.4.1

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

- aluminum
- iron
- carbon

Answer a

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

Answer b

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

Answer c

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

? Exercise 2.4.1

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

- sodium
- oxygen
- chlorine

Answer a

Sodium has 11 protons in its nucleus.

Answer b

Oxygen has 8 protons in its nucleus.

Answer c

Chlorine has 17 protons in its nucleus

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

✓ Example 2.4.2

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

- a. sulfur
- b. tungsten
- c. argon

Answer a

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

Answer b

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

Answer c

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

? Exercise 2.4.2

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

- a. magnesium
- b. potassium
- c. iodine

Answer a

Mg has 12 electrons.

Answer b

K has 19 electrons.

Answer c

I has 53 electrons.

Table 2.4.1: Some Common Elements and Their Atomic Numbers

Element	Atomic Number	Element	Atomic Nmbers
aluminum (Al)	13	magnesium (Mg)	12
americium (Am)	95	manganese (Mn)	25
argon (Ar)	18	mercury (Hg)	80
barium (Ba)	56	neon (Ne)	10
beryllium (Be)	4	nickel (Ni)	28
bromine (Br)	35	nitrogen (N)	7

Element	Atomic Number	Element	Atomic Numbers
calcium (Ca)	20	oxygen (O)	8
carbon (C)	6	phosphorus (P)	15
chlorine (Cl)	17	platinum (Pt)	78
chromium (Cr)	24	potassium (K)	19
cesium (Cs)	55	radon (Rn)	86
fluorine (F)	9	silver (Ag)	47
gallium (Ga)	31	sodium (Na)	11
gold (Au)	79	strontium (Sr)	38
helium (He)	2	sulfur (S)	16
hydrogen (H)	1	titanium (Ti)	22
iron (Fe)	26	tungsten (W)	74
iodine (I)	53	uranium (U)	92
lead (Pb)	82	zinc (Zn)	30
lithium (Li)	3	zirconium (Zr)	40

Isotopes

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

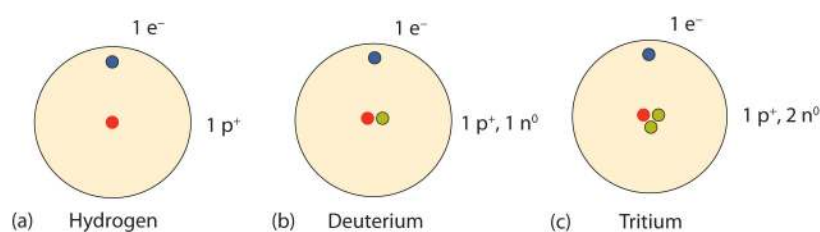


Figure 2.4.1: Isotopes of Hydrogen. Most

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.

An important series of isotopes is found with hydrogen atoms. Most hydrogen atoms have a nucleus with only a single proton. About 1 in 10,000 hydrogen nuclei, however, also has a neutron; this particular isotope is called *deuterium*. An extremely rare hydrogen isotope, *tritium*, has 1 proton and 2 neutrons in its nucleus. Figure 2.4.1 compares the three isotopes of hydrogen.

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

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

nucleus (and knowing the atomic number of that particular atom), you can determine the number of neutrons by subtracting the atomic number from the mass number.

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



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

✓ Example 2.4.3

How many protons and neutrons are in each atom?

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

Answer a

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

Answer b

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

? Exercise 2.4.3

How many protons and neutrons are in each atom?

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

Answer a

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

Answer b

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

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

Summary

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

Almost all of the mass of an atom is from the total protons and neutrons contained within a tiny (and therefore very dense) nucleus. The majority of the volume of an atom is the surrounding space in which the electrons reside. A representation of a carbon-12 atom is shown below in Figure 2.4.2.

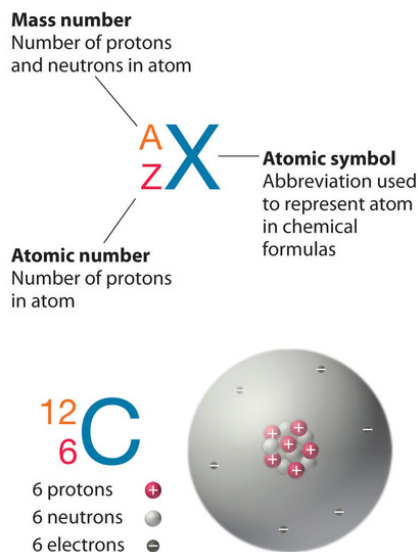


Figure 2.4.2: Formalism used for identifying specific nuclide (any particular kind of nucleus) The atomic symbol, X, is the abbreviation used to represent an atom in chemical formulas. The mass number, A, is the number of protons and neutrons in the atom, which is to the left of the X. The atomic number, Z, is the number of protons in the atom, which is to the left of the X and below the A.

Concept Review Exercises

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

Answers

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

Key Takeaways

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

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2.5: Atomic Masses

Learning Objectives

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

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

Atomic Mass Unit

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

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

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

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

Atomic Mass is the Weighted Average Mass of Isotopes

As stated above, most elements occur naturally as a mixture of two or more isotopes. Listed below (Table 2.5.1) are the naturally occurring isotopes of selected elements along with the percent natural abundance of each.

Table 2.5.1: Atomic Masses and Percent Abundances of Some Natural Isotopes

Element	Isotope (Symbol)	Percent Natural Abundance	Atomic Mass (amu)	Average Atomic Mass (amu)
Hydrogen	^1_1H	99.985	1.0078	1.0079
	^2_1H	0.015	2.0141	
	^3_1H	negligible	3.0160	
Carbon	$^{12}_6\text{C}$	98.89	12.000	12.011
	$^{13}_6\text{C}$	1.11	13.003	
	$^{14}_6\text{C}$	trace	14.003	
Oxygen	$^{16}_8\text{O}$	99.759	15.995	15.999
	$^{17}_8\text{O}$	0.037	16.995	
	$^{18}_8\text{O}$	0.204	17.999	
Chlorine	$^{35}_{17}\text{Cl}$	75.77	34.969	35.453
	$^{37}_{17}\text{Cl}$	24.23	36.966	
Copper	$^{63}_{29}\text{Cu}$	69.17	62.930	63.546
	$^{65}_{29}\text{Cu}$	30.83	64.928	

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

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

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

$$0.7577 (34.969 \text{ u}) + 0.2423 (36.966 \text{ u}) = 35.453 \text{ u}$$

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

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

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

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

$$0.99759 (15.995 \text{ u}) + 0.00037 (16.995 \text{ u}) + 0.00204 (17.999 \text{ u}) = 15.999 \text{ u}$$

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

✓ Example 2.5.1

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

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

Solution

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

$$0.99759 (15.995 \text{ u}) + 0.00037 (16.995 \text{ u}) + 0.00204 (17.999 \text{ u}) = 15.999 \text{ u}$$

2.5.1 Exercise

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

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

Answer

63.546 u

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

50 Sn Tin 118.71	atomic number atomic mass	6 C Carbon 12.011
--	---	---

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

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

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

✓ Example 2.5.2: Mass of Carbon

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

Solution

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

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

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

? Exercise 2.5.2: Mass of Tin

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

Answer

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

Concept Review Exercises

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

Answers

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

Key Takeaway

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

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2.6: Arrangements of Electrons

Learning Objectives

- Describe how electrons are grouped within atoms.

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

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

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

Table 2.6.1: Shells and Subshells

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

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

Table 2.6.2: Number of Electrons

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

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

We use numbers to indicate which shell an electron is in. As shown in Table 2.6.1, the first shell, closest to the nucleus and with the lowest-energy electrons, is shell 1. This first shell has only one subshell, which is labeled 1s and can hold a maximum of 2 electrons. We combine the shell and subshell labels when referring to the organization of electrons about a nucleus and use a superscript to indicate how many electrons are in a subshell. Thus, because a hydrogen atom has its single electron in the s subshell of the first shell, we use **1s¹** to describe the electronic structure of hydrogen. This structure is called an electron configuration. Electron configurations are shorthand descriptions of the arrangements of electrons in atoms. The electron configuration of a hydrogen atom is spoken out loud as “one-ess-one.”

Helium atoms have 2 electrons. Both electrons fit into the 1s subshell because s subshells can hold up to 2 electrons; therefore, the electron configuration for helium atoms is **1s²** (spoken as “one-ess-two”).

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

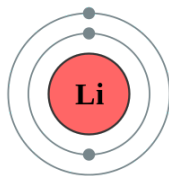


Figure 2.6.1: Shell diagram of lithium (Li) atom.

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

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

With neon, the 2p subshell is completely filled. Because the second shell has only two subshells, atoms with more electrons now must begin the third shell. The third shell has three subshells, labeled s, p, and d. The d subshell can hold a maximum of 10 electrons. The first two subshells of the third shell are filled in order—for example, the electron configuration of aluminum, with 13 electrons, is $1s^2 2s^2 2p^6 3s^2 3p^1$. However, a curious thing happens after the 3p subshell is filled: the 4s subshell begins to fill before the 3d subshell does. In fact, the exact ordering of subshells becomes more complicated at this point (after argon, with its 18 electrons), so we will not consider the electron configurations of larger atoms. A fourth subshell, the f subshell, is needed to complete the electron configurations for all elements. An f subshell can hold up to 14 electrons.

Electron filling always starts with 1s, the subshell closest to the nucleus. Next is 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, etc., shown in the electron shell filling order diagram in Figure 2.6.2. Follow each arrow in order **from top to bottom**. The subshells you reach along each arrow give the ordering of filling of subshells in larger atoms.

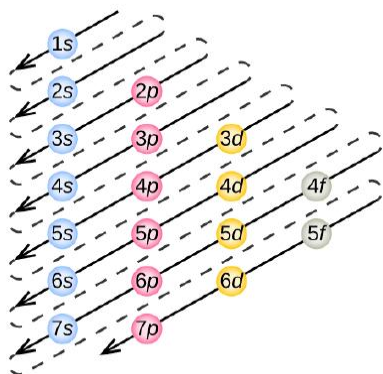


Figure 2.6.2: The order of electron filling in an atom.

✓ Example 2.6.1: Electronic Configuration of Phosphorus Atoms

Using Figure 2.6.2 as your guide, write the electron configuration of a neutral phosphorus atom. The atomic number of P is 15.

Solution

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

? Exercise 2.6.1: Electronic Configuration of Chlorine Atoms

Using Figure 2.6.2 as your guide, write the electron configuration of a neutral chlorine atom. The atomic number of Cl is 17.

Answer

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

Since the arrangement of the periodic table is based on the electron configurations, Figure 2.6.3 provides an alternative method for determining the electron configuration. The filling order simply **begins at the top left**, with hydrogen ($Z=1$) and includes each subshell as you proceed in increasing atomic number (Z) order.

Electron Configuration Table

The table shows the periodic table with subshells labeled in yellow boxes. The filling order is indicated by arrows: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p. A callout box for Hydrogen (H) shows its configuration: 1 electron in the 1s subshell.

Figure 2.6.3:

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

For example, the first row (Period 1) contains H and He only, because only two electrons are required to fill the 1s subshell. The second row s-block, contains only two elements, Li and Be, to fill the 2s subshell. This is followed by the second row p-block, containing 6 elements (B through Ne) since six electrons are required to fill the 2p subshell. The third row is similar to the second row elements. Two electrons are needed (Na and Mg) to fill the 3s subshell and six electrons are required (Al through Ar) to complete the 3p subshell. After filling the 3p block up to Ar, we see the next subshell will be 4s (K, Ca), followed by the 3d subshell, which are filled by ten electrons (Sc through Zn). The 4p subshell is filled next by six electrons (Ga through Kr). As you can see, the periodic table shown in Figure 2.6.3 provides a simple way to remember the order of filling the subshells in determining the electron configuration. The order of filling subshells is the same: **1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, etc.**

✓ Example 2.6.2: Aluminum

Using Figure 2.6.3 as your guide, write the electron configuration of neutral aluminum atom. The atomic number of Al is 13.

Solution

Aluminum has 13 electrons.

Start at Period 1 of the periodic table, Figure 2.6.3. Place two electrons in the 1s subshell ($1s^2$).

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

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

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

2.6.2 Exercise

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

Answer

Start at Period 1 of Figure 2.6.3. Place two electrons in the 1s subshell ($1s^2$).

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

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

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

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

Valence Electrons

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

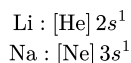
In the second period elements, the two electrons in the 1s sublevel are called **inner-shell electrons** and are not involved directly in the element's reactivity or in the formation of compounds. Lithium has a single electron in the second principal energy level and so we say that lithium has one valence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

The alkali metal sodium (atomic number 11) has one more electron than the neon atom. This electron must go into the lowest-energy subshell available, the 3s orbital, giving a $1s^2 2s^2 2p^6 3s^1$ configuration. The electrons occupying the outermost shell orbital(s) (highest value of n) are called valence electrons, and those occupying the inner shell orbitals are called **core electrons** (Figure \PageIndex{4}). Since the core electron shells correspond to noble gas electron configurations, we can abbreviate electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. For our sodium example, the symbol [Ne] represents core electrons, ($1s^2 2s^2 2p^6$) and our abbreviated or condensed configuration is [Ne] $3s^1$.



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

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



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

✓ Example 2.6.3

Examine the electron configuration of neutral phosphorus atoms in Example 2.6.1, $1s^2 2s^2 2p^6 3s^2 3p^3$ and write the abbreviated notation.

Solution

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

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

The 10 inner shell (core) electrons, $1s^2 2s^2 2p^6$ can be replaced by $[\text{Ne}]$ (see Figure 2.6.3). Abbreviated notation is : $[\text{Ne}]3s^2 3p^3$

? Exercise 2.6.3

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

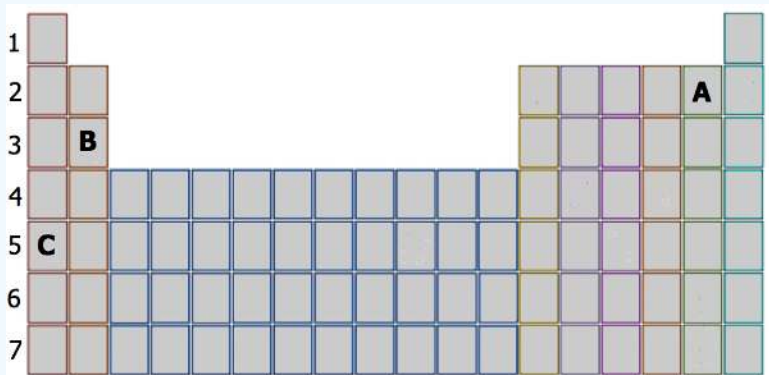
Answer

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

The 18 inner-shell (core) electrons, $1s^2 2s^2 2p^6 3s^2 3p^6$, can be replaced by $[\text{Ar}]$, see Figure 2.6.3. The abbreviated notation is: $[\text{Ar}]4s^2$

✓ Example 2.6.4

Based on their respective locations in the periodic table (use Figure 2.6.3), determine the number of valence electrons and the valence shell configuration of elements A, B and C.



Solution

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

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

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

2.6.4 Exercise

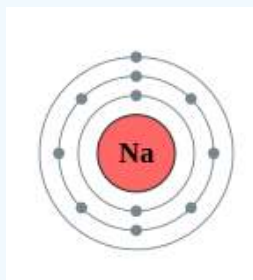
Using the location of Na in the periodic table (Figure 2.6.3), draw the shell diagram of sodium atom.

Answer

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

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

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



Concept Review Exercises

1. How are electrons organized in atoms?
2. What information does an electron configuration convey?
3. What is the difference between core electrons and valence electrons?

Answers

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

Key Takeaway

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

Exercises

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2.7: The Periodic Table

Learning Objectives

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

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

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

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

The periodic table is one of the cornerstones of chemistry because it organizes all the known elements on the basis of their chemical properties. A modern version is shown in Figure 2.7.1. Most periodic tables provide additional data (such as atomic mass) in a box that contains each element's symbol. The elements are listed in order of atomic number.

Period	Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1		1 H Hydrogen Nonmetal																	2 He Helium Noble Gas
2		3 Li Lithium Alkali Metal	4 Be Beryllium Alkaline Earth											5 B Boron Metalloid	6 C Carbon Nonmetal	7 N Nitrogen Nonmetal	8 O Oxygen Nonmetal	9 F Fluorine Halogen	10 Ne Neon Noble Gas
3		11 Na Sodium Alkali Metal	12 Mg Magnesium Alkaline Earth											13 Al Aluminum Post-transition	14 Si Silicon Metalloid	15 P Phosphorus Nonmetal	16 S Sulfur Nonmetal	17 Cl Chlorine Halogen	18 Ar Argon Noble Gas
4		19 K Potassium Alkali Metal	20 Ca Calcium Alkaline Earth	21 Sc Scandium Transition Metal	22 Ti Titanium Transition Metal	23 V Vanadium Transition Metal	24 Cr Chromium Transition Metal	25 Mn Manganese Transition Metal	26 Fe Iron Transition Metal	27 Co Cobalt Transition Metal	28 Ni Nickel Transition Metal	29 Cu Copper Transition Metal	30 Zn Zinc Transition Metal	31 Ga Gallium Post-transition	32 Ge Germanium Metalloid	33 As Arsenic Metalloid	34 Se Selenium Nonmetal	35 Br Bromine Halogen	36 Kr Krypton Noble Gas
5		37 Rb Rubidium Alkali Metal	38 Sr Strontium Alkaline Earth	39 Y Yttrium Transition Metal	40 Zr Zirconium Transition Metal	41 Nb Niobium Transition Metal	42 Mo Molybdenum Transition Metal	43 Tc Technetium Transition Metal	44 Ru Ruthenium Transition Metal	45 Rh Rhodium Transition Metal	46 Pd Palladium Transition Metal	47 Ag Silver Transition Metal	48 Cd Cadmium Transition Metal	49 In Indium Post-transition	50 Sn Tin Post-transition	51 Sb Antimony Metalloid	52 Te Tellurium Metalloid	53 I Iodine Halogen	54 Xe Xenon Noble Gas
6		55 Cs Cesium Alkali Metal	56 Ba Barium Alkaline Earth	*	72 Hf Hafnium Transition Metal	73 Ta Tantalum Transition Metal	74 W Tungsten Transition Metal	75 Re Rhenium Transition Metal	76 Os Osmium Transition Metal	77 Ir Iridium Transition Metal	78 Pt Platinum Transition Metal	79 Au Gold Transition Metal	80 Hg Mercury Transition Metal	81 Tl Thallium Post-transition	82 Pb Lead Post-transition	83 Bi Bismuth Post-transition	84 Po Polonium Metalloid	85 At Astatine Halogen	86 Rn Radon Noble Gas
7		87 Fr Francium Alkali Metal	88 Ra Radium Alkaline Earth	**	104 Rf Rutherfordium Transition Metal	105 Db Dubnium Transition Metal	106 Sg Seaborgium Transition Metal	107 Bh Bohrium Transition Metal	108 Hs Hassium Transition Metal	109 Mt Meitnerium Transition Metal	110 Ds Darmstadtium Transition Metal	111 Rg Roentgenium Transition Metal	112 Cn Copernicium Transition Metal	113 Nh Nihonium Post-transition	114 Fl Flerovium Post-transition	115 Mc Moscovium Post-transition	116 Lv Livermorium Post-transition	117 Ts Tennessine Halogen	118 Og Oganesson Noble Gas
	*	57 La Lanthanum Lanthanide	58 Ce Cerium Lanthanide	59 Pr Praseodymium Lanthanide	60 Nd Neodymium Lanthanide	61 Pm Promethium Lanthanide	62 Sm Samarium Lanthanide	63 Eu Europium Lanthanide	64 Gd Gadolinium Lanthanide	65 Tb Terbium Lanthanide	66 Dy Dysprosium Lanthanide	67 Ho Holmium Lanthanide	68 Er Erbium Lanthanide	69 Tm Thulium Lanthanide	70 Yb Ytterbium Lanthanide	71 Lu Lutetium Lanthanide			
	**	89 Ac Actinium Actinide	90 Th Thorium Actinide	91 Pa Protactinium Actinide	92 U Uranium Actinide	93 Np Neptunium Actinide	94 Pu Plutonium Actinide	95 Am Americium Actinide	96 Cm Curium Actinide	97 Bk Berkelium Actinide	98 Cf Californium Actinide	99 Es Einsteinium Actinide	100 Fm Fermium Actinide	101 Md Mendelevium Actinide	102 No Nobelium Actinide	103 Lr Lawrencium Actinide			

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

Features of the Periodic Table

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

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

Metals, Nonmetals and Metalloids

Certain elemental properties become apparent in a survey of the periodic table as a whole. Every element can be classified as either a metal, a nonmetal, or a semimetal, as shown in Figure 2.7.2. A metal is a substance that is shiny, typically (but not always) silvery in color, and an excellent conductor of electricity and heat. Metals are also malleable (they can be beaten into thin sheets) and ductile (they can be drawn into thin wires). A nonmetal is typically dull and a poor conductor of electricity and heat. Solid nonmetals are also very brittle. As shown in Figure 2.7.2, **metals** occupy the left three-fourths of the periodic table, while **nonmetals** (except for hydrogen) are clustered in the upper right-hand corner of the periodic table. The elements with properties intermediate between those of metals and nonmetals are called **semimetals** (or **metalloids**). Elements adjacent to the **bold zigzag** line in the right-hand portion of the periodic table have semimetal properties.

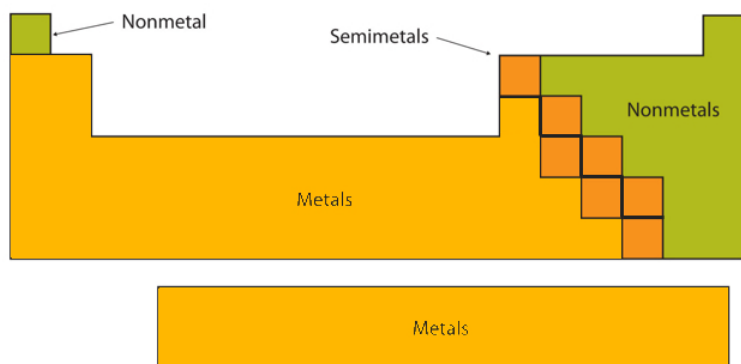


Figure 2.7.2: Types of Elements. Elements are either metals, nonmetals, or semimetals. Each group is located in a different part of the periodic table.

✓ Example 2.7.1

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

Solution

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

2.7.1 Exercise

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

Answer

metal

Representative, Transition and Inner-transition

Another way to categorize the elements of the periodic table is shown in Figure 2.7.3. The first two columns on the left and the last six columns on the right are called the **main group** or **representative** elements. The ten-column block between these columns

contains the **transition metals**. The two rows beneath the main body of the periodic table contain the inner transition metals. The elements in these two rows are also referred to as, respectively, the **lanthanide metals** and the **actinide metals**.

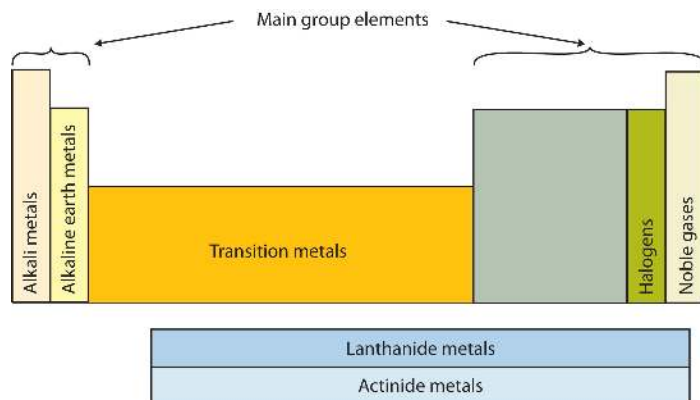


Figure 2.7.3: Special Names for Sections of the Periodic Table.

Some sections of the periodic table have special names. The elements lithium, sodium, potassium, rubidium, cesium, and francium are collectively known as alkali metals. Alkali metals are the first column. Alkaline earth metals are the second. Halogens are the second to last column. Noble gases are the last column.

To Your Health: Transition Metals in the Body

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

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

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

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

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

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

Group 1: The Alkali Metals

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

Group 2: The Alkaline Earth Metals

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

Group 17: The Halogens

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

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

Group 18: The Noble Gases

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

To Your Health: Radon

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

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

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

Why do elements in a given group have similar properties?

The periodic table is organized on the basis of similarities in elemental properties, but what explains these similarities? It turns out that the shape of the periodic table reflects the filling of subshells with electrons, as shown in Figure 2.7.4. Starting with the first period and going from left to right, the table reproduces the order of filling of the electron subshells in atoms. Furthermore, elements in the same *group* share the same valence shell electron configuration. For example, all elements in the first column have a single *s* electron in their valence shells, so their electron configurations can be described as ns^1 (where *n* represents the shell number). This last observation is crucial. Chemistry is largely the result of interactions between the valence electrons of different atoms. Thus, atoms that have **the same valence shell electron configuration** will have **similar chemistry**.

	← 1s →	
2s		2p
3s		3p
4s	3d	4p
5s	4d	5p
6s	5d	6p
4f		
5f		

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

✓ Example 2.7.1

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

- the alkaline earth metals
- the column of elements headed by carbon

Answer a

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

Answer b

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

? Exercise 2.7.1

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

- the halogens
- the column of elements headed by oxygen

Answer a

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

Answer b

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

Valence Electrons and Group Number

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

Table 2.7.1. The Group number and the number of valence electrons.

Periodic table group	Valence electrons
Group 1 (I) (alkali metals)	1

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

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

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

Atomic Radius

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

As mentioned earlier, the higher the shell number, the farther from the nucleus the electrons in that shell are likely to be. In other words, the size of an atom is generally determined by the number of the valence electron shell. Therefore, as we go down a column on the periodic table, the atomic radius increases. As we go *across* a period on the periodic table, however, electrons are being added to the *same* valence shell; meanwhile, more protons are being added to the nucleus, so the positive charge of the nucleus is increasing. The increasing positive charge attracts the electrons more strongly, pulling them closer to the nucleus. Consequently, as we go across a period, from left to right, the atomic radius decreases. These trends are seen clearly in Figure 2.7.5

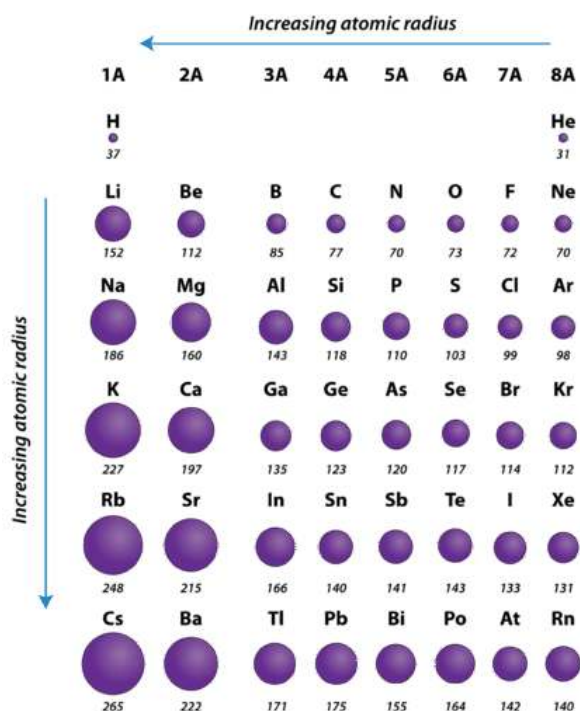


Figure 2.7.5 Trends on the Periodic Table. Atomic radii of the representative elements measured in picometers. The relative sizes of the atoms show several trends with regard to the structure of the periodic table. Atoms become larger going down a group and going from right to left across a period.

✓ Example 2.7.2

Using the periodic table (rather than Figure 2.7.5), which atom is larger?

- a. N or Bi
- b. Mg or Cl

Answer a

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

Answer b

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

? Exercise 2.7.2

Using the periodic table (rather than Figure 2.7.5), which atom is larger?

- a. Li or F
- b. Na or K

Answer a

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

Answer b

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

📌 Career Focus: Clinical Chemist

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

Concept Review Exercises

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

Answers

1. Elements are organized in order of increasing atomic number.
2.
 - a. the left three-quarters of the periodic table (to the left of the zigzag band)
 - b. the right quarter of the periodic table (to the right of the zigzag band)
 - c. the next-to-last column of the periodic table
 - d. the middle section of the periodic table

e. the last column of the periodic table

3. As you go across the periodic table, atomic radii decrease; as you go down the periodic table, atomic radii increase.

Key Takeaways

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

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

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

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

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

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

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

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

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

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

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

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CHAPTER OVERVIEW

3: Ionic Bonding and Simple Ionic Compounds

Template:Chem309Bennett

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 and Chapter 4, 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: Ionic Bonding and Simple Ionic Compounds \(Summary\)](#)

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3.1: Two Types of Bonding

Learning Objectives

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

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

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

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

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

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

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

✓ Example 3.1.1

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

Solution

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

Table explaining the solution to the example.

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

? Exercise 3.1.1

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

Answer

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

Key Takeaways

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

Exercises

1. What is the octet rule?
2. How are ionic bonds formed?
3. Why is an ionic compound unlikely to consist of two positively charged ions?
4. Why is an ionic compound unlikely to consist of two negatively charged ions?
5. A calcium atom has two valence electrons. Do you think it will lose two electrons or gain six electrons to obtain an octet in its outermost electron shell? Write the formula of the resulting ion.
6. An aluminum atom has three valence electrons. Do you think it will lose three electrons or gain five electrons to obtain an octet in its outermost electron shell? Write the formula of the resulting ion.
7. A selenium atom has six valence electrons. Do you think it will lose six electrons or gain two electrons to obtain an octet in its outermost electron shell? Write the formula of the resulting ion.
8. An iodine atom has seven valence electrons. Do you think it will lose seven electrons or gain one electron to obtain an octet in its outermost electron shell? Write the formula of the resulting ion.

Answers

1. The octet rule is the concept that atoms tend to have eight electrons in their valence electron shell.
2. Ionic bonds are formed by the attraction between oppositely charged ions.
3. Positive charges repel each other, so an ionic compound is not likely between two positively charged ions.
4. Negative charges repel each other also.
5. Ca atom is more likely to lose two electrons. It will become Ca^{2+} ion.
6. An Al atom is more likely to lose three electrons. It will become Al^{3+} ion.
7. Selenium is more likely to gain two electrons. It will become Se^{2-} ion.
8. Iodine is more likely to gain one electron. It will become I^- ion.

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3.2: Ions

Learning Objectives

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

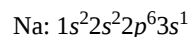
Most atoms do not have eight electrons in their valence electron shell. Some atoms have only a few electrons in their outer shell, while some atoms lack only one or two electrons to have an octet. In cases where an atom has three or fewer valence electrons, the atom may lose those valence electrons quite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

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

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

Electron Transfer

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



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

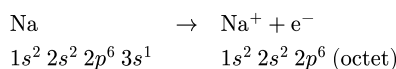


Figure 3.2.1 is a graphical depiction of this process.

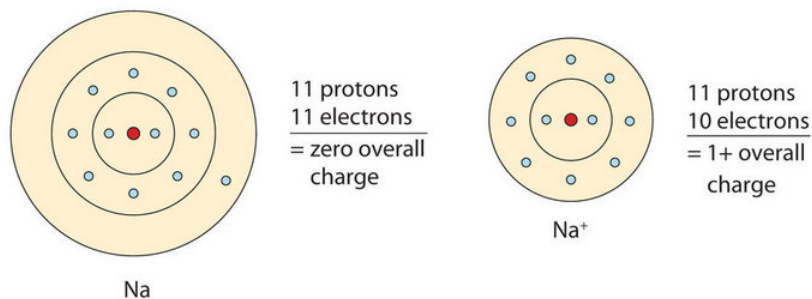


Figure 3.2.1: The Formation of a Sodium Ion. On

the left, a sodium atom has 11 electrons. On the right, the sodium ion only has 10 electrons and a 1+ charge.

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

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

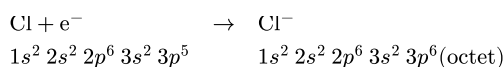


Figure 3.2.2 is a graphical depiction of this process.

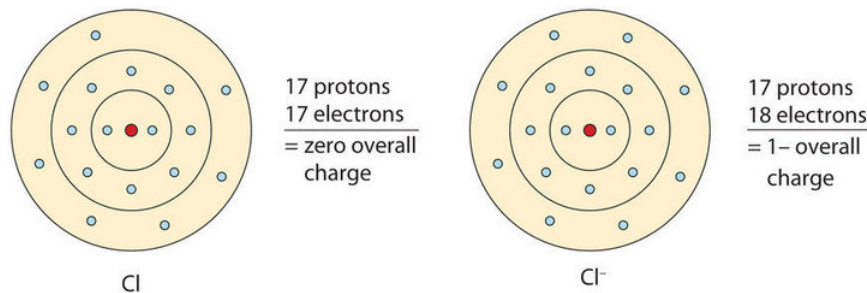


Figure 3.2.2: The Formation of a Chlorine Ion.

On the left, the chlorine atom has 17 electrons. On the right, the chloride ion has 18 electrons and has a 1- charge.

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

✓ Example 3.2.1

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

Solution

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

3.2.1 Exercise

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

Answer

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

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

1A							8A
H ⁺	2A		3A	4A	5A	6A	7A
Li ⁺					N ³⁻	O ²⁻	F ⁻
Na ⁺	Mg ²⁺		Al ³⁺		P ³⁻	S ²⁻	Cl ⁻
K ⁺	Ca ²⁺					Se ²⁻	Br ⁻
Rb ⁺	Sr ²⁺						I ⁻

Figure 3.2.3: Predicting Ionic Charges. The charge

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

✓ Example 3.2.2

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

- Mg⁺
- K⁺

Solution

(a) Mg is in Group 2A and has two valence electrons. It achieves octet by losing two electrons to form Mg²⁺ cation. Losing only one electron to form Mg⁺ does not make an octet, hence, Mg⁺ is not likely to form.

3.2.2Exercise

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

- S³⁻
- N³⁻

Answer

(a) S is in Group 6A and has six valence electrons. It achieves octet by gaining two electrons to form S²⁻ anion. Gaining three electrons to form S³⁻ does not make it octet, hence, S³⁻ is not likely to form.

Lewis Diagrams

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



and the representation for chlorine is as follows:



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

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

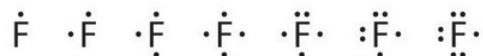
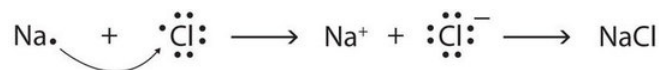


Figure 3.2.4 shows the electron configurations and Lewis diagrams of the elements lithium through neon, which is the entire second period of the periodic table. For the **main group** elements, the **number of valence electrons** is the **same as the group number** listed at the top of the periodic table.



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

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



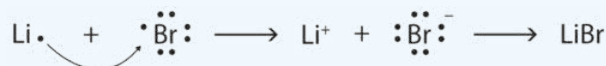
In representing the final formula, the dots are omitted.

✓ Example 3.2.3

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

Solution

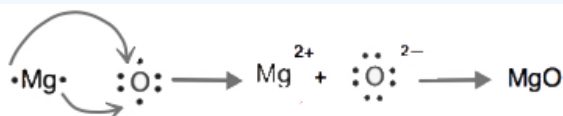
From the periodic table, we see that lithium is in the same column as sodium, so it will have the same valence shell electron configuration. That means that the neutral lithium atom will have the same Lewis diagram that the sodium atom has. Similarly, bromine is in the same column as chlorine, so it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



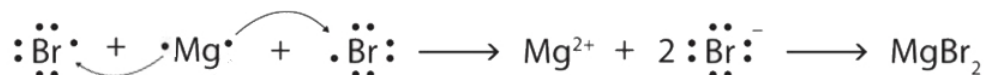
? Exercise 3.2.3

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

Answer



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

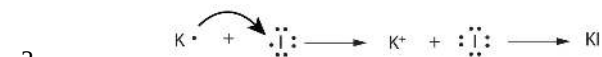


Notice that in this example there are two bromide ions (1– charge) needed for every one magnesium ion (2+ charge) in order for the overall charge of the compound to equal zero. This is called **charge balance**. The number of each type of ion is indicated in the

- d. S^{2-}
7. Write the electron configuration for each ion.
- Na^+
 - Be^{2+}
 - Cl^-
 - O^{2-}
8. Draw Lewis diagrams for the ions listed in Exercise 6. Also include Lewis diagrams for the respective neutral atoms as a comparison.
9. Draw Lewis diagrams for the ions listed in Exercise 7. Also include Lewis diagrams for the respective neutral atoms as a comparison.
10. Using Lewis diagrams, show the electron transfer for the formation of LiF.
11. Using Lewis diagrams, show the electron transfer for the formation of MgO.
12. Using Lewis diagrams, show the electron transfer for the formation of Li_2O .
13. Using Lewis diagrams, show the electron transfer for the formation of CaF_2 .
14. What characteristic charge do atoms in the first column of the periodic table have when they become ions?
15. What characteristic charge do atoms in the second column of the periodic table have when they become ions?
16. What characteristic charge do atoms in the third-to-last column of the periodic table have when they become ions?
17. What characteristic charge do atoms in the next-to-last column of the periodic table have when they become ions?

Answers

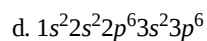
1. Cations (positive charged) and anions (negative charged).



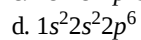
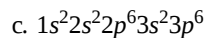
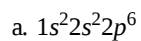
- 3.
- 1+
 - 2-
 - 2+
 - 1-
- 4.
- cation
 - anion
 - neither
 - cation
 - neither
 - neither

- 5.
- neither
 - anion
 - anion
 - cation
 - neither
 - neither

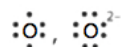
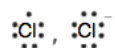
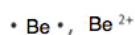
- 6.
- $1s^2$
 - $1s^2 2s^2 2p^6$
 - $1s^2 2s^2 2p^6$



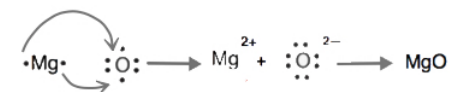
7.



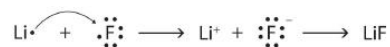
8.



9.



10.

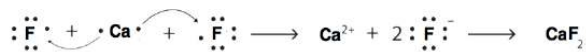


11.



13.

12.



14. 1^+

15. 2^+

16. 2^-

17. 1^-

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3.3: Formulas for Ionic Compounds

Learning Objectives

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

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

Ionic compounds exist as alternating positive and negative ions in regular, three-dimensional arrays called crystals (Figure 3.3.1). As you can see, there are no individual NaCl “particles” in the array; instead, there is a continuous lattice of alternating sodium and chloride ions. However, we can use the ratio of sodium ions to chloride ions, expressed in the lowest possible whole numbers, as a way of describing the compound. In the case of sodium chloride, the ratio of sodium ions to chloride ions, expressed in lowest whole numbers, is 1:1, so we use NaCl (one Na symbol and one Cl symbol) to represent the compound. Thus, NaCl is the chemical formula for sodium chloride, which is a concise way of describing the relative number of different ions in the compound. A macroscopic sample is composed of myriads of NaCl pairs; each individual pair called a **formula unit**. Although it is convenient to think that NaCl crystals are composed of individual NaCl units, Figure 3.3.1 shows that no single ion is exclusively associated with any other single ion. Each ion is surrounded by ions of opposite charge.

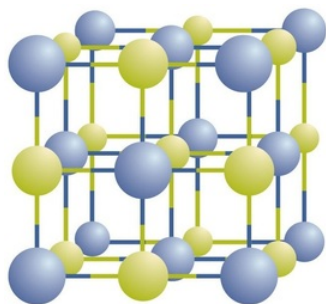


Figure 3.3.1: A Sodium Chloride Crystal. A crystal contains a three-dimensional array of alternating positive and negative ions. The precise pattern depends on the compound. A crystal of sodium chloride, shown here, is a collection of alternating sodium and chlorine ions.

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

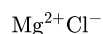
This rule is ultimately based on the fact that matter is, overall, electrically neutral.

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

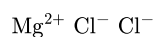
If we look at the ionic compound consisting of lithium ions and bromide ions, we see that the lithium ion has a 1+ charge and the bromide ion has a 1− charge. Only one ion of each is needed to balance these charges. The formula for lithium bromide is LiBr.

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

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



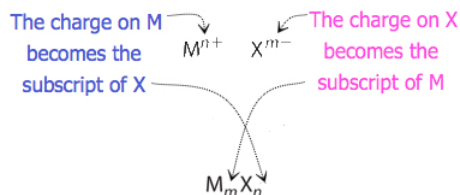
Combining one ion of each does not completely balance the positive and negative charges. The easiest way to balance these charges is to assume the presence of *two* chloride ions for each magnesium ion:



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

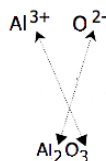
By convention, the lowest whole-number ratio of the ions is used in ionic formulas. There are exceptions for certain ions, such as Hg_2^{2+} .

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



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

Write the formula for the compound formed by aluminum and oxygen.



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

Figure 3.3.2: Crossing charges. One method for obtaining subscripts in the empirical formula is by crossing charges.

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

✓ Example 3.3.1

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

- the sodium ion and the sulfur ion
- the aluminum ion and the fluoride ion
- the $3+$ iron ion and the oxygen ion

Solution

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

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

? Exercise 3.3.1

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

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

Answer a:



Answer b:



Answer c:

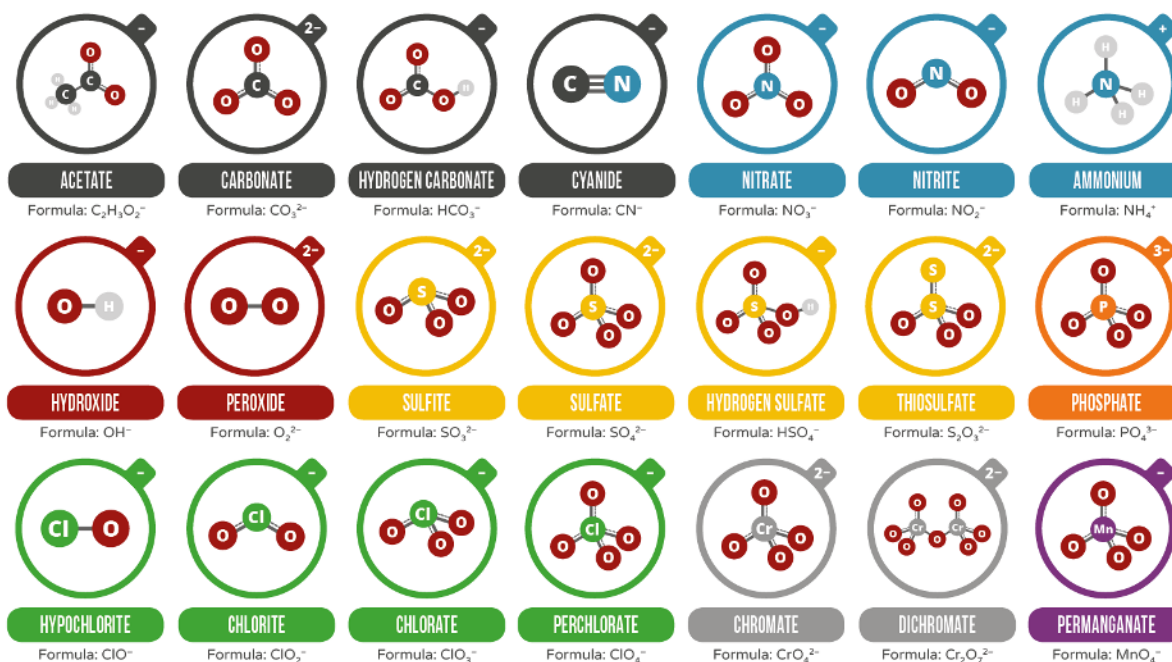


Polyatomic Ions

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

POLYATOMIC IONS: NAMES, FORMULAE & CHARGES

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



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Some Polyatomic Ions

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

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

Ion Name	Ion Formula
ammonium ion	NH_4^{+1}
hydroxide ion	OH^{-1}
cyanide ion	CN^{-1}
carbonate ion	CO_3^{-2}
bicarbonate or hydrogen carbonate	HCO_3^-
acetate ion	$\text{C}_2\text{H}_3\text{O}_2^{-1}$ or $\text{CH}_3\text{CO}_2^{-1}$
nitrate ion	NO_3^{-1}
nitrite ion	NO_2^{-1}
sulfate ion	SO_4^{-2}
sulfite ion	SO_3^{-2}
phosphate ion	PO_4^{-3}

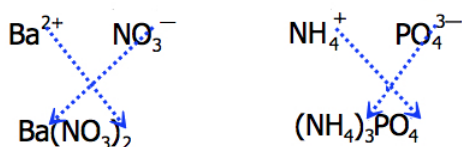
Ion Name	Ion Formula
phosphite ion	PO_3^{-3}

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

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

Write the formula for the compound formed by

- a. barium and nitrate b. ammonium and phosphate



The image asks a two-part question: Write the formula for the compound formed by (a) barium and nitrate, and (b) ammonium and phosphate. For (a), Ba has a charge of 2+ and NO_3 has a charge of -1. By crossing charges, the formula is $\text{Ba}(\text{NO}_3)_2$. For (b), NH_4 has a charge of +1 and PO_4 has a charge of 3-, so by crossing charges the formula is $(\text{NH}_4)_3\text{PO}_4$.

✓ Example 3.3.2

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

- the potassium ion and the sulfate ion
- the calcium ion and the nitrate ion

Solution

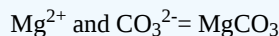
- Potassium ions have a charge of 1+, while sulfate ions have a charge of 2-. We will need two potassium ions to balance the charge on the sulfate ion, so the proper chemical formula is K_2SO_4 .
- Calcium ions have a charge of 2+, while nitrate ions have a charge of 1-. We will need two nitrate ions to balance the charge on each calcium ion. The formula for nitrate must be enclosed in parentheses. Thus, we write $\text{Ca}(\text{NO}_3)_2$ as the formula for this ionic compound.

? Exercise 3.3.2

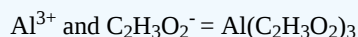
Write the chemical formula for an ionic compound composed of each pair of ions.

- the magnesium ion and the carbonate ion
- the aluminum ion and the acetate ion

Answer a:



Answer b:



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 discussed 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 $\text{Ba}(\text{NO}_3)_2$, 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.

- Na_2O
- PCl_3
- NH_4Cl
- OF_2

Solution

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

? Exercise 3.3.3

Identify each compound as ionic or not ionic.

- N_2O
- FeCl_3
- $(\text{NH}_4)_3\text{PO}_4$
- SOCl_2

Answer a:

not ionic

Answer b:

ionic

Answer c:

ionic

Answer d:

not ionic

Looking Closer: Blood and Seawater

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

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

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

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

Key Takeaways

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

EXERCISES

1. What information is contained in the formula of an ionic compound?
 - Why do the chemical formulas for some ionic compounds contain subscripts, while others do not?
3. Write the chemical formula for the ionic compound formed by each pair of ions.
 - a. Mg^{2+} and I^-
 - b. Na^+ and O^{2-}
4. Write the chemical formula for the ionic compound formed by each pair of ions.
 - a. Na^+ and Br^-
 - b. Mg^{2+} and Br^-
 - c. Mg^{2+} and S^{2-}
5. Write the chemical formula for the ionic compound formed by each pair of ions.

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

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

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

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

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

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

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

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

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

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

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

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

- a. NH_4^+ and NO_3^-
- b. H^+ and $\text{Cr}_2\text{O}_7^{2-}$
- c. Cu^+ and CO_3^{2-}
- d. Na^+ and HCO_3^-

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

- a. Ba and S
- b. Cs and I

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

- a. K and S
- b. Sc and Br

14. Which compounds would you predict to be ionic?

- a. Li_2O
- b. $(\text{NH}_4)_2\text{O}$
- c. CO_2
- d. FeSO_3
- e. C_6H_6
- f. $\text{C}_2\text{H}_6\text{O}$

15. Which compounds would you predict to be ionic?

- a. $\text{Ba}(\text{OH})_2$
- b. CH_2O
- c. NH_2CONH_2
- d. $(\text{NH}_4)_2\text{CrO}_4$
- e. C_8H_{18}
- f. NH_3

Answers

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

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

3.

- a. MgI_2
- b. Na_2O

4.

- a. NaBr
- b. MgBr_2
- c. MgS

5.

- a. KCl
- b. MgCl_2
- c. MgSe

6.

- a. Na_3N
- b. Mg_3N_2
- c. Al_2S_3

7.

- a. Li_3N
- b. Mg_3P_2
- c. Li_3P

8.

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

9.

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

10.

- a. $\text{Cr}(\text{NO}_3)_3$
- b. $\text{Fe}_3(\text{PO}_4)_2$
- c. CaCrO_4
- d. $\text{Al}(\text{OH})_3$

11.
 - a. NH_4NO_3
 - b. $\text{H}_2\text{Cr}_2\text{O}_7$
 - c. Cu_2CO_3
 - d. NaHCO_3
12.
 - a. Ba^{2+} , S^{2-} , BaS
 - b. Cs^+ , I^- , CsI
13.
 - a. K^+ , S^{2-} , K_2S
 - b. Sc^{3+} , Br^- , ScBr_3
14.
 - a. ionic
 - b. ionic
 - c. not ionic
 - d. ionic
 - e. not ionic
 - f. not ionic
15.
 - a. ionic
 - b. not ionic
 - c. not ionic
 - d. ionic
 - e. not ionic
 - f. not ionic

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3.4: Ionic Nomenclature

Learning Objectives

- To use the rules for naming ionic compounds

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

Naming Ions

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

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

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

Table 3.4.1: The Common System of Cation Names

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

The second system, called the **common system**, is not conventional but is still prevalent and used in the health sciences. This system recognizes that many metals have two common cations. The common system uses two suffixes (*-ic* and *-ous*) that are appended to the stem of the element name. The *-ic* suffix represents the greater of the two cation charges, and the *-ous* suffix represents the lower one. In many cases, the stem of the element name comes from the Latin name of the element. Table 3.4.1 lists the elements that use the common system, along with their respective cation names.

The name of a monatomic anion consists of the stem of the element name, the suffix *-ide*, and then the word *ion*. Thus, as we have already seen, Cl^- is “chlor-” + “-ide ion,” or the chloride ion. Similarly, O^{2-} is the oxide ion, Se^{2-} is the selenide ion, and so forth. Table 3.4.2 lists the names of some common monatomic ions.

Table 3.4.2: Some Monatomic Anions

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

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

✓ Example 3.4.1

Name each ion.

- Ca^{2+}
- S^{2-}
- SO_3^{2-}
- NH_4^{+}
- Cu^{+}

Answer a

the calcium ion

Answer b

the sulfide ion (from Table 3.4.2)

Answer c

the sulfite ion

Answer d

the ammonium ion

Answer e

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

? Exercise 3.4.1

Name each ion.

- Fe^{2+}
- Fe^{3+}
- SO_4^{2-}
- Ba^{2+}
- HCO_3^{-}

Answer a

the iron (II) or ferrous ion

Answer b

the iron (III) or ferric ion

Answer c

the sulfate ion

Answer d

the barium ion

Answer e

the bicarbonate ion or hydrogen carbonate ion

✓ Example 3.4.2

Write the formula for each ion.

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

Answer a

Br^-

Answer b

PO_4^{3-}

Answer c

Cu^{2+}

Answer d

Mg^{2+}

? Exercise 3.4.2

Write the formula for each ion.

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

Answer a

F^-

Answer b

CO_3^{2-}

Answer c

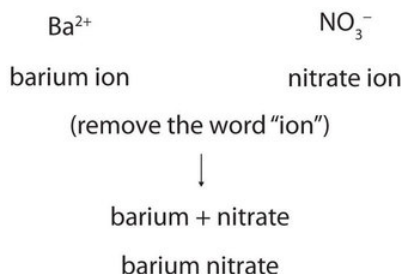
Fe^{2+}

Answer d

K^+

Naming Compounds

Now that we know how to name ions, we are ready to name ionic compounds. We do so by placing the name of the cation first, followed by the name of the anion, and dropping the word *ion* from both parts. For example, what is the name of the compound whose formula is $\text{Ba}(\text{NO}_3)_2$?



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. $\text{Ca}_3(\text{PO}_4)_2$
- b. $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$
- c. KCl
- d. CuCl
- e. SnF_2

Answer a

calcium phosphate

Answer b

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

Answer c

potassium chloride

Answer d

copper(I) chloride or cuprous chloride

Answer e

tin(II) fluoride or stannous fluoride

? Exercise 3.4.3

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

- a. ZnBr_2
- b. $\text{Fe}(\text{NO}_3)_3$
- c. Al_2O_3

d. CuF_2

e. AgF

Answer a

zinc bromide

Answer b

iron (III) nitrate or ferric nitrate

Answer c

aluminum oxide

Answer d

copper (II) fluoride or cupric fluoride

Answer e

silver fluoride

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

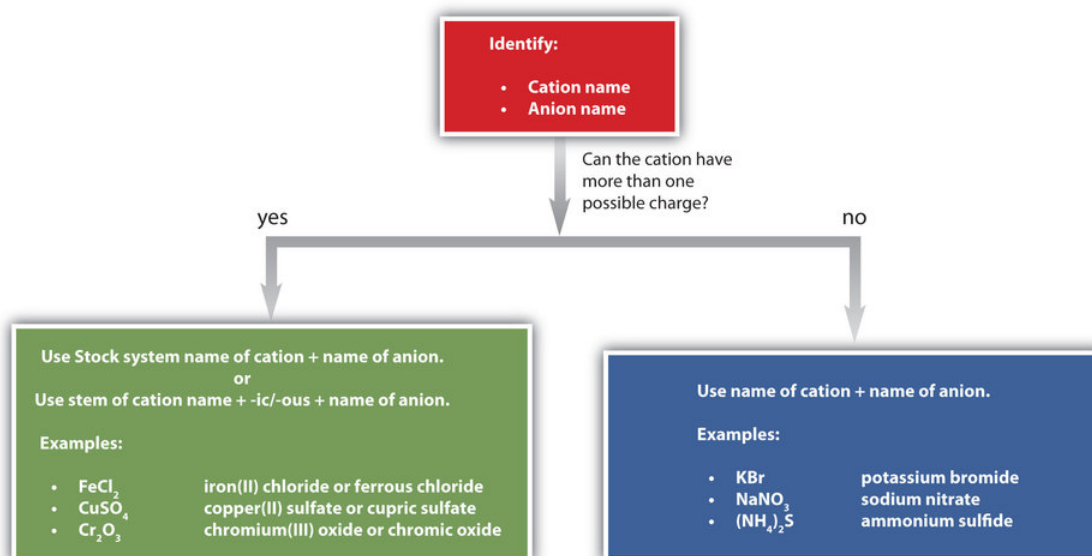


Figure 3.4.1: A

Guide to Naming Simple Ionic Compounds. Follow these steps to name a simple ionic compound. Identify the cation name and the anion name. If the cation can have more than one possible charge, either use the Stock system name of the cation and name of the anion, or use the stem of the cation name and -ic/-ous and the name of the anion. Examples of this would be FeCl_2 , which is iron(II) chloride or ferrous chloride, CuSO_4 , which is copper(II) sulfate or cupric sulfate, and Cr_2O_3 , which is chromium(III) oxide or chromic oxide. If the cation can not have more than one possible charge, use the name of the cation and the name of the anion. Examples of this would be KBr , which is potassium bromide, NaNO_3 , which is sodium nitrate, and $(\text{NH}_4)_2\text{S}$, which is ammonium sulfide.

KEY TAKEAWAY

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

EXERCISES

- Briefly describe the process for naming an ionic compound.
- In what order do the names of ions appear in the names of ionic compounds?
- Which ionic compounds can be named using two different systems? Give an example.
- Name each ion.

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

5. Name each ion.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

- a. NH_4^+ and NO_3^-
- b. K^+ and $\text{Cr}_2\text{O}_7^{2-}$
- c. Cu^+ and CO_3^{2-}
- d. Na^+ and HCO_3^-

14. Give two names for each compound.

- a. $\text{Al}(\text{HSO}_4)_3$
- b. $\text{Mg}(\text{HSO}_4)_2$

15. Give two names for each compound.

- a. $\text{Co}(\text{HCO}_3)_2$
- b. LiHCO_3

Answers

1. Name the cation and then the anion but don't use numerical prefixes.
2. the cation name followed by the anion name
3. Ionic compounds in which the cation can have more than one possible charge have two naming systems. FeCl_3 is either iron(III) chloride or ferric chloride (answers will vary).
4.
 - a. the radium ion
 - b. the phosphide ion
 - c. the dihydrogen phosphate ion
 - d. the tin(IV) ion or the stannic ion
5.
 - a. the cesium ion
 - b. the arsenide ion
 - c. the hydrogen sulfate ion
 - d. the tin(II) ion or the stannous ion
6.
 - a. sodium bromide
 - b. magnesium bromide
 - c. magnesium sulfide
7.
 - a. potassium chloride
 - b. magnesium chloride
 - c. magnesium selenide
8.
 - a. sodium nitride
 - b. magnesium nitride
 - c. aluminum sulfide
9.
 - a. lithium nitride
 - b. magnesium phosphide
 - c. lithium phosphide
10.
 - a. iron(III) bromide or ferric bromide
 - b. iron(II) bromide or ferrous bromide
 - c. gold(III) sulfide or auric sulfide
 - d. gold(I) sulfide or aurous sulfide
11.
 - a. chromium(III) oxide or chromic oxide

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

12.

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

13.

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

14.

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

15.

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

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

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

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

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

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

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

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

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

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

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CHAPTER OVERVIEW

4: Covalent Bonding and Simple Molecular Compounds

Template:Chem309Bennett

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: Covalent Compounds- Formulas and Names](#)
- [4.3: Multiple Covalent Bonds](#)
- [4.4: Polar Covalent Bonds and Electronegativity](#)
- [4.5: Characteristics of Molecules](#)
- [4.6: Intermolecular Forces](#)
- [4.7: Naming Binary Molecular Compounds](#)
- [4.S: Covalent Bonding and Simple Molecular Compounds \(Summary\)](#)

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4.1: Covalent Bonds

Learning Objectives

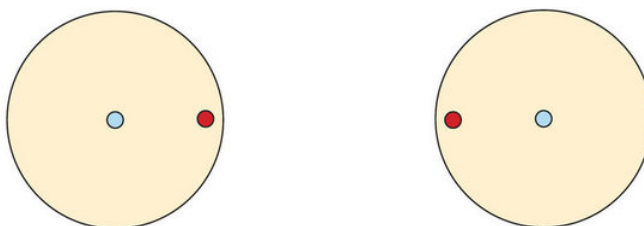
- To describe how a covalent bond forms.
- To apply the octet rule to covalent compounds

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

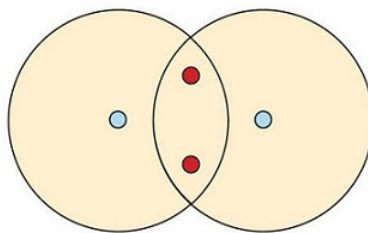
4.1.1 Electron Sharing

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

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



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



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

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



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



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



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

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

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

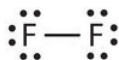


Each fluorine atom contributes one valence electron, making a single bond and giving each atom a complete valence shell, which fulfills the **octet** rule:



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

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



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

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

4.1.2 Covalent Bonds between Different Atoms

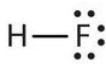
Now that we have looked at electron sharing between atoms of the same element, let us look at covalent bond formation between atoms of different elements. Consider a molecule composed of one hydrogen atom and one fluorine atom:



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



or



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

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

✓ Example 4.1.1

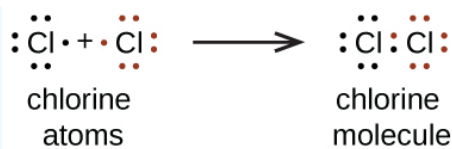
Use Lewis diagrams to indicate the formation of the following:

- Cl_2
- HBr

Solution

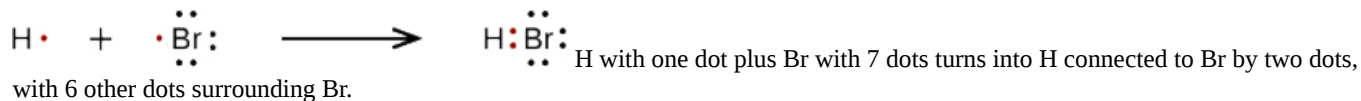
a. When two chlorine atoms form a chlorine molecule, they share one pair of electrons. In Cl_2 molecule, each chlorine atom is surrounded by an **octet** number of electrons.

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



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

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



? Exercise 4.1.1

Draw the Lewis diagram for each compound.

- a molecule composed of one chlorine atom and one fluorine atom
- a molecule composed of one hydrogen atom and one iodine atom

Answer a:

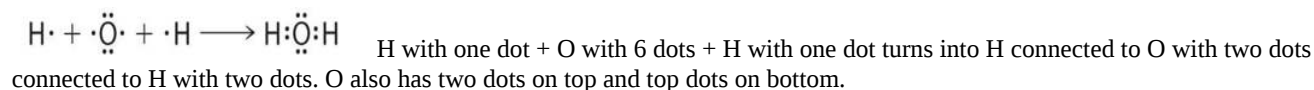


Answer b:

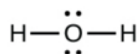


4.1.3 Covalent Bonds in Larger Molecules

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

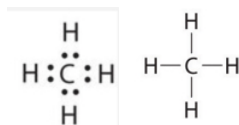


The structure on the right is the *Lewis electron structure*, or *Lewis structure*, for H₂O. With two bonding pairs and two lone pairs, the oxygen atom has now completed its **octet**. Moreover, by sharing a bonding pair with oxygen, each hydrogen atom now has a full valence shell of two electrons. Chemists usually indicate a bonding pair by a single line, as shown (below).



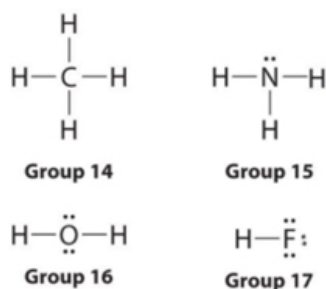
Water

Other large molecules are constructed in a similar fashion, with some atoms participating in more than one covalent bond. For example, methane (CH₄), the central carbon atom bonded to four hydrogen atoms, can be represented using either of the Lewis structures below. Again, sharing electrons between C and H atoms results in C achieving an octet while H achieving a duet number of electrons.



4.1.4 How Many Covalent Bonds Are Formed?

The number of bonds that an atom can form can often be predicted from the number of electrons needed to reach an octet (eight valence electrons). In the Lewis structure, the number of bonds formed by an element in a neutral compound is the same as the number of unpaired electrons it must share with other atoms to complete its octet of electrons. For example, each atom of a **group 4A** (14) element has four electrons in its outermost shell and therefore requires four more electrons to reach an octet. These four electrons can be gained by forming **four covalent bonds**, as illustrated here for carbon in CH₄ (methane). **Group 5A** (15) elements such as nitrogen have five valence electrons in the atomic Lewis symbol: one lone pair and three unpaired electrons. To obtain an octet, these atoms form **three covalent bonds**, as in NH₃ (ammonia). Oxygen and other atoms in **group 6A** (16) obtain an octet by forming **two covalent bonds**. Fluorine and the other halogens in **group 7A** (17) have seven valence electrons and can obtain an octet by forming **one covalent bond**.



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

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

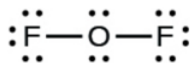
Atom (Group number)	Number of Bonds	Number of Lone Pairs
Carbon (Group 14 or 4A)	4	0
Nitrogen (Group 15 or 5A)	3	1
Oxygen (Group 16 or 6A)	2	2
Fluorine (Group 17 or 7A)	1	3

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

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

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.

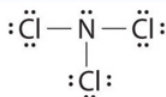
Examine the Lewis structure of OF_2 below. Count the number of bonds formed by each element. Based on the element's location in the periodic table, does it correspond to the expected number of bonds shown in Table 4.1? Does the Lewis structure below follow the octet rule?



$\ddot{\text{F}} \quad \ddot{\text{O}} \quad \ddot{\text{F}}$ F surrounded by 6 dots, connected to O with a long dash. O surrounded by 4 dots and connects to another F with a long dash. F surrounded by 6 dots.

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

Examine the Lewis structure of NCl_3 below. Count the number of bonds formed by each element. Based on the element's location in the periodic table, does it correspond to the expected number of bonds shown in Table 4.1? Does the Lewis structure below follow the octet rule?



Both Cl and N form the expected number of bonds. Cl (group 7A) has one bond and 3 lone pairs. The central atom N (group 5A) has 3 bonds and one lone pair. Yes, the Lewis structure of NCl_3 follows the octet rule.

- A covalent bond is formed between two atoms by sharing electrons.
- The number of bonds an element forms in a covalent compound is determined by the number of electrons it needs to reach octet.
- Hydrogen is an exception to the octet rule. H forms only one bond because it needs only two electrons.

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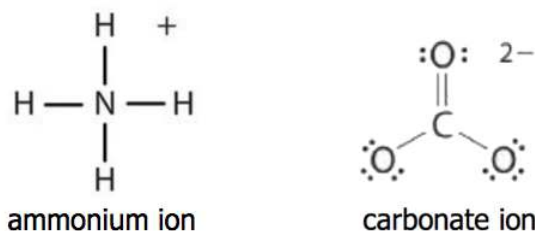
4.2: Covalent Compounds- Formulas and Names

COVALENT AND IONIC COMPOUNDS

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

As a general rule of thumb, compounds that involve a metal binding with either a non-metal or a semi-metal will display ionic bonding. Thus, the compound formed from sodium and chlorine will be ionic (a metal and a non-metal). Nitrogen monoxide (NO) will be a covalently bound molecule (two non-metals), silicon dioxide (SiO₂) will be a covalently bound molecule (a semi-metal and a non-metal) and MgCl₂ will be ionic (a metal and a non-metal).

A polyatomic ion is an ion composed of two or more atoms that have a charge as a group (poly = many). The ammonium ion (see figure below) consists of one nitrogen atom and four hydrogen atoms. Together, they comprise a single ion with a 1+ charge and a formula of NH₄⁺. The carbonate ion (see figure below) consists of one carbon atom and three oxygen atoms and carries an overall charge of 2⁻. The formula of the carbonate ion is CO₃²⁻.



The atoms of a polyatomic ion are tightly bonded together and so the entire ion behaves as a single unit. Several examples are found in Table 3.3.1. Nonmetal atoms in polyatomic ions are joined by covalent bonds, but the ion as a whole participates in ionic bonding. For example, ammonium chloride (NH₄Cl) has ionic bonding between a polyatomic ion, NH₄⁺, and Cl⁻ ions, but within the ammonium ion (NH₄⁺), the nitrogen and hydrogen atoms are connected by covalent bonds (shown above).

Both ionic and covalent bonding are also found in calcium carbonate. Calcium carbonate (CaCO₃) has ionic bonding between calcium ion Ca²⁺ and a polyatomic ion, CO₃²⁻, but within the carbonate ion (CO₃²⁻), the carbon and oxygen atoms are connected by covalent bonds (shown above).

4.2.0.1 Characteristics of Covalent (Molecular) Compounds

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

✓ Example 4.2.1

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

- Na₂O
- Na₃PO₄
- N₂O₄

Answer a

The elements in Na₂O are a metal and a nonmetal, which form ionic bonds.

Answer b

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

Answer c

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

? Exercise 4.2.1

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

- $\text{Ba}(\text{OH})_2$
- F_2
- PCl_3

Answer a:

both

Answer b:

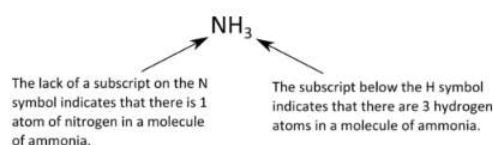
covalent

Answer c:

covalent

4.2.0.0.1 MOLECULAR FORMULAS

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



4.2.0.0.2 NAMING COVALENT COMPOUNDS

Naming *binary* (two-element) covalent compounds is similar to naming simple ionic compounds. The first element in the formula is simply listed using the name of the element. The second element is named by taking the stem of the element name and adding the suffix *-ide*. A system of numerical prefixes is used to specify the number of atoms in a molecule. Table 4.2.1 lists these numerical prefixes. Normally, no prefix is added to the first element's name if there is only one atom of the first element in a molecule. If the second element is oxygen, the trailing vowel is usually omitted from the end of a polysyllabic prefix but not a monosyllabic one (that is, we would say "monoxide" rather than "monooxide" and "trioxide" rather than "troxide").

Table 4.2.1: Numerical Prefixes for Naming Binary Covalent Compounds

Number of Atoms in Compound	Prefix on the Name of the Element
1	mono-*
2	di-
3	tri-

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

Number of Atoms in Compound	Prefix on the Name of the Element
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, *chlorine*, becomes *chloride*, and we attach the correct numerical prefix (“tetra-”) to indicate that the molecule contains four chlorine atoms. Putting these pieces together gives the name *carbon tetrachloride* for this compound.

✓ Example 4.2.2

Write the molecular formula for each compound.

- chlorine trifluoride
- phosphorus pentachloride
- sulfur dioxide
- 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.

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

? Exercise 4.2.2

Write the molecular formula for each compound.

- nitrogen dioxide
- dioxygen difluoride
- sulfur hexafluoride
- selenium monoxide

Answer a:

- NO_2

Answer b:

- O_2F_2

Answer c:

- SF_6

Answer d:

- SeO

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

✓ Example 4.2.3

Write the name for each compound.

- a. BrF_5
- b. S_2F_2
- c. CO

Solution

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

? Exercise 4.2.3

Write the name for each compound.

- a. CF_4
- b. SeCl_2
- c. SO_3

Answer a:

carbon tetrafluoride

Answer b:

selenium dichloride

Answer c:

sulfur trioxide

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

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

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

4.2.1 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?

4.2.2 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.

4.2.3 Key Takeaways

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

4.2.4 Exercises

1. Identify whether each compound has covalent bonds.
 - a. NaI
 - b. Na_2CO_3
 - c. N_2O
 - d. SiO_2
2. Identify whether each compound has covalent bonds.
 - a. C_2H_6
 - b. $\text{C}_6\text{H}_5\text{Cl}$
 - c. $\text{KC}_2\text{H}_3\text{O}_2$
 - d. $\text{Ca}(\text{OH})_2$
3. Identify whether each compound has ionic bonds, covalent bonds, or both.
 - a. Na_3PO_4
 - b. K_2O
 - c. COCl_2
 - d. CoCl_2
4. Identify whether each compound has ionic bonds, covalent bonds, or both.
 - a. FeCl_3
 - b. $\text{Fe}(\text{NO}_3)_3$
 - c. $(\text{NH}_2)_2\text{CO}$
 - d. SO_3
5. Which is the correct molecular formula— H_4Si or SiH_4 ? Explain.
6. Which is the correct molecular formula— SF_6 or F_6S ? Explain.
7. Write the name for each covalent compound.
 - a. SiF_4
 - b. NO_2
 - c. CS_2
 - d. P_2O_5
8. Write the name for each covalent compound.
 - a. CO
 - b. S_2O_3
 - c. BF_3
 - d. GeS_2
9. Write the formula for each covalent compound.
 - a. iodine trichloride
 - b. disulfur dibromide
 - c. arsenic trioxide
 - d. xenon hexafluoride
10. Write the formula for each covalent compound.
 - a. boron trichloride
 - b. carbon dioxide
 - c. tetraphosphorus decoxide

d. germanium dichloride

11. Write two covalent compounds that have common rather than systematic names.

12. What is the name of the simplest organic compound? What would its name be if it followed the nomenclature for binary covalent compounds?

4.2.5 Answers

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

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

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

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

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

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

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

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

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

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

11. H_2O and NH_3 (water and ammonia) (answers will vary)

12. CH_4 ; carbon tetrahydride

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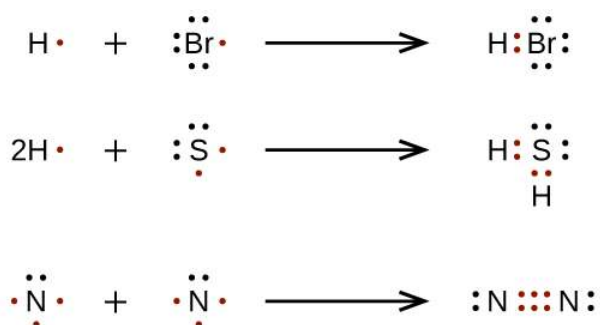
4.3: Multiple Covalent Bonds

Learning Objectives

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

4.3.0.1 DRAWING LEWIS STRUCTURES

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



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

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

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

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

$$\begin{array}{l}
 \text{O} + 2(\text{F}) = \text{OF}_2 \\
 6e^- + (2 \times 7e^-) = 20e^- \\
 \text{H} + \text{C} + \text{N} = \text{HCN} \\
 1e^- + 4e^- + 5e^- = 10e^-
 \end{array}$$

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



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

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

- In HCN, six electrons placed on N



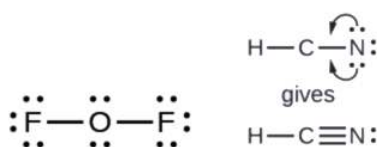
4. Place all remaining electrons on the central atom.

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



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

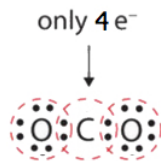
- In OF_2 , each atom has an octet as drawn, so nothing changes.
- In HCN, form two more C–N bonds



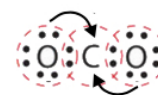
Finally, check to see if the total number of valence electrons are present in the Lewis structure. And then, inspect if the H atom has 2 electrons surrounding it and if each of the main group atoms is surrounded by 8 electrons.

4.3.0.0.1 MULTIPLE BONDS

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

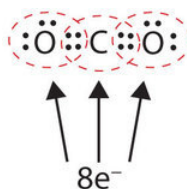


This does not give the carbon atom a complete octet; only four electrons are in its valence shell. This arrangement of shared



electrons is far from satisfactory.

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



In this arrangement, the carbon atom shares four electrons (two pairs) with the oxygen atom on the left and four electrons with the oxygen atom on the right. There are now eight electrons around each atom. Two pairs of electrons shared between two atoms make

a double bond between the atoms, which is represented by a double dash:



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



✓ Example 4.3.1

Draw the Lewis diagram for each molecule.

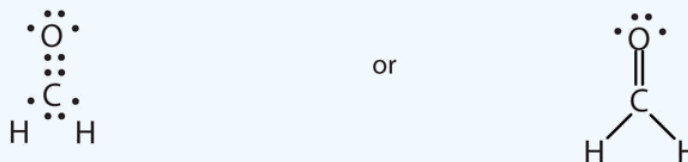
1. N_2
2. CH_2O (The carbon atom is the central atom.) One application of CH_2O , also called formaldehyde, is the preservation of biological specimens. Aqueous solutions of CH_2O are called formalin and have a sharp, characteristic (pungent) odor.

Solution

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



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



? Exercise 4.3.1

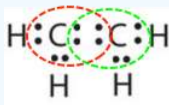
Draw the Lewis diagram for each molecule.

- a. O_2
- b. C_2H_4

Answer a:



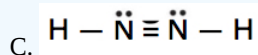
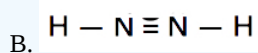
Answer b:



✓ Example 4.3.2

Which is the correct Lewis structure for N_2H_2 ?

A. $\text{H} - \ddot{\text{N}} = \ddot{\text{N}} - \text{H}$



Solution

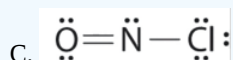
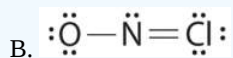
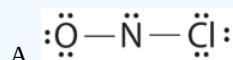
Lewis structure A is the correct answer. It has a total of $(2 \times 5e^-) + (2 \times 1e^-) = 12e^-$. Each of the N atoms satisfy the octet requirement and the H atoms follow the duet rule.

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

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

Exercise 4.3.2

Which is the correct Lewis structure for NOCl?



Answer

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

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

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

4.3.1 Key Takeaways

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

4.3.2 Exercises

1. What is one clue that a molecule has a multiple bond?
2. Draw the Lewis diagram for each of the following.
 - a. H_2O
 - b. NH_3
 - c. C_2H_6
 - d. CCl_4
3. Each molecule contains double bonds. Draw the Lewis diagram for each. The first element is the central atom.
 - a. CS_2
 - b. C_2F_4
 - c. COCl_2
4. Each molecule contains multiple bonds. Draw the Lewis diagram for each. Assume that the first element is the central atom, unless otherwise noted.
 - a. N_2

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

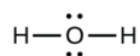
5. Explain why hydrogen atoms do not form double bonds.

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

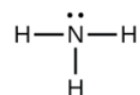
4.3.3 Answers

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

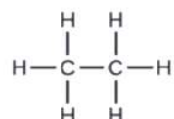
2. a.



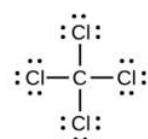
b.



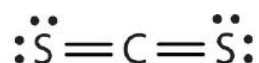
c.



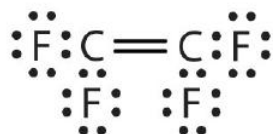
d.



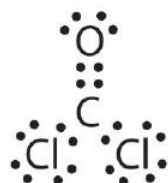
3. a.



b.

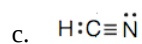


c.

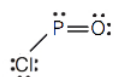


4. a. $\ddot{\text{N}} \equiv \ddot{\text{N}}$

b. $:\text{C} \equiv \text{O}:$



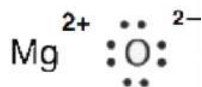
d.



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

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

This is the Lewis dot structure of MgO.



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4.4: Polar Covalent Bonds and Electronegativity

Learning Objectives

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

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

4.4.1 Bond Polarity

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

- A **nonpolar covalent bond** (Figure 4.4.1a) is one in which the electrons are shared *equally* between two atoms.
- A **polar covalent bond** (Figure 4.4.1b) is one in which one atom has a greater attraction for the electrons than the other atom.
- If the relative attraction of an atom for electrons is great enough, then the bond is an **ionic bond** (Figure 4.4.1c).

Electron density in a polar bond is distributed unevenly and is greater around the atom that attracts the electrons more than the other. For example, the electrons in the H–Cl bond of a hydrogen chloride molecule spend more time near the chlorine atom than near the hydrogen atom. Note that the shaded area around Cl in Figure 4.4.1b is much larger than it is around H. This imbalance in electron density results in a buildup of *partial negative charge* (designated as δ^-) on one side of the bond (Cl) and a *partial positive charge* (designated δ^+) on the other side of the bond (H).

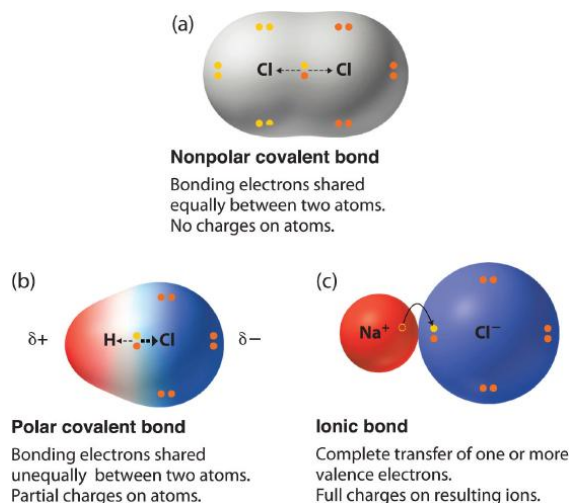


Figure 4.4.1: The Electron Distribution in a Nonpolar Covalent Bond, a Polar Covalent Bond, and an Ionic Bond Using Lewis Electron Structures. In a purely covalent bond (a), the bonding electrons are shared equally between the atoms. In a purely ionic bond (c), an electron has been transferred completely from one atom to the other. A polar covalent bond (b) is intermediate between the two extremes: the bonding electrons are shared unequally between the two atoms, and the electron distribution is asymmetrical with the electron density being greater around the more electronegative atom. Electron-rich (negatively charged) regions are shown in blue; electron-poor (positively charged) regions are shown in red.

Any covalent bond between atoms of different elements is a polar bond, but the degree of polarity varies widely. Some bonds between different elements are only minimally polar, while others are strongly polar. Ionic bonds can be considered the ultimate in polarity, with electrons being transferred rather than shared. To judge the relative polarity of a covalent bond, chemists use electronegativity, which is a relative measure of how strongly an atom attracts electrons when it forms a covalent bond.

4.4.2 Electronegativity

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

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

Electronegativity is a function of:

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

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

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

4.4.2.1 The Pauling Electronegativity Scale

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

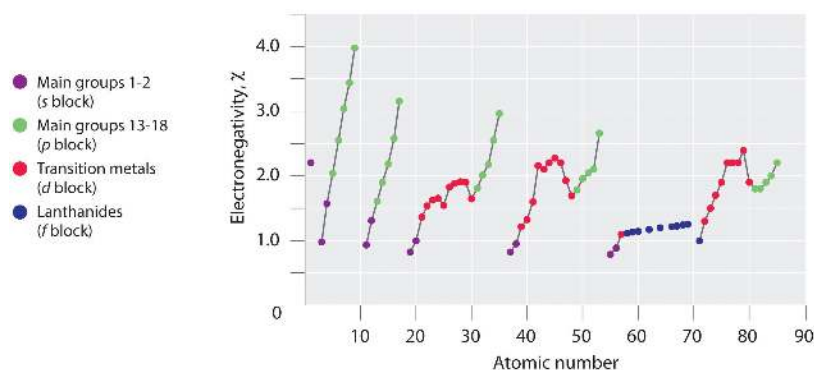
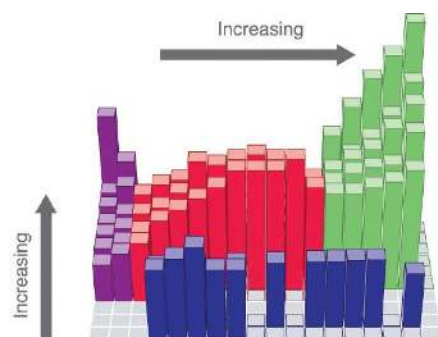


Figure 4.4.2: A Plot of Periodic Variation of

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

Periodic variations (trends) in Pauling's electronegativity values are illustrated in Figures 4.4.2 and 4.4.3. If we ignore the inert gases and elements for which no stable isotopes are known, we see that fluorine is the most electronegative element and cesium is the least electronegative nonradioactive element. Because electronegativities generally increase diagonally from the lower left to the upper right of the periodic table, elements lying on diagonal lines running from upper left to lower right tend to have comparable values (e.g., O and Cl, and N, S, and Br).



Electronegativity, χ

Figure 4.4.3: Pauling Electronegativity Values of the *s*-, *p*-, *d*-, and *f*-Block Elements. Values for most of the actinides are approximate. Elements for which no data are available are shown in gray. Source: Data from L. Pauling, *The Nature of the Chemical Bond*, 3rd ed. (1960). The *s* blocks are purple, the *p* blocks are green, the *d* blocks are red, and the *f* blocks are blue. Electronegativity increase from bottom to top and left to right.

The polarity of a covalent bond can be judged by determining the difference in the electronegativities of the two atoms making the bond. The greater the difference in electronegativities, the greater the imbalance of electron sharing in the bond. Although there are no hard and fast rules, the general rule, (see Figure 4.4.5), is if the difference in electronegativities is less than about 0.4, the bond is considered nonpolar; if the difference is greater than 0.4, the bond is considered polar. If the difference in electronegativities is large enough (generally greater than about 1.8), the resulting compound is considered ionic rather than covalent. An electronegativity difference of zero, of course, indicates a nonpolar covalent bond.

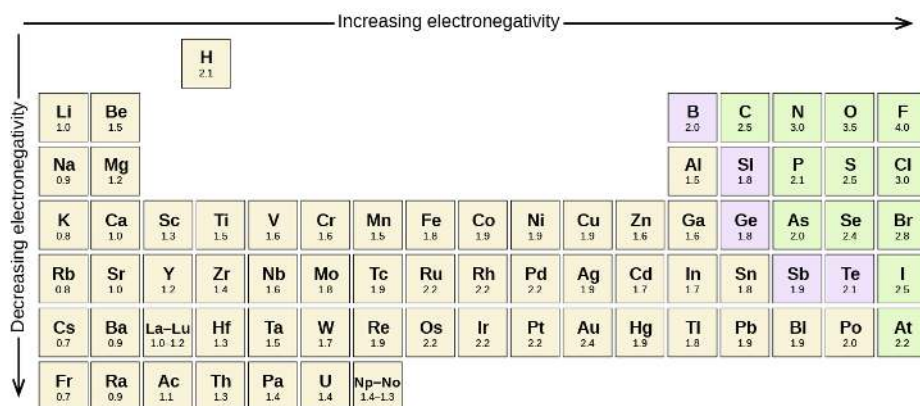
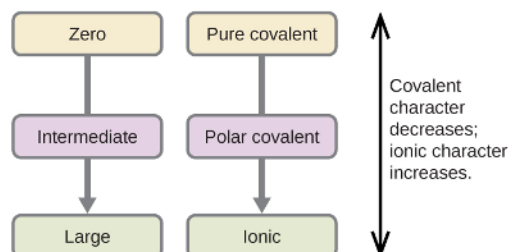


Figure 4.4.4 The electronegativity

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

Electronegativity
difference between
bonding atoms

Bond type



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

Figure 4.4.5: As the electronegativity

difference increases between two atoms, the bond becomes more ionic.

✓ Example 4.4.1

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

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

Solution

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

? Exercise 4.4.1

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

- a. C and O
- b. K and Br
- c. N and N
- d. Cs and F

Answer a:

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

Answer b:

The EN difference is greater than 1.8, hence ionic.

Answer c:

Identical atoms have zero EN difference, hence nonpolar.

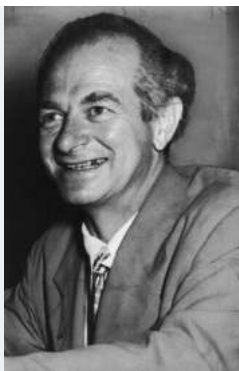
Answer d:

The EN difference is greater than 1.8, hence ionic.

Looking Closer: Linus Pauling

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

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



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

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

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4.5: Characteristics of Molecules

Learning Objectives

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

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

4.5.1 Molecular Mass

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

✓ Example 4.5.1

What is the molecular mass of each covalent compound?

- H_2O
- C_6H_6
- NO_2
- N_2O_5

Solution

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

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

This table finds the mass of atoms.

2 H:	$2 \times 1.01 =$	2.02 amu
1 O:		+ 16.00 amu
Total:		18.02 amu

The molecular mass of H_2O is **18.02** amu.

This table finds the mass of atoms.

6 C:	$6 \times 12.01 =$	72.06 amu
6 H:	$6 \times 1.01 =$	+ 6.06 amu
Total:		78.12 amu

The molecular mass of C_6H_6 is **78.12** amu.

This table finds the mass of atoms.

1 N:		14.01 amu
2 O:	$2 \times 16.00 =$	+ 32.00 amu
Total:		46.01 amu

The molecular mass of NO_2 is **46.01** amu.

This table finds the mass of atoms.

2 N:	$2 \times 14.01 =$	28.02 amu
5 O:	$5 \times 16.00 =$	+ 80.00 amu
Total:		108.02 amu

The molecular mass of N_2O_5 is **108.02** amu.

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

? Exercise 4.5.1

What is the molecular mass of each covalent compound?

- C_2H_2
- CO
- CO_2
- BF_3

Answer a:

26.04 amu

Answer b:

28.01 amu

Answer c:

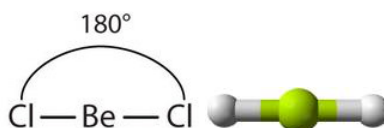
44.01 amu

Answer d:

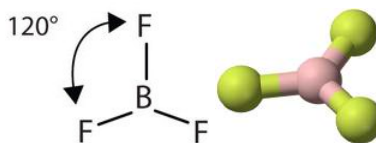
67.81 amu

4.5.2 Molecular Shape: VSEPR Theory

Unlike ionic compounds, with their extended crystal lattices, covalent molecules are discrete units with specific three-dimensional shapes. The shape of a molecule is determined by the fact that covalent bonds, which are composed of negatively charged electrons, tend to repel one another. This concept is called the **valence shell electron pair repulsion (VSEPR) theory**. For example, the two covalent bonds in BeCl_2 **stay as far from each other** as possible, ending up 180° apart from each other. The result is a **linear** molecule:



The three covalent bonds in BF_3 repel each other to form 120° angles in a plane, in a shape called **trigonal planar**:



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

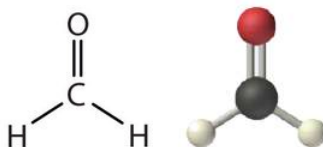
Try sticking three toothpicks into a marshmallow or a gumdrop and see if you can find different positions where your “bonds” are farther apart than the planar 120° orientation.

The four covalent bonds in CCl_4 arrange themselves three dimensionally, pointing toward the corner of a tetrahedron and making bond angles of 109.5° . CCl_4 is said to have a **tetrahedral** shape:

Table describes how to use the number of atoms around the central atom to determine the geometry of a molecule, as well as examples.

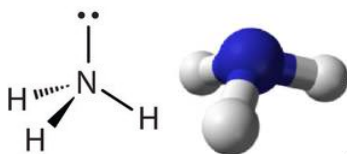
Atoms Around Central Atom	Geometry	Example
2 AB_2	Linear	BeCl_2
3 AB_3	Trigonal Planar	BF_3
4 AB_4	Tetrahedral	CCl_4

In determining the shapes of molecules, it is useful to first determine the Lewis diagram for a molecule. The shapes of molecules with multiple bonds are determined by treating the multiple bonds as one bond. Thus, formaldehyde (CH_2O) has a shape similar to that of BF_3 . It is **trigonal planar**.

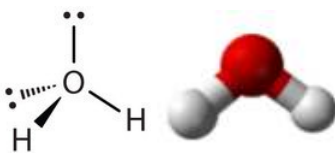


4.5.2.1 Molecules With Lone Pairs Around Central Atom

Molecules with lone electron pairs around the central atom have a shape based on the position of the atoms, not the electron pairs. For example, NH_3 has **one lone electron pair** and **three bonded electron pairs**. These four electron pairs repel each other and adopt a tetrahedral arrangement. However, the shape of the molecule is described in terms of the positions of the atoms, not the lone electron pairs. Thus, NH_3 is said to have a **trigonal pyramidal** shape, not a tetrahedral one.



Similarly, H_2O has **two lone pairs** of electrons around the central oxygen atom and **two bonded electron pairs**. Although the four electron pairs adopt a tetrahedral arrangement, the shape of the molecule is described by the positions of the atoms only. The shape of H_2O is **bent** with an approximate 109.5° angle.

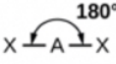
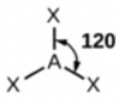
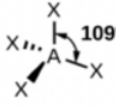


In summary, to determine the molecular geometry:

Step 1: Draw the Lewis structure.

Step 2: Count the number of bonds (a double/triple bond counts as one) and lone pairs around the **central atom**.

Step 3: Use Table 4.5.1 to determine the molecular geometry.

Number of bonds and lone pairs	Number of bonds	1 lone pair	2 lone pairs
	0 lone pair		
2	 Linear		
3	 Trigonal planar	 Bent or angular	 Lone Pair
4	 Tetrahedral	 Trigonal pyramid	
			 Bent or angular

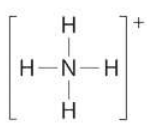
If a molecule has 2 bonds and 0 lone pairs, it is linear.

If a molecule has 3 bonds and 0 lone pairs, it is trigonal planar. If a molecule has 3 bonds and 1 lone pair, it is bent or angular. If a molecule has 4 bonds and 0 lone pairs, it is tetrahedral. If a molecule has 4 bonds and 1 lone pair, it is trigonal pyramid. If a molecule has 4 bonds and 2 lone pairs, it is bent or angular.

Table 4.5.1: The molecular geometry depends on the number of bonds and lone pairs around the **central atom, A**.

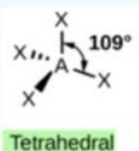
✓ Example 4.5.1

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

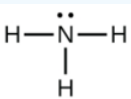


Solution

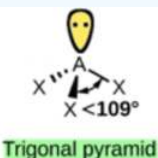
In ammonium ion, the central atom N has 4 bonds and no lone pair. It is equivalent to the below in Table 4.5.1. Hence, this is *tetrahedral*.



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

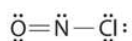


It is equivalent to the below in Table 4.5.1. Hence, the shape of this molecule is *trigonal pyramid*.



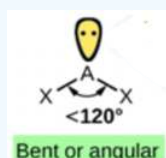
4.5.1 Exercise

What is the molecular shape of nitrosyl chloride, a highly corrosive, reddish-orange gas? Its Lewis structure is shown below.



Answer

Focus on the central atom, N. It has a double bond to O, count this as one bond. It also has a single bond to Cl. Thus, N has 2 bonds and one lone pair. These 3 electron pairs will spread out 120 degrees from each other. But, since the shape is defined by the arrangement of the atoms only, the shape is bent or angular. If you consult Table 4.5.1, this molecule is equivalent to the below. Hence, two bonds and one lone pair has a *bent or angular* shape.



4.5.3 Molecular Polarity

In general, a molecule is nonpolar if all its bonds are nonpolar. Examples are I_2 , O_2 , H_2 , CH_4 , C_2H_6 and C_3H_8 .

In general, a molecule is polar if it contains polar bonds EXCEPT when the bond polarities cancel each other. As mentioned in Section 4.4, the shape of the CO_2 molecule (linear) orients the two $\text{C}=\text{O}$ polar bonds **directly opposite** each other, thus **cancelling** each other's effect. **Carbon dioxide** (CO_2) is a **nonpolar** molecule.

On the other hand, water (as discussed above) is a bent molecule because of the two lone pairs on the central oxygen atom. Because of the bent shape, the dipoles do not cancel each other out and the water molecule is **polar**. In the figure below, the individual $\text{H}-\text{O}$ polar bonds represented by the two red arrows are not directly opposite each other. These two dipoles don't cancel each other out. In fact, the net dipole (blue arrow) points upward. There is a resultant partial positive charge at one end (between the two H atoms) and a partial negative charge on the other end (where O is located). The uneven distribution of charge or the overall dipole is shown by the blue arrow below (Figure 4.5.1). Hence, **water is polar** (has + and - poles) while **carbon dioxide is nonpolar**.

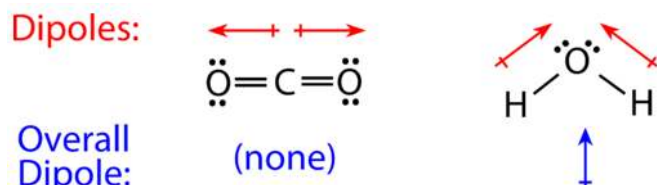
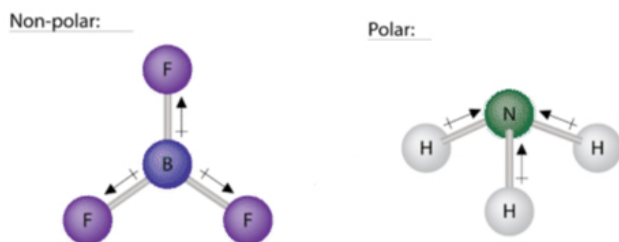


Figure 4.5.1: The molecular geometry of a molecule (linear vs.

bent) affects its polarity.

Similarly, in BF_3 (trigonal planar), the effect of a $\text{B}-\text{F}$ bond is cancelled by the sum of the other two $\text{B}-\text{F}$ bonds (see video). Hence, a trigonal planar molecule (BF_3) is nonpolar because the bond polarities cancel each other, but a trigonal pyramidal molecule (NH_3) is polar.



planar vs. trigonal pyramid) affects its polarity.

Figure 4.5.2: The molecular geometry of a molecule (trigonal

Some other molecules are shown in the figure below. Notice that a tetrahedral molecule such as CCl_4 is **nonpolar**. However, if the peripheral atoms are not of the same electronegativity, the bond polarities don't cancel and the molecule becomes **polar**, as in CH_3Cl .

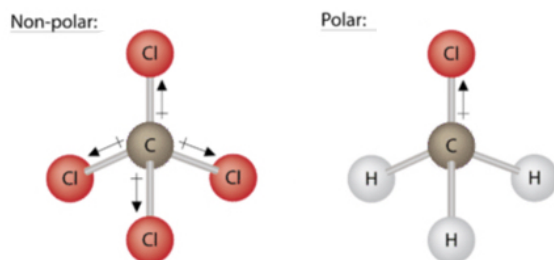


Figure 4.5.3: The same molecular geometry but peripheral bonds are of different electronegativity. CCl_4 is nonpolar but CH_3Cl is polar.

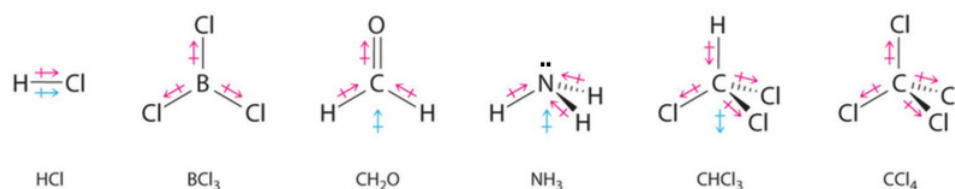


Figure 4.5.4: Molecules with Polar Bonds. Individual bond dipole moments are indicated in red. Due to their different three-dimensional geometry, some molecules with polar bonds have a net dipole moment (HCl , CH_2O , NH_3 , and CHCl_3), indicated in blue, whereas others do not because the bond dipoles cancel due to symmetry (BCl_3 and CCl_4).

4.5.4 Physical Properties of Molecular Compounds

The physical state and properties of a particular compound depend in large part on the type of chemical bonding it displays. **Molecular compounds**, sometimes called covalent compounds, display a wide range of physical properties due to the different types of intermolecular attractions such as different kinds of polar interactions. The melting and boiling points of molecular compounds are generally quite low compared to those of **ionic compounds**. This is because the energy required to disrupt the **intermolecular forces** (discussed in Section 8.1) between molecules is far less than the energy required to break the ionic bonds in a crystalline ionic compound. Since molecular compounds are composed of neutral molecules, their electrical conductivity is generally quite poor, whether in the solid or liquid state. Ionic compounds do not conduct electricity in the solid state because of their rigid structure, but conduct well when either molten or dissolved into a solution. The water solubility of molecular compounds is variable and depends primarily on the type of intermolecular forces involved. Substances that exhibit hydrogen bonding or dipole-dipole forces are generally water soluble, whereas those that exhibit only London dispersion forces are generally insoluble. Most, but not all, ionic compounds are quite soluble in water. The table below summarizes some of the differences between ionic and molecular compounds.

Table 4.5.2: Comparison of Ionic and Molecular Compounds

Property	Ionic Compounds	Molecular Compounds
Type of elements	Metal and nonmetal	Nonmetals only
Bonding	Ionic - transfer of electron(s) between atoms	Covalent - sharing of pair(s) of electrons between atoms
Representative unit	Formula unit	Molecule
Physical state at room temperature	Solid	Gas, liquid, or solid
Water solubility	Usually high	Variable
Melting and boiling temperatures	Generally high	Generally low
Electrical conductivity	Good when molten or in solution	Poor

In summary, covalent compounds are softer, have lower boiling and melting points, are more flammable, are less soluble in water and do not conduct electricity compared to ionic compounds. The individual melting and boiling points, solubility and other physical properties of molecular compounds depend on molecular polarity.

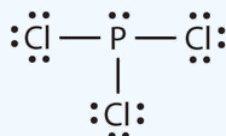
✓ Example 4.5.2

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

- PCl_3
- CO_2

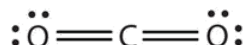
Solution

a. The Lewis diagram for PCl_3 is as follows:



Focus on the central atom, P that has 3 bonds and one lone pair. The four electron pairs arrange themselves tetrahedrally, but the lone electron pair is not considered in describing the molecular shape. Like NH_3 , this molecule is *pyramidal*. The 3 P-Cl bonds don't cancel each other. This is *polar*.

- The Lewis diagram for CO_2 is as follows:



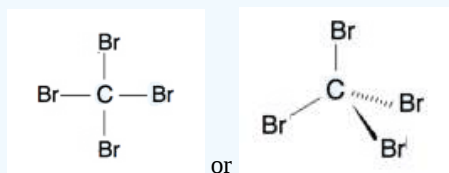
Focus on the central atom, C. The multiple bonds are treated as one group, hence C has 2 bonds and zero lone pair. CO_2 has only two groups of electrons that repel each other. They will direct themselves 180° apart from each other, so CO_2 molecules are *linear*. This is highly symmetrical, with the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

? Exercise 4.5.2

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

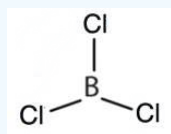
- CBr_4
- BCl_3

Answer a:



The Lewis structure shows 4 groups attached to the central atom, hence *tetrahedral*. All the 4 groups are identical and the shape is symmetrical. Hence, it is *nonpolar*.

Answer b:



The Lewis diagram shows 3 groups attached to the central atom, hence *trigonal planar*. All the 3 groups are identical and shape is symmetrical, hence, it is *nonpolar*.

4.5.5 Key Takeaways

- A molecule has a certain mass, called the molecular mass.
- Simple molecules have geometries that can be determined from VSEPR theory.
- Polar molecules result from differences in electronegativity of the atoms in the molecule.
- Dipoles that are directly opposite one another cancel each other out.

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4.6: Intermolecular Forces

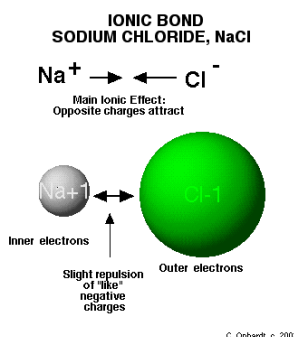
The physical properties of melting point, boiling point, vapor pressure, evaporation, viscosity, surface tension, and solubility are related to the strength of attractive forces between molecules. These attractive forces are called Intermolecular Forces. The amount of "stick togetherness" is important in the interpretation of the various properties listed above.

4.6.1 Introduction

There are four types of intermolecular forces. Most of the intermolecular forces are identical to bonding between atoms in a single molecule. Intermolecular forces just extend the thinking to forces between molecules and follows the patterns already set by the bonding within molecules.

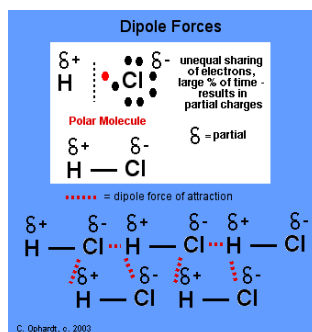
4.6.2 Ionic Forces

The forces holding ions together in ionic solids are electrostatic forces. Opposite charges attract each other. These are the strongest intermolecular forces. **Ionic forces** hold many ions in a crystal lattice structure.



4.6.3 Dipole Forces

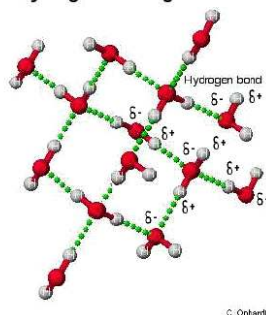
Polar covalent molecules are sometimes described as "dipoles", meaning that the molecule has two "poles". One end (pole) of the molecule has a partial positive charge while the other end has a partial negative charge. The molecules will orientate themselves so that the opposite charges attract principle operates effectively. For example, hydrochloric acid (HCl) is a polar molecule with the partial positive charge on the hydrogen and the partial negative charge on the chlorine. A network of partial + and - charges attract molecules to each other.



4.6.4 Hydrogen Bonding

The **hydrogen bond** is really a special case of dipole forces. A hydrogen bond is the attractive force between the hydrogen attached to an electronegative atom of one molecule and an electronegative atom of a different molecule. Usually the electronegative atom is oxygen, nitrogen, or fluorine. In other words - The hydrogen on one molecule attached to O or N that is attracted to an O or N of a different molecule.

Hydrogen Bonding in Water

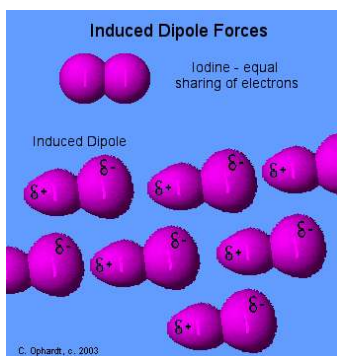


C. Ophardt, c. 2003

In the graphic below, the hydrogen is partially positive and attracted to the partially negative charge on the oxygen or nitrogen. Because oxygen has two lone pairs, two different hydrogen bonds can be made to each oxygen. This is a very specific bond as indicated. Some combinations that are not hydrogen bonds include: hydrogen to another hydrogen or hydrogen to a carbon.

4.6.5 London Dispersion or Induced Dipole or Van der Waals Forces

Forces between essentially non-polar molecules are the weakest of all intermolecular forces. "Temporary dipoles" are formed by the shifting of electron clouds within molecules. These temporary dipoles attract or repel the electron clouds of nearby non-polar molecules. The temporary dipoles may exist for only a fraction of a second but a force of attraction also exist for that fraction of time. The strength of induced dipole forces depends on how easily electron clouds can be distorted. Large atoms or molecules with many electrons far removed from the nucleus are more easily distorted.



C. Ophardt, c. 2003

4.6.6 Contributors

- Charles Ophardt, Professor Emeritus, Elmhurst College
- [Virtual Chembook](#)

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4.7: Naming Binary Molecular Compounds

Learning Objectives

- Name binary molecular compounds.

Naming *binary* (two-element) covalent compounds is very similar to naming simple ionic compounds. The first element in the formula is simply listed using the name of the element. The second element is named by taking the stem of the element name and adding the suffix *-ide*. Unlike for ionic compounds, molecular compounds can be formed using the same elements in different ratios. Therefore, it is important to indicate the number of each type of atom, using a system of numerical prefixes, listed in Table 4.7.1. Normally, no prefix is added to the first element's name if there is only one atom of the first element in a molecule. If the second element is oxygen, the trailing vowel is usually omitted from the end of a polysyllabic prefix but not a monosyllabic one (that is, we would say "monoxide" rather than "monooxide" and "trioxide" rather than "troxide").

Table 4.7.1: 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, *chlorine*, becomes *chloride*, 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 4.7.1

Write the molecular formula for each compound.

- chlorine trifluoride
- phosphorus pentachloride
- sulfur dioxide
- 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.

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

? Exercise 4.7.1

Write the molecular formula for each compound.

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

Answer a:

a. NO_2

Answer b:

O_2F_2

Answer c:

SF_6

Answer d:

SeO

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

✓ Example 4.7.2

Write the name for each compound.

- a. BrF_5
- b. S_2F_2
- c. CO

Solution

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

? Exercise 4.7.2

Write the name for each compound.

- a. CF_4
- b. SeCl_2
- c. SO_3

Answer a:

carbon tetrafluoride

Answer b:

selenium dichloride

Answer c:

sulfur trioxide

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

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

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

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

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

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

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

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

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

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

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

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CHAPTER OVERVIEW

5: Classification and Balancing of Chemical Reactions

[5.1: Chemical Equations](#)

[5.2: Balancing Chemical Equations](#)

[5.3: Acids, Bases, and Neutralization Reactions](#)

[5.4: Redox Reactions](#)

[5.5: Recognizing Redox Reactions](#)

[5.6: Net Ionic Equations](#)

[5.7: Le Chatelier's Principle](#)

[5.S: Introduction to Chemical Reactions \(Summary\)](#)

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5.1: Chemical Equations

5.1.1 Learning Objectives

- Define *chemical reaction*.
- Understand the Law of Conservation of Matter

Water (H₂O) is composed of hydrogen and oxygen. Suppose we imagine a process in which we take some elemental hydrogen (H₂) and elemental oxygen (O₂) 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 5.1.1 shows a rather dramatic example of this very reaction.

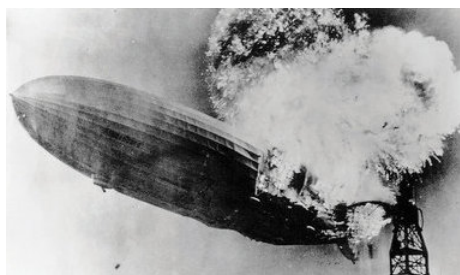


Figure 5.1.1: The Formation of Water. Hydrogen and oxygen combine to form water.

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

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



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:



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 5.1.2).

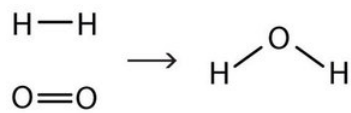


Figure 5.1.2: Balanced—Yes or No? By counting the atoms of each element, we can see that the reaction is not balanced as written.

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:



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:



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 now **balanced** (Figure 5.1.3). Note: The diatomic oxygen has a coefficient of 1, which typically is not written but assumed in balanced chemical equations.

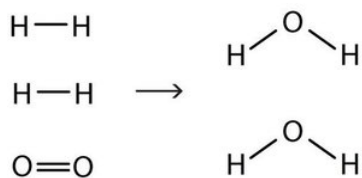


Figure 5.1.3: Balanced—Yes or No? By counting the atoms of each element, we can see that the reaction is now balanced.

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

5.1.15.1.2 Example

Is each chemical equation balanced?

- $2\text{Na}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2\text{Na}_2\text{O}(\text{s})$
- $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\ell)$
- $\text{AgNO}_3(\text{aq}) + 2\text{KCl}(\text{aq}) \rightarrow \text{AgCl}(\text{s}) + \text{KNO}_3(\text{aq})$

5.1.2.1 Solution

- 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.
- 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.
- 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.

5.1.15.1.3 Exercise

Is each chemical equation balanced?

- $2\text{Hg}(\ell) + \text{O}_2(\text{g}) \rightarrow \text{Hg}_2\text{O}_{2(\text{s})}$
- $\text{C}_2\text{H}_{4(\text{g})} + 2\text{O}_{2(\text{g})} \rightarrow 2\text{CO}_{2(\text{g})} + 2\text{H}_2\text{O}(\ell)$
- $\text{Mg}(\text{NO}_3)_{2(\text{s})} + 2\text{Li}(\text{s}) \rightarrow \text{Mg}(\text{s}) + 2\text{LiNO}_{3(\text{s})}$

Answer a:

balanced

Answer b:

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

Answer c:

balanced

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5.2: Balancing Chemical Equations

Learning Objectives

- Balance chemical equations.

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

Below are guidelines for writing and balancing chemical equations.

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

For example, to balance the equation

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



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

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

(5.2.2)

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



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

(5.2.4)

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:



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

(5.2.6)

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

✓ Example 5.2.2

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

Solution

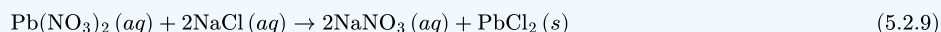
Step 1: Write the skeleton equation with the correct formulas.



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

Reactants	Products	
1 Pb atom	1 Pb atom	
2 NO_3^- ions	1 NO_3^- ions	(5.2.8)
1 Na atom	1 Na atom	
1 Cl atom	2 Cl atoms	

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



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

Reactants	Products	
1 Pb atom	1 Pb atom	
2 NO_3^- ions	2 NO_3^- ions	(5.2.10)
2 Na atom	2 Na atom	
2 Cl atom	2 Cl atoms	

Step 5: Think about the result.

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

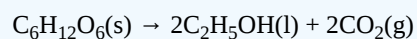
? Exercise 5.2.2

Fermentation is a biochemical process that enables yeast cells to live in the absence of oxygen. Humans have exploited it for centuries to produce wine and beer and make bread rise. In fermentation, sugars such as glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) are converted to ethanol ($\text{C}_2\text{H}_5\text{OH}$) and carbon dioxide CO_2 . Write a balanced chemical reaction for the fermentation of glucose.



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

Answer



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5.3: Acids, Bases, and Neutralization Reactions

Learning Objectives

- Identify an acid-base neutralization reaction and predict its products.

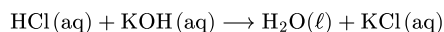
An **acid** is any compound that produces hydrogen ions (H^+) in an aqueous solution, and the chemical opposite of an acid is a **base**, which is a compound that produces hydroxide ions (OH^-) in an aqueous solution. These original definitions were proposed by Arrhenius (the same person who proposed ion dissociation) in 1884, so they are referred to as the **Arrhenius definition** of an acid and a base, respectively.

You may recognize that, based on the description of a hydrogen atom, an H^+ ion is a hydrogen atom that has lost its lone electron; that is, H^+ is simply a proton. Do we really have bare protons moving about in aqueous solution? No. What is more likely is that the H^+ ion has attached itself to one (or more) water molecule(s). To represent this chemically, we define the **hydronium ion** as H_3O^+ , which represents an additional proton attached to a water molecule. We use the hydronium ion as the more logical way that a hydrogen ion appears in an aqueous solution, although in many chemical reactions H^+ and H_3O^+ are treated equivalently.

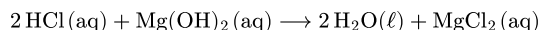
The reaction of an acid and a base is called a **neutralization reaction**. Although acids and bases have their own unique chemistries, the acid and base "cancel" each other's chemistry to produce a rather innocuous substance—water. In fact, the general reaction between an acid and a base is:



where the term **salt** is generally used to define any ionic compound (soluble or insoluble) that is formed from a reaction between an acid and a base. (In chemistry, the word *salt* refers to more than just table salt.) For example, the balanced chemical equation for the reaction between $\text{HCl}(\text{aq})$ and $\text{KOH}(\text{aq})$ is



where the salt is KCl. By counting the number of atoms of each element, we find that only one water molecule is formed as a product. However, in the reaction between $\text{HCl}(\text{aq})$ and $\text{Mg}(\text{OH})_2(\text{aq})$, additional molecules of HCl and H_2O are required to balance the chemical equation:



Here, the salt is MgCl_2 . (This is one of several reactions that take place when a type of antacid—a base—is used to treat stomach acid.)

Example 5.3.1:

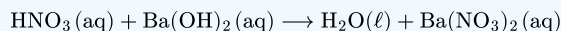
Write the neutralization reactions between each acid and base.

- $\text{HNO}_3(\text{aq})$ and $\text{Ba}(\text{OH})_2(\text{aq})$
- $\text{H}_3\text{PO}_4(\text{aq})$ and $\text{Ca}(\text{OH})_2(\text{aq})$

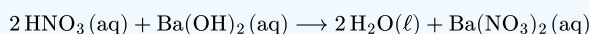
Solution

First, we will write the chemical equation with the formulas of the reactants and the expected products; then we will balance the equation.

- The expected products are water and barium nitrate, so the initial chemical reaction is

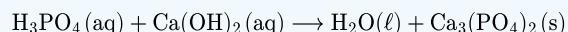


To balance the equation, we need to realize that there will be two H_2O molecules, so two HNO_3 molecules are required:

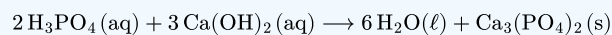


This chemical equation is now balanced.

- The expected products are water and calcium phosphate, so the initial chemical equation is



According to the solubility rules, $\text{Ca}_3(\text{PO}_4)_2$ is insoluble, so it has an (s) phase label. To balance this equation, we need two phosphate ions and three calcium ions. We end up with six water molecules to balance the equation:

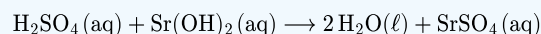


This chemical equation is now balanced.

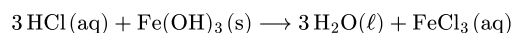
Exercise 5.3.1

Write the neutralization reaction between $\text{H}_2\text{SO}_4(\text{aq})$ and $\text{Sr}(\text{OH})_2(\text{aq})$.

Answer



Neutralization reactions are one type of chemical reaction that proceeds even if one reactant is not in the aqueous phase. For example, the chemical reaction between $\text{HCl}(\text{aq})$ and $\text{Fe}(\text{OH})_3(\text{s})$ still proceeds according to the equation:



even though $\text{Fe}(\text{OH})_3$ is not soluble. When one realizes that $\text{Fe}(\text{OH})_3(\text{s})$ is a component of rust, this explains why some cleaning solutions for rust stains contain acids—the neutralization reaction produces products that are soluble and wash away. (Washing with acids like HCl is one way to remove rust and rust stains, but HCl must be used with caution!)

5.3.1 Key Takeaways

- The Arrhenius definition of an acid is a substance that increases the amount of H^+ in an aqueous solution.
- The Arrhenius definition of a base is a substance that increases the amount of OH^- in an aqueous solution.
- Neutralization is the reaction of an acid and a base, which forms water and a salt.

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5.4: Redox Reactions

Learning Objectives

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

When zinc metal is submerged into a quantity of aqueous HCl, the following reaction occurs (Figure 5.4.1):

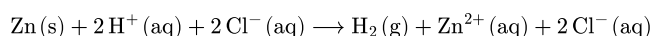


This is one example of what is sometimes called a *single replacement reaction* because Zn replaces H in combination with Cl.



Figure 5.4.1: Zinc Metal plus Hydrochloric Acid. It is fairly obvious that zinc metal reacts with aqueous hydrochloric acid! The bubbles are hydrogen gas (right side of Equation 5.4.1).

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

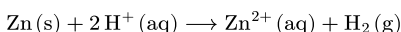


Viewed this way, the net reaction seems to be a charge transfer between zinc and hydrogen atoms. (There is no net change experienced by the chloride ion.) In fact, electrons are being transferred from the zinc atoms to the hydrogen atoms (which ultimately make a molecule of diatomic hydrogen), changing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

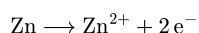
To understand electron-transfer reactions like the one between zinc metal and hydrogen ions, chemists separate them into two parts: one part focuses on the loss of electrons, and one part focuses on the gain of electrons. The loss of electrons is called **oxidation**. The gain of electrons is called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

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

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

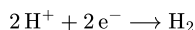


zinc atoms are oxidized to Zn^{2+} . The **half reaction for the oxidation** reaction, omitting phase labels, is as follows:



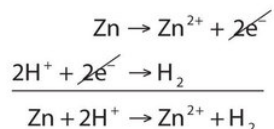
This half reaction is balanced in terms of the number of zinc atoms, and it also shows the two electrons that are needed as products to account for the zinc atom losing two negative charges to become a $2+$ ion. With half reactions, there is one more item to balance: the overall charge on each side of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



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.



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.)

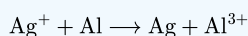
Redox reactions are often balanced by balancing each individual half reaction and then combining the two balanced half reactions. Sometimes a half reaction must have all of its coefficients multiplied by some integer for all the electrons to cancel. The following example demonstrates this process.

✓ Example 5.4.1: Reducing Silver Ions

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

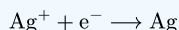
Solution

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



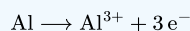
The equation looks balanced as it is written. However, when we compare the overall charges on each side of the equation, we find a charge of +1 on the left but a charge of +3 on the right. This equation is not properly balanced. To balance it, let us write the two half reactions. Silver ions are reduced,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

Reduction half-reaction:

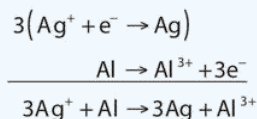


Aluminum is oxidized, losing three electrons to change from Al to Al^{3+} :

Oxidation half-reaction:



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



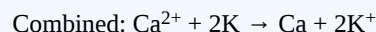
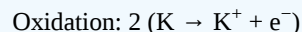
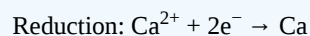
Now the equation is balanced, not only in terms of elements but also in terms of charge.

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

? Exercise 5.4.1

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

Answer



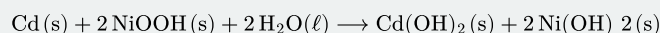
- The **substance oxidized** is the reactant that had undergone oxidation: K
- The **substance reduced** is the reactant that had undergone reduction: Ca^{2+}
- The **reducing agent** is the same as the substance oxidized: K
- The **oxidizing agent** is the same as the substance reduced: Ca^{2+}

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

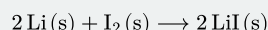
📌 To Your Health: Redox Reactions and Pacemaker Batteries

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

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



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:

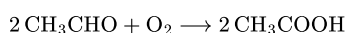


Lithium is oxidized, and iodine is reduced. Although the lithium/iodine battery cannot be recharged, one of its advantages is that it lasts up to 10 years. Thus, a person with a pacemaker does not have to worry about periodic recharging; about once per decade a person requires minor surgery to replace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



Figure 5.4.1: A small button battery like this is used to power a watch, pacemaker, or calculator. (CC BY-SA; Gerhard H Wrodnigg via Wikipedia)

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



Thus, acetaldehyde is being oxidized.

Similarly, reduction and oxidation can be defined in terms of the gain or loss of hydrogen atoms. If a molecule adds hydrogen atoms, it is being reduced. If a molecule loses hydrogen atoms, the molecule is being oxidized. For example, in the conversion of acetaldehyde into ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), hydrogen atoms are added to acetaldehyde, so the acetaldehyde is being reduced:

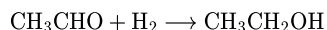


Table 5.4.1: Oxidation-Reduction Reactions and the Changes in Oxygen and Hydrogen.

Process	Change in oxygen (some reactions)	Change in hydrogen (some reactions)
Oxidation	gain	lose
Reduction	lose	gain

✓ Example 5.4.2

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

- $\text{N}_2 \rightarrow \text{NH}_3$
- $\text{CH}_3\text{CH}_2\text{OHCH}_3 \rightarrow \text{CH}_3\text{COCH}_3$
- $\text{HCHO} \rightarrow \text{HCOOH}$

Solution

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

? Exercise 5.4.2

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

- $\text{CH}_4 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$
- $\text{NO}_2 \rightarrow \text{N}_2$
- $\text{CH}_2=\text{CH}_2 \rightarrow \text{CH}_3\text{CH}_3$

Answer a:

Oxygen is being added. Oxidation is occurring.

Answer b:

Oxygen is being removed. Reduction is occurring.

Answer a:

Hydrogen is being added. Reduction is occurring.

5.4.1 Key Takeaway

Chemical reactions in which electrons are transferred are called oxidation-reduction, or redox, reactions. Oxidation is the loss of electrons. Reduction is the gain of electrons. Oxidation and reduction always occur together, even though they can be written as separate chemical equations.

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5.5: Recognizing Redox Reactions

Learning Objectives

- Assign oxidation numbers to atoms in simple compounds.
- Recognize a reaction as an oxidation-reduction reaction.

Redox reactions require that we keep track of the electrons assigned to each atom in a chemical reaction. How do we do that? We use **oxidation numbers** to keep track of electrons in atoms. Oxidation numbers are assigned to atoms based on four rules. Oxidation numbers are not necessarily equal to the charge on the atom (although sometimes they can be); we must keep the concepts of charge and oxidation numbers separate.

Assigning Oxidation Numbers

The rules for assigning oxidation numbers to atoms are as follows:

1. Atoms in their elemental state are assigned an oxidation number of 0.
2. Atoms in monatomic (i.e., one-atom) ions are assigned an oxidation number equal to their charge. Oxidation numbers are usually written with the sign first, then the magnitude, to differentiate them from charges.
3. In compounds, fluorine is assigned a -1 oxidation number; oxygen is usually assigned a -2 oxidation number (except in peroxide compounds [where it is -1] and in binary compounds with fluorine [where it is positive]); and hydrogen is usually assigned a $+1$ oxidation number (except when it exists as the hydride ion $[H^-]$, in which case rule 2 prevails).
4. In compounds, all other atoms are assigned an oxidation number so that the sum of the oxidation numbers on all the atoms in the species equals the charge on the species (which is zero if the species is neutral).

Here are some examples for practice. In H_2 , both H atoms have an oxidation number of 0 by rule 1. In $MgCl_2$, magnesium has an oxidation number of $+2$, while chlorine has an oxidation number of -1 by rule 2. In H_2O , the H atoms each have an oxidation number of $+1$, while the O atom has an oxidation number of -2 , even though hydrogen and oxygen do not exist as ions in this compound (rule 3). By contrast, by rule 3, each H atom in hydrogen peroxide (H_2O_2) has an oxidation number of $+1$, while each O atom has an oxidation number of -1 . We can use rule 4 to determine oxidation numbers for the atoms in SO_2 . Each O atom has an oxidation number of -2 ; for the sum of the oxidation numbers to equal the charge on the species (which is zero), the S atom is assigned an oxidation number of $+4$. Does this mean that the sulfur atom has a $4+$ charge on it? No, it means only that the S atom is assigned a $+4$ oxidation number by our rules of apportioning electrons among the atoms in a compound.

Example 5.5.1

Assign oxidation numbers to the atoms in each substance.

1. Cl_2
2. GeO_2
3. $Ca(NO_3)_2$

Solution

1. Cl_2 is the elemental form of chlorine. Rule 1 states each atom has an oxidation number of 0.
2. By rule 3, oxygen is normally assigned an oxidation number of -2 . For the sum of the oxidation numbers to equal the charge on the species (zero), the Ge atom is assigned an oxidation number of $+4$.
3. $Ca(NO_3)_2$ can be separated into two parts: the Ca^{2+} ion and the NO_3^- ion. Considering these separately, the Ca^{2+} ion has an oxidation number of $+2$ by rule 2. Now consider the NO_3^- ion. Oxygen is assigned an oxidation number of -2 , and there are three of them. According to rule 4, the sum of the oxidation numbers on all atoms must equal the charge on the species, so we have the simple algebraic equation $x + 3(-2) = -1$

where x is the oxidation number of the N atom and the -1 represents the charge on the species. Evaluating for x ,

$$x + (-6) = -1 \quad x = +5$$

Thus the oxidation number on the N atom in the NO_3^- ion is $+5$.

Answer

H: +1; O: -2; P: +5

✓ Example 5.5.2:

$$2\text{Na} + \text{Br}_2 \longrightarrow 2\text{NaBr}$$
$$\underset{0}{2Na} + \underset{0}{Br_2} \rightarrow \underset{+1-1}{2NaBr}$$

$$2\text{Na} + \text{Br}_2 \longrightarrow 2\text{NaBr}$$

ox # 0 0 +1 -1

Oxidation

$$2\text{Na} + \text{Br}_2 \longrightarrow 2\text{NaBr}$$

ox # 0 0 +1 -1

Reduction

? Exercise 5.5.2

$$\text{C} + \text{O}_2 \longrightarrow \text{CO}_2$$

Answer

C is being oxidized from 0 to +4; O is being reduced from 0 to -2.

$$6H^+(aq) + 2MnO_4^-(aq) + 5H_2O_2(l) \rightarrow 2Mn^{2+}(aq) + 5O_2(g) + 8H_2O(l)$$

✓ Food and Drink Application: Fortifying Food with Iron

<https://med.libretexts.org/@go/page/60574>

human biology (although the body does contain an enzyme to reduce Fe^{3+} to Fe^{2+} , so Fe^{3+} must have some biological significance, albeit minor). To ensure that we ingest enough iron, many foods are enriched with iron. Although Fe^{2+} compounds are the most logical substances to use, some foods use "reduced iron" as an ingredient (bread and breakfast cereals are the most well-known examples). Reduced iron is simply iron metal; iron is added as a fine metallic powder. The metallic iron is oxidized to Fe^{2+} in the digestive system and then absorbed by the body, but the question remains: Why are we ingesting metallic iron? Why not just use Fe^{2+} salts as an additive?



Figure 5.5.1 Ingredients. Many prepared foods list reduced iron in their ingredients list. The ingredients list contains Flour (Contains: wheat flour, malted barley flour, niacin, reduced iron, thiamine mononitrate, riboflavin, folic acid), water, sourdough (6.4%) (contains: water, flour [wheat flour, malted barley flour, niacin, reduced iron, thiamine mononitrate, riboflavin, folic acid], yeast), salt, wheat germ, semolina (contains: durum wheat semolina, niacin, ferrous sulphate, thiamine mononitrate, riboflavin, folic acid).

Although it is difficult to establish conclusive reasons, a search of scientific and medical literature suggests a few reasons. One reason is that fine iron filings do not affect the taste of the product. The size of the iron powder (several dozen micrometers) is not noticeable when chewing iron-supplemented foods, and the tongue does not detect any changes in flavor that can be detected when using Fe^{2+} salts. Fe^{2+} compounds can affect other properties of foodstuffs during preparation and cooking, like dough pliability, yeast growth, and color. Finally, of the common iron substances that might be used, metallic iron is the least expensive. These factors appear to be among the reasons why metallic iron is the supplement of choice in some foods.

5.5.1 Key Takeaways

- Oxidation numbers are used to keep track of electrons in atoms.
- There are rules for assigning oxidation numbers to atoms.
- Oxidation is an increase in oxidation number (loss of electrons); reduction is a decrease in oxidation number (gain of electrons).

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5.6: Net Ionic Equations

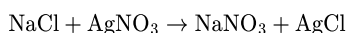
Learning Objectives

- Write ionic and net ionic equations for chemical reactions involving ions.

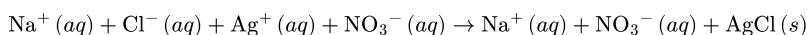
At sports events around the world, a small number of athletes fiercely compete on fields and in stadiums. They get tired, dirty, and sometimes hurt as they try to win the game. Surrounding them are thousands of spectators watching and cheering. Would the game be different without the spectators? Definitely! Spectators provide encouragement to the team and generate enthusiasm. Although the spectators are not playing the game, they are certainly a part of the process.

5.6.1 Net Ionic Equations

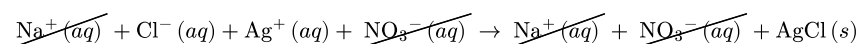
We can write a molecular equation for the formation of silver chloride precipitate:



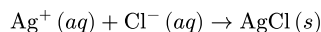
The corresponding **ionic equation** is written to show the *ions* that are dissolved in solution:



If you look carefully at the ionic equation, you will notice that the sodium ion and the nitrate ion appear unchanged on both sides of the equation. When the two solutions are mixed, neither the Na^+ nor the NO_3^- ions participate in the reaction. They can be eliminated from the reaction.



A **spectator ion** is an ion that does not take part in the chemical reaction and is found in solution both before and after the reaction. In the above reaction, the sodium ion and the nitrate ion are both spectator ions. The equation can now be written without the spectator ions:



The **net ionic equation** is the chemical equation that shows only those elements, compounds, and ions that are directly involved in the chemical reaction. Notice that in writing the net ionic equation, the positively-charged silver cation was written first on the reactant side, followed by the negatively-charged chloride anion. This is somewhat customary because that is the order in which the ions must be written in the silver chloride product. However, it is not absolutely necessary to order the reactants in this way.

Net ionic equations must be balanced by both mass and charge. Balancing by mass means ensuring that there are equal masses of each element on the product and reactant sides. Balancing by charge means making sure that the overall charge is the same on both sides of the equation. In the above equation, the overall charge is zero, or neutral, on both sides of the equation. As a general rule, if you balance the molecular equation properly, the net ionic equation will end up being balanced by both mass and charge.

Example 5.6.1

When aqueous solutions of copper (II) chloride and potassium phosphate are mixed, a precipitate of copper (II) phosphate is formed. Write a balanced net ionic equation for this reaction.

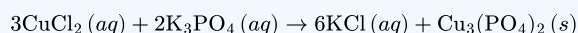
Solution

Step 1: Plan the problem.

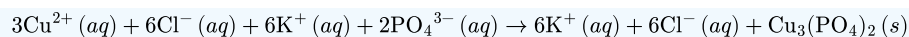
Write and balance the molecular equation first, making sure that all formulas are correct. Then write the ionic equation, showing all aqueous substances as ions. Carry through any coefficients. Finally, eliminate spectator ions and write the net ionic equation.

Step 2: Solve.

Molecular equation:

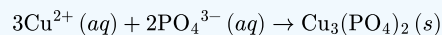


Ionic equation:



Notice that the balance of the equation is carried through when writing the dissociated ions. For example, there are six chloride ions on the reactant side because the coefficient of 3 is multiplied by the subscript of 2 on the copper (II) chloride formula. The spectator ions, K^{+} and Cl^{-} , can be eliminated.

Net ionic equation:



Step 3: Think about your result.

For a precipitation reaction, the net ionic equation always shows the two ions that come together to form the precipitate. The equation is balanced by mass and charge.

5.6.2 Summary

- A spectator ion is an ion that does not take part in the chemical reaction and is found in solution both before and after the reaction.
- The net ionic equation is the chemical equation that shows only those elements, compounds, and ions that are directly involved in the chemical reaction.
- An example of writing a net ionic equation is outlined.

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5.7: Le Chatelier's Principle

Learning Outcomes

- Define Le Chatelier's principle.
- Predict how the change in amounts of substances, temperature, or pressure will affect amounts of reactants and products present at equilibrium.

Le Chatelier's Principle

Chemical equilibrium was studied by the French chemist Henri Le Chatelier (1850 - 1936) and his description of how a system responds to a stress to equilibrium has become known as **Le Chatelier's principle**: When a chemical system that is at equilibrium is disturbed by a stress, the system will respond in order to relieve the stress. Stresses to a chemical system involve changes in the concentrations of reactants or products, changes in the temperature of the system, or changes in the pressure of the system. We will discuss each of these stresses separately. The change to the equilibrium position in every case is either a favoring of the forward reaction or a favoring of the reverse reaction. When the forward reaction is favored, the concentrations of products increase, while the concentrations of reactants decrease. When the reverse reaction is favored, the concentrations of the products decrease, while the concentrations of reactants increase.

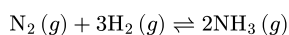
Original Equilibrium	Favored Reaction	Result
$A \rightleftharpoons B$	Forward: $A \rightarrow B$	[A] decreases; [B] increases
$A \rightleftharpoons B$	Reverse: $A \leftarrow B$	[A] increases; [B] decreases



Figure 9.6.1: *Henri Le Chatelier.*

Effect of Concentration

A change in concentration of one of the substances in an equilibrium system typically involves either the addition or the removal of one of the reactants or products. Consider the Haber-Bosch process for the industrial production of ammonia from nitrogen and hydrogen gases.



If the concentration of one substance in a system is increased, the system will respond by favoring the reaction that removes that substance. When more N_2 is added, the forward reaction will be favored because the forward reaction uses up N_2 and converts it to NH_3 . The forward reaction speeds up temporarily as a result of the addition of a reactant. The position of equilibrium shifts as more NH_3 is produced. The concentration of NH_3 increases, while the concentrations of N_2 and H_2 decrease. After some time passes, equilibrium is reestablished with new concentrations of all three substance. As can be seen in the figure below, if more N_2 is added, a new equilibrium is achieved by the system. The new concentration of NH_3 is higher because of the favoring of the forward reaction. The new concentration of the H_2 is lower. The concentration of N_2 is higher than in the original equilibrium, but went down slightly following the addition of the N_2 that disturbed the original equilibrium. By responding in this way, the value of the equilibrium constant for the reaction, K_{eq} , does not change as a result of the stress to the system.

In other words, the amount of each substance is different but the ratio of the amount of each remains the same.

If more NH_3 were added, the reverse reaction would be favored. This "favoring" of a reaction means temporarily speeding up the reaction in that direction until equilibrium is reestablished. Recall that once equilibrium is reestablished, the rates of the forward and reverse reactions are again equal. The addition of NH_3 would result in increased formation of the reactants, N_2 and H_2 .

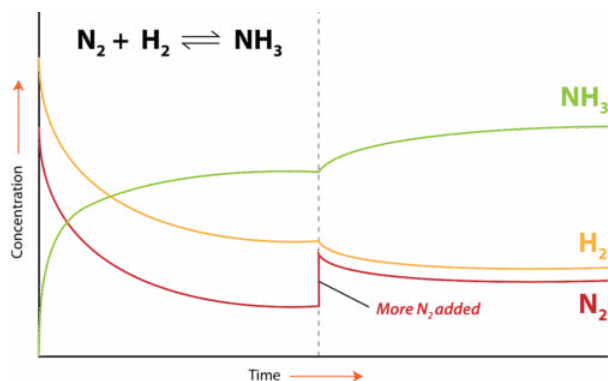


Figure 9.6.2: The Haber-Bosch process is an equilibrium between

reactants N_2 and H_2 and product NH_3 .

An equilibrium can also be disrupted by the removal of one of the substances. If the concentration of a substance is decreased, the system will respond by favoring the reaction that replaces that substance. In the industrial Haber-Bosch process, NH_3 is removed from the equilibrium system as the reaction proceeds. As a result, the forward reaction is favored so that more NH_3 is produced. The concentrations of N_2 and H_2 decrease. Continued removal of NH_3 will eventually force the reaction to go to completion until all of the reactants are used up. If either N_2 or H_2 were removed from the equilibrium system, the reverse reaction would be favored and the concentration of NH_3 would decrease.

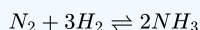
The effect of changes in concentration on an equilibrium system according to Le Chatelier's principle is summarized in the table below.

Table 9.6.1

Stress	Response
addition of reactant	forward reaction favored
addition of product	reverse reaction favored
removal of reactant	reverse reaction favored
removal of product	forward reaction favored

✓ Example 5.7.1

Given this reaction at equilibrium:



How will it affect the reaction if the equilibrium is stressed by each change?

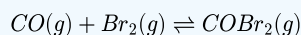
1. H_2 is added.
2. NH_3 is added.
3. NH_3 is removed.

Solution

1. If H_2 is added, there is now more reactant, so the reaction will shift to the right (toward products) to reduce the added H_2 .
2. If NH_3 is added, there is now more product, so the reaction will shift to the left (toward reactants) to reduce the added NH_3 .
3. If NH_3 is removed, there is now less product, so the reaction will shift to the right (toward products) to replace the product removed.

5.7.1Exercise

Given this reaction at equilibrium:



How will it affect the reaction if the equilibrium is stressed by each change?

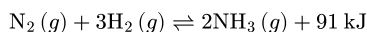
1. Br₂ is removed.
2. COBr₂ is added.

Answer

1. shift to the left (toward reactants)
2. shift to the left (toward reactants)

Effect of Temperature

Increasing or decreasing the temperature of a system at equilibrium is also a stress to the system. The equation for the Haber-Bosch process is written again below, as a thermochemical equation (i.e. it contains information about the energy gained or lost when the reaction occurs).



The forward reaction is the exothermic direction: the formation of NH₃ releases heat which is why that is shown as a product. The reverse reaction is the endothermic direction: as NH₃ decomposes to N₂ and H₂, heat is absorbed. An increase in the temperature for this is like adding a product because heat is being released by the reaction. If we add a product then the reaction proceeds towards the formation of more reactants. Reducing the temperature for this system would be similar to removing a product which would favor the formation of more products. The amount of NH₃ will increase and the amount of N₂ and H₂ will decrease.

For changes in concentration, the system responds in such a way that the value of the equilibrium constant, K_{eq} is unchanged. However, a change in temperature shifts the equilibrium and the K_{eq} value either increases or decreases. As discussed in the previous section, values of K_{eq} are dependent on the temperature. When the temperature of the system for the Haber-Bosch process is increased, the resultant shift in equilibrium towards the reactants means that the K_{eq} value decreases. When the temperature is decreased, the shift in equilibrium towards the products means that the K_{eq} value increases.

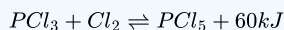
Le Chatelier's principle as related to temperature changes can be illustrated easily by the reaction in which dinitrogen tetroxide is in equilibrium with nitrogen dioxide.



Dinitrogen tetroxide (N₂O₄) is colorless, while nitrogen dioxide (NO₂) is dark brown in color. When N₂O₄ breaks down into NO₂, heat is absorbed (endothermic) according to the forward reaction above. Therefore, an increase in temperature (adding heat) of the system will favor the forward reaction. Conversely, a decrease in temperature (removing heat) will favor the reverse reaction.

✓ Example 5.7.2

Predict the effect of increasing the temperature on this equilibrium.

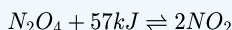


Solution

Because energy is listed as a product, it is being produced, so the reaction is exothermic. If the temperature is increasing, a product is being added to the equilibrium, so the equilibrium shifts to minimize the addition of extra product: it shifts to the left (back toward reactants).

5.7.2Exercise

Predict the effect of decreasing the temperature on this equilibrium.



Answer

Equilibrium shifts to the left (toward reactants).

Effect of Pressure

Changing the pressure of an equilibrium system in which gases are involved is also a stress to the system. A change in the pressure on a liquid or a solid has a negligible effect. We will return again the equilibrium for the Haber-Bosch process. Imagine the gases are contained in a closed system in which the volume of the system is controlled by an adjustable piston as shown in the figure below.

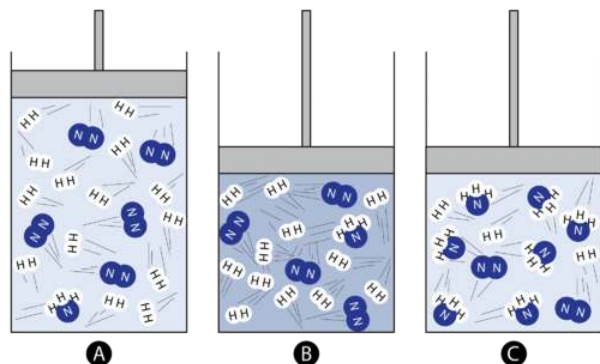


Figure 9.6.3: Effect of pressure on equilibrium. (A) is at equilibrium, (B) increase of pressure through decreased volume, and (C) equilibrium is reestablished.

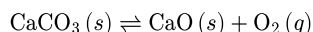
On the far left, the reaction system contains primarily N₂ and H₂, with only one molecule of NH₃ present. As the piston is pushed inwards, the pressure of the system increases according to Boyle's law. This is a stress to the equilibrium. In the middle image, the same number of molecules is now confined in a smaller space and so the pressure has increased. According to Le Chatelier's principle, the system responds in order to relieve the stress. In the image on the right, the forward reaction has been favored and more NH₃ is produced. The overall result is a decrease in the number of gas molecules in the entire system. This in turn decreases the pressure and provides a relief to the original stress of a pressure increase. An increase in pressure on an equilibrium system favors the reaction which products fewer total moles of gas. In this case, it is the forward reaction that is favored.

A decrease in pressure on the above system could be achieved by pulling the piston outward, increasing the container volume. The equilibrium would respond by favoring the reverse reaction in which NH₃ decomposes to N₂ and H₂. This is because the overall number of gas molecules would increase and so would the pressure. A decrease in pressure on an equilibrium system favors the reaction which produces more total moles of gas. This is summarized in the table below.

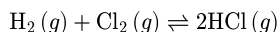
Table 9.6.2

Stress	Response
pressure increase	reaction produces fewer gas molecules
pressure decrease	reaction produces more gas molecules

Like changes in concentration, the K_{eq} value for a given reaction is unchanged by a change in pressure. The amounts of each substance will change but the ratio will not. It is important to remember when analyzing the effect of a pressure change on equilibrium that only gases are affected. If a certain reaction involves liquids or solids, they should be ignored. For example, calcium carbonate decomposes according to the equilibrium reaction:

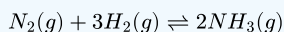


Oxygen is the only gas in the system. An increase in the pressure of the system slows the rate of decomposition of CaCO₃ because the reverse reaction is favored. When a system contains equal moles of gas on both sides of the equation, pressure has no effect on the equilibrium position, as in the formation of HCl from H₂ and Cl₂.



✓ Example 5.7.3

What is the effect on this equilibrium if pressure is increased?

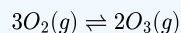


Solution

According to Le Chatelier's principle, if pressure is increased, then the equilibrium shifts to the side with the fewer number of moles of gas. This particular reaction shows a total of 4 mol of gas as reactants and 2 mol of gas as products, so the reaction shifts to the right (toward the products side).

5.7.3 Exercise

What is the effect on this equilibrium if pressure is decreased?



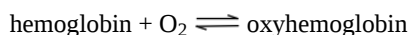
Answer

Reaction shifts to the left (toward reactants).

Application of Le Chatelier's Principle

Oxygen transport by the blood

In aerobic respiration, oxygen is transported to the cells where it is combined with glucose and metabolized to carbon dioxide, which then moves back to the lungs from which it is expelled.



The partial pressure of O_2 in the air is 0.2 atm, sufficient to allow these molecules to be taken up by hemoglobin (the red pigment of blood) in which it becomes loosely bound in a complex known as oxyhemoglobin. At the ends of the capillaries which deliver the blood to the tissues, the O_2 concentration is reduced by about 50% owing to its consumption by the cells. This shifts the equilibrium to the left, releasing the oxygen so it can diffuse into the cells.

Key Takeaways

- In a reaction at equilibrium, the introduction of more products will shift the mass balance towards more reactants, and the introduction of more reactants will lead to the formation of more products, but the *ratio of Products/Reactants (equilibrium constant)*, K is unchanged.
- If temperature is changed, the numeric value K will change. If a reaction is *exothermic* (releases heat), an increase in the **temperature** will force the equilibrium to the left, causing the system to absorb heat and thus partially offsetting the rise in temperature. The opposite effect occurs for *endothermic* reactions, which are shifted to the right by rising temperature.
- The effect of **pressure** on an equilibrium is significant only for reactions which involve different numbers of moles of gases on the two sides of the equation. An increase in the total pressure will shift to the side with fewer moles of gas. A decrease in pressure will shift to the side with more moles of gas.

Contributors and Attributions

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5.S: Introduction to Chemical Reactions (Summary)

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

Scientific **laws** are general statements that apply to a wide variety of circumstances. One important law in chemistry is the **law of conservation of matter**, which states that in any closed system, the amount of matter stays constant.

Chemical equations are used to represent **chemical reactions**. **Reactants** change chemically into **products**. The law of conservation of matter requires that a proper chemical equation be **balanced**. **Coefficients** are used to show the relative numbers of reactant and product molecules.

In **stoichiometry**, quantities of reactants and/or products can be related to each other using the balanced chemical equation. The coefficients in a balanced chemical reaction are used to devise the proper ratios that relate the number of molecules of one substance to the number of molecules of another substance.

Chemical reactions can be classified by type. **Combination reactions** (also called **composition reactions**) make a substance from other substances. **Decomposition reactions** break one substance down into multiple substances. **Combustion reactions** combine molecular oxygen with the atoms of another reactant.

Oxidation reactions are reactions in which an atom loses an electron. **Reduction reactions** are reactions in which an atom gains an electron. These two processes always occur together, so they are collectively referred to as **oxidation-reduction** (or **redox**) **reactions**. The species being oxidized is called the **reducing agent**, while the species being reduced is the **oxidizing agent**. Alternate definitions of oxidation and reduction focus on the gain or loss of oxygen atoms, or the loss or gain of hydrogen atoms. Redox reactions are easily balanced if the overall reaction is first separated into **half reactions**, which are individually balanced.

Oxidation-reduction reactions are common in organic and biological chemistry. **Respiration**, the process by which we inhale and metabolize oxygen, is a series of redox reactions. In the absence of oxygen, redox reactions still occur in a process called **anaerobic metabolism**. **Antioxidants** such as ascorbic acid also play a part in the human diet, acting as reducing agents in various biochemical reactions. **Photosynthesis**, the process by which plants convert water and carbon dioxide to glucose, is also based on redox reactions.

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CHAPTER OVERVIEW

6: Organic Chemistry of Hydrocarbons

Template:Chem309Bennett

Hydrocarbons are organic compounds that contain **only** carbon and hydrogen. The four general classes of hydrocarbons are: alkanes, alkenes, alkynes and arenes. Aromatic compounds derive their names from the fact that many of these compounds in the early days of discovery were grouped because they were oils with fragrant odors.

- [6.1: Introduction to Organic Chemistry](#)
- [6.2: Condensed Structural and Line-Angle Formulas](#)
- [6.3: Structures and Names of Alkanes](#)
- [6.4: Branched-Chain Alkanes](#)
- [6.5: Cycloalkanes](#)
- [6.6: IUPAC Nomenclature](#)
- [6.7: Alkenes- Structure and Nomenclature](#)
- [6.8: Alkenes- Cis-Tran Isomerization](#)
- [6.9: Alkynes](#)
- [6.10: Aromatic Compounds](#)
- [6.11: Aromatic Compounds- Structure and Nomenclature](#)
- [6.12: Physical Properties of Hydrocarbons](#)
- [6.13: Chapter Summary](#)
- [6.E: Unsaturated and Aromatic Hydrocarbons \(Exercises\)](#)

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6.1: Introduction to Organic Chemistry

Learning Objectives

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

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

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

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

6.1.0.1 Alkanes

The simplest organic compounds are the **hydrocarbons**, compounds composed of carbon and hydrogen atoms only. Some hydrocarbons have only single bonds and appear as a chain (which can be a straight chain or can have branches) of carbon atoms also bonded to hydrogen atoms. These hydrocarbons are called **alkanes (saturated hydrocarbons)**. Each alkane has a characteristic, systematic name depending on the number of carbon atoms in the molecule. These names consist of a stem that indicates the number of carbon atoms in the chain plus the ending -ane. The stem meth- means one carbon atom, so methane is an alkane with one carbon atom. Similarly, the stem eth- means two carbon atoms; ethane is an alkane with two carbon atoms. Continuing, the stem prop- means three carbon atoms, so propane is an alkane with three carbon atoms. The stem but- means four carbon atoms; butane is an alkane with four carbon atoms. Figure 6.1.1 gives the Lewis structures, condensed structural formulas and molecular formulas of the four simplest alkanes. In the **condensed structural formula**, the covalent bonds are understood to exist between each carbon and the hydrogens associated with it, as well as between carbon atoms.

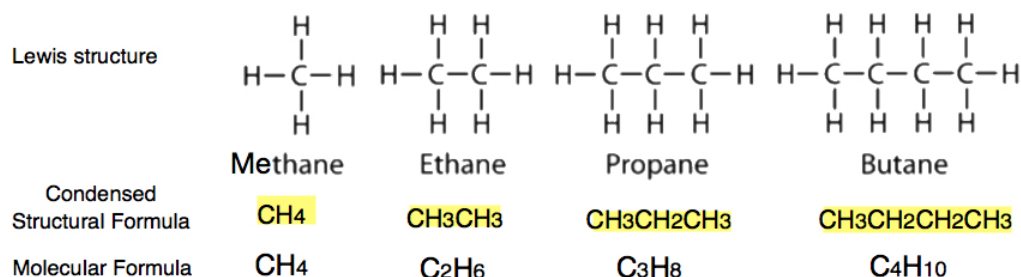


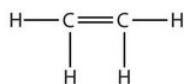
Figure 6.1.1:

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

6.1.0.1 Alkenes

Some hydrocarbons have one or more carbon-carbon double bonds (denoted C=C). These hydrocarbons are called alkenes. Figure 6.1.2 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.

ethene, C_2H_4



propene, C_3H_6

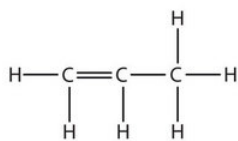


Figure 6.1.2: Formulas and Molecular Models of the Two Simplest Alkenes. Ethene is commonly called ethylene, while propene is commonly called propylene.

6.1.0.1 Alkynes

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



Ethyne

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

To Your Health: Saturated and Unsaturated Fats

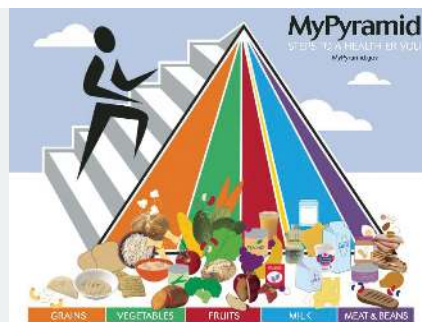
Hydrocarbons are not the only compounds that can have carbon–carbon double bonds. A group of compounds called fats can have them as well, and their presence or absence in the human diet is becoming increasingly correlated with health issues.

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

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

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

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



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

6.1.0.1 Functional Groups

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

If an OH group (also called a hydroxyl group) is substituted for a hydrogen atom in a hydrocarbon molecule, the compound is an alcohol. Alcohols are named using the parent hydrocarbon name but with the final $-e$ dropped and the suffix $-ol$ attached. The two simplest alcohols are methanol and ethanol. Figure 6.1.4 shows their formulas along with a molecular model of each.

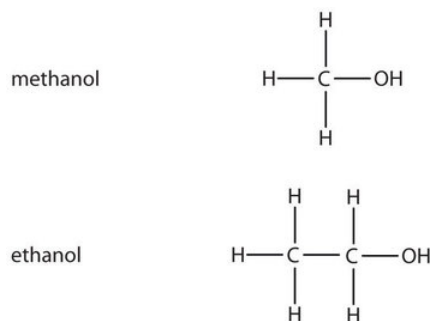


Figure 6.1.4: The Two Simplest Organic Alcohol Compounds. Alcohols have an OH functional group in the molecule.

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

Alcohol

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

Another important family of organic compounds has a carboxyl group, in which a carbon atom is double-bonded to an oxygen atom and to an OH group. Compounds with a carboxyl functional group are called carboxylic acids, and their names end in $-oic\ acid$. Figure 6.1.5 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 .

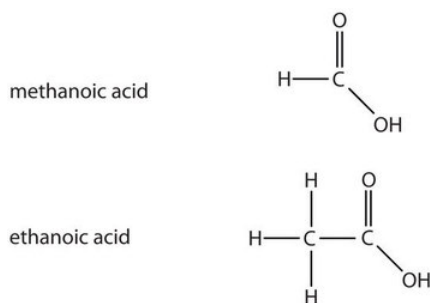


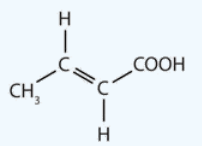
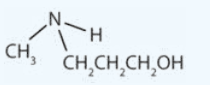
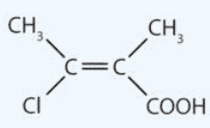
Figure 6.1.5: The Two Smallest Organic Acids. The two smallest carboxylic acids are formic acid (found in the stingers of ants) and acetic acid (found in vinegar).

The condensed structures of methanoic acid and ethanoic acid are **HCOOH** and **CH₃COOH**, respectively.

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

✓ Example 6.1.1

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

- a. 
- b. 
- c. 
- d. CH₃CH₂CH₂CH₂OH

Answer a

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

Answer b

This molecule has an alcohol functional group.

Answer c

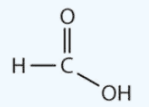
This molecule has a carbon-carbon double bond and a carboxyl functional group.

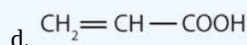
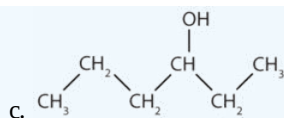
Answer d

This molecule has an alcohol functional group.

? Exercise 6.1.1

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

- a. CH₃C ≡ CCH₃
- b. 



Answer a:

triple bond (alkyne)

Answer b:

carboxyl group

Answer c:

alcohol group

Answer d:

double bond (alkene) and carboxyl group

Career Focus: Forensic Chemist

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

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

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

6.1.1 Key Takeaways

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

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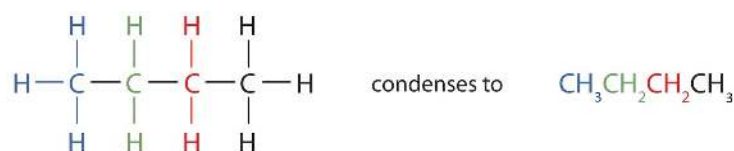
6.2: Condensed Structural and Line-Angle Formulas

Learning Objectives

- Write condensed structural formulas for alkanes given complete structural formulas.
- Draw line-angle formulas given structural formulas.

We use several kinds of formulas to describe organic compounds. A *molecular formula* shows only the kinds and numbers of atoms in a molecule. For example, the molecular formula C_4H_{10} tells us there are 4 carbon atoms and 10 hydrogen atoms in a molecule, but it doesn't distinguish between butane and isobutane. A structural formula shows all the carbon and hydrogen atoms and the bonds attaching them. Thus, structural formulas identify the specific isomers by showing the order of attachment of the various atoms.

Unfortunately, structural formulas are difficult to type/write and take up a lot of space. Chemists often use condensed structural formulas to alleviate these problems. The condensed formulas show hydrogen atoms right next to the carbon atoms to which they are attached, as illustrated for butane:



The ultimate condensed formula is a line-angle formula, in which carbon atoms are implied at the corners and ends of lines, and each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds. For example, we can represent pentane ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$) and isopentane [$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$] as follows:



Parentheses in condensed structural formulas indicate that the enclosed grouping of atoms is attached to the adjacent carbon atom.

6.2.1 Key Takeaways

- Condensed chemical formulas show the hydrogen atoms (or other atoms or groups) right next to the carbon atoms to which they are attached.
- Line-angle formulas imply a carbon atom at the corners and ends of lines. Each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds.

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6.3: Structures and Names of Alkanes

As we begin our study of organic compounds with the hydrocarbons, the simplest organic compounds, 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. In these structures, each carbon atom is bonded to four other atoms (hydrogen or carbon)—the most possible; there are no double or in the molecules.

Consider the series in Figure 2.1.4. 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.

The principle of homology allows us to write a general formula for alkanes: $\text{C}_n\text{H}_{2n+2}$. 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 $\text{C}_8\text{H}_{(2 \times 8) + 2} = \text{C}_8\text{H}_{18}$.

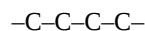
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6.4: Branched-Chain Alkanes

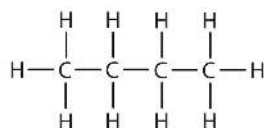
Learning Objectives

- To learn how alkane molecules can have branched chains and recognize compounds that are isomers.

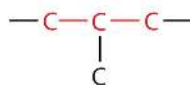
We can write the structure of butane (C_4H_{10}) by stringing four carbon atoms in a row,



and then adding enough hydrogen atoms to give each carbon atom four bonds:



The compound butane has this structure, but there is another way to put 4 carbon atoms and 10 hydrogen atoms together. Place 3 of the carbon atoms in a row and then branch the fourth one off the middle carbon atom:



Now we add enough hydrogen atoms to give each carbon four bonds.

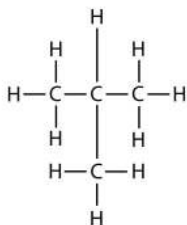


Figure 6.4.1).

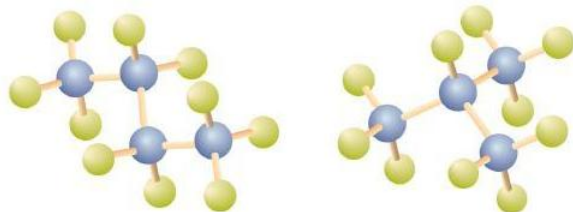
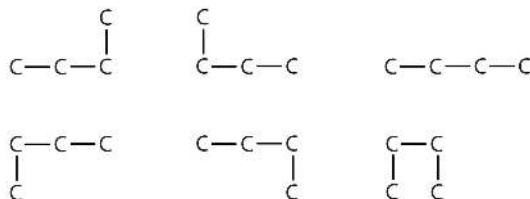


Figure 6.4.1: Butane and Isobutane. The ball-and-stick models of these two compounds show them to be isomers; both have the molecular formula C_4H_{10} .

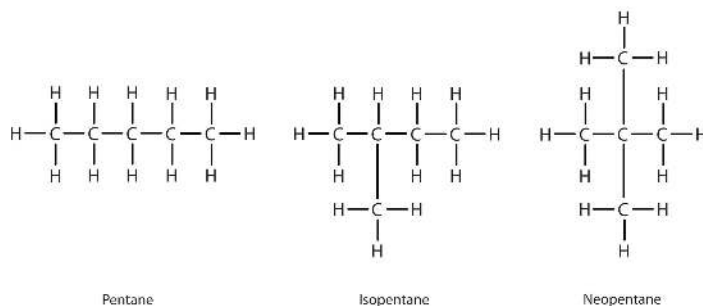
Notice that C_4H_{10} is depicted with a bent chain in Figure 6.4.1. The four-carbon chain may be bent in various ways because the groups can rotate freely about the C–C bonds. However, this rotation does not change the identity of the compound. It is important to realize that bending a chain does *not* change the identity of the compound; all of the following represent the same compound, butane:



The structure of isobutane shows a continuous chain of three carbon atoms only, with the fourth attached as a branch off the middle carbon atom of the continuous chain, which is different from the structures of butane (compare the two structures in Figure 6.4.1).

Unlike C_4H_{10} , the compounds methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) do not exist in isomeric forms because there is only one way to arrange the atoms in each formula so that each carbon atom has four bonds.

Next beyond C_4H_{10} in the homologous series is pentane. Each compound has the same molecular formula: C_5H_{12} . (Table 12.1.1 from the previous section has a column identifying the number of possible isomers for the first 10 straight-chain alkanes.) The compound at the far left is pentane because it has all five carbon atoms in a continuous chain. The compound in the middle is isopentane; like isobutane, it has a one CH_3 branch off the second carbon atom of the continuous chain. The compound at the far right, discovered after the other two, was named neopentane (from the Greek *neos*, meaning “new”). Although all three have the same molecular formula, they have different properties, including boiling points: pentane, $36.1^\circ C$; isopentane, $27.7^\circ C$; and neopentane, $9.5^\circ C$.



A continuous (unbranched) chain of carbon atoms is often called a *straight chain* even though the tetrahedral arrangement about each carbon gives it a zigzag shape. Straight-chain alkanes are sometimes called *normal alkanes*, and their names are given the prefix *n*-. For example, butane is called *n*-butane. We will not use that prefix here because it is not a part of the system established by the International Union of Pure and Applied Chemistry.

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6.5: Cycloalkanes

Learning Objectives

- To name cycloalkanes given their formulas and write formulas for these compounds given their names.

The hydrocarbons we have encountered so far have been composed of molecules with open-ended chains of carbon atoms. When a chain contains three or more carbon atoms, the atoms can join to form *ring* or *cyclic* structures. The simplest of these cyclic hydrocarbons has the formula C_3H_6 . Each carbon atom has two hydrogen atoms attached (Figure 6.5.1) and is called cyclopropane.

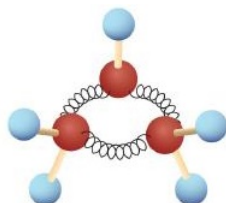
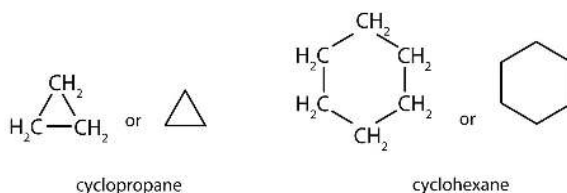


Figure 6.5.1: Ball-and-Spring Model of Cyclopropane. The springs are bent to join the carbon atoms.

6.5.1 To Your Health: Cyclopropane as an Anesthetic

With its boiling point of -33°C , cyclopropane is a gas at room temperature. It is also a potent, quick-acting anesthetic with few undesirable side effects in the body. It is no longer used in surgery, however, because it forms explosive mixtures with air at nearly all concentrations.

The cycloalkanes—cyclic hydrocarbons with only single bonds—are named by adding the prefix *cyclo-* to the name of the open-chain compound having the same number of carbon atoms as there are in the ring. Thus the name for the cyclic compound C_4H_8 is cyclobutane. The carbon atoms in cyclic compounds can be represented by *line-angle formulas* that result in regular geometric figures. Keep in mind, however, that each corner of the geometric figure represents a carbon atom plus as many hydrogen atoms as needed to give each carbon atom four bonds.



Some cyclic compounds have substituent groups attached. Example 6.5.1 interprets the name of a cycloalkane with a single substituent group.

✓ Example 6.5.1

Draw the structure for each compound.

- cyclopentane
- methylcyclobutane

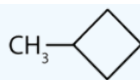
Solution a

The name *cyclopentane* indicates a cyclic (cyclo) alkane with five (pent-) carbon atoms. It can be represented as a pentagon.



Solution b

The name *methylcyclobutane* indicates a cyclic alkane with four (but-) carbon atoms in the cyclic part. It can be represented as a square with a CH_3 group attached.



? Exercise 6.5.1

Draw the structure for each compound.

- cycloheptane
- ethylcyclohexane

The properties of cyclic hydrocarbons are generally quite similar to those of the corresponding open-chain compounds. So cycloalkanes (with the exception of cyclopropane, which has a highly strained ring) act very much like noncyclic alkanes. Cyclic structures containing five or six carbon atoms, such as cyclopentane and cyclohexane, are particularly stable. We will see later that some carbohydrates (sugars) form five- or six-membered rings in solution.

The cyclopropane ring is strained because the C–C–C angles are 60°, and the preferred (tetrahedral) bond angle is 109.5°. (This strain is readily evident when you try to build a ball-and-stick model of cyclopropane; see Figure 6.5.1.) Cyclopentane and cyclohexane rings have little strain because the C–C–C angles are near the preferred angles.

6.5.2 Key Takeaway

- Many organic compounds have cyclic structures.

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6.6: IUPAC Nomenclature

Learning Objectives

- To name alkanes by the IUPAC system and write formulas for alkanes given IUPAC names

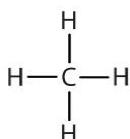
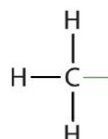
As noted in previously, the number of isomers increases rapidly as the number of carbon atoms increases. There are 3 pentanes, 5 hexanes, 9 heptanes, and 18 octanes. It would be difficult to assign unique individual names that we could remember. A systematic way of naming hydrocarbons and other organic compounds has been devised by the International Union of Pure and Applied Chemistry (IUPAC). These rules, used worldwide, are known as the IUPAC System of Nomenclature. (Some of the names we used earlier, such as isobutane, isopentane, and neopentane, do not follow these rules and are called *common names*.) A stem name (Table 6.6.1) 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 6.6.1: 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 6.6.2. Alkyl groups are not independent molecules; they are parts of molecules that we consider as a unit to name compounds systematically.

Table 6.6.2: Common Alkyl Groups

Parent Alkane		Alkyl Group		Condensed Structural Formula
methane		methyl		CH ₃ –

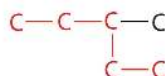
*There are four butyl groups, two derived from butane and two from isobutane. We will introduce the other three where appropriate.

Parent Alkane		Alkyl Group		Condensed Structural Formula
ethane		ethyl		CH_3CH_2-
propane		propyl		$\text{CH}_3\text{CH}_2\text{CH}_2-$
		isopropyl		$(\text{CH}_3)_2\text{CH}-$
butane		butyl*		$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-$

*There are four butyl groups, two derived from butane and two from isobutane. We will introduce the other three where appropriate.

Simplified IUPAC rules for naming alkanes are as follows (demonstrated in Example 6.6.1).

- Name alkanes according to the LCC (longest continuous chain) of carbon atoms in the molecule (rather than the total number of carbon atoms).** This LCC, considered the parent chain, determines the base name, to which we add the suffix *-ane* to indicate that the molecule is an alkane.
- 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.)



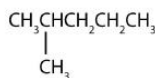
- Place the names of the substituent groups in alphabetical order before the name of the parent compound.** If the same alkyl group appears more than once, the numbers of all the carbon atoms to which it is attached are expressed. If the same group appears more than once on the same carbon atom, the 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.

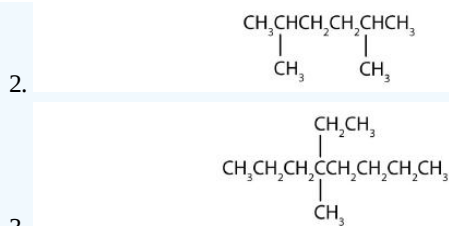
When these rules are followed, every unique compound receives its own exclusive name. The rules enable us to not only name a compound from a given structure but also draw a structure from a given name. The best way to learn how to use the IUPAC system is to put it to work, not just memorize the rules. It's easier than it looks.

Example 6.6.1

Name each compound.

1.



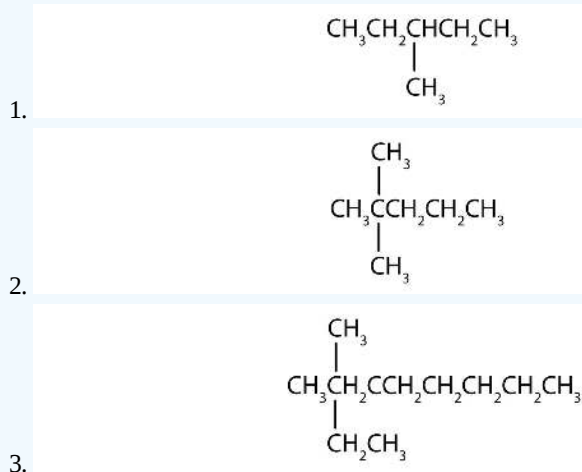


Solution

1. The long chain carbon (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 6.6.1

Name each compound.



Example 6.6.2

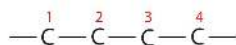
Draw the structure for each compound.

- a. 2,3-dimethylbutane
- b. 4-isopropyl-2-methylheptane

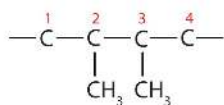
Solution

In drawing structures, always start with the parent chain.

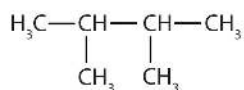
- a. The parent chain is butane, indicating four carbon atoms in the LCC.



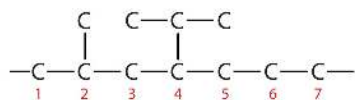
Then add the groups at their proper positions. You can number the parent chain from either direction as long as you are consistent; just don't change directions before the structure is done. The name indicates two methyl (CH₃) groups, one on the second carbon atom and one on the third.



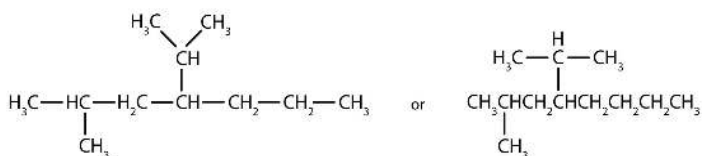
Finally, fill in all the hydrogen atoms, keeping in mind that each carbon atom must have four bonds.



- b. The parent chain is heptane in this case, indicating seven carbon atoms in the LCC. $-C-C-C-C-C-C-C-$
Adding the groups at their proper positions gives



Filling in all the hydrogen atoms gives the following condensed structural formulas:



Note that the bonds (dashes) can be shown or not; sometimes they are needed for spacing.

Exercise 6.6.2

Draw the structure for each compound.

- 4-ethyloctane
- 3-ethyl-2-methylpentane
- 3,3,5-trimethylheptane

6.6.1 Key Takeaway

- Alkanes have both common names and systematic names, specified by IUPAC.

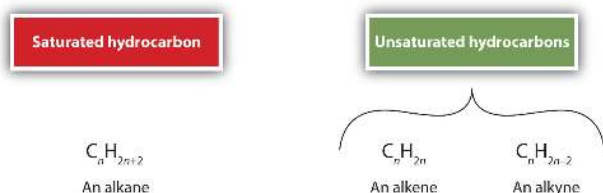
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6.7: Alkenes- Structure and Nomenclature

Learning Objectives

- To name alkenes given formulas and write formulas for alkenes given names.

As noted before, alkenes are hydrocarbons with carbon-to-carbon double bonds ($R_2C=CR_2$) and alkynes are hydrocarbons with carbon-to-carbon triple bonds ($R-C\equiv C-R$). Collectively, they are called unsaturated hydrocarbons because they have fewer hydrogen atoms than does an alkane with the same number of carbon atoms, as is indicated in the following general formulas:

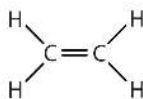


Some representative alkenes—their names, structures, and physical properties—are given in Table 6.7.1.

Table 6.7.1: Physical Properties of Some Selected Alkenes

IUPAC Name	Molecular Formula	Condensed Structural Formula	Melting Point (°C)	Boiling Point (°C)
ethene	C_2H_4	$CH_2=CH_2$	−169	−104
propene	C_3H_6	$CH_2=CHCH_3$	−185	−47
1-butene	C_4H_8	$CH_2=CHCH_2CH_3$	−185	−6
1-pentene	C_5H_{10}	$CH_2=CH(CH_2)_2CH_3$	−138	30
1-hexene	C_6H_{12}	$CH_2=CH(CH_2)_3CH_3$	−140	63
1-heptene	C_7H_{14}	$CH_2=CH(CH_2)_4CH_3$	−119	94
1-octene	C_8H_{16}	$CH_2=CH(CH_2)_5CH_3$	−102	121

We used only condensed structural formulas in Table 6.7.1. Thus, $CH_2=CH_2$ stands for



The double bond is shared by the two carbons and does not involve the hydrogen atoms, although the condensed formula does not make this point obvious. Note that the molecular formula for ethene is C_2H_4 , whereas that for ethane is C_2H_6 .

The first two alkenes in Table 6.7.1, ethene and propene, are most often called by their common names—ethylene and propylene, respectively (Figure 6.7.1). 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.

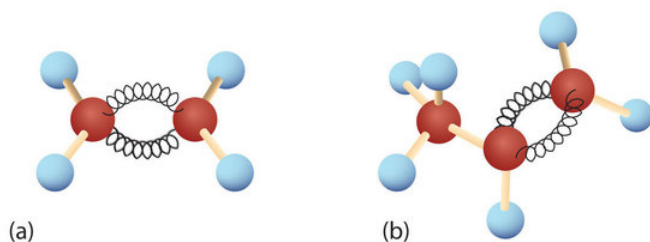
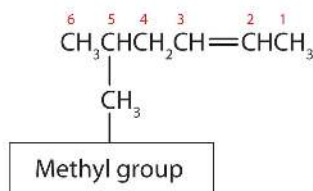


Figure 6.7.1: Ethene and Propene. The ball-and-spring models of ethene/ethylene (a) and propene/propylene (b) show their respective shapes, especially bond angles.

Although there is only one alkene with the formula C_2H_4 (ethene) and only one with the formula C_3H_6 (propene), there are several alkenes with the formula C_4H_8 .

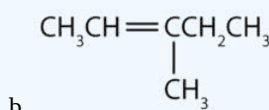
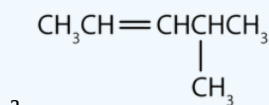
Here are some basic rules for naming alkenes from the International Union of Pure and Applied Chemistry (IUPAC):

1. The longest chain of carbon atoms *containing the double bond* is considered the parent chain. It is named using the same stem as the alkane having the same number of carbon atoms but ends in *-ene* to identify it as an alkene. Thus the compound $CH_2=CHCH_3$ is *propene*.
2. If there are four or more carbon atoms in a chain, we must indicate the position of the double bond. The carbon atoms are numbered so that the first of the two that are doubly bonded is given the lower of the two possible numbers. The compound $CH_3CH=CHCH_2CH_3$, for example, has the double bond between the second and third carbon atoms. Its name is 2-pentene (not 3-pentene).
3. Substituent groups are named as with alkanes, and their position is indicated by a number. Thus, the structure below is 5-methyl-2-hexene. Note that the numbering of the parent chain is always done in such a way as to give the double bond the lowest number, even if that causes a substituent to have a higher number. *The double bond always has priority in numbering.*



✓ Example 6.7.1

Name each compound.

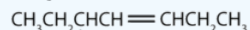
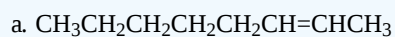


Solution

- a. The longest chain containing the double bond has five carbon atoms, so the compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the fourth carbon atom (rule 3), so the compound's name is 4-methyl-2-pentene.
- b. The longest chain containing the double bond has five carbon atoms, so the parent compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the third carbon atom (rule 3), so the compound's name is 3-methyl-2-pentene.

? Exercise 6.7.1

Name each compound.

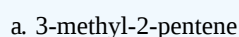


Answer

Just as there are cycloalkanes, there are *cycloalkenes*. These compounds are named like alkenes, but with the prefix *cyclo-* attached to the beginning of the parent alkene name.

✓ Example 6.7.2

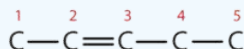
Draw the structure for each compound.



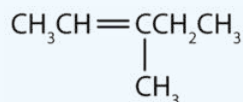
Solution

a.

First write the parent chain of five carbon atoms: C–C–C–C–C. Then add the double bond between the second and third carbon atoms:

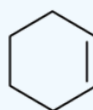


Now place the methyl group on the third carbon atom and add enough hydrogen atoms to give each carbon atom a total of four bonds.



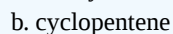
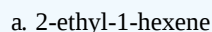
b

First, consider what each of the three parts of the name means. *Cyclo* means a ring compound, *hex* means 6 carbon atoms, and *-ene* means a double bond.



? Exercise 6.7.2

Draw the structure for each compound.



6.7.1 Key Takeaway

- Alkenes are hydrocarbons with a carbon-to-carbon double bond.

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6.8: Alkenes- Cis-Tran Isomerization

Learning Objectives

- Recognize that alkenes that can exist as cis-trans isomers.
- Classify isomers as cis or trans.
- Draw structures for cis-trans isomers given their names.

There is free rotation about the carbon-to-carbon single bonds (C–C) in alkanes. In contrast, the structure of alkenes requires that the carbon atoms of a double bond and the two atoms bonded to each carbon atom all lie in a single plane, and that each doubly bonded carbon atom lies in the center of a triangle. This part of the molecule's structure is rigid; rotation about doubly bonded carbon atoms is *not* possible without rupturing the bond. Look at the two chlorinated hydrocarbons in Figure 6.8.1.

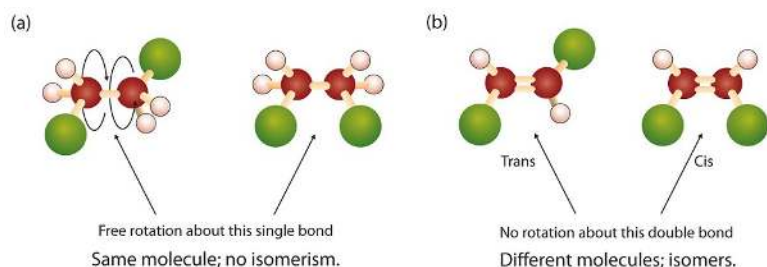


Figure 6.8.1: Rotation about Bonds. In 1,2-

dichloroethane (a), free rotation about the C–C bond allows the two structures to be interconverted by a twist of one end relative to the other. In 1,2-dichloroethene (b), restricted rotation about the double bond means that the relative positions of substituent groups above or below the double bond are significant.

In 1,2-dichloroethane (part (a) of Figure 6.8.1), there is free rotation about the C–C bond. The two models shown represent exactly the same molecule; they are *not* isomers. You can draw structural formulas that look different, but if you bear in mind the possibility of this free rotation about single bonds, you should recognize that these two structures represent the same molecule:



In 1,2-dichloroethene (Figure 6.8.1b), however, restricted rotation about the double bond means that the relative positions of substituent groups above or below the double bond become significant. This leads to a special kind of isomerism. The isomer in which the two chlorine (Cl) atoms lie on the same side of the molecule is called the *cis* isomer (Latin *cis*, meaning “on this side”) and is named *cis*-1,2-dichloroethene. The isomer with the two Cl atoms on opposite sides of the molecule is the *trans* isomer (Latin *trans*, meaning “across”) and is named *trans*-1,2-dichloroethene. These two compounds are *cis-trans* isomers (or *geometric isomers*), compounds that have different configurations (groups permanently in different places in space) because of the presence of a rigid structure in their molecule.

Consider the alkene with the condensed structural formula $\text{CH}_3\text{CH}=\text{CHCH}_3$. We could name it 2-butene, but there are actually two such compounds; the double bond results in *cis-trans* isomerism (Figure 6.8.2).

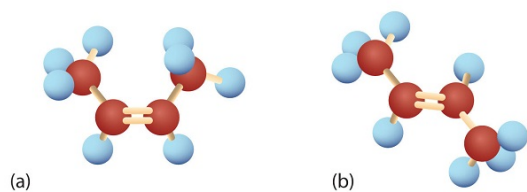


Figure 6.8.2: Ball-and-Spring Models of (a) Cis-2-Butene and (b) Trans-2-

Butene. *Cis-trans* isomers have different physical, chemical, and physiological properties.

Cis-2-butene has both methyl groups on the same side of the molecule. *Trans*-2-butene has the methyl groups on opposite sides of the molecule. Their structural formulas are as follows:

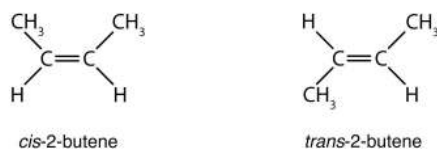


Figure 6.8.3: Models of (left) *Cis-2-Butene* and (right) *Trans-2-Butene*.

Note, however, that the presence of a double bond does **not** necessarily lead to cis-trans isomerism (Figure 6.8.4). We can draw two *seemingly* different propenes:



Figure 6.8.4: Different views of the propene molecule (flip vertically). These are not isomers.

However, these two structures are not really different from each other. If you could pick up either molecule from the page and flip it over top to bottom, you would see that the two formulas are identical. Thus there are two requirements for cis-trans isomerism:

1. Rotation must be restricted in the molecule.
2. There must be **two nonidentical groups on each** doubly bonded carbon atom.

In these propene structures, the second requirement for cis-trans isomerism is not fulfilled. One of the doubly bonded carbon atoms does have two different groups attached, but the rules require that *both* carbon atoms have two different groups. In general, the following statements hold true in cis-trans isomerism:

- Alkenes with a $\text{C}=\text{CH}_2$ unit do not exist as cis-trans isomers.
- Alkenes with a $\text{C}=\text{CR}_2$ unit, where the two R groups are the same, do not exist as cis-trans isomers.
- Alkenes of the type $\text{R}-\text{CH}=\text{CH}-\text{R}$ 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 $\text{C}=\text{C}$ bond with one non-hydrogen group attached to each of the carbons, cis/trans nomenclature described 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 $\text{C}=\text{C}$ bond, with a methyl group and a bromine on one carbon, and an ethyl group on the other, it is neither trans nor cis, since it is not clear whether the ethyl group is trans to the bromine or the methyl. This is addressed with a more advanced [E,Z Convention](#) [E] [E] [E] discussed elsewhere.

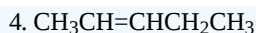
Cis-trans isomerism also occurs in cyclic compounds. In ring structures, groups are unable to rotate about any of the ring carbon-carbon bonds. Therefore, groups can be either on the same side of the ring (cis) or on opposite sides of the ring (trans). For our purposes here, we represent all cycloalkanes as planar structures, and we indicate the positions of the groups, either above or below the plane of the ring.



✓ Example 6.8.1

Which compounds can exist as cis-trans (geometric) isomers? Draw them.

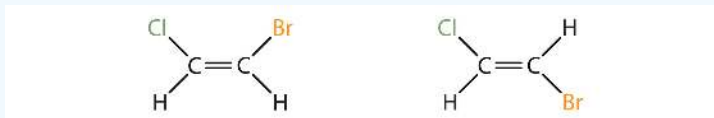
1. $\text{CHCl}=\text{CHBr}$
2. $\text{CH}_2=\text{CBrCH}_3$
3. $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{CH}_3$



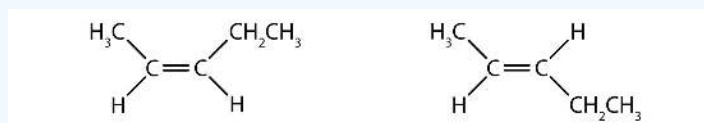
Solution

All four structures have a double bond and thus meet rule 1 for cis-trans isomerism.

1. This compound meets rule 2; it has two nonidentical groups on *each* carbon atom (H and Cl on one and H and Br on the other). It exists as both cis and trans isomers:



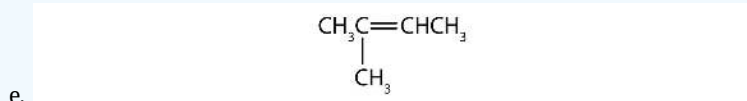
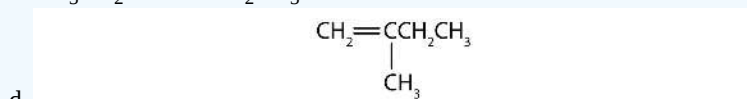
2. This compound has two hydrogen atoms on one of its doubly bonded carbon atoms; it fails rule 2 and does not exist as cis and trans isomers.
3. This compound has two methyl (CH_3) groups on one of its doubly bonded carbon atoms. It fails rule 2 and does not exist as cis and trans isomers.
4. This compound meets rule 2; it has two nonidentical groups on *each* carbon atom and exists as both cis and trans isomers:



? Exercise 6.8.1

Which compounds can exist as cis-trans isomers? Draw them.

- a. $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_3$
- b. $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_3$
- c. $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_3$



6.8.1 Key Takeaway

- Cis-trans (geometric) isomerism exists when there is restricted rotation in a molecule and there are two nonidentical groups on *each* doubly bonded carbon atom.

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6.9: Alkynes

Learning Objectives

- Describe the general physical and chemical properties of alkynes.
- Name alkynes given formulas and write formulas for alkynes given names.

The simplest alkyne—a hydrocarbon with carbon-to-carbon triple bond—has the molecular formula C_2H_2 and is known by its common name—acetylene (Figure 6.9.1). Its structure is $H-C\equiv C-H$.

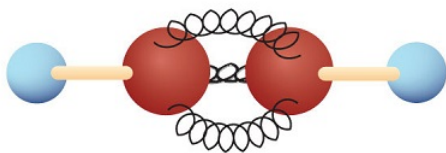


Figure 6.9.1: Ball-and-Spring Model of Acetylene. Acetylene (ethyne) is the simplest member of the alkyne family.

Acetylene is used in oxyacetylene torches for cutting and welding metals. The flame from such a torch can be very hot. Most acetylene, however, is converted to chemical intermediates that are used to make vinyl and acrylic plastics, fibers, resins, and a variety of other products.

Alkynes are similar to alkenes in both physical and chemical properties. For example, alkynes undergo many of the typical addition reactions of alkenes. The International Union of Pure and Applied Chemistry (IUPAC) names for alkynes parallel those of alkenes, except that the family ending is *-yne* rather than *-ene*. The IUPAC name for acetylene is ethyne. The names of other alkynes are illustrated in the following exercises.

6.9.1 Key Takeaway

- Alkynes are hydrocarbons with carbon-to-carbon triple bonds and properties much like those of alkenes.

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6.10: Aromatic Compounds

Learning Objectives

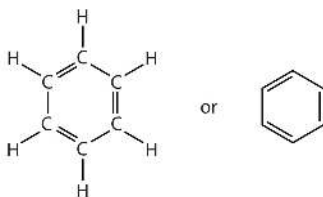
- To describe the bonding in benzene and the way typical reactions of benzene differ from those of the alkenes.

Next we consider a class of hydrocarbons with molecular formulas like those of unsaturated hydrocarbons, but which, unlike the alkenes, do not readily undergo addition reactions. These compounds comprise a distinct class, called aromatic hydrocarbons, with unique structures and properties. We start with the simplest of these compounds. Benzene (C_6H_6) is of great commercial importance, but it also has noteworthy health effects.

The formula C_6H_6 seems to indicate that benzene has a high degree of unsaturation. (Hexane, the saturated hydrocarbon with six carbon atoms has the formula C_6H_{14} —eight more hydrogen atoms than benzene.) However, despite the seeming low level of saturation, benzene is rather unreactive. It does not, for example, react readily with bromine, which, is a test for unsaturation.

Benzene is a liquid that smells like gasoline, boils at $80^\circ C$, and freezes at $5.5^\circ C$. 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.

6.10.1 Key Takeaway

- Aromatic hydrocarbons appear to be unsaturated, but they have a special type of bonding and do not undergo addition reactions.

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6.11: Aromatic Compounds- Structure and Nomenclature

Learning Objectives

- Recognize aromatic compounds from structural formulas.
- Name aromatic compounds given formulas.
- Write formulas for aromatic compounds given their names.

Historically, benzene-like substances were called aromatic hydrocarbons because they had distinctive aromas. Today, an aromatic compound is any compound that contains a benzene ring or has certain benzene-like properties (but not necessarily a strong aroma). You can recognize the aromatic compounds in this text by the presence of one or more benzene rings in their structure. Some representative aromatic compounds and their uses are listed in Table 6.11.1, where the benzene ring is represented as C_6H_5 .

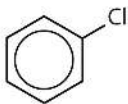
Table 6.11.1: Some Representative Aromatic Compounds

Name	Structure	Typical Uses
aniline	$C_6H_5-NH_2$	starting material for the synthesis of dyes, drugs, resins, varnishes, perfumes; solvent; vulcanizing rubber
benzoic acid	C_6H_5-COOH	food preservative; starting material for the synthesis of dyes and other organic compounds; curing of tobacco
bromobenzene	C_6H_5-Br	starting material for the synthesis of many other aromatic compounds; solvent; motor oil additive
nitrobenzene	$C_6H_5-NO_2$	starting material for the synthesis of aniline; solvent for cellulose nitrate; in soaps and shoe polish
phenol	C_6H_5-OH	disinfectant; starting material for the synthesis of resins, drugs, and other organic compounds
toluene	$C_6H_5-CH_3$	solvent; gasoline octane booster; starting material for the synthesis of benzoic acid, benzaldehyde, and many other organic compounds

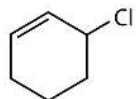
✓ Example 6.11.1

Which compounds are aromatic?

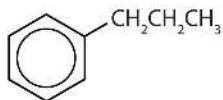
1.

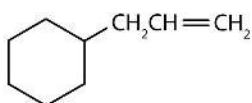


2.



3.





4.

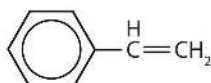
Solution

1. The compound has a benzene ring (with a chlorine atom substituted for one of the hydrogen atoms); it is aromatic.
2. The compound is cyclic, but it does not have a benzene ring; it is not aromatic.
3. The compound has a benzene ring (with a propyl group substituted for one of the hydrogen atoms); it is aromatic.
4. The compound is cyclic, but it does not have a benzene ring; it is not aromatic.

? Exercise 6.11.1

Which compounds are aromatic?

1.



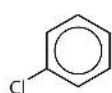
2.



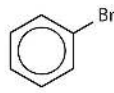
3.



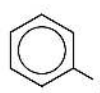
In the International Union of Pure and Applied Chemistry (IUPAC) system, aromatic hydrocarbons are named as derivatives of benzene. Figure 6.11.1 shows four examples. In these structures, it is immaterial whether the single substituent is written at the top, side, or bottom of the ring; a hexagon is symmetrical, and therefore all positions are equivalent.



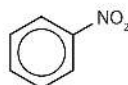
Chlorobenzene



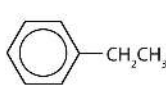
Bromobenzene



Iodobenzene



Nitrobenzene

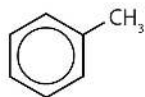


Ethylbenzene

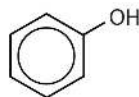
Figure 6.11.1: Some Benzene Derivatives. These compounds are named

in the usual way with the group that replaces a hydrogen atom named as a substituent group: Cl as chloro, Br as bromo, I as iodo, NO₂ as nitro, and CH₃CH₂ as ethyl.

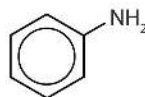
Although some compounds are referred to exclusively by IUPAC names, some are more frequently denoted by common names, as is indicated in Table 6.11.1.



Toluene



Phenol



Aniline

When there is more than one substituent, the corners of the hexagon are no longer equivalent, so we must designate the relative positions. There are three possible disubstituted benzenes, and we can use numbers to distinguish them (Figure 6.11.2). We start numbering at the carbon atom to which one of the groups is attached and count toward the carbon atom that bears the other substituent group by the shortest path.

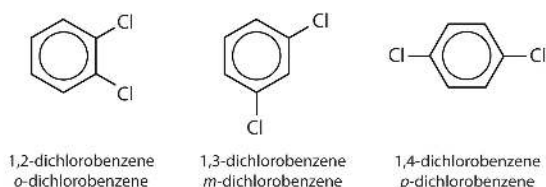
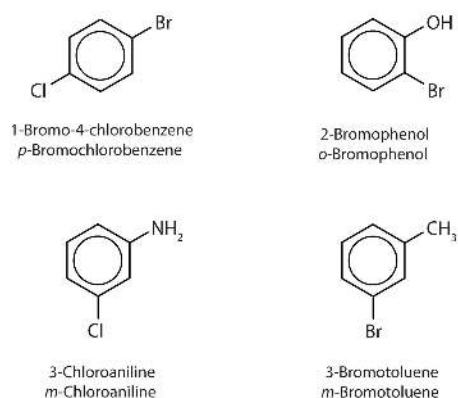


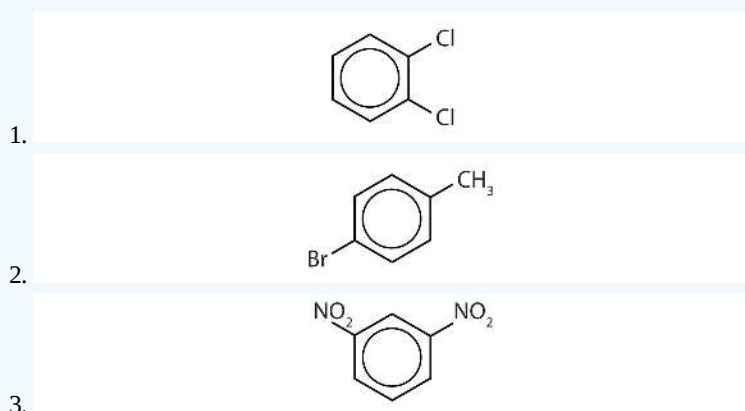
Figure 6.11.2: The Three Isomeric Dichlorobenzenes

In Figure 6.11.2, common names are also used: the prefix *ortho* (*o*-) for 1,2-disubstitution, *meta* (*m*-) for 1,3-disubstitution, and *para* (*p*-) for 1,4-disubstitution. The substituent names are listed in alphabetical order. The first substituent is given the lowest number. When a common name is used, the carbon atom that bears the group responsible for the name is given the number 1:



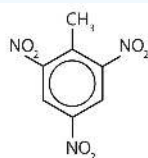
✓ Example 6.11.2

Name each compound using both the common name and the IUPAC name.



Solution

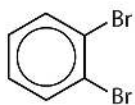
- The benzene ring has two chlorine atoms (dichloro) in the first and second positions. The compound is *o*-dichlorobenzene or 1,2-dichlorobenzene.
- The benzene ring has a methyl (CH₃) group. The compound is therefore named as a derivative of toluene. The bromine atom is on the fourth carbon atom, counting from the methyl group. The compound is *p*-bromotoluene or 4-bromotoluene.
- The benzene ring has two nitro (NO₂) groups in the first and third positions. It is *m*-dinitrobenzene or 1,3-dinitrobenzene.
- Note: The nitro (NO₂) group is a common substituent in aromatic compounds. Many nitro compounds are explosive, most notably 2,4,6-trinitrotoluene (TNT).



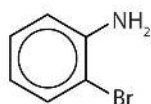
? Exercise 6.11.2

Name each compound using both the common name and the IUPAC name.

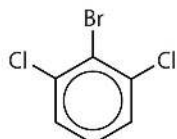
1.



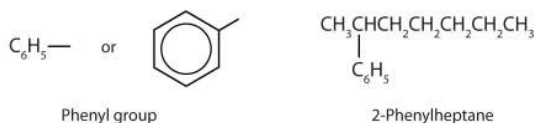
2.



3.



- Sometimes an aromatic group is found as a substituent bonded to a nonaromatic entity or to another aromatic ring. The group of atoms remaining when a hydrogen atom is removed from an aromatic compound is called an aryl group. The most common aryl group is derived from benzene (C_6H_6) by removing one hydrogen atom (C_6H_5) and is called a *phenyl* group, from *pheno*, an old name for benzene.



6.11.1 Polycyclic Aromatic Hydrocarbons

Some common aromatic hydrocarbons consist of fused benzene rings—rings that share a common side. These compounds are called polycyclic aromatic hydrocarbons (PAHs).



The three examples shown here are colorless, crystalline solids generally obtained from coal tar. Naphthalene has a pungent odor and is used in mothballs. Anthracene is used in the manufacture of certain dyes. Steroids, a large group of naturally occurring substances, contain the phenanthrene structure.

6.11.2 To Your Health: Polycyclic Aromatic Hydrocarbons and Cancer

The intense heating required for distilling coal tar results in the formation of PAHs. For many years, it has been known that workers in coal-tar refineries are susceptible to a type of skin cancer known as tar cancer. Investigations have shown that a number of PAHs are carcinogens. One of the most active carcinogenic compounds, benzopyrene, occurs in coal tar and has also been isolated from cigarette smoke, automobile exhaust gases, and charcoal-broiled steaks. It is estimated that more than 1,000 t of benzopyrene are emitted into the air over the United States each year. Only a few milligrams of benzopyrene per kilogram of body weight are required to induce cancer in experimental animals.

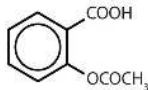
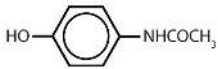
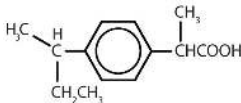
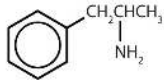
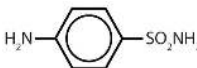
6.11.3 Biologically Important Compounds with Benzene Rings

Substances containing the benzene ring are common in both animals and plants, although they are more abundant in the latter. Plants can synthesize the benzene ring from carbon dioxide, water, and inorganic materials. Animals cannot synthesize it, but they are dependent on certain aromatic compounds for survival and therefore must obtain them from food. Phenylalanine, tyrosine, and

tryptophan (essential amino acids) and vitamins K, B₂ (riboflavin), and B₉ (folic acid) all contain the benzene ring. Many important drugs, a few of which are shown in Table 6.11.2, also feature a benzene ring.

So far we have studied only aromatic compounds with carbon-containing rings. However, many cyclic compounds have an element other than carbon atoms in the ring. These compounds, called *heterocyclic compounds*, are discussed later. Some of these are heterocyclic aromatic compounds.

Table 6.11.2: Some Drugs That Contain a Benzene Ring

Name	Structure
aspirin	
acetaminophen	
ibuprofen	
amphetamine	
sulfanilamide	

6.11.4 Key Takeaway

- Aromatic compounds contain a benzene ring or have certain benzene-like properties; for our purposes, you can recognize aromatic compounds by the presence of one or more benzene rings in their structure.

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6.12: Physical Properties of Hydrocarbons

Learning Objectives

- To identify the physical properties of alkanes and describe trends in these properties.

Because alkanes have relatively predictable physical properties and undergo relatively few chemical reactions other than combustion, they serve as a basis of comparison for the properties of many other organic compound families. Let's consider their physical properties first.

Table 6.12.1 describes some of the properties of some of the first 10 straight-chain alkanes. Because alkane molecules are nonpolar, they are insoluble in water, which is a polar solvent, but are soluble in nonpolar and slightly polar solvents. Consequently, alkanes themselves are commonly used as solvents for organic substances of low polarity, such as fats, oils, and waxes. Nearly all alkanes have densities less than 1.0 g/mL and are therefore less dense than water (the density of H₂O is 1.00 g/mL at 20°C). These properties explain why oil and grease do not mix with water but rather float on its surface.

Table 6.12.1: Physical Properties of Some Alkanes

Molecular Name	Formula	Melting Point (°C)	Boiling Point (°C)	Density (20°C)*	Physical State (at 20°C)
methane	CH ₄	−182	−164	0.668 g/L	gas
ethane	C ₂ H ₆	−183	−89	1.265 g/L	gas
propane	C ₃ H ₈	−190	−42	1.867 g/L	gas
butane	C ₄ H ₁₀	−138	−1	2.493 g/L	gas
pentane	C ₅ H ₁₂	−130	36	0.626 g/mL	liquid
hexane	C ₆ H ₁₄	−95	69	0.659 g/mL	liquid
octane	C ₈ H ₁₈	−57	125	0.703 g/mL	liquid
decane	C ₁₀ H ₂₂	−30	174	0.730 g/mL	liquid

*Note the change in units going from gases (grams per liter) to liquids (grams per milliliter). Gas densities are at 1 atm pressure.



Figure 6.12.1: Oil Spills. Crude oil coats the water's surface in the Gulf of Mexico after the *Deepwater Horizon* oil rig sank following an explosion. The leak was a mile below the surface, making it difficult to estimate the size of the spill. One liter of oil can create a slick 2.5 hectares (6.3 acres) in size. This and similar spills provide a reminder that hydrocarbons and water don't mix. Source: Photo courtesy of NASA Goddard / MODIS Rapid Response Team, [NASA.gov](https://www.nasa.gov), [Topics, Earth Features, Oil Spill](https://www.nasa.gov)(opens in new window) [www.nasa.gov].

Also shown in Table 6.12.1 are the boiling points of the straight-chain alkanes increase with increasing molar mass. This general rule holds true for the straight-chain homologs of all organic compound families. Larger molecules have greater surface areas and consequently interact more strongly; more energy is therefore required to separate them. For a given molar mass, the boiling points of alkanes are relatively low because these nonpolar molecules have only weak dispersion forces to hold them together in the liquid state.

📌 Looking Closer: An Alkane Basis for Properties of Other Compounds

(a)

$$\begin{array}{c} \text{H}_2\text{C}-\text{O}-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2 \\ | \\ \text{HC}-\text{O}-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2 \\ | \\ \text{H}_2\text{C}-\text{O}-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2 \end{array}$$

(b)

$$\text{CH CH CH CH CH CH CH CH CH CH CH CH CH CH CH CH}$$

Figure 6.12.2: 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

6.12.1 Key Takeaway

- Alkanes are nonpolar compounds that are low boiling and insoluble in water.

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6.13: Chapter Summary

Template:HideTOC

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

Organic chemistry is the chemistry of carbon compounds, and **inorganic chemistry** is the chemistry of all the other elements. Carbon atoms can form stable covalent bonds with other carbon atoms and with atoms of other elements, and this property allows the formation the tens of millions of organic compounds. **Hydrocarbons** contain only hydrogen and carbon atoms.

Hydrocarbons in which each carbon atom is bonded to four other atoms are called **alkanes** or **saturated hydrocarbons**. They have the general formula C_nH_{2n+2} . Any given alkane differs from the next one in a series by a CH_2 unit. Any family of compounds in which adjacent members differ from each other by a definite factor is called a **homologous series**.

Carbon atoms in alkanes can form straight chains or branched chains. Two or more compounds having the same molecular formula but different structural formulas are **isomers** of each other. There are no isomeric forms for the three smallest alkanes; beginning with C_4H_{10} , all other alkanes have isomeric forms.

A **structural formula** shows all the carbon and hydrogen atoms and how they are attached to one another. A **condensed structural formula** shows the hydrogen atoms right next to the carbon atoms to which they are attached. A **line-angle formula** is a formula in which carbon atoms are implied at the corners and ends of lines. Each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds.

The **IUPAC System of Nomenclature** provides rules for naming organic compounds. An **alkyl group** is a unit formed by removing one hydrogen atom from an alkane.

The physical properties of alkanes reflect the fact that alkane molecules are nonpolar. Alkanes are insoluble in water and less dense than water.

Alkanes are generally unreactive toward laboratory acids, bases, oxidizing agents, and reducing agents. They do burn (undergo **combustion reactions**).

Alkanes react with halogens by substituting one or more halogen atoms for hydrogen atoms to form **halogenated hydrocarbons**. An **alkyl halide (haloalkane)** is a compound resulting from the replacement of a hydrogen atom of an alkane with a halogen atom.

Cycloalkanes are hydrocarbons whose molecules are closed rings rather than straight or branched chains. A **cyclic hydrocarbon** is a hydrocarbon with a ring of carbon atoms.

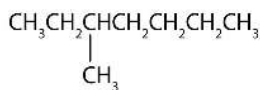
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6.E: Unsaturated and Aromatic Hydrocarbons (Exercises)

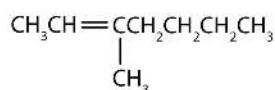
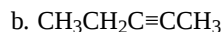
6.E.1 13.1: Alkenes- Structures and Names

6.E.2 Concept Review Exercises

- Briefly identify the important distinctions between a saturated hydrocarbon and an unsaturated hydrocarbon.
- Briefly identify the important distinctions between an alkene and an alkane.
- Classify each compound as saturated or unsaturated. Identify each as an alkane, an alkene, or an alkyne.



a.



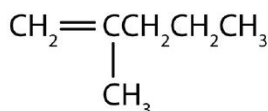
c.

6.E.3 Answers

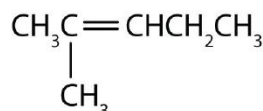
- Unsaturated hydrocarbons have double or triple bonds and are quite reactive; saturated hydrocarbons have only single bonds and are rather unreactive.
- An alkene has a double bond; an alkane has single bonds only.
- saturated; alkane
 - unsaturated; alkyne
 - unsaturated; alkene

6.E.4 Exercises

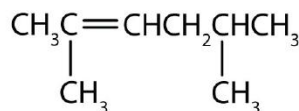
- Draw the structure for each compound.
 - 2-methyl-2-pentene
 - 2,3-dimethyl-1-butene
 - cyclohexene
- Draw the structure for each compound.
 - 5-methyl-1-hexene
 - 3-ethyl-2-pentene
 - 4-methyl-2-hexene
- Name each compound according to the IUPAC system.



a.

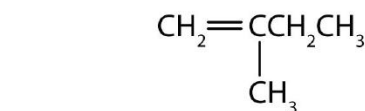


b.

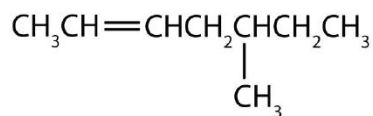


c.

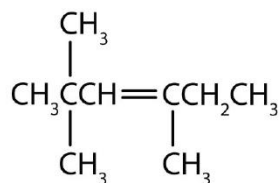
- Name each compound according to the IUPAC system.



a.

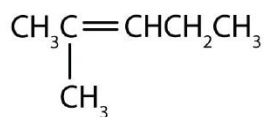


b.

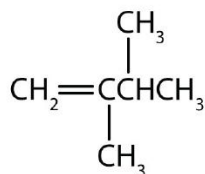


c.

6.E.5 Answers



1. a.



b.



c.

3. a. 2-methyl-1-pentene
- b. 2-methyl-2-pentene
- c. 2,5-dimethyl-2-hexene

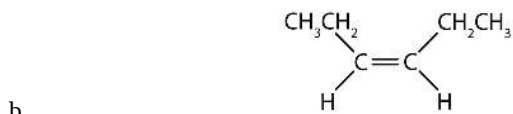
6.E.6 13.2: Cis-Trans Isomers (Geometric Isomers)

6.E.7 Concept Review Exercises

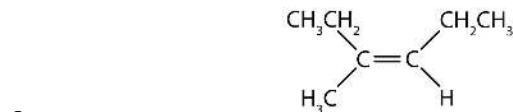
1. What are cis-trans (geometric) isomers? What two types of compounds can exhibit cis-trans isomerism?
2. Classify each compound as a cis isomer, a trans isomer, or neither.



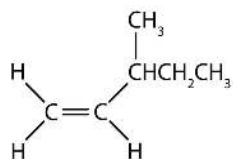
a.



b.



c.



d.

6.E.8 Answers

1. Cis-trans isomers are compounds that have different configurations (groups permanently in different places in space) because of the presence of a rigid structure in their molecule. Alkenes and cyclic compounds can exhibit cis-trans isomerism.
2. a. trans (the two hydrogen atoms are on opposite sides)
b. cis (the two hydrogen atoms are on the same side, as are the two ethyl groups)
c. cis (the two ethyl groups are on the same side)
d. neither (flipping the bond does not change the molecule. There are no isomers for this molecule)

6.E.9

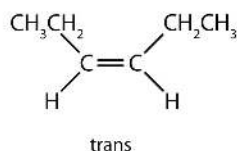
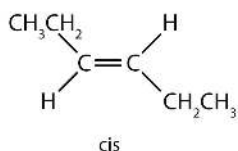
6.E.10 Exercises

1. Draw the structures of the cis-trans isomers for each compound. Label them cis and trans. If no cis-trans isomers exist, write none.
 - a. 2-bromo-2-pentene
 - b. 3-hexene
 - c. 4-methyl-2-pentene
 - d. 1,1-dibromo-1-butene
 - e. 2-butenic acid ($\text{CH}_3\text{CH}=\text{CHCOOH}$)
2. Draw the structures of the cis-trans isomers for each compound. Label them cis and trans. If no cis-trans isomers exist, write none.
 - a. 2,3-dimethyl-2-pentene
 - b. 1,1-dimethyl-2-ethylcyclopropane
 - c. 1,2-dimethylcyclohexane
 - d. 5-methyl-2-hexene
 - e. 1,2,3-trimethylcyclopropane

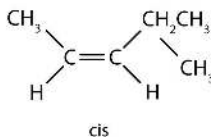
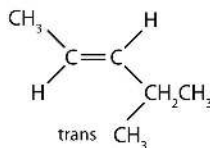
6.E.11 Answer

1. a: none. There are two distinct geometric isomers, but since there are there are four different groups off the double bond, these are both cis/trans isomers (they are technically E/Z isomers discussed elsewhere).

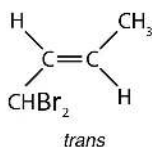
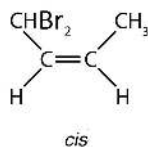
b:

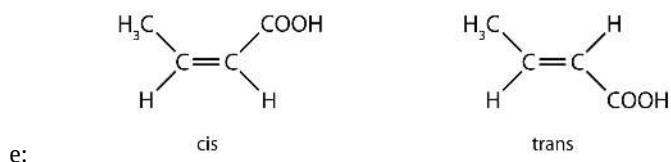


c:



d:





6.E.12

6.E.13 13.3: Physical Properties of Alkenes

6.E.14 Concept Review Exercises

- Briefly describe the physical properties of alkenes. How do these properties compare to those of the alkanes?
- Without consulting tables, arrange the following alkenes in order of increasing boiling point: 1-butene, ethene, 1-hexene, and propene.

6.E.15 Answers

- Alkenes have physical properties (low boiling points, insoluble in water) quite similar to those of their corresponding alkanes.
- ethene < propene < 1-butene < 1-hexene

6.E.16 Exercises

- Without referring to a table or other reference, predict which member of each pair has the higher boiling point.
 - 1-pentene or 1-butene
 - 3-heptene or 3-nonene
- Which is a good solvent for cyclohexene, pentane or water?

6.E.17 Answer

- 1-pentene
 - 3-nonene

6.E.18 13.4: Chemical Properties of Alkenes

6.E.19 Concept Review Exercises

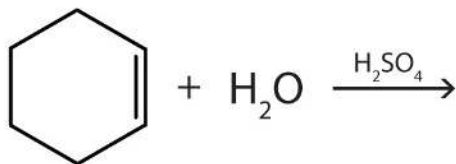
- What is the principal difference in properties between alkenes and alkanes? How are they alike?
- If $\text{C}_{12}\text{H}_{24}$ reacts with HBr in an addition reaction, what is the molecular formula of the product?

6.E.20 Answers

- Alkenes undergo addition reactions; alkanes do not. Both burn.
- $\text{C}_{12}\text{H}_{24}\text{Br}_2$

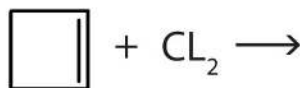
6.E.21 Exercises

- Complete each equation.
 - $(\text{CH}_3)_2\text{C}=\text{CH}_2 + \text{Br}_2 \rightarrow$
 - $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_3 + \text{H}_2 \xrightarrow{\text{Ni}}$



c.

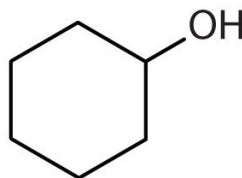
- Complete each equation.
 - $\text{CH}_2=\text{CHCH}=\text{CH}_2 + 2\text{H}_2 \xrightarrow{\text{Ni}}$
 - $(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2 + \text{H}_2\text{O} \xrightarrow{\text{H}_2\text{SO}_4}$



c.

6.E.22 Answer

1. a. $(\text{CH}_3)_2\text{CBrCH}_2\text{Br}$
b. $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$



c.

6.E.23 13.5: Polymers

6.E.24 Concept Review Exercises

1. What is a monomer? What is a polymer? How do polymer molecules differ from the molecules we have discussed in earlier sections of this chapter?
2. What is addition polymerization? What structural feature usually characterizes molecules used as monomers in addition polymerization?
3. What is the molecular formula of a polymer molecule formed by the addition polymerization of 175 molecules of vinyl chloride ($\text{CH}_2=\text{CHCl}$)?

6.E.25 Answers

1. Monomers are small molecules that can be assembled into giant molecules referred to as polymers, which are much larger than the molecules we discussed earlier in this chapter.
2. In addition polymerization, the monomers add to one another in such a way that the polymer contains all the atoms of the starting monomers.
3. $\text{C}_{350}\text{H}_{525}\text{Cl}_{175}$

6.E.26 Exercises

1. Write the condensed structural formula of the monomer from which Saran is formed. A segment of the Saran molecule has the following structure: $\text{CH}_2\text{CCl}_2\text{CH}_2\text{CCl}_2\text{CH}_2\text{CCl}_2\text{CH}_2\text{CCl}_2$.
2. Write the condensed structural formula for the section of a molecule formed from four units of the monomer $\text{CH}_2=\text{CHF}$.

6.E.27 Answer

1. $\text{H}_2\text{C}=\text{CCl}_2$

6.E.28 13.6: Alkynes

6.E.29 Concept Review Exercises

1. Briefly identify the important differences between an alkene and an alkyne. How are they similar?
2. The alkene $(\text{CH}_3)_2\text{CHCH}_2\text{CH}=\text{CH}_2$ is named 4-methyl-1-pentene. What is the name of $(\text{CH}_3)_2\text{CHCH}_2\text{C}\equiv\text{CH}$?
3. Do alkynes show cis-trans isomerism? Explain.

6.E.30 Answers

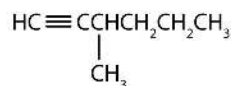
1. Alkenes have double bonds; alkynes have triple bonds. Both undergo addition reactions.
2. 4-methyl-1-pentyne
3. No; a triply bonded carbon atom can form only one other bond. It would have to have two groups attached to show cis-trans isomerism.

6.E.31 Exercises

1. Draw the structure for each compound.
 - a. acetylene
 - b. 3-methyl-1-hexyne
2. Draw the structure for each compound.
 - a. 4-methyl-2-hexyne
 - b. 3-octyne
3. Name each alkyne.
 - a. $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$
 - b. $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CCH}_3$

6.E.32 Answers

1. a. $\text{H}-\text{C}\equiv\text{C}-\text{H}$



- b.
3. a. 1-pentyne
- b. 2-hexyne

6.E.33

6.E.34 13.7: Aromatic Compounds- Benzene

6.E.35 Concept Review Exercises

1. How do the typical reactions of benzene differ from those of the alkenes?
2. Briefly describe the bonding in benzene.
3. What does the circle mean in the chemist's representation of benzene?

6.E.36 Answers

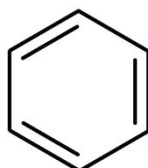
1. Benzene is rather unreactive toward addition reactions compared to an alkene.
2. Valence electrons are shared equally by all six carbon atoms (that is, the electrons are delocalized).
3. The six electrons are shared equally by all six carbon atoms.

6.E.37

6.E.38 Exercises

1. Draw the structure of benzene as if it had alternate single and double bonds.
2. Draw the structure of benzene as chemists usually represent it today.

6.E.39 Answer



- 1.

6.E.40

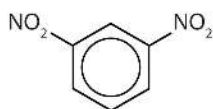
6.E.41 13.8: Structure and Nomenclature of Aromatic Compounds

6.E.42 Concept Review Exercises

- Briefly identify the important characteristics of an aromatic compound.
- What is meant by the prefixes *meta*, *ortho*, or *para*? Give the name and draw the structure for a compound that illustrates each.
- What is a phenyl group? Give the structure for 3-phenyloctane.

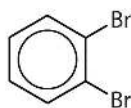
6.E.43 Answers

- An aromatic compound is any compound that contains a benzene ring or has certain benzene-like properties.
- meta* = 1,3 disubstitution; (answers will vary)



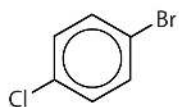
m-dinitrobenzene or 1,3-dinitrobenzene

ortho = 1,2 disubstitution



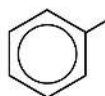
o-dibromobenzene or 1,2-dibromobenzene

para = 1,4 disubstitution or 1-bromo-4-chlorobenzene

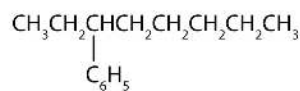


p-bromochlorobenzene or 1-bromo-4-chlorobenzene

- phenyl group: C_6H_5 or

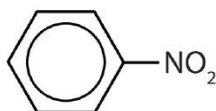


3-phenyloctane:

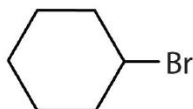


6.E.44 Exercises

- Is each compound aromatic?

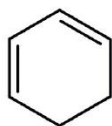


a.

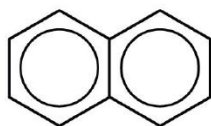


b.

- Is each compound aromatic?



a.



b.

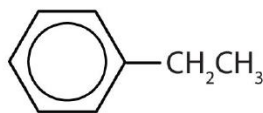
3. Draw the structure for each compound.

- toluene
- m*-diethylbenzene
- 3,5-dinitrotoluene

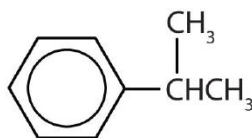
4. Draw the structure for each compound.

- p*-dichlorobenzene
- naphthalene
- 1,2,4-trimethylbenzene

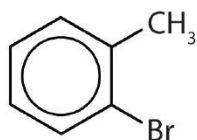
5. Name each compound with its IUPAC name.



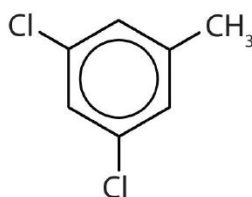
a.



b.

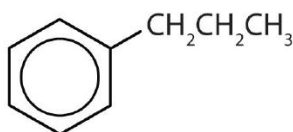


c.



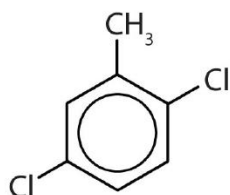
d.

6. Name each compound with its IUPAC name.

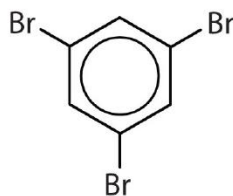


a.

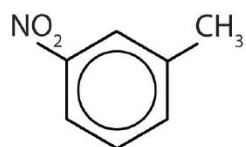
b.



c.



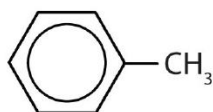
d.



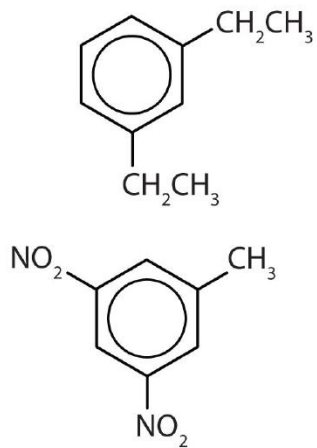
6.E.45 Answers

1. a. yes
- b. no

3. a.



b.



c.

5. a. ethylbenzene
- b. isopropylbenzene
- c. *o*-bromotoluene
- d. 3,5-dichlorotoluene

6.E.46

6.E.47

6.E.48

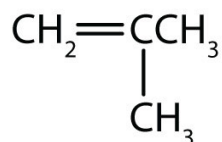
6.E.49

6.E.50

6.E.51

6.E.52 Additional Exercises

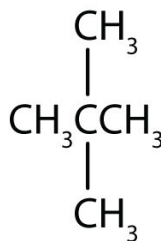
1. Classify each compound as saturated or unsaturated.



a.

b. $\text{CH}_3\text{C}\equiv\text{CCH}_3$

2. Classify each compound as saturated or unsaturated.



a.

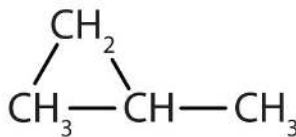


b.

3. Give the molecular formula for each compound.



a.



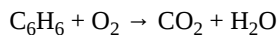
b.

4. When three isomeric pentenes—X, Y, and Z—are hydrogenated, all three form 2-methylbutane. The addition of Cl_2 to Y gives 1,2-dichloro-3-methylbutane, and the addition of Cl_2 to Z gives 1,2-dichloro-2-methylbutane. Draw the original structures for X, Y, and Z.

5. Pentane and 1-pentene are both colorless, low-boiling liquids. Describe a simple test that distinguishes the two compounds. Indicate what you would observe.

6. Draw and name all the alkene cis-trans isomers corresponding to the molecular formula C_5H_{10} . (Hint: there are only two.)

7. The complete combustion of benzene forms carbon dioxide and water:



Balance the equation. What mass, in grams, of carbon dioxide is formed by the complete combustion of 39.0 g of benzene?

8. Describe a physiological effect of some PAHs.

9. What are some of the hazards associated with the use of benzene?

10. What is wrong with each name? Draw the structure and give the correct name for each compound.

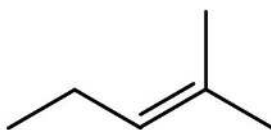
- 2-methyl-4-heptene
- 2-ethyl-2-hexene
- 2,2-dimethyl-3-pentene

11. What is wrong with each name?

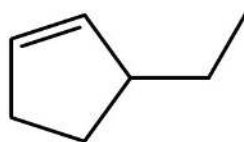
- 2-bromobenzene
- 3,3-dichlorotoluene
- 1,4-dimethylnitrobenzene

12. Following are line-angle formulas for three compounds. Draw the structure and give the name for each.

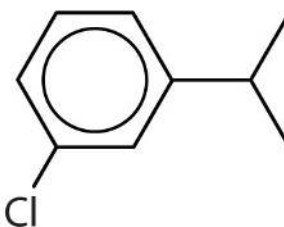
a.



b.

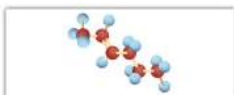


c.

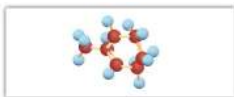


13. Following are ball-and-stick molecular models for three compounds (blue balls represent H atoms; red balls are C atoms). Write the condensed structural formula and give the name for each.

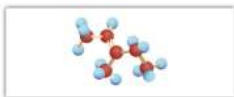
a.



b.



c.



6.E.53 Answers

1.

- a. unsaturated
- b. unsaturated

3.

- a. C_6H_{10}
- b. C_4H_8

5. Add bromine solution (reddish-brown) to each. Pentane will not react, and the reddish-brown color persists; 1-pentene will react, leaving a colorless solution.

7. $2C_6H_6 + 15O_2 \rightarrow 12CO_2 + 6H_2O$; 132 g

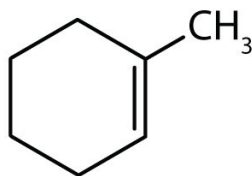
9. carcinogenic, flammable

11.

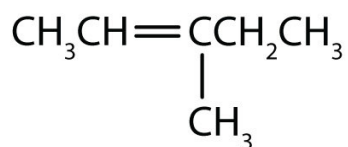
- a. number not needed
- b. can't have two groups on one carbon atom on a benzene ring
- c. can't have a substituent on the same carbon atom as the nitro group

13.

- a. $CH_3CH=CHCH_2CH_2CH_3$; 2-hexene



b.



c.

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CHAPTER OVERVIEW

7: Organic Compounds of Oxygen

Ethanol and resveratrol, a phenol, are representatives of two of the families of oxygen-containing compounds that we consider in this chapter. Two other classes, aldehydes and ketones, are formed by the oxidation of alcohols. Ethers, another class, are made by the dehydration of alcohols.

- [7.1: Prelude to Organic Compounds of Oxygen](#)
- [7.2: Organic Compounds with Functional Groups](#)
- [7.3: Alcohols - Nomenclature and Classification](#)
- [7.4: Physical Properties of Alcohols](#)
- [7.5: Phenols](#)
- [7.6: Ethers](#)
- [7.7: Aldehydes and Ketones- Structure and Names](#)
- [7.8: Properties of Aldehydes and Ketones](#)
- [7.S: Organic Compounds of Oxygen \(Summary\)](#)

Template:HideTOC

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7.1: Prelude to Organic Compounds of Oxygen

One of the more familiar chemical compounds on Earth is ethyl alcohol (ethanol). As the intoxicant in alcoholic beverages, ethanol is often simply called alcohol. If ethanol is diluted, as it is in wine, beer, or mixed drinks with about 1 oz of liquor, and if it is consumed in small quantities, it is relatively safe. In excess—four or more drinks in a few hours—it causes intoxication, which is characterized by a loss of coordination, nausea and vomiting, and memory blackouts.

Excessive ingestion of ethanol over a long period of time leads to cirrhosis of the liver, alteration of brain cell function, nerve damage, and strong physiological addiction. Alcoholism—an addiction to ethanol—is the most serious drug problem in the United States. Heavy drinking shortens a person's life span by contributing to diseases of the liver, the cardiovascular system, and virtually every other organ of the body.

In small quantities—one or two drinks a day—ethanol might promote health. In addition to the possible benefits of modest amounts of ethanol, a chemical in red wines, resveratrol, is thought to lower the risk of heart disease. Resveratrol, found in red grapes, is an antioxidant. It inhibits the oxidation of cholesterol and subsequent clogging of the arteries. One need not drink wine to get the benefits of resveratrol, however. It can be obtained by eating the grapes or drinking red grape juice.

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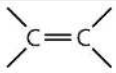
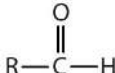
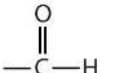
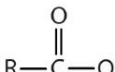
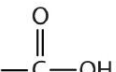
7.2: Organic Compounds with Functional Groups

Learning Objectives

- to describe functional groups and explain why they are useful in the study of organic chemistry.

Previously, we considered several kinds of hydrocarbons. Now we examine some of the many organic compounds that contain functional groups. We first introduced the idea of the functional group, a specific structural arrangement of atoms or bonds that imparts a characteristic chemical reactivity to the molecule. If you understand the behavior of a particular functional group, you will know a great deal about the general properties of that class of compounds. In this chapter, we make a brief yet systematic study of some of organic compound families. Each family is based on a common, simple functional group that contains an oxygen atom or a nitrogen atom. Some common functional groups are listed in Table 7.2.1.

Table 7.2.1: Selected Organic Functional Groups

Name of Family	General Formula	Functional Group	Suffix*
alkane	RH	none	-ane
alkene	$R_2C=CR_2$		-ene
alkyne	$RC\equiv CR$	$-C\equiv C-$	-yne
alcohol	ROH	-OH	-ol
thiol	RSH	-SH	-thiol
ether	ROR	-O-	ether
aldehyde			-al
ketone			-one
carboxylic acid			-oic acid

*Ethers do not have a suffix in their common name; all ethers end with the word *ether*.

Summary

The functional group, a structural arrangement of atoms and/or bonds, is largely responsible for the properties of organic compound families.

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7.3: Alcohols - Nomenclature and Classification

Learning Objectives

- Identify the general structure for an alcohol.
- Identify the structural feature that classifies alcohols as primary, secondary, or tertiary.
- Name alcohols with both common names and IUPAC names

An alcohol is an organic compound with a hydroxyl (OH) functional group on an aliphatic carbon atom. Because OH is the functional group of all alcohols, we often represent alcohols by the general formula ROH, where R is an alkyl group. Alcohols are common in nature. Most people are familiar with ethyl alcohol (ethanol), the active ingredient in alcoholic beverages, but this compound is only one of a family of organic compounds known as alcohols. The family also includes such familiar substances as cholesterol and the carbohydrates. Methanol (CH₃OH) and ethanol (CH₃CH₂OH) are the first two members of the homologous series of alcohols.

7.3.1 Nomenclature of Alcohols

Alcohols with one to four carbon atoms are frequently called by common names, in which the name of the alkyl group is followed by the word *alcohol*:



Structural formula of methyl alcohol, ethyl alcohol, propyl alcohol, and isopropyl alcohol with the methyl, ethyl propyl, and isopropyl groups highlighted in green.

According to the International Union of Pure and Applied Chemistry (IUPAC), alcohols are named by changing the ending of the parent alkane name to *-ol*. Here are some basic IUPAC rules for naming alcohols:

- The longest continuous chain (LCC) of carbon atoms containing the OH group is taken as the parent compound—an alkane with the same number of carbon atoms. The chain is numbered from the end nearest the OH group.
- The number that indicates the position of the OH group is prefixed to the name of the parent hydrocarbon, and the *-e* ending of the parent alkane is replaced by the suffix *-ol*. (In cyclic alcohols, the carbon atom bearing the OH group is designated C1, but the 1 is not used in the name.) Substituents are named and numbered as in alkanes.
- If more than one OH group appears in the same molecule (polyhydroxy alcohols), suffixes such as *-diol* and *-triol* are used. In these cases, the *-e* ending of the parent alkane is retained.

Figure 7.3.1 shows some examples of the application of these rules.

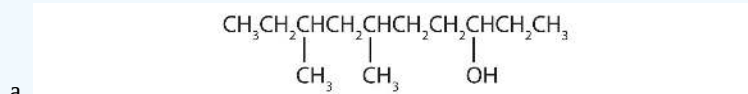
Structures of 2-methylbutan-2-ol, 3,5-dimethylhexan-1-ol, 6-methylheptan-3-ol, 2-bromo-5-chlorocyclopentanol are shown to highlight rules 1 and 2. 1,2-ethanediol and propane-1,2,3-triol are shown to highlight rule 3.

Figure 7.3.1: IUPAC Rules for Alcohols. The names and structures of some alcohols demonstrate the use of IUPAC rules.

✓ Example 7.3.1

Give the IUPAC name for each compound.

From left to right, there are ten carbon on the alkane straight chain with methyl groups emerging from carbon 3 and 5 and a hydroxyl group on carbon 8.

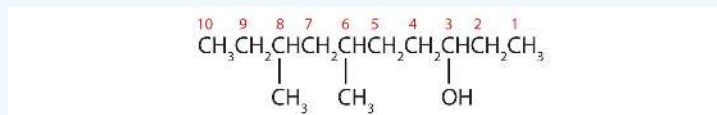


a.

b. HOCH₂CH₂CH₂CH₂CH₂OH

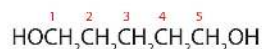
Solution

Ten carbon atoms in the LCC makes the compound a derivative of decane (rule 1), and the OH on the third carbon atom makes it a 3-decanol (rule 2).



The carbon atoms are numbered from the end closest to the OH group. That fixes the two methyl (CH₃) groups at the sixth and eighth positions. The name is 6,8-dimethyl-3-decanol (not 3,5-dimethyl-8-decanol).

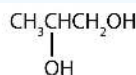
Five carbon atoms in the LCC make the compound a derivative of pentane. Two OH groups on the first and fifth carbon atoms make the compound a diol and give the name 1,5-pentanediol (rule 3).



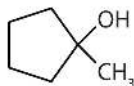
? Exercise 7.3.1

Give the IUPAC name for each compound.

a.



b.



Answer

a. 1,2-propadiol

b. 1-methyl-1-cyclopentanol

✓ Example 7.3.2

Draw the structure for each compound.

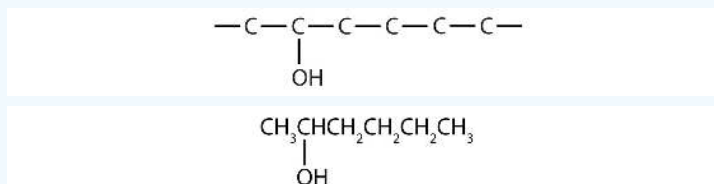
a. 2-hexanol

b. 3-methyl-2-pentanol

Solution

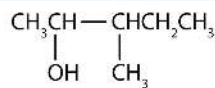
a. The ending *-ol* indicates an alcohol (the OH functional group), and the *hex-* stem tells us that there are six carbon atoms in the LCC. We start by drawing a chain of six carbon atoms: —C—C—C—C—C—C— .

The 2 indicates that the OH group is attached to the second carbon atom.



- b. The ending *-ol* indicates an alcohol (the OH functional group), and the *pen-* stem tells us that there are six carbon atoms in the LCC. We start by drawing a chain of five carbon atoms: --C--C--C--C--C-- . The numbers indicate that there is a methyl (CH_3) group on the third carbon atom and an OH group on the second carbon atom.

The 3- indicates there is a methyl- on carbon 3 and the 2- indicates that the -OH is attached to carbon 2.



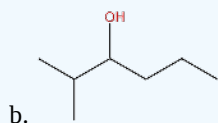
? Exercise 7.3.1

Draw the structure for each compound.

- 3-heptanol
- 2-methyl-3-hexanol

Answer

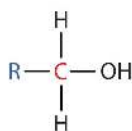
a.  3-Heptanol | C7H16O | ChemSpider



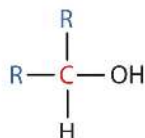
7.3.2 Classification of Alcohols

Some of the properties of alcohols depend on the number of carbon atoms attached to the specific carbon atom that is attached to the OH group. Alcohols can be grouped into three classes on this basis.

- A primary (1°) alcohol is one in which the carbon atom (in red) with the OH group is attached to *one* other carbon atom (in blue). Its general formula is RCH_2OH .



- A secondary (2°) alcohol is one in which the carbon atom (in red) with the OH group is attached to *two* other carbon atoms (in blue). Its general formula is R_2CHOH .



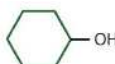
- A tertiary (3°) alcohol is one in which the carbon atom (in red) with the OH group is attached to *three* other carbon atoms (in blue). Its general formula is R_3COH .



Table 7.3.1 names and classifies some of the simpler alcohols. Some of the common names reflect a compound's classification as secondary (*sec*-) or tertiary (*tert*-). These designations are not used in the IUPAC nomenclature system for alcohols. Note that there are four butyl alcohols in the table, corresponding to the four butyl groups: the butyl group ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$) discussed before, and three others:



Table 7.3.1: Classification and Nomenclature of Some Alcohols

Condensed Structural Formula	Class of Alcohol	Common Name	IUPAC Name
CH_3OH	—	methyl alcohol	methanol
$\text{CH}_3\text{CH}_2\text{OH}$	primary	ethyl alcohol	ethanol
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	primary	propyl alcohol	1-propanol
$(\text{CH}_3)_2\text{CHOH}$	secondary	isopropyl alcohol	2-propanol
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	primary	butyl alcohol	1-butanol
$\text{CH}_3\text{CH}_2\text{CHOHCH}_3$	secondary	<i>sec</i> -butyl alcohol	2-butanol
$(\text{CH}_3)_2\text{CHCH}_2\text{OH}$	primary	isobutyl alcohol	2-methyl-1-propanol
$(\text{CH}_3)_3\text{COH}$	tertiary	<i>tert</i> -butyl alcohol	2-methyl-2-propanol
	secondary	cyclohexyl alcohol	cyclohexanol

Summary

In the IUPAC system, alcohols are named by changing the ending of the parent alkane name to *-ol*. Alcohols are classified according to the number of carbon atoms attached to the carbon atom that is attached to the OH group.

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7.4: Physical Properties of Alcohols

Learning Objectives

- Explain why the boiling points of alcohols are higher than those of ethers and alkanes of similar molar masses.
- Explain why alcohols and ethers of four or fewer carbon atoms are soluble in water while comparable alkanes are not soluble.

Alcohols can be considered derivatives of water (H_2O ; also written as HOH).



Like the $\text{H}-\text{O}-\text{H}$ bond in water, the $\text{R}-\text{O}-\text{H}$ bond is bent, and alcohol molecules are polar. This relationship is particularly apparent in small molecules and reflected in the physical and chemical properties of alcohols with low molar mass. Replacing a hydrogen atom from an alkane with an OH group allows the molecules to associate through hydrogen bonding (Figure 7.4.1).

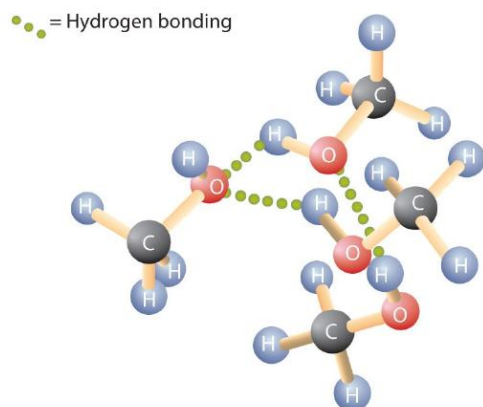


Figure 7.4.1: Intermolecular Hydrogen Bonding in Methanol. The OH groups of alcohol molecules make hydrogen bonding possible.

Recall that physical properties are determined to a large extent by the type of intermolecular forces. Table 7.4.1 lists the molar masses and the boiling points of some common compounds. The table shows that substances with similar molar masses can have quite different boiling points.

Table 7.4.1: Comparison of Boiling Points and Molar Masses

Formula	Name	Molar Mass	Boiling Point ($^{\circ}\text{C}$)
CH_4	methane	16	-164
HOH	water	18	100
C_2H_6	ethane	30	-89
CH_3OH	methanol	32	65
C_3H_8	propane	44	-42
$\text{CH}_3\text{CH}_2\text{OH}$	ethanol	46	78
C_4H_{10}	butane	58	-1
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	1-propanol	60	97

Alkanes are nonpolar and are thus associated only through relatively weak dispersion forces. Alkanes with one to four carbon atoms are gases at room temperature. In contrast, even methanol (with one carbon atom) is a liquid at room temperature. Hydrogen

bonding greatly increases the boiling points of alcohols compared to hydrocarbons of comparable molar mass. The boiling point is a rough measure of the amount of energy necessary to separate a liquid molecule from its nearest neighbors. If the molecules interact through hydrogen bonding, a relatively large quantity of energy must be supplied to break those intermolecular attractions. Only then can the molecule escape from the liquid into the gaseous state.

Alcohols can also engage in hydrogen bonding with water molecules (Figure 7.4.2). Thus, whereas the hydrocarbons are insoluble in water, alcohols with one to three carbon atoms are completely soluble. As the length of the chain increases, however, the solubility of alcohols in water decreases; the molecules become more like hydrocarbons and less like water. The alcohol 1-decanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$) is essentially insoluble in water. We frequently find that the borderline of solubility in a family of organic compounds occurs at four or five carbon atoms.

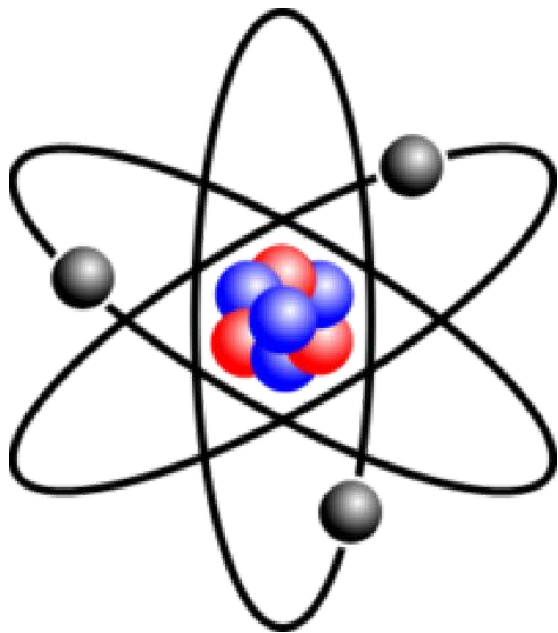


Figure 7.4.2: Hydrogen Bonding between Methanol Molecules and Water Molecules. Hydrogen bonding between the OH of methanol and water molecules accounts for the solubility of methanol in water.

Summary

Alcohols have higher boiling points than do ethers and alkanes of similar molar masses because the OH group allows alcohol molecules to engage in hydrogen bonding. Alcohols of four or fewer carbon atoms are soluble in water because the alcohol molecules engage in hydrogen bonding with water molecules; comparable alkane molecules cannot engage in hydrogen bonding.

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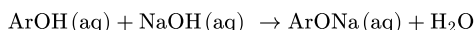
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7.5: Phenols

Learning Objectives

- To describe the structure and uses of some phenols

Compounds in which an OH group is attached directly to an aromatic ring are designated ArOH and called phenols. Phenols differ from alcohols in that they are slightly acidic in water. They react with aqueous sodium hydroxide (NaOH) to form salts.



The parent compound, C₆H₅OH, is itself called phenol. (An old name, emphasizing its slight acidity, was *carbolic acid*.) Phenol is a white crystalline compound that has a distinctive (“hospital smell”) odor.

Figure 7.5.1: (Left) Structure of Phenol (right) Approximately two grams of phenol in glass vial. from Wikipedia

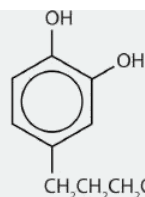
To Your Health: Phenols and Us

Phenols are widely used as antiseptics (substances that kill microorganisms on living tissue) and as disinfectants (substances intended to kill microorganisms on inanimate objects such as furniture or floors). The first widely used antiseptic was phenol. Joseph Lister used it for antiseptic surgery in 1867. Phenol is toxic to humans, however, and can cause severe burns when applied to the skin. In the bloodstream, it is a systemic poison—that is, one that is carried to and affects all parts of the body. Its severe side effects led to searches for safer antiseptics, a number of which have been found.



An operation in 1753, painted by Gaspare Traversi, of a surgery before antiseptics were used.

One safer phenolic antiseptic is 4-hexylresorcinol (4-hexyl-1,3-dihydroxybenzene; resorcinol is the common name for 1,3-dihydroxybenzene, and 4-hexylresorcinol has a hexyl group on the fourth carbon atom of the resorcinol ring). It is much more powerful than phenol as a germicide and has fewer undesirable side effects. Indeed, it is safe enough to be used as the active ingredient in some mouthwashes and throat lozenges.



The compound 4-hexylresorcinol is mild enough to be used as the active ingredient in antiseptic preparations for use on the skin.

The compound 4-hexylresorcinol is mild enough to be used as the active ingredient in antiseptic preparations for use on the skin.

Summary

Phenols are compounds in which an OH group is attached directly to an aromatic ring. Many phenols are used as antiseptics.

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7.6: Ethers

Learning Objectives

- Describe the structural difference between an alcohol and an ether that affects physical characteristics and reactivity of each.
- Name simple ethers.
- Describe the structure and uses of some ethers.

With the general formula ROR' , an ether may be considered a derivative of water in which both hydrogen atoms are replaced by alkyl or aryl groups. It may also be considered a derivative of an alcohol (ROH) in which the hydrogen atom of the OH group is been replaced by a second alkyl or aryl group:



Simple ethers have simple common names, formed from the names of the groups attached to oxygen atom, followed by the generic name *ether*. For example, $CH_3-O-CH_2CH_2CH_3$ is methyl propyl ether. If both groups are the same, the group name should be preceded by the prefix *di-*, as in dimethyl ether (CH_3-O-CH_3) and diethyl ether $CH_3CH_2-O-CH_2CH_3$.

Ether molecules have no hydrogen atom on the oxygen atom (that is, no OH group). Therefore there is no intermolecular hydrogen bonding between ether molecules, and ethers therefore have quite low boiling points for a given molar mass. Indeed, ethers have boiling points about the same as those of alkanes of comparable molar mass and much lower than those of the corresponding alcohols (Table 7.6.1).

Table 7.6.1: Comparison of Boiling Points of Alkanes, Alcohols, and Ethers

Condensed Structural Formula	Name	Molar Mass	Boiling Point ($^{\circ}C$)	Intermolecular Hydrogen Bonding in Pure Liquid?
$CH_3CH_2CH_3$	propane	44	-42	no
CH_3OCH_3	dimethyl ether	46	-25	no
CH_3CH_2OH	ethyl alcohol	46	78	yes
$CH_3CH_2CH_2CH_2CH_3$	pentane	72	36	no
$CH_3CH_2OCH_2CH_3$	diethyl ether	74	35	no
$CH_3CH_2CH_2CH_2OH$	butyl alcohol	74	117	yes

Ether molecules do have an oxygen atom, however, and engage in hydrogen bonding with water molecules. Consequently, an ether has about the same solubility in water as the alcohol that is isomeric with it. For example, dimethyl ether and ethanol (both having the molecular formula C_2H_6O) are completely soluble in water, whereas diethyl ether and 1-butanol (both $C_4H_{10}O$) are barely soluble in water (8 g/100 mL of water).

✓ Example 7.6.1

What is the common name for each ether?

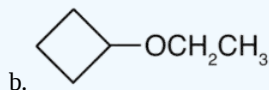
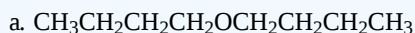
- a. $CH_3CH_2CH_2OCH_2CH_2CH_3$
 CH_3CHOCH_3
 $|$
 CH_3
- b.

Solution

- a. The carbon groups on either side of the oxygen atom are propyl ($CH_3CH_2CH_2$) groups, so the compound is dipropyl ether.
- b. The three-carbon group is attached by the middle carbon atom, so it is an isopropyl group. The one-carbon group is a methyl group. The compound is isopropyl methyl ether.

? Exercise 7.6.1

What is the common name for each ether?



Answer

a. dibutylether

b. cyclobutyl ethyl ether

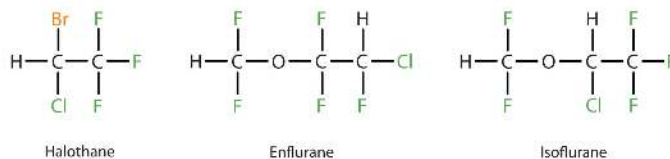
📌 To Your Health: Ethers as General Anesthetics

A *general anesthetic* acts on the brain to produce unconsciousness and a general insensitivity to feeling or pain. Diethyl ether ($\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$) was the first general anesthetic to be used.



William Morton, a Boston dentist, introduced diethyl ether into surgical practice in 1846. This painting shows an operation in Boston in 1846 in which diethyl ether was used as an anesthetic. Inhalation of ether vapor produces unconsciousness by depressing the activity of the central nervous system. Source: Painting of William Morton by Ernest Board.

Diethyl ether is relatively safe because there is a fairly wide gap between the dose that produces an effective level of anesthesia and the lethal dose. However, because it is highly flammable and has the added disadvantage of causing nausea, it has been replaced by newer inhalant anesthetics, including the fluorine-containing compounds halothane, enflurane, and isoflurane. Unfortunately, the safety of these compounds for operating room personnel has been questioned. For example, female operating room workers exposed to halothane suffer a higher rate of miscarriages than women in the general population.



These three modern, inhalant, halogen-containing, anesthetic compounds are less flammable than diethyl ether.

Summary

To give ethers common names, simply name the groups attached to the oxygen atom, followed by the generic name *ether*. If both groups are the same, the group name should be preceded by the prefix *di-*. Ether molecules have no OH group and thus no intermolecular hydrogen bonding. Ethers therefore have quite low boiling points for a given molar mass. Ether molecules have an

oxygen atom and can engage in hydrogen bonding with water molecules. An ether molecule has about the same solubility in water as the alcohol that is isomeric with it.

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7.7: Aldehydes and Ketones- Structure and Names

Learning Objectives

- Identify the general structure for an aldehyde and a ketone.
- Use common names to name aldehydes and ketones.
- Use the IUPAC system to name aldehydes and ketones.

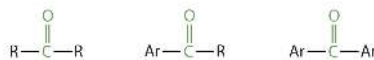
The next functional group we consider, the carbonyl group, has a carbon-to-oxygen double bond.



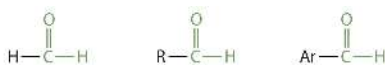
Carbonyl groups define two related families of organic compounds: the aldehydes and the ketones.

The carbonyl group is ubiquitous in biological compounds. It is found in carbohydrates, fats, proteins, nucleic acids, hormones, and vitamins—organic compounds critical to living systems.

In a ketone, two carbon groups are attached to the carbonyl carbon atom. The following general formulas, in which R represents an alkyl group and Ar stands for an aryl group, represent ketones.



In an aldehyde, at least one of the attached groups must be a hydrogen atom. The following compounds are aldehydes:

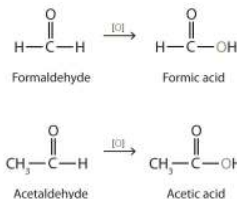


In condensed formulas, we use CHO to identify an aldehyde rather than COH, which might be confused with an alcohol. This follows the general rule that in condensed structural formulas H comes after the atom it is attached to (usually C, N, or O).

The carbon-to-oxygen double bond is not shown but understood to be present. Because they contain the same functional group, aldehydes and ketones share many common properties, but they still differ enough to warrant their classification into two families.

7.7.1 Naming Aldehydes and Ketones

Both common and International Union of Pure and Applied Chemistry (IUPAC) names are frequently used for aldehydes and ketones, with common names predominating for the lower homologs. The common names of aldehydes are taken from the names of the acids into which the aldehydes can be converted by *oxidation*.



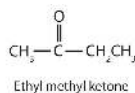
The stems for the common names of the first four aldehydes are as follows:

- 1 carbon atom: *form-*
- 2 carbon atoms: *acet-*
- 3 carbon atoms: *propion-*
- 4 carbon atoms: *butyr-*

Because the carbonyl group in a ketone must be attached to two carbon groups, the simplest ketone has three carbon atoms. It is widely known as *acetone*, a unique name unrelated to other common names for ketones.



Generally, the common names of ketones consist of the names of the groups attached to the carbonyl group, followed by the word *ketone*. (Note the similarity to the naming of ethers.) Another name for acetone, then, is *dimethyl ketone*. The ketone with four carbon atoms is ethyl methyl ketone.



✓ Example 7.7.1

Classify each compound as an aldehyde or a ketone. Give the common name for each ketone.

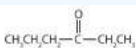
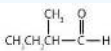
- $\text{CH}_3\text{CH}_2\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$
- $\text{CH}_3\text{CH}_2\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2\text{CH}_2\text{CH}_3$
- $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\underset{\text{CH}_3}{\text{CH}}\text{CH}_3$

Solution

1. This compound has the carbonyl group on an end carbon atom, so it is an aldehyde.
2. This compound has the carbonyl group on an interior carbon atom, so it is a ketone. Both alkyl groups are propyl groups. The name is therefore dipropyl ketone.
3. This compound has the carbonyl group between two alkyl groups, so it is a ketone. One alkyl group has three carbon atoms and is attached by the middle carbon atom; it is an isopropyl group. A group with one carbon atom is a methyl group. The name is therefore isopropyl methyl ketone.

? Exercise 7.7.1

Classify each compound as an aldehyde or a ketone. Give the common name for each ketone.

1. 
2. 

Answer

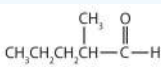
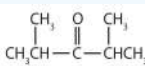
1. 3-hexanone
2. 2-methylbutanal

Here are some simple IUPAC rules for naming aldehydes and ketones:

- The stem names of aldehydes and ketones are derived from those of the parent alkanes, defined by the longest continuous chain (LCC) of carbon atoms that contains the functional group.
- For an aldehyde, drop the *-e* from the alkane name and add the ending *-al*. Methanal is the IUPAC name for formaldehyde, and ethanal is the name for acetaldehyde.
- For a ketone, drop the *-e* from the alkane name and add the ending *-one*. Propanone is the IUPAC name for acetone, and butanone is the name for ethyl methyl ketone.
- To indicate the position of a substituent on an aldehyde, the carbonyl carbon atom is always considered to be C1; it is unnecessary to designate this group by number.
- To indicate the position of a substituent on a ketone, number the chain in the manner that gives the carbonyl carbon atom the lowest possible number. In cyclic ketones, it is understood that the carbonyl carbon atom is C1.

✓ Example 7.7.2

Give the IUPAC name for each compound.

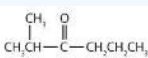
- a. 
- b. 
- c. 

Solution

- a. There are five carbon atoms in the LCC. The methyl group (CH₃) is a substituent on the second carbon atom of the chain; the aldehyde carbon atom is always C1. The name is derived from pentane. Dropping the *-e* and adding the ending *-al* gives pentanal. The methyl group on the second carbon atom makes the name 2-methylpentanal.
- b. There are five carbon atoms in the LCC. The carbonyl carbon atom is C3, and there are methyl groups on C2 and C4. The IUPAC name is 2,4-dimethyl-3-pentanone.
- c. There are six carbon atoms in the ring. The compound is cyclohexanone. No number is needed to indicate the position of the carbonyl group because all six carbon atoms are equivalent.

? Exercise 7.7.1

Give the IUPAC name for each compound.

- a. 
- b. 
- c. 

Answer

- a. 2,3-dimethylbutanal
- b. 2-methyl-3-hexanone
- c. cyclobutanone

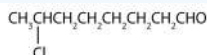
✓ Example 7.7.3

Draw the structure for each compound.

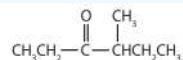
- a. 7-chlorooctanal
- b. 4-methyl-3-hexanone

Solution

- a. The *octan-* part of the name tells us that the LCC has eight carbon atoms. There is a chlorine (Cl) atom on the seventh carbon atom; numbering from the carbonyl group and counting the carbonyl carbon atom as C1, we place the Cl atom on the seventh carbon atom.



- b. The *hexan-* part of the name tells us that the LCC has six carbon atoms. The 3 means that the carbonyl carbon atom is C3 in this chain, and the 4 tells us that there is a methyl (CH_3) group at C4:

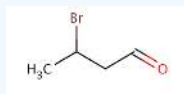


? Exercise 7.7.1

Draw the structure for each compound.

- 3-bromo-butanal
- 7-bromo-4-methyl-2-heptanone

Answer



a.

b.  7-Bromo-4-methyl-2-heptanone | C8H15BrO | ChemSpider

Summary

The common names of aldehydes are taken from the names of the corresponding carboxylic acids: formaldehyde, acetaldehyde, and so on. The common names of ketones, like those of ethers, consist of the names of the groups attached to the carbonyl group, followed by the word *ketone*. Stem names of aldehydes and ketones are derived from those of the parent alkanes, using an *-al* ending for an aldehydes and an *-one* ending for a ketone.

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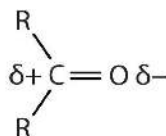


7.8: Properties of Aldehydes and Ketones

Learning Objectives

- Explain why the boiling points of aldehydes and ketones are higher than those of ethers and alkanes of similar molar masses but lower than those of comparable alcohols.
- Compare the solubilities in water of aldehydes and ketones of four or fewer carbon atoms with the solubilities of comparable alkanes and alcohols.
- Name the typical reactions take place with aldehydes and ketones.
- Describe some of the uses of common aldehydes and ketones.

The carbon-to-oxygen double bond is quite polar, more polar than a carbon-to-oxygen single bond. The electronegative oxygen atom has a much greater attraction for the bonding electron pairs than does the carbon atom. The carbon atom has a partial positive charge, and the oxygen atom has a partial negative charge:



In aldehydes and ketones, this charge separation leads to dipole-dipole interactions that are great enough to significantly affect the boiling points. Table 7.8.1 shows that the polar single bonds in ethers have little such effect, whereas hydrogen bonding between alcohol molecules is even stronger.

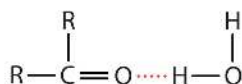
Table 7.8.1: Boiling Points of Compounds Having Similar Molar Masses but Different Types of Intermolecular Forces

Compound	Family	Molar Mass	Type of Intermolecular Forces	Boiling Point (°C)
CH ₃ CH ₂ CH ₂ CH ₃	alkane	58	dispersion only	-1
CH ₃ OCH ₂ CH ₃	ether	60	weak dipole	6
CH ₃ CH ₂ CHO	aldehyde	58	strong dipole	49
CH ₃ CH ₂ CH ₂ OH	alcohol	60	hydrogen bonding	97

Formaldehyde is a gas at room temperature. Acetaldehyde boils at 20°C; in an open vessel, it boils away in a warm room. Most other common aldehydes are liquids at room temperature.

Although the lower members of the homologous series have pungent odors, many higher aldehydes have pleasant odors and are used in perfumes and artificial flavorings. As for the ketones, acetone has a pleasant odor, but most of the higher homologs have rather bland odors.

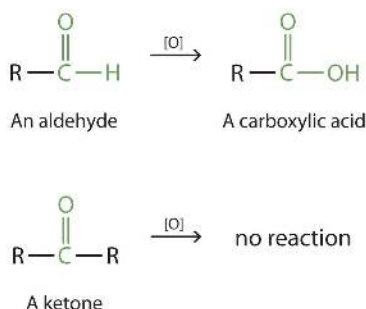
The oxygen atom of the carbonyl group engages in hydrogen bonding with a water molecule.



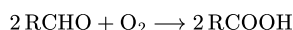
The solubility of aldehydes is therefore about the same as that of alcohols and ethers. Formaldehyde, acetaldehyde, and acetone are soluble in water. As the carbon chain increases in length, solubility in water decreases. The borderline of solubility occurs at about four carbon atoms per oxygen atom. All aldehydes and ketones are soluble in organic solvents and, in general, are less dense than water.

7.8.1 Oxidation of Aldehydes and Ketones

Aldehydes and ketones are much alike in many of their reactions, owing to the presence of the carbonyl functional group in both. They differ greatly, however, in one most important type of reaction: oxidation. Aldehydes are readily oxidized to carboxylic acids, whereas ketones resist oxidation.



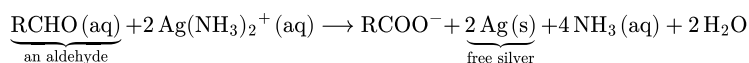
The aldehydes are, in fact, among the most easily oxidized of organic compounds. They are oxidized by oxygen (O_2) in air to carboxylic acids.



The ease of oxidation helps chemists identify aldehydes. A sufficiently mild oxidizing agent can distinguish aldehydes not only from ketones but also from alcohols. **Tollens' reagent**, for example, is an alkaline solution of silver (Ag^+) ion complexed with ammonia (NH_3), which keeps the Ag^+ ion in solution.



When Tollens' reagent oxidizes an aldehyde, the Ag^+ ion is reduced to free silver (Ag).



Deposited on a clean glass surface, the silver produces a mirror (Figure 7.8.1). Ordinary ketones do not react with Tollens' reagent.

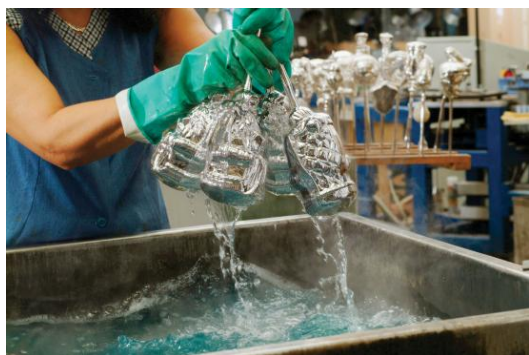


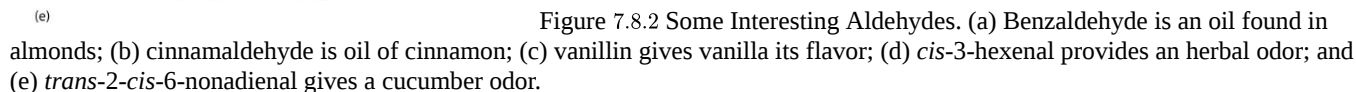
Figure 7.8.1: Aldehyde Reactions. A reaction related to the Tollens' reaction is often used to silver mirrors. These ornaments were silvered by such a reaction. Glucose, a simple sugar with an aldehyde functional group, is used as the reducing agent. Source: Photo courtesy of Krebs Glas Lauscha, commons.wikimedia.org/wiki/File:Silvering.jpg. A person wearing gloves is holding a bunch of ornaments that she has just lifted from a basin containing a solution.

Although ketones resist oxidation by ordinary laboratory oxidizing agents, they undergo combustion, as do aldehydes.

7.8.2 Some Common Carbonyl Compounds

Formaldehyde has an irritating odor. Because of its reactivity, it is difficult to handle in the gaseous state. For many uses, it is therefore dissolved in water and sold as a 37% to 40% aqueous solution called *formalin*. Formaldehyde denatures proteins, rendering them insoluble in water and resistant to bacterial decay. For this reason, formalin is used in embalming solutions and in preserving biological specimens.

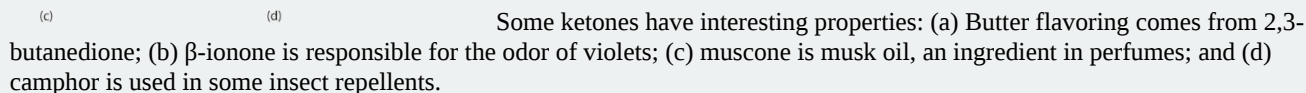
Acetaldehyde is an extremely volatile, colorless liquid. It is a starting material for the preparation of many other organic compounds. Acetaldehyde is formed as a metabolite in the fermentation of sugars and in the detoxification of alcohol in the liver. Aldehydes are the active components of many other familiar materials (Figure 7.8.2).



Acetone is the simplest and most important ketone. Because it is miscible with water as well as with most organic solvents, its chief use is as an industrial solvent (for example, for paints and lacquers). It is also the chief ingredient in some brands of nail polish remover.

Acetone is formed in the human body as a by-product of lipid metabolism. Normally, acetone does not accumulate to an appreciable extent because it is oxidized to carbon dioxide and water. The normal concentration of acetone in the human body is less than 1 mg/100 mL of blood. In certain disease states, such as uncontrolled diabetes mellitus, the acetone concentration rises to higher levels. It is then excreted in the urine, where it is easily detected. In severe cases, its odor can be noted on the breath.

Ketones are also the active components of other familiar substances, some of which are noted in the accompanying figure.



Certain steroid hormones have the ketone functional group as a part of their structure. Two examples are progesterone, a hormone secreted by the ovaries that stimulates the growth of cells in the uterine wall and prepares it for attachment of a fertilized egg, and testosterone, the main male sex hormone. These and other sex hormones affect our development and our lives in fundamental ways.

Summary

The polar carbon-to-oxygen double bond causes aldehydes and ketones to have higher boiling points than those of ethers and alkanes of similar molar masses but lower than those of comparable alcohols that engage in intermolecular hydrogen bonding. Aldehydes are readily oxidized to carboxylic acids, whereas ketones resist oxidation.

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7.S: Organic Compounds of Oxygen (Summary)

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

A **functional group** is any atom or atom group that confers characteristic properties to a family of compounds.

The hydroxyl group (OH) is the functional group of the **alcohols**. The alcohols are represented by the general formula ROH. Alcohols are derived from alkanes by replacing one or more hydrogen atoms by an OH group. A **primary (1°) alcohol** (RCH_2OH) has the OH group on a carbon atom attached to one other carbon atom; a **secondary (2°) alcohol** (R_2CHOH) has the OH group on a carbon atom attached to two other carbon atoms; and a **tertiary (3°) alcohol** (R_3COH) has the OH group on a carbon atom attached to three other carbon atoms.

The ability to engage in hydrogen bonding greatly increases the boiling points of alcohols compared to hydrocarbons of comparable molar mass. Alcohols can also engage in hydrogen bonding with water molecules, and those with up to about four carbon atoms are soluble in water.

Many alcohols can be synthesized by the hydration of alkenes. Common alcohols include methanol, ethanol, and isopropyl alcohol. Methanol is quite poisonous. It can cause blindness or even death. Ethanol can be prepared from ethylene or made by fermentation. It is the “alcohol” in alcoholic beverages. On occasion, people drink methanol by mistake, thinking it is the beverage alcohol. On occasion, unscrupulous bootleggers, sell methanol to unsuspecting customers. In either case, the results are often tragic.

Rubbing alcohol is usually a 70% aqueous solution of isopropyl alcohol. Ethanol is also used in some rubbing alcohol formulations.

When water is removed from an alcohol in a dehydration step, the result is either an alkene or an ether, depending on the reaction conditions. Primary alcohols are oxidized to aldehydes or carboxylic acids, and secondary alcohols are oxidized to ketones. Tertiary alcohols are not easily oxidized.

Phenols (ArOH) are compounds having the OH group attached to an aromatic ring.

Ethers (ROR' , ROAr , ArOAr) are compounds in which an oxygen atom is joined to two organic groups.

The **carbonyl group**, a carbon-to-oxygen double bond, is the defining feature of **aldehydes** and **ketones**. In aldehydes at least one bond on the carbonyl group is a carbon-to-hydrogen bond; in ketones, both available bonds on the carbonyl carbon atom are carbon-to-carbon bonds. Aldehydes are synthesized by the oxidation of primary alcohols. The aldehyde can be further oxidized to a carboxylic acid. Ketones are prepared by the oxidation of secondary alcohols. Mild oxidizing agents oxidize aldehydes to carboxylic acids. Ketones are not oxidized by these reagents.

A **thiol** is a compound with an SH functional group, this will be addressed later when we address proteins as macromolecules.

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CHAPTER OVERVIEW

8: Acids and Bases

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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.

[8.1: Brønsted-Lowry Definition of Acids and Bases](#)

[8.2: Water is both an Acid and a Base](#)

[8.3: The Strengths of Acids and Bases](#)

[8.4: pH and Kw](#)

[8.5: Buffers](#)

[8.6: Chapter Summary](#)

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8.1: Brønsted-Lowry Definition of Acids and Bases

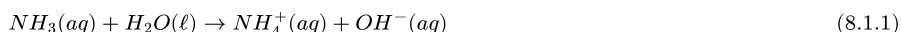
Learning Objectives

1. Recognize a compound as a Brønsted-Lowry acid or a Brønsted-Lowry base.
2. Illustrate the proton transfer process that defines a Brønsted-Lowry acid-base reaction.

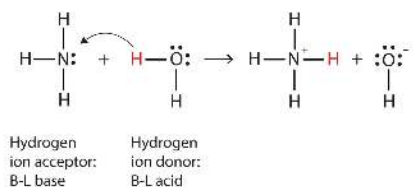
Ammonia (NH_3) increases the hydroxide ion concentration in aqueous solution by reacting with water rather than releasing hydroxide ions directly. In fact, the Arrhenius definitions of an acid and a base focus on hydrogen ions and hydroxide ions. Are there more fundamental definitions for acids and bases?

In 1923, the Danish scientist Johannes Brønsted and the English scientist Thomas Lowry independently proposed new definitions for acids and bases. Rather than considering both hydrogen and hydroxide ions, they focused on the hydrogen ion only. A Brønsted-Lowry acid is a compound that supplies a hydrogen ion in a reaction. A Brønsted-Lowry base, conversely, is a compound that accepts a hydrogen ion in a reaction. Thus, the Brønsted-Lowry definitions of an acid and a base focus on the movement of hydrogen ions in a reaction, rather than on the production of hydrogen ions and hydroxide ions in an aqueous solution.

Let us use the reaction of ammonia in water to demonstrate the Brønsted-Lowry definitions of an acid and a base. Ammonia and water molecules are reactants, while the ammonium ion and the hydroxide ion are products:



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.

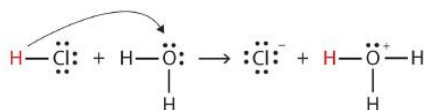
Is an Arrhenius acid like hydrochloric acid still an acid in the Brønsted-Lowry sense? Yes, but it requires us to understand what really happens when HCl is dissolved in water. Recall that the hydrogen *atom* is a single proton surrounded by a single electron. To make the hydrogen *ion*, we remove the 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 :



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 H₂O 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, **H₂O 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, H₂O 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 H₂O a base in this circumstance.

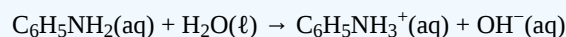
All Arrhenius acids and bases are Brønsted-Lowry acids and bases as well. However, not all Brønsted-Lowry acids and bases are Arrhenius acids and bases.

✓ Example 8.1.1

Aniline (C₆H₅NH₂) is slightly soluble in water. It has a nitrogen atom that can accept a hydrogen ion from a water molecule just like the nitrogen atom in ammonia does. Write the chemical equation for this reaction and identify the Brønsted-Lowry acid and base.

Solution

C₆H₅NH₂ and H₂O are the reactants. When C₆H₅NH₂ accepts a proton from H₂O, it gains an extra H and a positive charge and leaves an OH[−] ion behind. The reaction is as follows:

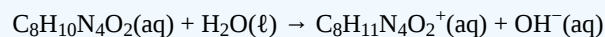


Because C₆H₅NH₂ accepts a proton, it is the Brønsted-Lowry base. The H₂O molecule, because it donates a proton, is the Brønsted-Lowry acid.

? Exercise 8.1.1

Caffeine (C₈H₁₀N₄O₂) is a stimulant found in coffees and teas. When dissolved in water, it can accept a proton from a water molecule. Write the chemical equation for this process and identify the Brønsted-Lowry acid and base.

Answer



B-L base B-L acid

The Brønsted-Lowry definitions of an acid and a base can be applied to chemical reactions that occur in solvents other than water. The following example illustrates.

✓ Example 8.1.2

Sodium amide (NaNH₂) dissolves in methanol (CH₃OH) and separates into sodium ions and amide ions (NH₂[−]). The amide ions react with methanol to make ammonia and the methoxide ion (CH₃O[−]). Write a balanced chemical equation for this process and identify the Brønsted-Lowry acid and base.

Solution

The equation for the reaction is between NH₂[−] and CH₃OH to make NH₃ and CH₃O[−] is as follows:

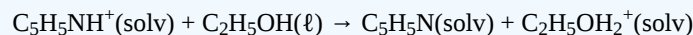


The label (*solv*) indicates that the species are dissolved in some solvent, in contrast to (*aq*), which specifies an aqueous (H₂O) solution. In this reaction, we see that the NH₂[−] ion accepts a proton from a CH₃OH molecule to make an NH₃ molecule. Thus, as the proton acceptor, NH₂[−] is the Brønsted-Lowry base. As the proton donor, CH₃OH is the Brønsted-Lowry acid.

? Exercise 8.1.2

Pyridinium chloride ($\text{C}_5\text{H}_5\text{NHCl}$) dissolves in ethanol ($\text{C}_2\text{H}_5\text{OH}$) and separates into pyridinium ions ($\text{C}_5\text{H}_5\text{NH}^+$) and chloride ions. The pyridinium ion can transfer a hydrogen ion to a solvent molecule. Write a balanced chemical equation for this process and identify the Brønsted-Lowry acid and base.

Answer



B-L acid B-L base

8.1.1 Application in Everyday Life

Many people like to put lemon juice or vinegar, both of which are acids, on cooked fish (Figure 8.1.1). It turns out that fish have volatile amines (bases) in their systems, which are neutralized by the acids to yield involatile ammonium salts. This reduces the odor of the fish, and also adds a “sour” taste that we seem to enjoy.

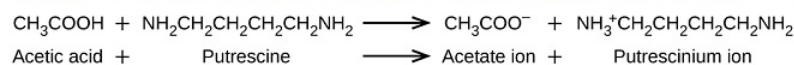


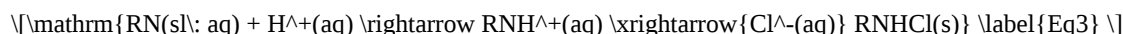
Figure 8.1.1: A neutralization reaction

takes place between citric acid or acetic acid (proton donors) in lemons or vinegar and putrescine (proton acceptor) in the flesh of fish. (CC BY 4.0; OpenStax)

Pickling is a method used to preserve vegetables using a naturally produced acidic environment. The vegetable, such as a cucumber, is placed in a sealed jar submerged in a brine solution. The brine solution favors the growth of beneficial bacteria and suppresses the growth of harmful bacteria. The beneficial bacteria feed on starches in the cucumber and produce lactic acid as a waste product in a process called fermentation. The lactic acid eventually increases the acidity of the brine to a level that kills any harmful bacteria, which require a basic environment. Without the harmful bacteria consuming the cucumbers they are able to last much longer than if they were unprotected. A byproduct of the pickling process changes the flavor of the vegetables with the acid making them taste sour.

8.1.2 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 [$\text{HCl}(\text{aq})$]. 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:



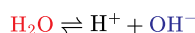
where RN represents some organic compound containing nitrogen. The label (*sl aq*) means “slightly aqueous,” indicating that the compound RN is only slightly soluble. Drugs that are modified in this way are called *hydrochloride salts*. Examples include the powerful painkiller codeine, which is commonly administered as codeine hydrochloride. Acids other than hydrochloric acid are also used. Hydrobromic acid, for example, gives *hydrobromide salts*. Dextromethorphan, an ingredient in many cough medicines, is dispensed as dextromethorphan hydrobromide. The accompanying figure shows another medication (lidocaine) as a hydrochloride salt.



Figure used with permission from Wikipedia.

8.1.3 Conjugate Acid-Base Pairs

According to the Bronsted-Lowry theory of acids and bases, an acid is a proton donor and a base is a proton acceptor. Once an acid has given up a proton, the part that remains is called the acid's **conjugate base**. This species is a base because it can accept a proton (to re-form the acid). The conjugate base of HF (first example below) is fluoride ion, F^- .



Similarly, the part of the base that remains after a base accepts a proton is called the base's **conjugate acid**. This species is an acid because it can give up a proton (and thus re-form the base). The conjugate acid of fluoride ion, F^- (first example below) is HF.



To summarize, the conjugate base of HF is fluoride ion, F^- , and the conjugate acid of fluoride ion, F^- , is HF. The HF/ F^- pair is referred to as a conjugate acid-base pair. The difference in the formulas of a conjugate acid-base pair (example: HF and F^-) is H^+ . The table below lists conjugate acid-base pairs for your reference so that you can figure out the strategy of identifying them. For any given acid or base, you should be able to give its conjugate base or conjugate acid. The formula of an acid's conjugate base is generated by **removing a proton** (H^+) from the acid formula. The formula of the base's conjugate acid is formed by **adding a proton** (H^+) to the formula of the base.

Table 8.1.1. Conjugate acid-base pairs.

Conjugate Acid	Conjugate Base
H_3O^+	H_2O
H_2O	OH^-
H_2SO_4	HSO_4^-
HSO_4^-	SO_4^{2-}
NH_4^+	NH_3

Conjugate Acid	Conjugate Base
NH_3	NH_2^-
CH_3COOH	CH_3COO^-
CH_3NH_3^+	CH_3NH_2

✓ Example 8.1.3 : Conjugate Pairs

Write the formula of the conjugate base of (a) HCl and (b) HCO_3^- .

Write the formula of the conjugate acid of (c) CH_3NH_2 and (d) OH^- .

Solution:

A conjugate base is formed by removing a proton (H^+). A conjugate acid is formed by accepting a proton (H^+).

- After HCl donates a proton, a Cl^- ion is produced, and so Cl^- is the conjugate base.
- After hydrogen carbonate ion, HCO_3^- , donates a proton, its conjugate base, CO_3^{2-} is produced.
- After accepting a proton (H^+), CH_3NH_2 is converted to CH_3NH_3^+ , its conjugate acid.
- After accepting a proton (H^+), OH^- is converted to H_2O , its conjugate acid.

8.1.3 Exercise : Conjugate Pairs

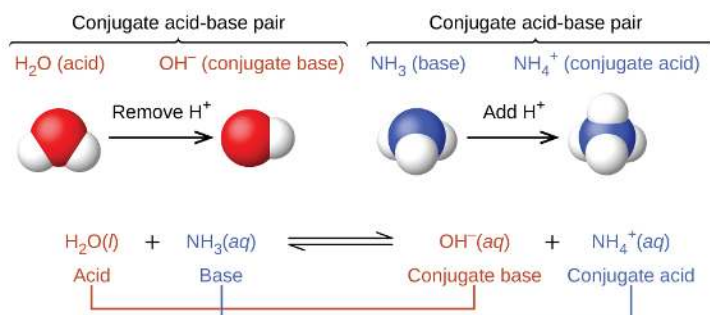
Write the formula of the conjugate base of (a) HNO_2 and (b) H_2CO_3 .

Write the formula of the conjugate acid of (c) $\text{C}_6\text{H}_5\text{NH}_2$ and (d) HCO_3^- .

Answer

- NO_2^- is the conjugate base of HNO_2 .
- HCO_3^- is the conjugate base of H_2CO_3
- $\text{C}_6\text{H}_5\text{NH}_3^+$ is the conjugate acid of $\text{C}_6\text{H}_5\text{NH}_2$.
- H_2CO_3 is the conjugate acid of HCO_3^-

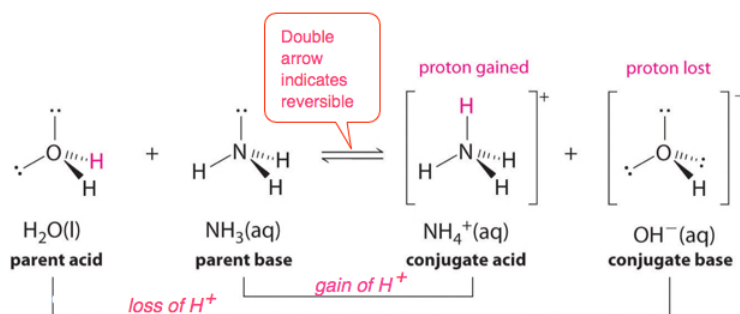
In the reaction of ammonia with water to give ammonium ions and hydroxide ions, ammonia acts as a base by accepting a proton from a water molecule, which in this case means that water is acting as an acid. In the reverse reaction, an ammonium ion acts as an acid by donating a proton to a hydroxide ion, and the hydroxide ion acts as a base. The **conjugate acid-base pairs** for this reaction are $\text{NH}_4^+/\text{NH}_3$ and $\text{H}_2\text{O}/\text{OH}^-$. This means that the conjugate acid of the base NH_3 is NH_4^+ while the conjugate base of the acid NH_4^+ is NH_3 . Similarly, the conjugate base of the acid H_2O is OH^- , and the conjugate acid of the base OH^- is H_2O .



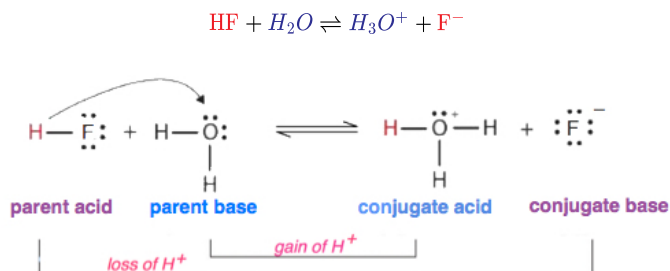
This figure has three parts in two rows. In the first row, two diagrams of acid-base pairs are shown. On the left, a space filling model of H_2O is shown with a red O atom at the center and two smaller white H atoms attached in a bent shape. Above this model is the label " H_2O (acid)" in purple. An arrow points right, which is labeled "Remove H^+ ". To the right is another space filling model with a single red O atom to which a single smaller white H atom is attached. The label in purple above this model reads, " OH^- (conjugate base)". Above both of these red and white models is an upward pointing bracket that is labeled "Conjugate acid-base".

pair.” To the right is a space filling model with a central blue N atom to which three smaller white H atoms are attached in a triangular pyramid arrangement. A label in green above reads “N H subscript 3 (base).” An arrow labeled “Add H superscript plus” points right. To the right of the arrow is another space filling model with a blue central N atom and four smaller white H atoms in a tetrahedral arrangement. The green label above reads “N H subscript 3 superscript plus (conjugate acid).” Above both of these blue and white models is an upward pointing bracket that is labeled “Conjugate acid-base pair.” The second row of the figure shows the chemical reaction, H subscript 2 O (l) is shown in purple, and is labeled below in purple as “acid,” plus N H subscript 3 (a q) in green, labeled below in green as “base,” followed by a double sided arrow and O H superscript negative (a q) in purple, labeled in purple as “conjugate base,” plus N H subscript 4 superscript plus (a q) in green, which is labeled in green as “conjugate acid.” The acid on the left side of the equation is connected to the conjugate base on the right with a purple line. Similarly, the base on the left is connected to the conjugate acid on the right side.

In the **forward** reaction, the parent acid is H₂O and the parent base is NH₃(shown in the illustration below). The acid H₂O loses a proton (H⁺) to form its conjugate base OH⁻. The base NH₃ gains a proton, to produce its conjugate acid NH₄⁺. In the **reverse** reaction, the acid NH₄⁺ loses a proton (H⁺) to form its conjugate base NH₃. The base OH⁻ gains a proton, to produce its conjugate acid H₂O.

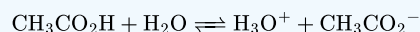


When hydrogen fluoride (HF) dissolves in water and ionizes, protons are transferred from hydrogen fluoride (parent acid) molecules to water (parent base) molecules, yielding hydronium ions (conjugate acid of water) and fluoride ions (conjugate base of HF):



✓ Example 8.1.3

Identify the conjugate acid-base pairs in this equilibrium.

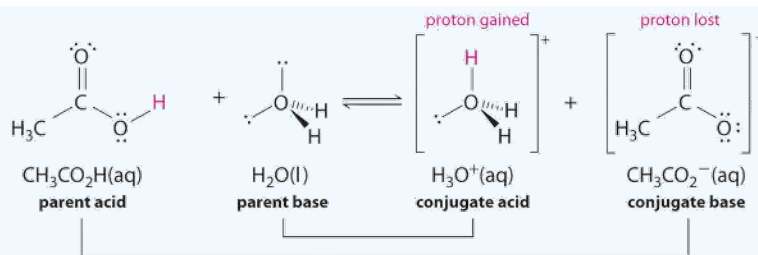


Solution

Similarly, in the reaction of acetic acid with water, acetic acid **donates** a proton to water, which acts as the base. In the reverse reaction, H₃O⁺ is the acid that donates a proton to the acetate ion, which acts as the base.

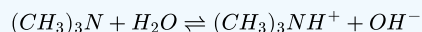
Once again, we have two conjugate acid–base pairs:

- the parent acid and its conjugate base (CH₃CO₂H/CH₃CO₂⁻) and
- the parent base and its conjugate acid (H₃O⁺/H₂O).



✓ Example 8.1.4

Identify the conjugate acid-base pairs in this equilibrium.



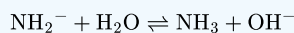
Solution

One pair is H_2O and OH^- , where H_2O has one more H^+ and is the conjugate acid, while OH^- has one less H^+ and is the conjugate base.

The other pair consists of $(\text{CH}_3)_3\text{N}$ and $(\text{CH}_3)_3\text{NH}^+$, where $(\text{CH}_3)_3\text{NH}^+$ is the conjugate acid (it has an additional proton) and $(\text{CH}_3)_3\text{N}$ is the conjugate base.

? Exercise 8.1.4

Identify the conjugate acid-base pairs in this equilibrium.



Answer:

H_2O (acid) and OH^- (base); NH_2^- (base) and NH_3 (acid)

The use of conjugate acid-base pairs allows us to make a very simple statement about relative strengths of acids and bases. *The stronger an acid, the weaker its conjugate base, and, conversely, the stronger a base, the weaker its conjugate acid.*

8.1.4 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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8.2: Water is both an Acid and a Base

Learning Objectives

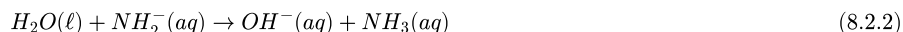
- To write chemical equations for water acting as an acid and as a base.

Water (H_2O) is an interesting compound in many respects. Here, we will consider its ability to behave as an acid or a base.

In some circumstances, a water molecule will accept a proton and thus act as a **Brønsted-Lowry base**. We saw an example in the dissolving of HCl in H_2O :



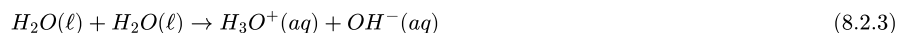
In other circumstances, a water molecule can donate a proton and thus act as a **Brønsted-Lowry acid**. For example, in the presence of the amide ion (see Example 4 in Section 10.2), a water molecule donates a proton, making ammonia as a product:



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:



This process is called the **autoionization of water** (Figure 8.2.1) and occurs in every sample of water, whether it is pure or part of a solution. Autoionization occurs to some extent in any amphiprotic liquid. (For comparison, liquid ammonia undergoes autoionization as well, but only about 1 molecule in a million billion (1 in 10^{15}) reacts with another ammonia molecule.)

Note

It is rare to truly have pure water. Water exposed to air will usually be slightly acidic because dissolved carbon dioxide gas, or carbonic acid, decreases the pH slightly below 7. Alternatively, dissolved minerals, like calcium carbonate (limestone), can make water slightly basic.

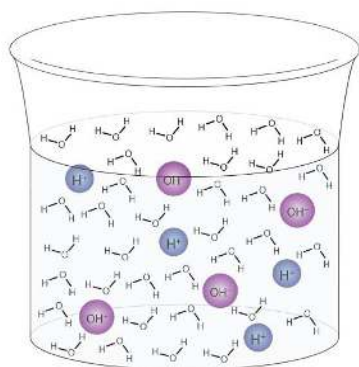


Figure 8.2.1 Autoionization. A small fraction of water molecules—approximately 6 in 100 million—ionize spontaneously into hydronium ions and hydroxide ions. This picture necessarily overrepresents the amount of autoionization that really occurs in pure water.

✓ Example 8.2.1

Identify water as either a Brønsted-Lowry acid or a Brønsted-Lowry base.

1. $\text{H}_2\text{O}(\ell) + \text{NO}_2^-(\text{aq}) \rightarrow \text{HNO}_2(\text{aq}) + \text{OH}^-(\text{aq})$
2. $\text{HC}_2\text{H}_3\text{O}_2(\text{aq}) + \text{H}_2\text{O}(\ell) \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{C}_2\text{H}_3\text{O}_2^-(\text{aq})$

Solution

1. In this reaction, the water molecule donates a proton to the NO_2^- ion, making $\text{OH}^-(\text{aq})$. As the proton donor, H_2O acts as a Brønsted-Lowry acid.
2. In this reaction, the water molecule accepts a proton from $\text{HC}_2\text{H}_3\text{O}_2$, becoming $\text{H}_3\text{O}^+(\text{aq})$. As the proton acceptor, H_2O is a Brønsted-Lowry base.

? Exercise 8.2.2

Identify water as either a Brønsted-Lowry acid or a Brønsted-Lowry base.

1. $\text{HCOOH}(\text{aq}) + \text{H}_2\text{O}(\ell) \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{HCOO}^-(\text{aq})$
2. $\text{H}_2\text{O}(\ell) + \text{PO}_4^{3-}(\text{aq}) \rightarrow \text{OH}^-(\text{aq}) + \text{HPO}_4^{2-}(\text{aq})$

Answer

1. H_2O acts as the proton acceptor (Brønsted-Lowry base)
2. H_2O acts as the proton donor (Brønsted-Lowry acid)

8.2.1 Key Takeaway

- Water molecules can act as both an acid and a base, depending on the conditions.

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8.3: The Strengths of Acids and Bases

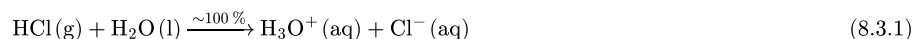
Learning Objectives

- Describe the difference between strong and weak acids and bases.
- Describe how a chemical reaction reaches chemical equilibrium.
- Define the pH scale and use it to describe acids and bases.

Acids and bases do not all demonstrate the same degree of chemical activity in solution. Different acids and bases have different strengths.

8.3.1 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:



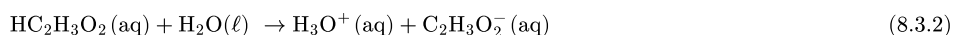
HCl(aq) is one example of a **strong acid**, which is a compound that is essentially **100% ionized** in aqueous solution. There are very few strong acids. The important ones are listed in Table 8.3.1.

Table 8.3.1: Strong Acids and Bases (All in Aqueous Solution)

Acids	Bases
HCl	LiOH
HBr	NaOH
HI	KOH
HNO ₃	Mg(OH) ₂
H ₂ SO 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 8.3.1.

If an acid is **not listed** in Table 8.3.1, 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 (HC₂H₃O₂) is a weak acid. The ionization reaction for acetic acid is as follows:

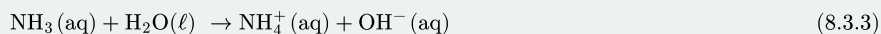


Depending on the concentration of HC₂H₃O₂, the ionization reaction may occur only for 1%–5% of the acetic acid molecules.

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 [HC₂H₃O₂(aq)]. In a medicine chest, one may find a bottle of **vitamin C** tablets; the chemical name of vitamin C is ascorbic acid (HC₆H₇O₆).

One of the more familiar household bases is ammonia (NH₃), 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:



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.

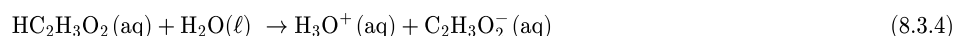


Figure 8.3.1: (left) Bottles of alkaline drain cleaners containing sodium hydroxide can dissolve greases and hair. (right) Chemical burns caused by sodium hydroxide solution photographed 44 hours after exposure. Figures used with permission from Wikipedia.

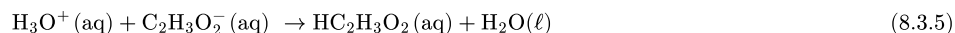
Perhaps the most dangerous household chemical is the lye-based drain cleaner. Lye is a common name for sodium hydroxide, although it is also used as a synonym for potassium hydroxide. Lye is an extremely caustic chemical that can react with grease, hair, food particles, and other substances that may 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.

8.3.2 Chemical Equilibrium in Weak Acids and Bases

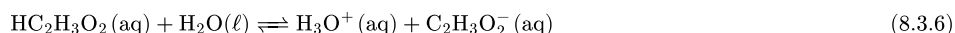
The behavior of **weak acids and bases** illustrates a key concept in chemistry. Does the chemical reaction describing the ionization of a weak acid or base just stop when the acid or base is done ionizing? Actually, no. Rather, the reverse process—the reformation of the molecular form of the acid or base—occurs, ultimately at the same rate as the ionization process. For example, the ionization of the weak acid $\text{HC}_2\text{H}_3\text{O}_2(\text{aq})$ is as follows:



The reverse process also begins to occur:



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:



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 8.3.1: Partial Ionization

Write the equilibrium chemical equation for the partial ionization of each weak acid or base.

- $\text{HNO}_2(\text{aq})$
- $\text{C}_5\text{H}_5\text{N}(\text{aq})$

Solution

- $\text{HNO}_2(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{NO}_2^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
- $\text{C}_5\text{H}_5\text{N}(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{C}_5\text{H}_5\text{NH}^+(\text{aq}) + \text{OH}^-(\text{aq})$

? Exercise 8.3.1

Write the equilibrium chemical equation for the partial ionization of each weak acid or base.

- $\text{HF}(\text{aq})$

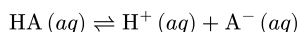
- b. $\text{AgOH}_{(aq)}$
c. $\text{CH}_3\text{NH}_2(aq)$

Answer

- a. $\text{HF}(aq) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{F}^-(aq) + \text{H}_3\text{O}^+(aq)$
b. $\text{AgOH}(aq) \rightleftharpoons \text{Ag}^+(aq) + \text{OH}^-(aq)$
c. $\text{CH}_3\text{NH}_2(aq) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{CH}_3\text{NH}_3^+(aq) + \text{OH}^-(aq)$

8.3.3 Acid Ionization Constant, K_a

The ionization for a general weak acid, HA, can be written as follows:



Because the acid is weak, an equilibrium expression can be written. An **acid ionization constant** (K_a) is the equilibrium constant for the ionization of an acid.

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

The acid ionization represents the fraction of the original acid that has been ionized in solution. Therefore, the numerical value of K_a is a reflection of the strength of the acid. Weak acids with relatively higher K_a values are stronger than acids with relatively lower K_a values. Because strong acids are essentially 100% ionized, the concentration of the acid in the denominator is nearly zero and the K_a value approaches infinity. For this reason, K_a values are generally reported for weak acids only.

The table below is a listing of acid ionization constants for several acids. Note that polyprotic acids have a distinct ionization constant for each ionization step, with each successive ionization constant being smaller than the previous one.

Table 8.3.2: Acid Ionization Constants at 25°C

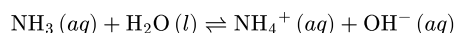
Name of Acid	Ionization Equation	K_a
Sulfuric acid	$\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}^+ + \text{HSO}_4^-$ $\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$	very large 1.3×10^{-2}
Hydrofluoric acid	$\text{HF} \rightleftharpoons \text{H}^+ + \text{F}^-$	7.1×10^{-4}
Nitrous acid	$\text{HNO}_2 \rightleftharpoons \text{H}^+ + \text{NO}_2^-$	4.5×10^{-4}
Benzoic acid	$\text{C}_6\text{H}_5\text{COOH} \rightleftharpoons \text{H}^+ + \text{C}_6\text{H}_5\text{COO}^-$	6.5×10^{-5}
Acetic acid	$\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^-$	1.8×10^{-5}
Carbonic acid	$\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$ $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$	4.2×10^{-7} 4.8×10^{-11}

Hydrofluoric acid $\text{HF}_{(aq)}$ reacts directly with glass (very few chemicals react with glass). Hydrofluoric acid is used in glass etching.

8.3.4 Strong and Weak Bases and Base Ionization Constant, K_b

As with acids, bases can either be strong or weak, depending on their extent of ionization. A **strong base** is a base, which ionizes completely in an aqueous solution. The most common strong bases are soluble metal hydroxide compounds such as potassium hydroxide. Some metal hydroxides are not as strong simply because they are not as soluble. Calcium hydroxide is only slightly soluble in water, but the portion that does dissolve also dissociates into ions.

A **weak base** is a base that ionizes only slightly in an aqueous solution. Recall that a base can be defined as a substance, which accepts a hydrogen ion from another substance. When a weak base such as ammonia is dissolved in water, it accepts an H^+ ion from water, forming the hydroxide ion and the conjugate acid of the base, the ammonium ion.



The equilibrium greatly favors the reactants and the extent of ionization of the ammonia molecule is very small.

An equilibrium expression can be written for the reactions of weak bases with water. Because the concentration of water is extremely large and virtually constant, the water is not included in the expression. A **base ionization constant** (K_b) is the equilibrium constant for the ionization of a base. For ammonia the expression is:

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

The numerical value of K_b is a reflection of the strength of the base. Weak bases with relatively higher K_b values are stronger than bases with relatively lower K_b values. Table 8.3.3 is a listing of base ionization constants for several weak bases.

Table 8.3.3: Base Ionization Constants at 25°C

Name of Base	Ionization Equation	K_b
Methylamine	$\text{CH}_3\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{NH}_3^+ + \text{OH}^-$	5.6×10^{-4}
Ammonia	$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$	1.8×10^{-5}
Pyridine	$\text{C}_5\text{H}_5\text{N} + \text{H}_2\text{O} \rightleftharpoons \text{C}_5\text{H}_5\text{NH}^+ + \text{OH}^-$	1.7×10^{-9}
Acetate ion	$\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^-$	5.6×10^{-10}
Fluoride ion	$\text{F}^- + \text{H}_2\text{O} \rightleftharpoons \text{HF} + \text{OH}^-$	1.4×10^{-11}
Urea	$\text{H}_2\text{NCONH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{NCONH}_3^+ + \text{OH}^-$	1.5×10^{-14}

8.3.5 The Ion-Product of Water

As we have already seen, H_2O can act as an acid or a base. Within any given sample of water, some H_2O molecules are acting as acids, and other H_2O molecules are acting as bases. The chemical equation is as follows:

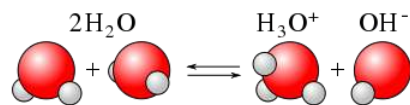
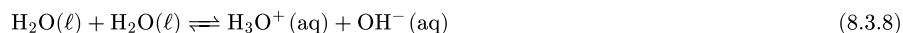
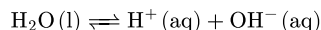


Figure 8.3.2: Autoionization of water, giving hydroxide and hydronium ions.

Similar to a weak acid, the autoionization of water is an equilibrium process, and is more properly written as follows:



We often use the simplified form of the reaction:



The equilibrium constant for the autoionization of water is referred to as the ion-product for water and is given the symbol K_w .

$$K_w = [\text{H}^+][\text{OH}^-]$$

The **ion-product of water** (K_w) is the mathematical product of the concentration of hydrogen ions and hydroxide ions. Note that H_2O is not included in the ion-product expression because it is a pure liquid. The value of K_w is very small, in accordance with a reaction that favors the reactants. At 25°C, the experimentally determined value of K_w in pure water is 1.0×10^{-14} .

$$K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

In a sample of pure water, the concentrations of hydrogen and hydroxide ions are equal to one another. Pure water or any other aqueous solution in which this ratio holds is said to be **neutral**. To find the molarity of each ion, the square root of K_w is taken.

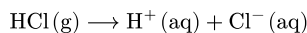
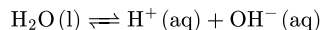
$$[\text{H}^+] = [\text{OH}^-] = 1.0 \times 10^{-7}$$

The product of these two concentrations is 1.0×10^{-14}

$$[\text{H}^+] \times [\text{OH}^-] = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

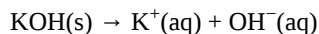
- For acids, the concentration of H^+ or $[\text{H}^+]$ is greater than $1.0 \times 10^{-7} \text{ M}$
- For bases, the concentration of OH^- or $[\text{OH}^-]$ is greater than $1.0 \times 10^{-7} \text{ M}$.

Aqueous HCl is an example of acidic solution. Hydrogen chloride (HCl) ionizes to produce H^+ and Cl^- ions upon dissolving in water. This **increases the concentration of H^+ ions** in the solution. According to **Le Chatelier's principle**, the equilibrium represented by



is **forced to the left**, towards the reactant. As a result, the **concentration of the hydroxide ion decreases**.

Now, consider KOH (aq), a **basic solution**. Solid potassium hydroxide (KOH) dissociates in water to yield potassium ions and hydroxide ions.



The **increase in concentration of the OH^- ions** will cause a decrease in the concentration of the H^+ ions.

No matter whether the aqueous solution is an acid, a base, or neutral: and the ion-product of $[\text{H}^+][\text{OH}^-]$ remains constant.

- For acidic solutions, $[\text{H}^+]$ is greater than $[\text{OH}^-]$.
- For basic solutions, $[\text{OH}^-]$ is greater than $[\text{H}^+]$.
- For neutral solutions, $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$

This means that if you know $[\text{H}^+]$ for a solution, you can calculate what $[\text{OH}^-]$ has to be for the product to equal 1.0×10^{-14} , or if you know $[\text{OH}^-]$, you can calculate $[\text{H}^+]$. This also implies that as one concentration goes up, the other must go down to compensate so that their product always equals the value of K_w .

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \quad (8.3.9)$$

✓ Example 8.3.2

Hydrochloric acid (HCl) is a strong acid, meaning it is 100% ionized in solution. What is the $[\text{H}^+]$ and the $[\text{OH}^-]$ in a solution of $2.0 \times 10^{-3} \text{ M}$ HCl?

Solution

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

Known

- $[\text{HCl}] = 2.0 \times 10^{-3} \text{ M}$
- $K_w = 1.0 \times 10^{-14}$

Unknown

- $[\text{H}^+] = ? \text{ M}$
- $[\text{OH}^-] = ? \text{ M}$

Because HCl is 100% ionized, the concentration of H^+ ions in solution will be equal to the original concentration of HCl. Each HCl molecule that was originally present ionizes into one H^+ ion and one Cl^- ion. The concentration of OH^- can then be determined from the $[\text{H}^+]$ and K_w .

Step 2: Solve.

$$[\text{H}^+] = 2.0 \times 10^{-3} \text{ M}$$

$$K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

$$[\text{OH}^-] = K_w / [\text{H}^+] = 1.0 \times 10^{-14} / 2.0 \times 10^{-3} = 5.0 \times 10^{-12} \text{ M}$$

Step 3: Think about your result.

The $[\text{H}^+]$ is much higher than the $[\text{OH}^-]$ because the solution is acidic. As with other equilibrium constants, the unit for K_w is customarily omitted.

8.3.2 Exercise

Sodium hydroxide (NaOH) is a strong base. What is the $[H^+]$ and the $[OH^-]$ in a 0.001 M NaOH solution at 25 °C?

Answer

$[OH^-] = 0.001M$ or $1 \times 10^{-3}M$; $[H^+] = 1 \times 10^{-11}M$.

8.3.6 The pH Scale

One qualitative measure of the strength of an acid or a base solution is the pH scale, which is based on the concentration of the hydronium (or hydrogen) ion in aqueous solution.

$$pH = -\log[H^+]$$

or

$$pH = -\log[H_3O^+]$$

Figure 8.3.3 illustrates this relationship, along with some examples of various solutions. Because hydrogen ion concentrations are generally less than one (for example $1.3 \times 10^{-3} M$), the log of the number will be a negative number. To make pH even easier to work with, pH is defined as the **negative log of $[H_3O^+]$** , which will give a positive value for pH.

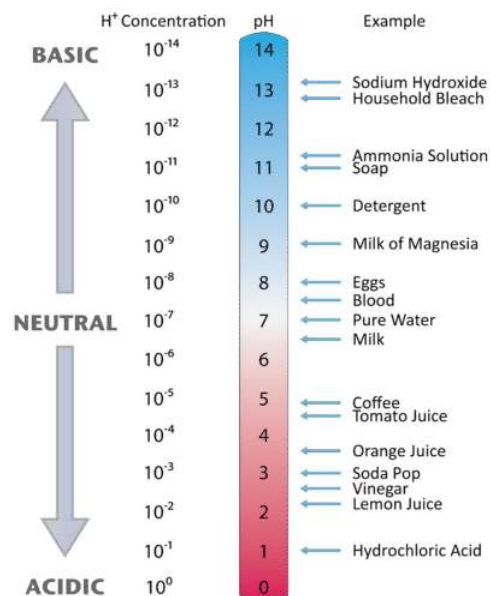


Figure 8.3.3: The relationship between $[H^+]$ and pH values for several common materials.

A neutral (neither acidic nor basic) solution has a pH of 7. A pH below 7 means that a solution is acidic, with lower values of pH corresponding to increasingly acidic solutions. A pH greater than 7 indicates a basic solution, with higher values of pH corresponding to increasingly basic solutions. Thus, given the pH of several solutions, you can state which ones are acidic, which ones are basic, and which are more acidic or basic than others. These are summarized in Table 8.3.4.

Table 8.3.4: Acidic, Basic and Neutral pH Values

Acidic, Basic and Neutral pH Values

Classification	Relative Ion Concentrations	pH at 25 °C
acidic	$[H^+] > [OH^-]$	$pH < 7$
neutral	$[H^+] = [OH^-]$	$pH = 7$
basic	$[H^+] < [OH^-]$	$pH > 7$

✓ Example 8.3.3

Find the pH, given the $[H^+]$ of the following:

- $1 \times 10^{-3} \text{ M}$
- $2.5 \times 10^{-11} \text{ M}$
- $4.7 \times 10^{-9} \text{ M}$

Solution

$$\text{pH} = -\log [H_3O^+]$$

Substitute the known quantity into the equation and solve. Use a scientific calculator for b and c.

- $\text{pH} = -\log [1 \times 10^{-3}] = 3.\underline{0}$ (1 decimal place since 1 has 1 significant figure)
- $\text{pH} = -\log [2.5 \times 10^{-11}] = 10.\underline{60}$ (2 decimal places since 2.5 has 2 significant figures)
- $\text{pH} = -\log [4.7 \times 10^{-9}] = 8.\underline{33}$ (2 decimal places since 4.7 has 2 significant figures)

Note on significant figures:

Because the number(s) before the decimal point in the pH value relate to the power on 10, the number of digits *after* the decimal point (underlined) is what determines the number of significant figures in the final answer.

8.3.3Exercise

Find the pH, given $[H^+]$ of the following:

- $5.8 \times 10^{-4} \text{ M}$
- $1.0 \times 10^{-7} \text{ M}$

Answer

- 3.24
- 7.00

Table 8.3.5 lists the pH of several common solutions. The most acidic among the listed solutions is battery acid with the lowest pH value (0.3). The most basic is 1M NaOH solution with the highest pH value of 14.0. Notice that some biological fluids (stomach acid and urine) are nowhere near neutral. You may also notice that many food products are slightly acidic. They are acidic because they contain solutions of weak acids. If the acid components of these foods were strong acids, the food would likely be inedible.

Table 8.3.5: 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 ₂ O	7

Solution	pH
(human) blood	7.3–7.5
sea water	8
antacid (milk of magnesia)	10.5
NH ₃ (1 M)	11.6
bleach	12.6
NaOH (1 M)	14.0

✓ Example 8.3.4

Label each solution as acidic, basic, or neutral based only on the stated *pH*.

- milk of magnesia, *pH* = 10.5
- pure water, *pH* = 7
- wine, *pH* = 3.0

Solution

- With a *pH* greater than 7, milk of magnesia is basic. (Milk of magnesia is largely Mg(OH)₂.)
- Pure water, with a *pH* of 7, is neutral.
- With a *pH* of less than 7, wine is acidic.

8.3.4 Exercise

Identify each substance as acidic, basic, or neutral based only on the stated *pH*.

- human blood with *pH* = 7.4
- household ammonia with *pH* = 11.0
- cherries with *pH* = 3.6

Answer

- slightly basic
- basic
- acidic

8.3.7 Acid Rain

Normal rainwater has a *pH* between 5 and 6 due to the presence of dissolved CO₂ which forms carbonic acid:



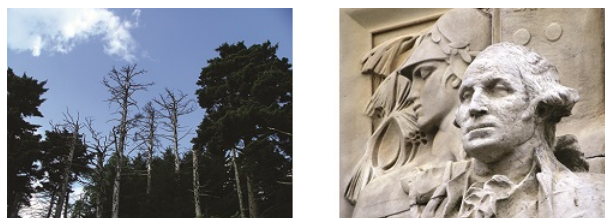
Acid rain is rainwater that has a *pH* of less than 5, due to a variety of nonmetal oxides, including CO₂, SO₂, SO₃, NO, and NO₂ being dissolved in the water and reacting with it to form not only carbonic acid, but sulfuric acid and nitric acid. The formation and subsequent ionization of sulfuric acid are shown here:



Carbon dioxide is naturally present in the atmosphere because we and most other organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or when we burn wood or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also stems from burning fossil fuels, which have traces of sulfur, and from the process of “roasting” ores of metal sulfides in metal-refining processes. Oxides of nitrogen are

formed in internal combustion engines where the high temperatures make it possible for the nitrogen and oxygen in air to chemically combine.

Acid rain is a particular problem in industrial areas where the products of combustion and smelting are released into the air without being stripped of sulfur and nitrogen oxides. In North America and Europe until the 1980s, it was responsible for the destruction of forests and freshwater lakes, when the acidity of the rain actually killed trees, damaged soil, and made lakes uninhabitable for all but the most acid-tolerant species. Acid rain also corrodes statuary and building facades that are made of marble and limestone (Figure 8.3.4). Regulations limiting the amount of sulfur and nitrogen oxides that can be released into the atmosphere by industry and automobiles have reduced the severity of acid damage to both natural and manmade environments in North America and Europe. It is now a growing problem in industrial areas of China and India.



(a)

(b)

Figure 8.3.4: (a) Acid rain makes trees more susceptible to drought and

insect infestation, and depletes nutrients in the soil. (b) It also corrodes statues that are carved from marble or limestone. (credit a: modification of work by Chris M Morris; credit b: modification of work by “Eden, Janine and Jim”/Flickr) Two photos are shown. Photograph a on the left shows the upper portion of trees against a bright blue sky. The tops of several trees at the center of the photograph have bare branches and appear to be dead. Image b shows a statue of a man that appears to from the revolutionary war era in either marble or limestone.

8.3.8 Key Takeaways

- Acids and bases can be strong or weak depending on the extent of ionization in solution.
- Most chemical reactions reach equilibrium at which point there is no net change.
- The ion-product of $[H^+][OH^-]$ in an aqueous solution remains constant.
- A **pH** value is simply the *negative* of the logarithm of the H^+ ion concentration ($-\log[H^+]$).
- The pH scale is used to succinctly communicate the acidity or basicity of a solution.
- A solution is **acidic** if $pH < 7$.
- A solution is **basic** if $pH > 7$.
- A solution is **neutral** if $pH = 7$.

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8.4: pH and Kw

Skills to Develop

- To define the pH scale as a measure of acidity of a solution

Because of its *amphoteric* nature (i.e., acts as both an acid or a base), water does not always remain as H_2O molecules. In fact, two water molecules react to form *hydronium* and hydroxide ions:



This is also called the self-ionization of water. The concentration of H_3O^+ and OH^- are equal in pure water because of the 1:1 stoichiometric ratio of Equation 8.4.1. The molarity of H_3O^+ and OH^- in water are also both $1.0 \times 10^{-7} M$ at $25^\circ C$. Therefore, a constant of water (K_w) is created to show the equilibrium condition for the self-ionization of water. The product of the molarity of hydronium and hydroxide ion is always 1.0×10^{-14} .

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \quad (8.4.2)$$

This equations also applies to all aqueous solutions. However, K_w does change at different temperatures, which affects the pH range discussed below.

Note

H^+ and H_3O^+ is often used interchangeably to represent the hydrated proton, commonly call the *hydronium ion*.

8.4.1 pH

Because K_w is constant (1.0×10^{-14} at $25^\circ C$, the pK_w is 14, the constant of water determines the range of the pH scale. To understand what the pK_w is, it is important to understand first what the "p" means in pOH, and pH. The Danish biochemist Søren Sørensen proposed the term pH to refer to the "potential of hydrogen ion." He defined the "p" as the negative of the logarithm, -log, of $[H^+]$. Therefore the pH is the negative logarithm of the molarity of H. The pOH is the negative logarithm of the molarity of OH^- and the pK_w is the negative logarithm of the constant of water. These definitions give the following equations:

$$pH = -\log[H^+] \quad (8.4.3)$$

$$pOH = -\log[OH^-] \quad (8.4.4)$$

$$pK_w = -\log[K_w] \quad (8.4.5)$$

A logarithm, used in the above equations, of a number is how much a power is raised to a particular base in order to produce that number. To simplify this, look at the equation: $\log_b a = x$. This correlates to $b^x = a$. A simple example of this would be $\log_{10} 100 = 2$, or $10^2 = 100$. It is assumed that the base of Logarithms is ten if it is not stated. So for the sake of pH and pOH problems it will always be ten. When x is a negative number that means you are dividing it by the power. So, if $\log_{10} 0.01 = -2$ which can be written $10^{-2} = 0.01$, then 10^{-2} also means $1/10^2$. The log function can be found on your scientific calculator. Now if we apply this to pH and pOH we can better understand how we calculate the values.

At room temperature,

$$K_w = 1.0 \times 10^{-14} \quad (8.4.6)$$

So

$$pK_w = -\log[1.0 \times 10^{-14}] \quad (8.4.7)$$

Using the properties of logarithms, Equation 8.4.7 can be rewritten as

$$10^{-pK_w} = 10^{-14}. \quad (8.4.8)$$

By substituting, we see that pK_w is 14. The equation also shows that each increasing unit on the scale decreases by the factor of ten on the concentration of H^+ . For example, a pH of 1 has a molarity ten times more concentrated than a solution of pH 2.

Since

$$pK_w = 14 \quad (8.4.9)$$

$$pK_w = pH + pOH = 14 \quad (8.4.10)$$

Note

The pH scale is *logarithmic*, meaning that an increase or decrease of an integer value changes the concentration by a tenfold. For example, a pH of 3 is ten times more acidic than a pH of 4. Likewise, a pH of 3 is one hundred times more acidic than a pH of 5. Similarly a pH of 11 is ten times more basic than a pH of 10.

8.4.2 The Effective Range of the pH Scale

It is common that the pH scale is argued to range from 0-14 or perhaps 1-14 but neither is correct. The pH range does not have an upper nor lower bound, since as defined above, the pH is an indication of concentration of H^+ . For example, at a pH of zero the hydronium ion concentration is one molar, while at pH 14 the hydroxide ion concentration is one molar. Typically the concentrations of H^+ in water in most solutions fall between a range of 1 M (pH=0) and 10^{-14} M (pH=14). Hence a range of 0 to 14 provides sensible (**but not absolute**) "bookends" for the scale (Figure 8.4.1). One can go somewhat below zero and somewhat above 14 in water, because the concentrations of hydronium ions or hydroxide ions can exceed one molar. Figure 1 depicts the pH scale with common solutions and where they are on the scale.

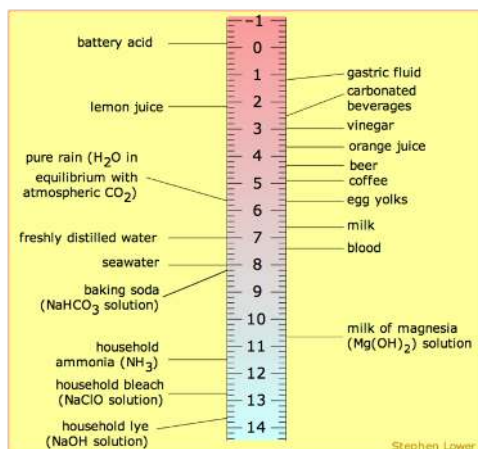


Figure 8.4.1: Solutions and the placement of them on pH scale

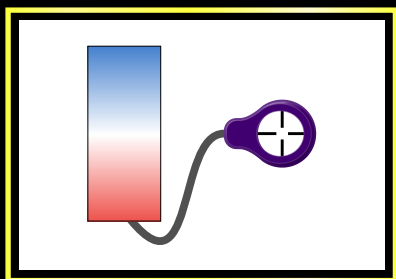
- From the range 7-14, a solution is basic. The pOH should be looked in the perspective of OH^- instead of H^+ . Whenever the value of pOH is greater than 7, then it is considered basic. And therefore there are more OH^- than H^+ in the solution
- At pH 7, the substance or solution is at neutral and means that the concentration of H^+ and OH^- ion is the same.
- From the range 1-7, a solution is acidic. So, whenever the value of a pH is less than 7, it is considered acidic. There are more H^+ than OH^- in an acidic solution.

Note

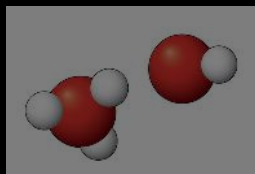
The pH scale does **not** have an upper nor lower bound. Negative pH values are possible

The following PhET simulation helps to build an intuition of the pH scale.

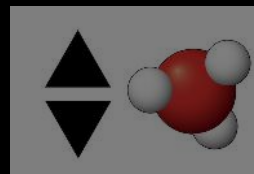
pH Scale



Macro



Micro



My Solution



Example 8.4.1

If the concentration of $NaOH$ in a solution is $2.5 \times 10^{-4} M$, what is the concentration of H_3O^+ ?

SOLUTION

Because

$$1.0 \times 10^{-14} = [H_3O^+][OH^-]$$

to find the concentration of H_3O^+ , solve for the $[H_3O^+]$.

$$\frac{1.0 \times 10^{-14}}{[OH^-]} = [H_3O^+]$$

$$\frac{1.0 \times 10^{-14}}{2.5 \times 10^{-4}} = [H_3O^+] = 4.0 \times 10^{-11} M$$

Example 8.4.2

- Find the pH of a solution of 0.002 M of HCl.
- Find the pH of a solution of 0.00005 M NaOH.

SOLUTION

- The equation for pH is $-\log [H^+]$

$$[H^+] = 2.0 \times 10^{-3} M$$

$$pH = -\log[2.0 \times 10^{-3}] = 2.70$$

b. The equation for pOH is $-\log [\text{OH}^-]$

$$[\text{OH}^-] = 5.0 \times 10^{-5} \text{ M}$$

$$pOH = -\log[5.0 \times 10^{-5}] = 4.30$$

$$pK_w = pH + pOH$$

and

$$pH = pK_w - pOH$$

then

$$pH = 14 - 4.30 = 9.70$$

8.4.3 Living Systems

Molecules that make up or are produced by living organisms usually function within a narrow pH range (near neutral) and a narrow temperature range (body temperature). Many biological solutions, such as blood, have a pH near neutral. pH influences the structure and the function of many enzymes (protein catalysts) in living systems. Many of these enzymes have narrow ranges of pH activity (Table 8.4.1).

Table 8.4.1: pH in Living Systems

Compartment	pH
Gastric Acid	1
Lysosomes	4.5
Granules of Chromaffin Cells	5.5
Human Skin	5.5
Urine	6
Neutral H ₂ O at 37 °C	6.81
Cytosol	7.2
Cerebrospinal Fluid	7.3
Blood	7.43-7.45
Mitochondrial Matrix	7.5
Pancreas Secretions	8.1

Cellular pH is so important that death may occur within hours if a person becomes acidotic (having increased acidity in the blood). As one can see pH is critical to life, biochemistry, and important chemical reactions. Common examples of how pH plays a very important role in our daily lives are given below:

- Water in swimming pool is maintained by checking its pH. Acidic or basic chemicals can be added if the water becomes too acidic or too basic.
- Whenever we get a heartburn, more acid build up in the stomach and causes pain. We need to take antacid tablets (a base) to neutralize excess acid in the stomach.
- The pH of blood is slightly basic. A fluctuation in the pH of the blood can cause serious harm to vital organs in the body.
- Certain diseases are diagnosed only by checking the pH of blood and urine.
- Certain crops thrive better at certain pH range.
- Enzymes activate at a certain pH in our body.

8.4.4 Contributors

- Emmellin Tung (UCD), Sharon Tsao (UCD), Divya Singh (UCD), Patrick Gormley ([Lapeer Community School District](#))

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8.5: Buffers

Learning Objectives

- To define *buffer* and describe how it reacts with an acid or a base.

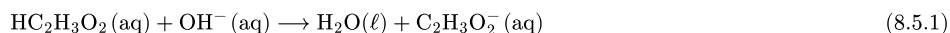
Weak acids are relatively common, even in the foods we eat. But we occasionally come across a strong acid or base, such as stomach acid, that has a strongly acidic pH of 1–2. By definition, strong acids and bases can produce a relatively large amount of hydrogen or hydroxide ions and, as a consequence, have a marked chemical activity. In addition, very small amounts of strong acids and bases can change the pH of a solution very quickly. If 1 mL of stomach acid [which we will approximate as 0.05 M HCl(aq)] is added to the bloodstream, and if no correcting mechanism is present, the pH of the blood would go from about 7.4 to about 4.9—a pH that is not conducive to continued living. Fortunately, the body has a mechanism for minimizing such dramatic pH changes.

The mechanism involves a **buffer**, a solution that resists dramatic changes in pH. A *buffer* (or *buffered*) solution is one that resists a change in its pH when H^+ or OH^- ions are added or removed owing to some other reaction taking place in the same solution. Buffers do so by being composed of certain pairs of solutes: either a **weak acid plus its conjugate base** or a **weak base plus its conjugate acid**.

For example, a buffer can be composed of dissolved **acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$, a weak acid) and sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2$)**. Sodium acetate is a salt that dissociates into sodium ions and acetate ions in solution. For as long as acetic acid and acetate ions are present in significant amounts a solution, this can resist dramatic pH changes. Another example of a buffer is a solution containing **ammonia (NH_3 , a weak base) and ammonium chloride (NH_4Cl)**. Ammonium acetate is also a salt that dissociates into ammonium ions and chloride ions in solution. The presence of ammonium ions with ammonia molecules satisfies the requisite condition for a buffer solution.

8.5.1 How Buffers Work

The essential component of a buffer system is a **conjugate acid-base pair** whose concentration is fairly high in relation to the concentrations of added H^+ or OH^- it is expected to buffer against. Let us use an acetic acid–sodium acetate buffer to demonstrate how buffers work. If a strong base—a source of OH^- (aq) ions—is added to the buffer solution, those hydroxide ions will react with the acetic acid in an acid-base reaction:



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 $\text{HC}_2\text{H}_3\text{O}_2$ 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:



Rather than changing the pH dramatically and making the solution acidic, the added hydrogen ions react to make molecules of a weak acid. Figure 8.5.1 illustrates both actions of a buffer.

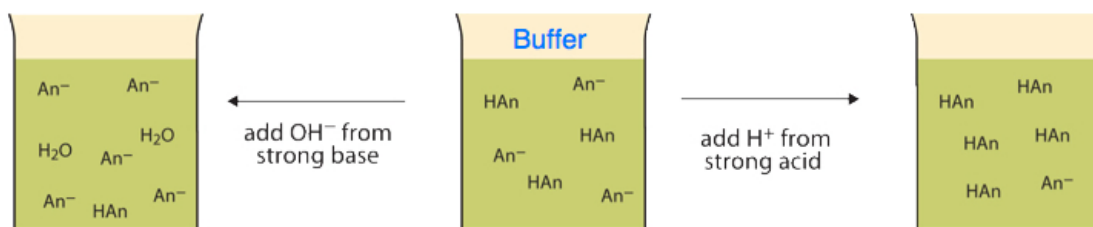


Figure 8.5.1: The Action of Buffers. Buffers can react with both strong acids (top) and strong bases (bottom) to minimize large changes in pH.

A simple buffer system might be a 0.2 M solution of sodium acetate; the conjugate pair here is acetic acid HAc and its conjugate base, the acetate ion Ac^- . The idea is that this conjugate pair "pool" will be available to gobble up any small ($\leq 10^{-3}$ M) addition of H^+ or OH^- that may result from other processes going on in the solution.

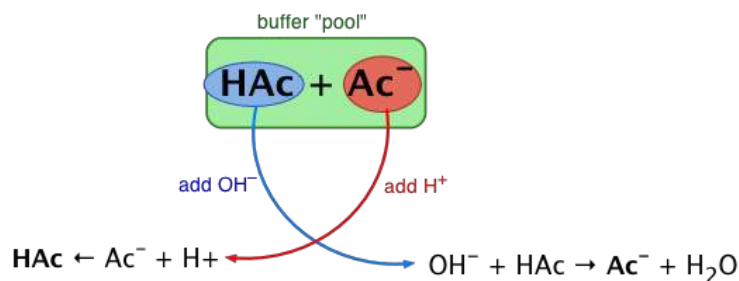


Figure 8.5.2: How HAc/Ac buffer works

Buffers work well only for limited amounts of added strong acid or base. Once either solute is all reacted, the solution is no longer a buffer, and rapid changes in pH may occur. We say that a buffer has a certain capacity. Buffers that have more solute dissolved in them to start with have larger capacities, as might be expected.

Buffers made from weak bases and salts of weak bases act similarly. For example, in a buffer containing NH_3 and NH_4Cl , ammonia molecules can react with any excess hydrogen ions introduced by strong acids:



while the ammonium ion $[\text{NH}_4^+(aq)]$ can react with any hydroxide ions introduced by strong bases:

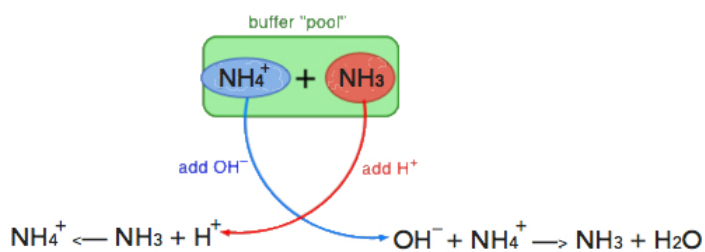


Figure 8.5.3: How $\text{NH}_4^+/\text{NH}_3$ buffer works

✓ Example 8.5.1

Which solute combinations can make a buffer solution? Assume all are aqueous solutions.

- HCHO_2 and NaCHO_2
- HCl and NaCl
- CH_3NH_2 and $\text{CH}_3\text{NH}_3\text{Cl}$
- NH_3 and NaOH

Solution

- Formic acid (HCHO_2) is a weak acid, while NaCHO_2 is a salt supplying —formate ion (CHO_2^-), the conjugate base of HCHO_2 . The combination of these two solutes would make a buffer solution.
- Hydrochloric acid (HCl) is a strong acid, not a weak acid, so the combination of these two solutes would not make a buffer solution.
- Methylamine (CH_3NH_2) is like ammonia, a weak base. The compound $\text{CH}_3\text{NH}_3\text{Cl}$ is a salt supplying CH_3NH_3^+ , the conjugate acid of CH_3NH_2 . The combination of these two solutes would make a buffer solution.
- Ammonia (NH_3) is a weak base, but NaOH is a strong base. The combination of these two solutes would not make a buffer solution.

? Exercise 8.5.1

Which solute combinations can make a buffer solution? Assume all are aqueous solutions.

- NaHCO_3 and NaCl
- H_3PO_4 and NaH_2PO_4
- NH_3 and $(\text{NH}_4)_3\text{PO}_4$
- NaOH and NaCl

Answer

- H_3PO_4 (weak acid) and H_2PO_4^- (conjugate base of H_3PO_4) make a buffer.
- NH_3 (weak base) and NH_4^+ (conjugate acid of NH_3) make a buffer

✓ Food and Drink App: The Acid That Eases Pain

Although medicines are not exactly "food and drink," we do ingest them, so let's take a look at an acid that is probably the most common medicine: acetylsalicylic acid, also known as aspirin. Aspirin is well known as a pain reliever and antipyretic (fever reducer).

The structure of aspirin is shown in the accompanying figure. The acid part is circled; it is the H atom in that part that can be donated as aspirin acts as a Brønsted-Lowry acid. Because it is not given in Table 10.5.1, acetylsalicylic acid is a weak acid. However, it is still an acid, and given that some people consume relatively large amounts of aspirin daily, its acidic nature can cause problems in the stomach lining, despite the stomach's defenses against its own stomach acid.

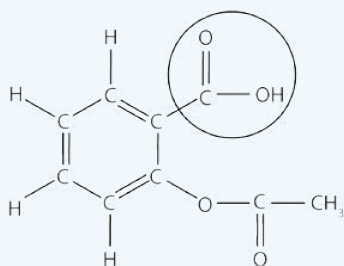


Figure 8.5.4 The Molecular Structure of Aspirin. The circled

atoms are the acid part of the molecule.

Because the acid properties of aspirin may be problematic, many aspirin brands offer a "buffered aspirin" form of the medicine. In these cases, the aspirin also contains a buffering agent—usually MgO —that regulates the acidity of the aspirin to minimize its acidic side effects.

As useful and common as aspirin is, it was formally marketed as a drug starting in 1899. The U.S. Food and Drug Administration (FDA), the governmental agency charged with overseeing and approving drugs in the United States, wasn't formed until 1906. Some have argued that if the FDA had been formed before aspirin was introduced, aspirin may never have gotten approval due to its potential for side effects—gastrointestinal bleeding, ringing in the ears, Reye's syndrome (a liver problem), and some allergic reactions. However, recently aspirin has been touted for its effects in lessening heart attacks and strokes, so it is likely that aspirin is here to stay.

Buffer solutions are essential components of all living organisms.

- Our blood is buffered to maintain a pH of 7.4 that must remain unchanged as metabolically-generated CO_2 (carbonic acid) is added and then removed by our lungs.
- Buffers in the oceans, in natural waters such as lakes and streams, and within soils help maintain their environmental stability against acid rain and increases in atmospheric CO_2 .
- Many industrial processes, such as brewing, require buffer control, as do research studies in biochemistry and physiology that involve enzymes, are active only within certain pH ranges.

The pH in living systems (Figure \(\PageIndex{1}\)) is maintained by buffer systems.

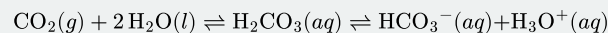
Table 7.3.2: pH in Living Systems

Compartment	pH
Gastric Acid	1
Lysosomes	4.5
Granules of Chromaffin Cells	5.5
Human Skin	5.5
Urine	6
Neutral H_2O at 37 °C	6.81
Cytosol	7.2
Cerebrospinal Fluid	7.3
Blood	7.43-7.45
Mitochondrial Matrix	7.5
Pancreas Secretions	8.1

Human blood has a buffering system to minimize extreme changes in pH. One buffer in blood is based on the presence of HCO_3^- and H_2CO_3 [H_2CO_3 is another way to write $\text{CO}_2(\text{aq})$]. With this buffer present, even if some stomach acid were to find its way directly into the bloodstream, the change in the pH of blood would be minimal. Inside many of the body's cells, there is a buffering system based on phosphate ions.

Medicine: The Buffer System in Blood

The normal pH of human blood is about 7.4. The carbonate buffer system in the blood uses the following equilibrium reaction:



The concentration of carbonic acid, H_2CO_3 is approximately 0.0012 M, and the concentration of the hydrogen carbonate ion, HCO_3^- , is around 0.024 M. Using the Henderson-Hasselbalch equation and the pK_a of carbonic acid at body temperature, we can calculate the pH of blood:

$$\text{pH} = \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]} = 6.1 + \log \frac{0.024}{0.0012} = 7.4$$

The fact that the H_2CO_3 concentration is significantly lower than that of the HCO_3^- ion may seem unusual, but this imbalance is due to the fact that most of the by-products of our metabolism that enter our bloodstream are acidic. Therefore, there must be a larger proportion of base than acid, so that the capacity of the buffer will not be exceeded.

Lactic acid is produced in our muscles when we exercise. As the lactic acid enters the bloodstream, it is neutralized by the HCO_3^- ion, producing H_2CO_3 . An enzyme then accelerates the breakdown of the excess carbonic acid to carbon dioxide and water, which can be eliminated by breathing. In fact, in addition to the regulating effects of the carbonate buffering system on the pH of blood, the body uses breathing to regulate blood pH. If the pH of the blood decreases too far, an increase in breathing removes CO_2 from the blood through the lungs driving the equilibrium reaction such that $[\text{H}_3\text{O}^+]$ is lowered. If the blood is too

alkaline, a lower breath rate increases CO_2 concentration in the blood, driving the equilibrium reaction the other way, increasing $[\text{H}^+]$ and restoring an appropriate pH.

Career Focus: Blood Bank Technology Specialist

At this point in this text, you should have the idea that the chemistry of blood is fairly complex. Because of this, people who work with blood must be specially trained to work with it properly.

A blood bank technology specialist is trained to perform routine and special tests on blood samples from blood banks or transfusion centers. This specialist measures the pH of blood, types it (according to the blood's ABO+/- type, Rh factors, and other typing schemes), tests it for the presence or absence of various diseases, and uses the blood to determine if a patient has any of several medical problems, such as anemia. A blood bank technology specialist may also interview and prepare donors to give blood and may actually collect the blood donation.

Blood bank technology specialists are well trained. Typically, they require a college degree with at least a year of special training in blood biology and chemistry. In the United States, training must conform to standards established by the American Association of Blood Banks.

8.5.2 Key Takeaway

- A buffer is a solution that resists sudden changes in pH.

8.5.3 Concept Review Exercise

1. Explain how a buffer prevents large changes in pH.

8.5.4 Answer

1. A buffer has components that react with both strong acids and strong bases to resist sudden changes in pH.

8.5.5 Exercises

1. Describe a buffer. What two related chemical components are required to make a buffer?
2. Can a buffer be made by combining a strong acid with a strong base? Why or why not?
3. Which solute combinations can make a buffer? Assume all are aqueous solutions.
 1. HCl and NaCl
 2. HNO_2 and NaNO_2
 3. NH_4NO_3 and HNO_3
 4. NH_4NO_3 and NH_3
4. Which solute combinations can make a buffer? Assume all are aqueous solutions.
 1. H_3PO_4 and Na_3PO_4
 2. NaHCO_3 and Na_2CO_3
 3. NaNO_3 and $\text{Ca}(\text{NO}_3)_2$
 4. HN_3 and NH_3
5. For each combination in Exercise 3 that is a buffer, write the chemical equations for the reactions of the buffer components when a strong acid and a strong base is added.
6. For each combination in Exercise 4 that is a buffer, write the chemical equations for the reaction of the buffer components when a strong acid and a strong base is added.
7. The complete phosphate buffer system is based on four substances: H_3PO_4 , H_2PO_4^- , HPO_4^{2-} , and PO_4^{3-} . What different buffer solutions can be made from these substances?
8. Explain why NaBr cannot be a component in either an acidic or a basic buffer.
9. Explain why $\text{Mg}(\text{NO}_3)_2$ cannot be a component in either an acidic or a basic buffer.

8.5.5.1 Answers

1. A buffer resists sudden changes in pH. It has a weak acid or base and a salt of that weak acid or base.
2. No. Combining a strong acid and a strong base will produce salt and water. Excess strong acid or strong base will not act as a buffer.

3.
 1. not a buffer
 2. buffer
 3. not a buffer
 4. buffer
4.
 1. not a buffer
 2. buffer
 3. not a buffer
 4. not a buffer
5. 3b: strong acid: $\text{H}^+ + \text{NO}_2^- \rightarrow \text{HNO}_2$; strong base: $\text{OH}^- + \text{HNO}_2 \rightarrow \text{H}_2\text{O} + \text{NO}_2^-$; 3d: strong acid: $\text{H}^+ + \text{NH}_3 \rightarrow \text{NH}_4^+$; strong base: $\text{OH}^- + \text{NH}_4^+ \rightarrow \text{H}_2\text{O} + \text{NH}_3$
6. 4b: strong acid: $\text{H}^+ + \text{CO}_3^{2-} \rightarrow \text{HCO}_3^-$; strong base: $\text{OH}^- + \text{HCO}_3^- \rightarrow \text{H}_2\text{O} + \text{CO}_3^{2-}$;
7. Buffers can be made by combining H_3PO_4 and H_2PO_4^- , H_2PO_4^- and HPO_4^{2-} , and HPO_4^{2-} and PO_4^{3-} .
8. NaBr splits up into two ions in solution, Na^+ and Br^- . Na^+ will not react with any added base knowing that NaOH is a strong base. Br^- will not react with any added acid knowing that HBr is a strong acid. Because NaBr will not react with any added base or acid, it does not resist change in pH and is not a buffer.
9. $\text{Mg}(\text{NO}_3)_2$ includes two types of ions, Mg^{2+} and NO_3^- . $\text{Mg}(\text{OH})_2$ is strong base and completely dissociates (100% falls apart), so Mg^{2+} will not react with any added base (0% combines with OH^-). HNO_3 is strong acid and completely dissociates (100% falls apart), so NO_3^- will not react with any added acid (0% combines with H^+). Because $\text{Mg}(\text{NO}_3)_2$ will not react with any added base or acid, it does not resist change in pH and is not a buffer.

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8.6: Chapter Summary

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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CHAPTER OVERVIEW

9: Organic Acids and Bases and Some of Their Derivatives

Organic acids have been known for ages. Prehistoric people likely made acetic acid when their fermentation reactions went awry and produced vinegar instead of wine. The Sumerians (2900–1800 BCE) used vinegar as a condiment, a preservative, an antibiotic, and a detergent. Citric acid was discovered by an Islamic alchemist, Jabir Ibn Hayyan (also known as Geber), in the 8th century, and crystalline citric acid was first isolated from lemon juice in 1784 by the Swedish chemist Carl Wilhelm Scheele. Medieval scholars in Europe were aware that the crisp, tart flavor of citrus fruits is caused by citric acid. Naturalists of the 17th century knew that the sting of a red ant's bite was due to an organic acid that the ant injected into the wound. The acetic acid of vinegar, the formic acid of red ants, and the citric acid of fruits all belong to the same family of compounds—carboxylic acids. Soaps are salts of long-chain carboxylic acids. Prehistoric people also knew about organic bases—by smell if not by name; amines are the organic bases produced when animal tissue decays. The organic compounds that we consider in this chapter are organic acids and bases. We will also consider two derivatives of carboxylic acids: esters and amides. An ester is derived from a carboxylic acid and an alcohol. Fats and oils are esters, as are many important fragrances and flavors. An amide is derived from a carboxylic acid and either ammonia or an amine. Proteins, often called “the stuff of life,” are polyamides.

[9.1: Prelude to Organic Acids and Bases and Some of Their Derivatives](#)

[9.2: Carboxylic Acids - Structures and Names](#)

[9.3: The Formation of Carboxylic Acids](#)

[9.4: Physical Properties of Carboxylic Acids](#)

[9.5: Chemical Properties of Carboxylic Acids- Ionization and Neutralization](#)

[9.6: Esters - Structures and Names](#)

[9.7: Physical Properties of Esters](#)

[9.8: Preparation of Esters](#)

[9.9: Hydrolysis of Esters](#)

[9.S: Organic Acids and Bases and Some of Their Derivatives \(Summary\)](#)

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9.1: Prelude to Organic Acids and Bases and Some of Their Derivatives

Organic acids have been known for ages. Prehistoric people likely made acetic acid when their fermentation reactions went awry and produced vinegar instead of wine. The Sumerians (2900–1800 BCE) used vinegar as a condiment, a preservative, an antibiotic, and a detergent. Citric acid was discovered by an Islamic alchemist, Jabir Ibn Hayyan (also known as Geber), in the 8th century, and crystalline citric acid was first isolated from lemon juice in 1784 by the Swedish chemist Carl Wilhelm Scheele. Medieval scholars in Europe were aware that the crisp, tart flavor of citrus fruits is caused by citric acid. Naturalists of the 17th century knew that the sting of a red ant's bite was due to an organic acid that the ant injected into the wound. The acetic acid of vinegar, the formic acid of red ants, and the citric acid of fruits all belong to the same family of compounds—carboxylic acids. Soaps are salts of long-chain carboxylic acids.

Prehistoric people also knew about organic bases—by smell if not by name; amines are the organic bases produced when animal tissue decays.

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9.2: Carboxylic Acids - Structures and Names

Learning Objectives

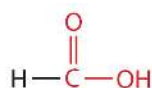
- Name carboxylic acids with common names.
- Name carboxylic acids according to IUPAC nomenclature.

Carboxylic acids occur widely in nature, often combined with alcohols or other functional groups, as in fats, oils, and waxes. They are components of many foods, medicines, and household products (Figure 9.2.1). Not surprisingly, many of them are best known by common names based on Latin and Greek words that describe their source.



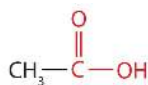
Figure 9.2.1: Carboxylic Acids in the Home. Carboxylic acids occur in many common household items. (a) Vinegar contains acetic acid, (b) aspirin is acetylsalicylic acid, (c) vitamin C is ascorbic acid, (d) lemons contain citric acid, and (e) spinach contains oxalic acid. © Thinkstock

The simplest carboxylic acid, formic acid (HCOOH), was first obtained by the distillation of ants (Latin *formica*, meaning “ant”). The bites of some ants inject formic acid, and the stings of wasps and bees contain formic acid (as well as other poisonous materials).



Formic acid

The next higher homolog is acetic acid, which is made by fermenting cider and honey in the presence of oxygen. This fermentation produces vinegar, a solution containing 4%–10% acetic acid, plus a number of other compounds that add to its flavor. Acetic acid is probably the most familiar weak acid used in educational and industrial chemistry laboratories.



Acetic acid

Pure acetic acid solidifies at 16.6°C , only slightly below normal room temperature. In the poorly heated laboratories of the late 19th and early 20th centuries in northern North America and Europe, acetic acid often “froze” on the storage shelf. For that

reason, pure acetic acid (sometimes called concentrated acetic acid) came to be known as *glacial acetic acid*, a name that survives to this day.

The third homolog, propionic acid ($\text{CH}_3\text{CH}_2\text{COOH}$), is seldom encountered in everyday life. The fourth homolog, butyric acid ($\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$), is one of the most foul-smelling substances imaginable. It is found in rancid butter and is one of the ingredients of body odor. By recognizing extremely small amounts of this and other chemicals, bloodhounds are able to track fugitives. Models of the first four carboxylic acids are shown in Figure 9.2.2.

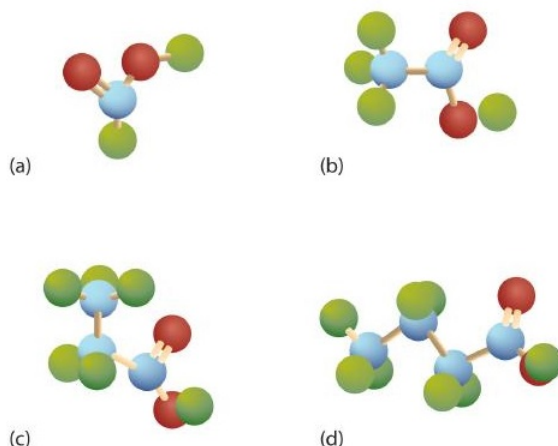
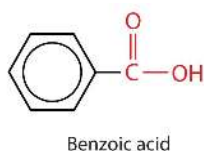
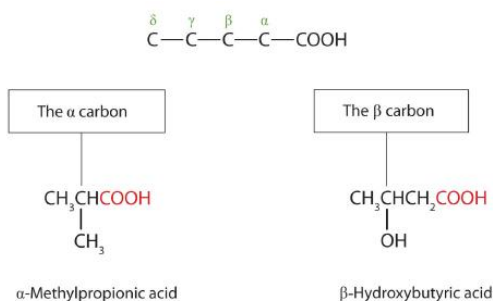


Figure 9.2.2: Ball-and-Stick Models of Carboxylic Acids. Carboxylic acids feature a carbon atom doubly bonded to an oxygen atom and also joined to an OH group. The four acids illustrated here are formic acid (a), acetic acid (b), propionic acid (c), and butyric acid (d).

The acid with the carboxyl group attached directly to a benzene ring is called benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$).



The common names of carboxylic acids use Greek letters (α , β , γ , δ , and so forth), not numbers, to designate the position of substituent groups in acids. These letters refer to the position of the carbon atom in relation to the carboxyl carbon atom.



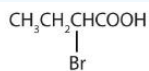
In the nomenclature system of the International Union of Pure and Applied Chemistry (IUPAC), the parent hydrocarbon is the one that corresponds to the longest continuous chain (LCC) containing the carboxyl group. The *-e* ending of the parent alkane is replaced by the suffix *-oic* and the word *acid*. For example, the carboxylic acid derived from pentane is pentanoic acid ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$). As with aldehydes, the carboxyl carbon atom is counted first; numbers are used to indicate any substituted carbon atoms in the parent chain.

Greek letters are used with common names; numbers are used with IUPAC names.

✓ Example 9.2.1

Give the common and IUPAC names for each compound.

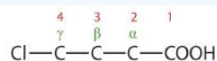
1. $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{COOH}$



2.

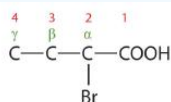
9.2.1 Solution

1. The LCC contains four carbon atoms; the compound is therefore named as a substituted butyric (or butanoic) acid.



The chlorine atom is attached to the γ -carbon in the common system or C4 in the IUPAC system. The compound is γ -chlorobutyric acid or 4-chlorobutanoic acid.

2. The LCC contains four carbon atoms; the compound is therefore named as a substituted butyric (or butanoic) acid.



The bromine (Br) atom is at the α -carbon in the common system or C2 in the IUPAC system. The compound is α -bromobutyric acid or 2-bromobutanoic acid.

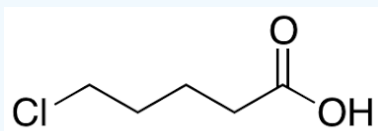
? Exercise 9.2.1

Give the IUPAC name for each compound.

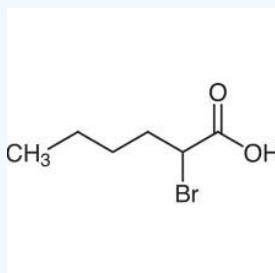
- a. $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$
b. $(\text{CH}_3)_2\text{CHCH}_2\text{CHBrCOOH}$

Answer

- a. 5-chloropentaonic acid



- b. 2-bromohexanoic acid



✓ Example 9.2.2

Write the condensed structural formula for β -chloropropionic acid.

Solution

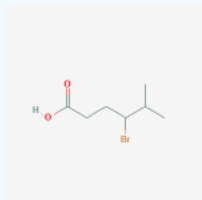
Propionic acid has three carbon atoms: $\text{C}-\text{C}-\text{COOH}$. Attach a chlorine (Cl) atom to the parent chain at the beta carbon atom, the second one from the carboxyl group: $\text{Cl}-\text{C}-\text{C}-\text{COOH}$. Then add enough hydrogen atoms to give each carbon atom four

bonds: $\text{ClCH}_2\text{CH}_2\text{COOH}$.

? Exercise 9.2.1

Write the condensed structural formula for 4-bromo-5-methylhexanoic acid.

Answer



9.2.2 Key Takeaways

- Simple carboxylic acids are best known by common names based on Latin and Greek words that describe their source (e.g., formic acid, Latin *formica*, meaning “ant”).
- Greek letters, not numbers, designate the position of substituted acids in the common naming convention.
- IUPAC names are derived from the LCC of the parent hydrocarbon with the *-e* ending of the parent alkane replaced by the suffix *-oic* and the word *acid*.

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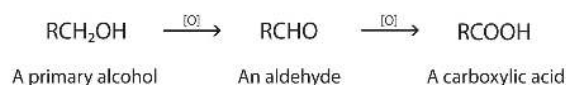
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9.3: The Formation of Carboxylic Acids

Learning Objectives

- To describe the preparation of carboxylic acids.

As we noted previously, the oxidation of aldehydes or primary alcohols forms carboxylic acids:



In the presence of an oxidizing agent, ethanol is oxidized to acetaldehyde, which is then oxidized to acetic acid.



This process also occurs in the liver, where enzymes catalyze the oxidation of ethanol to acetic acid.



Acetic acid can be further oxidized to carbon dioxide and water.

Summary

Whether in the laboratory or in the body, the oxidation of aldehydes or primary alcohols forms carboxylic acids.

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9.4: Physical Properties of Carboxylic Acids

Learning Objectives

- Compare the boiling points of carboxylic acids with alcohols of similar molar mass.
- Compare the solubilities of carboxylic acids in water with the solubilities of comparable alkanes and alcohols in water.

Many carboxylic acids are colorless liquids with disagreeable odors. The carboxylic acids with 5 to 10 carbon atoms all have “goaty” odors (explaining the odor of Limburger cheese). These acids are also produced by the action of skin bacteria on human sebum (skin oils), which accounts for the odor of poorly ventilated locker rooms. The acids with more than 10 carbon atoms are waxlike solids, and their odor diminishes with increasing molar mass and resultant decreasing volatility.

Carboxylic acids exhibit strong hydrogen bonding between molecules. They therefore have high boiling points compared to other substances of comparable molar mass.

The carboxyl group readily engages in hydrogen bonding with water molecules (Figure 9.4.1). The acids with one to four carbon atoms are completely miscible with water. Solubility decreases as the carbon chain length increases because dipole forces become less important and dispersion forces become more predominant. Hexanoic acid [$\text{CH}_3(\text{CH}_2)_4\text{COOH}$] is barely soluble in water (about 1.0 g/100 g of water). Palmitic acid [$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$], with its large nonpolar hydrocarbon component, is essentially insoluble in water. The carboxylic acids generally are soluble in such organic solvents as ethanol, toluene, and diethyl ether.

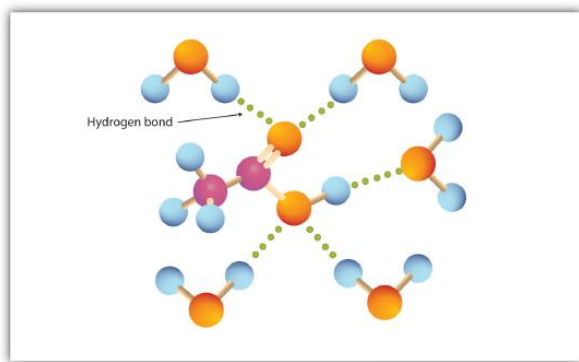


Figure 9.4.1: Hydrogen Bonding between an Acetic Acid Molecule and Water Molecules. Carboxylic acids of low molar mass are quite soluble in water.

Table 15.4.1 lists some physical properties for selected carboxylic acids. The first six are homologs. Notice that the boiling points increase with increasing molar mass, but the melting points show no regular pattern.

Table 9.4.1: Physical Constants of Carboxylic Acids

Condensed Structural Formula	Name of Acid	Melting Point (°C)	Boiling Point (°C)	Solubility (g/100 g of Water)
HCOOH	formic acid	8	100	miscible
CH ₃ COOH	acetic acid	17	118	miscible
CH ₃ CH ₂ COOH	propionic acid	−22	141	miscible
CH ₃ (CH ₂) ₂ COOH	butyric acid	−5	163	miscible
CH ₃ (CH ₂) ₃ COOH	valeric acid	−35	187	5
CH ₃ (CH ₂) ₄ COOH	caproic acid	−3	205	1.1
C ₆ H ₅ COOH	benzoic acid	122	249	0.29

9.4.1 Key Takeaways

- Carboxylic acids have high boiling points compared to other substances of comparable molar mass. Boiling points increase with molar mass.

- Carboxylic acids having one to four carbon atoms are completely miscible with water. Solubility decreases with molar mass.

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9.5: Chemical Properties of Carboxylic Acids- Ionization and Neutralization

Learning Objectives

- Name the typical reactions that take place with carboxylic acids.
- Describe how carboxylic acids react with basic compounds.

Water-soluble carboxylic acids ionize slightly in water to form moderately acidic solutions. 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:

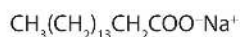


In these reactions, the carboxylic acids act like inorganic acids: they neutralize basic compounds. With solutions of carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions, they also form carbon dioxide gas.

Carboxylic acid salts are named in the same manner as inorganic salts: the name of the cation is followed by the name of the organic anion. The name of the anion is obtained by dropping the *-ic* ending of the acid name and replacing it with the suffix *-ate*. This rule applies whether we are using common names or International Union of Pure and Applied Chemistry (IUPAC) names:

$\text{CH}_3\text{COO}^-\text{Li}^+$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COO}^-\text{K}^+$	$\text{C}_6\text{H}_5\text{COO}^-\text{Na}^+$
Lithium acetate (lithium ethanoate)	Potassium butyrate (potassium butanoate)	Sodium benzoate

The salts of long-chain carboxylic acids are called soaps. We discuss the chemistry of soaps elsewhere.



Sodium palmitate (a soap)

✓ Example 9.5.1

Write an equation for each reaction.

- the ionization of propionic acid in water (H_2O)
- the neutralization of propionic acid with aqueous sodium hydroxide (NaOH)

Solution

Propionic acid has three carbon atoms, so its formula is $\text{CH}_3\text{CH}_2\text{COOH}$.

- Propionic acid ionizes in water to form a propionate ion and a hydronium (H_3O^+) ion. $\text{CH}_3\text{CH}_2\text{COOH}(\text{aq}) + \text{H}_2\text{O}(\ell) \rightarrow \text{CH}_3\text{CH}_2\text{COO}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
- Propionic acid reacts with $\text{NaOH}(\text{aq})$ to form sodium propionate and water. $\text{CH}_3\text{CH}_2\text{COOH}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{CH}_3\text{CH}_2\text{COO}^-\text{Na}^+(\text{aq}) + \text{H}_2\text{O}(\ell)$

? Exercise 9.5.1

Write an equation for each reaction.

- the ionization of $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ in water.
- the ionization of propionic acid in water.

Answer

- $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}(\text{aq}) + \text{H}_2\text{O}(\ell) \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{COO}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
- $\text{CH}_3\text{CH}_2\text{COOH}(\text{aq}) + \text{H}_2\text{O}(\ell) \rightarrow \text{CH}_3\text{CH}_2\text{COO}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$

✓ Example 9.5.2

Write an equation for the reaction of decanoic acid with each compound.

- aqueous sodium hydroxide (NaOH)
- aqueous sodium bicarbonate (NaHCO_3)

Solution

- Decanoic acid has 10 carbon atoms. It reacts with NaOH to form a salt and water (H_2O). $\text{CH}_3(\text{CH}_2)_8\text{COOH} + \text{NaOH}(\text{aq}) \rightarrow \text{CH}_3(\text{CH}_2)_8\text{COO}^-\text{Na}^+(\text{aq}) + \text{H}_2\text{O}(\ell)$
- With NaHCO_3 , the products are a salt, H_2O , and carbon dioxide (CO_2). $\text{CH}_3(\text{CH}_2)_8\text{COOH} + \text{NaHCO}_3(\text{aq}) \rightarrow \text{CH}_3(\text{CH}_2)_8\text{COO}^-\text{Na}^+(\text{aq}) + \text{H}_2\text{O}(\ell) + \text{CO}_2(\text{g})$

? Exercise 9.5.3

Write an equation for the reaction of butyric acid with each compound.

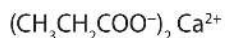
- aqueous sodium hydroxide (NaOH)
- aqueous sodium bicarbonate (NaHCO_3)

9.5.1 Solution

- $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{COO}^-\text{Na}^+(\text{aq}) + \text{H}_2\text{O}(\ell)$
- $\text{CH}_3(\text{CH}_2)_2\text{COOH} + \text{NaHCO}_3(\text{aq}) \rightarrow \text{CH}_3(\text{CH}_2)_2\text{COO}^-\text{Na}^+(\text{aq}) + \text{H}_2\text{O}(\ell) + \text{CO}_2(\text{g})$

📌 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.



Calcium propionate



Potassium sorbate

9.5.2 Key Takeaways

- Soluble carboxylic acids are weak acids in aqueous solutions.
- Carboxylic acids neutralize bases to form salts.

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9.6: Esters - Structures and Names

Learning Objectives

- Identify the general structure for an ester.
- Use common names to name esters.
- Name esters according to the IUPAC system.

Esters have the general formula RCOOR' , where R may be a hydrogen atom, an alkyl group, or an aryl group, and R' may be an alkyl group or an aryl group but *not* a hydrogen atom. (If it were hydrogen atom, the compound would be a carboxylic acid.) Figure 9.6.1 shows models for two common esters.

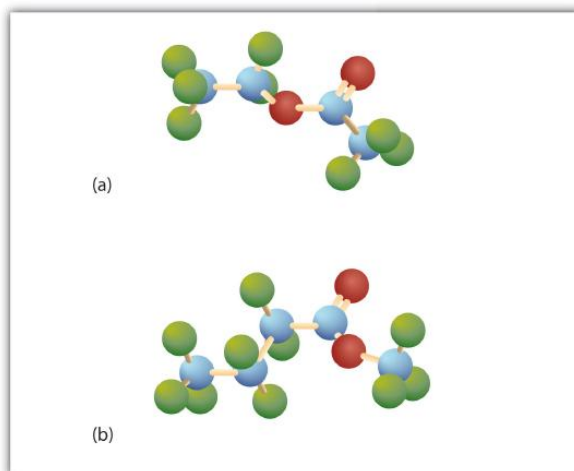


Figure 9.6.1: The Structure of Esters. Esters feature a carbon-to-oxygen double bond that is also singly bonded to a second oxygen atom, which is then joined to an alkyl or an aryl group. The esters shown here are ethyl acetate (a) and methyl butyrate (b).

Esters occur widely in nature. Unlike carboxylic acids, esters generally have pleasant odors and are often responsible for the characteristic fragrances of fruits and flowers. Once a flower or fruit has been chemically analyzed, flavor chemists can attempt to duplicate the natural odor or taste. Both natural and synthetic esters are used in perfumes and as flavoring agents.

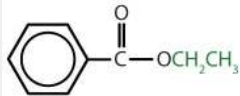
Fats and vegetable oils are esters of long-chain fatty acids and glycerol. Esters of phosphoric acid are of the utmost importance to life.

9.6.1 Names of Esters

Although esters are covalent compounds and salts are ionic, esters are named in a manner similar to that used for naming salts. The group name of the alkyl or aryl portion is given first and is followed by the name of the acid portion. In both common and International Union of Pure and Applied Chemistry (IUPAC) nomenclature, the *-ic* ending of the parent acid is replaced by the suffix *-ate* (Table 9.6.1).

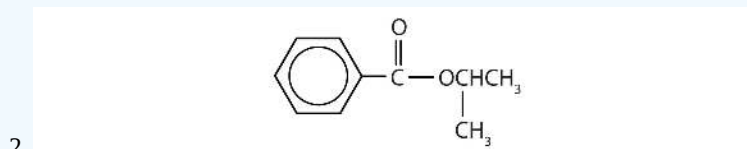
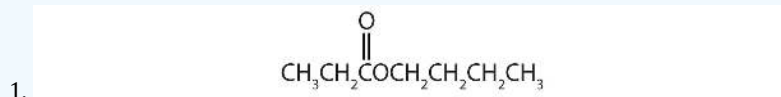
Table 9.6.1: Nomenclature of Esters

Condensed Structural Formula	Common Name	IUPAC Name
HCOOCH_3	methyl formate	methyl methanoate
$\text{CH}_3\text{COOCH}_3$	methyl acetate	methyl ethanoate
$\text{CH}_3\text{COOCH}_2\text{CH}_3$	ethyl acetate	ethyl ethanoate
$\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3$	ethyl propionate	ethyl propanoate
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}(\text{CH}_3)_2$	isopropyl butyrate	isopropyl butanoate

Condensed Structural Formula	Common Name	IUPAC Name
	ethyl benzoate	ethyl benzoate

✓ Example 9.6.1

Give the common and IUPAC names for each compound.



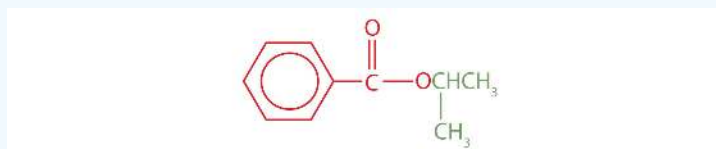
Solution

The alkyl group attached directly to the oxygen atom is a butyl group (in green).



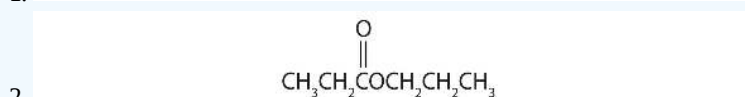
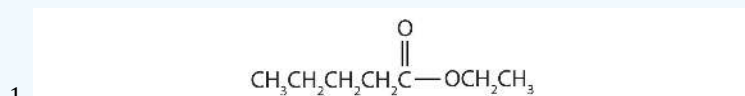
The part of the molecule derived from the carboxylic acid (in red) has three carbon atoms. It is called propionate (common) or propanoate (IUPAC). The ester is therefore butyl propionate or butyl propanoate.

1. An alkyl group (in green) is attached directly to the oxygen atom by its middle carbon atom; it is an isopropyl group. The part derived from the acid (that is, the benzene ring and the carbonyl group, in red) is benzoate. The ester is therefore isopropyl benzoate (both the common name and the IUPAC name).



? Exercise 9.6.1

Give the IUPAC names for each compound.



Answer

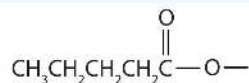
1. ethyl pentanoate
2. propyl propanoate

✓ Example 9.6.2

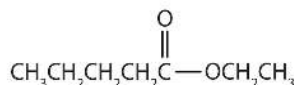
Draw the structure for ethyl pentanoate.

Solution

Start with the portion from the acid. Draw the pentanoate (five carbon atoms) group first; keeping in mind that the last carbon atom is a part of the carboxyl group.



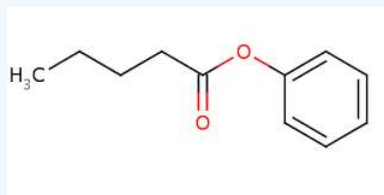
Then attach the ethyl group to the bond that ordinarily holds the hydrogen atom in the carboxyl group.



? Exercise 9.6.1

Draw the structure for phenyl pentanoate.

Answer



9.6.2 Key Takeaway

- An ester has an OR group attached to the carbon atom of a carbonyl group.

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9.7: Physical Properties of Esters

Learning Objectives

- Compare the boiling points of esters with alcohols of similar molar mass.
- Compare the solubilities of esters in water with the solubilities of comparable alkanes and alcohols in water.

Ester molecules are polar but have no hydrogen atom attached directly to an oxygen atom. They are therefore incapable of engaging in intermolecular hydrogen bonding with one another and thus have considerably lower boiling points than their isomeric carboxylic acids counterparts. Because ester molecules can engage in hydrogen bonding with water molecules, however, esters of low molar mass are somewhat soluble in water. Borderline solubility occurs in those molecules that have three to five carbon atoms. Table 9.7.1 lists the physical properties of some common esters.

Esters are common solvents. Ethyl acetate is used to extract organic solutes from aqueous solutions—for example, to remove caffeine from coffee. It also is used to remove nail polish and paint. Cellulose nitrate is dissolved in ethyl acetate and butyl acetate to form lacquers. The solvent evaporates as the lacquer “dries,” leaving a thin film on the surface. High boiling esters are used as softeners (plasticizers) for brittle plastics.

Table 9.7.1: Physical Properties of Some Esters

Condensed Structural Formula	Name	Molar Mass	Melting Point (°C)	Boiling Point (°C)	Aroma
HCOOCH_3	methyl formate	60	−99	32	
$\text{HCOOCH}_2\text{CH}_3$	ethyl formate	74	−80	54	rum
$\text{CH}_3\text{COOCH}_3$	methyl acetate	74	−98	57	
$\text{CH}_3\text{COOCH}_2\text{CH}_3$	ethyl acetate	88	−84	77	
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_3$	methyl butyrate	102	−85	102	apple
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3$	ethyl butyrate	116	−101	121	pineapple
$\text{CH}_3\text{COO}(\text{CH}_2)_4\text{CH}_3$	pentyl acetate	130	−71	148	pear
$\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$	isopentyl acetate	130	−79	142	banana
$\text{CH}_3\text{COOCH}_2\text{C}_6\text{H}_5$	benzyl acetate	150	−51	215	jasmine
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COO}(\text{CH}_2)_4\text{CH}_3$	pentyl butyrate	158	−73	185	apricot
$\text{CH}_3\text{COO}(\text{CH}_2)_7\text{CH}_3$	octyl acetate	172	−39	210	orange

Summary

Esters have polar bonds but do not engage in hydrogen bonding and are therefore intermediate in boiling points between the nonpolar alkanes and the alcohols, which engage in hydrogen bonding. Ester molecules can engage in hydrogen bonding with water, so esters of low molar mass are therefore somewhat soluble in water.

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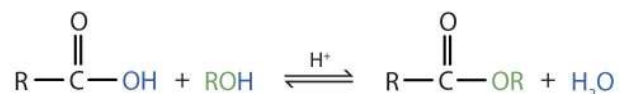
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9.8: Preparation of Esters

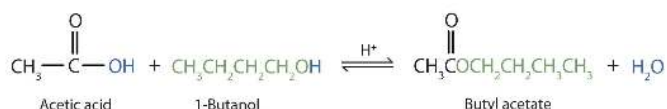
Learning Objectives

- To identify and describe the substances from which most esters are prepared.

Some esters can be prepared by esterification, a reaction in which a carboxylic acid and an alcohol, heated in the presence of a mineral acid catalyst, form an ester and water:



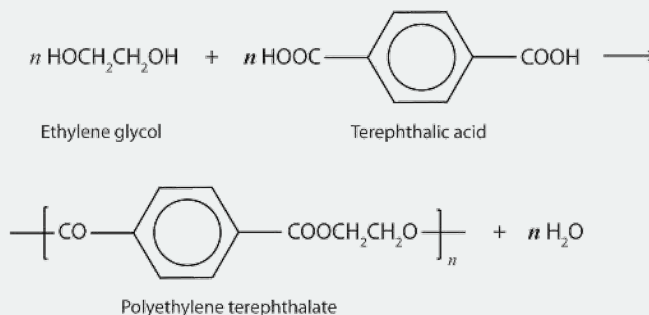
The reaction is reversible. As a specific example of an esterification reaction, butyl acetate can be made from acetic acid and 1-butanol.



A Closer Look: Condensation Polymers

A commercially important esterification reaction is condensation polymerization, in which a reaction occurs between a dicarboxylic acid and a dihydric alcohol (diol), with the elimination of water. Such a reaction yields an ester that contains a free (unreacted) carboxyl group at one end and a free alcohol group at the other end. Further condensation reactions then occur, producing polyester polymers.

The most important polyester, polyethylene terephthalate (PET), is made from terephthalic acid and ethylene glycol monomers:



Polyester molecules make excellent fibers and are used in many fabrics. A knitted polyester tube, which is biologically inert, can be used in surgery to repair or replace diseased sections of blood vessels. PET is used to make bottles for soda pop and other beverages. It is also formed into films called Mylar. When magnetically coated, Mylar tape is used in audio- and videocassettes. Synthetic arteries can be made from PET, polytetrafluoroethylene, and other polymers.

Summary

Esters are made by the reaction of a carboxylic acid with an alcohol, a process that is called esterification.

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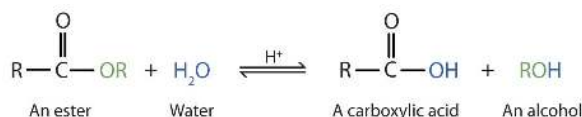
9.9: Hydrolysis of Esters

Learning Objectives

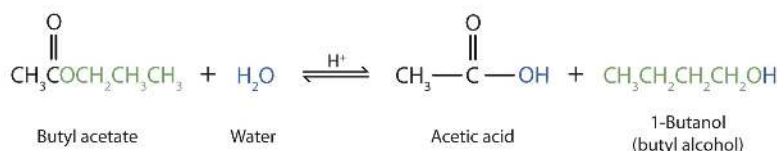
- Describe the typical reaction that takes place with esters.
- Identify the products of an acidic hydrolysis of an ester.
- Identify the products of a basic hydrolysis of an ester.

Esters are neutral compounds, unlike the acids from which they are formed. In typical reactions, the alkoxy (OR') group of an ester is replaced by another group. One such reaction is hydrolysis, literally "splitting with water." The hydrolysis of esters is catalyzed by either an acid or a base.

Acidic hydrolysis is simply the reverse of **esterification**. The ester is heated with a large excess of water containing a strong-acid catalyst. Like esterification, the reaction is reversible and does not go to completion.



As a specific example, butyl acetate and water react to form acetic acid and 1-butanol. The reaction is reversible and does not go to completion.

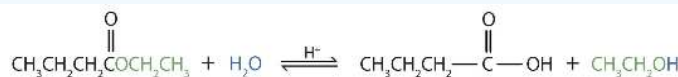


✓ Example 9.9.1

Write an equation for the acidic hydrolysis of ethyl butyrate ($\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3$) and name the products.

Solution

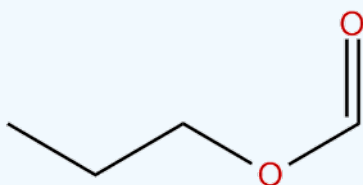
Remember that in acidic hydrolysis, water (HOH) splits the ester bond. The H of HOH joins to the oxygen atom in the OR part of the original ester, and the OH of HOH joins to the carbonyl carbon atom:



The products are butyric acid (butanoic acid) and ethanol.

? Exercise 9.9.1

Name the following compound and determine the products of acid hydrolysis

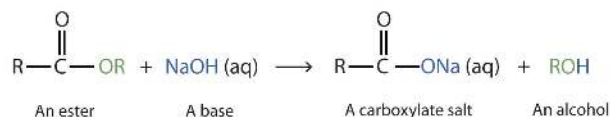


Answer

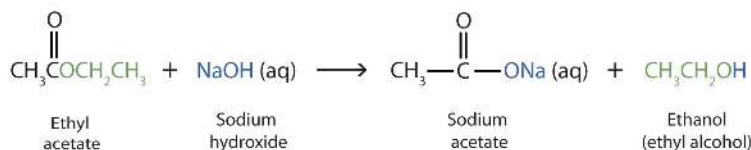
Name: propyl methanoate

Products: Methanoic acid (acid) and propanol (alcohol)

When a base (such as sodium hydroxide [NaOH] or potassium hydroxide [KOH]) is used to hydrolyze an ester, the products are a carboxylate salt and an alcohol. Because soaps are prepared by the alkaline hydrolysis of fats and oils, alkaline hydrolysis of esters is called saponification (Latin *sapon*, meaning “soap,” and *facere*, meaning “to make”). In a saponification reaction, the base is a reactant, not simply a catalyst. The reaction goes to completion:



As a specific example, ethyl acetate and NaOH react to form sodium acetate and ethanol:

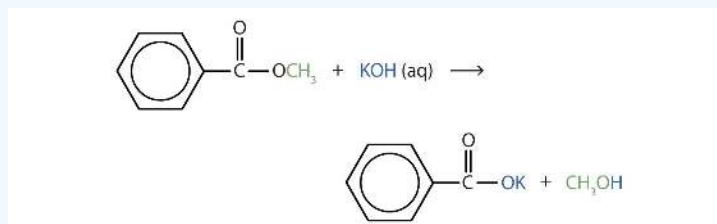


✓ Example 9.9.2

Write an equation for the hydrolysis of methyl benzoate in a potassium hydroxide solution.

Solution

In basic hydrolysis, the molecule of the base splits the ester linkage. The acid portion of the ester ends up as the *salt* of the acid (in this case, the potassium salt). The alcohol portion of the ester ends up as the free alcohol.



? Exercise 9.9.2

Write the equation for the hydrolysis of ethyl propanoate in a sodium hydroxide solution.

 Solved: Write the structural formulas of the reaction products whe... | Chegg.com

Summary

Hydrolysis is a most important reaction of esters. Acidic hydrolysis of an ester gives a carboxylic acid and an alcohol. Basic hydrolysis of an ester gives a carboxylate salt and an alcohol.

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9.S: Organic Acids and Bases and Some of Their Derivatives (Summary)

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

A **carboxylic acid** (RCOOH) contains the functional group COOH , called the **carboxyl group**, which has an OH group attached to a carbonyl carbon atom. An **ester** (RCOOR') has an OR' group attached to a carbonyl carbon atom. We will see a similar structure later when we discuss **amines** and **amides**. An **amine** is derived from ammonia (NH_3), with one, two, or all three of the hydrogen atoms of NH_3 replaced by an alkyl (or an aryl) group. The **amide** functional group has a carbonyl group joined to a nitrogen atom from NH_3 or an amine.

There are many familiar carboxylic acids. The R group may be a hydrogen atom (as in formic acid, HCOOH), an alkyl group (as in acetic acid, CH_3COOH), or an aryl group (as in benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$). The location of substituents along the carbon chain is indicated by a Greek letter (for common names) or a number (for names from the International Union of Pure and Applied Chemistry).

A carboxylic acid is formed by the oxidation of an aldehyde with the same number of carbon atoms. Because aldehydes are formed from primary alcohols, these alcohols are also a starting material for carboxylic acids.

Carboxylic acids have strong, often disagreeable, odors. They are highly polar molecules and readily engage in hydrogen bonding, so they have relatively high boiling points.

Carboxylic acids are weak acids. They react with bases to form salts and with carbonates and bicarbonates to form carbon dioxide gas and the salt of the acid.

Esters are pleasant-smelling compounds that are responsible for the fragrances of flowers and fruits. They have lower boiling points than comparable carboxylic acids because, even though ester molecules are somewhat polar, they cannot engage in hydrogen bonding. However, with water, esters can engage in hydrogen bonding; consequently, the low molar mass esters are soluble in water. Esters can be synthesized by **esterification**, in which a carboxylic acid and an alcohol are combined under acidic conditions. Esters are neutral compounds that undergo **hydrolysis**, a reaction with water. Under acidic conditions, hydrolysis is essentially the reverse of esterification. When carried out under basic conditions, the process is called **saponification**.

Inorganic acids also react with alcohols to form esters. Some of the most important esters in biochemistry are those formed from phosphoric acid.

Organic compounds containing a carbonyl group bonded to a nitrogen atom are amides, and the carbon-to-nitrogen bond is an amide linkage (or a peptide linkage). Most amides are colorless and odorless, and the lighter ones are soluble in water. Because they are polar molecules, amides have comparatively high boiling points and melting points. Amides are synthesized from carboxylic acids and NH_3 or amines. Amides are neutral compounds. They resist hydrolysis in water, but acids, bases, and enzymes catalyze the reaction.

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CHAPTER OVERVIEW

10: Functional Group Reactions

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There is a very large, often intimidating, number of organic chemistry reactions. These are the "tools" of a chemist, and to use these tools effectively, we must organize them in a sensible manner and look for patterns of reactivity that permit us make plausible predictions. Most of these reactions occur at special sites of reactivity known as functional groups, and these constitute one organizational scheme that helps us catalog and remember reactions. Ultimately, the best way to achieve proficiency in organic chemistry is to understand how reactions take place, and to recognize the various factors that influence their course. Functional groups are atoms or small groups of atoms (two to four) that exhibit a characteristic reactivity when treated with certain reagents. A particular functional group will almost always display its characteristic chemical behavior when it is present in a compound. Because of this, the discussion of organic reactions is often organized according to functional groups.

[10.1: Oxidation-Reduction \(Redox\) Reactions](#)

[10.2: Redox Reactions in Organic Chemistry](#)

[10.3: Reactions that Form Alcohols](#)

[10.4: Reactions of Alcohols](#)

[10.5: The Formation of Carboxylic Acids](#)

[10.6: Properties of Esters](#)

[10.7: Hydrolysis of Esters](#)

[10.8: Hydrolysis of Amides](#)

[10.9: Summary](#)

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10.1: Oxidation-Reduction (Redox) Reactions

Learning Objectives

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

When zinc metal is submerged into a quantity of aqueous HCl, the following reaction occurs (Figure 10.1.1):

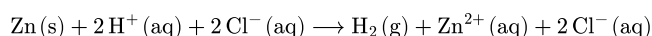


This is one example of what is sometimes called a *single replacement reaction* because Zn replaces H in combination with Cl.



Figure 10.1.1: Zinc Metal plus Hydrochloric Acid. It is fairly obvious that zinc metal reacts with aqueous hydrochloric acid! The bubbles are hydrogen gas (right side of Equation 10.1.1).

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

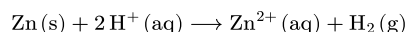


Viewed this way, the net reaction seems to be a charge transfer between zinc and hydrogen atoms. (There is no net change experienced by the chloride ion.) In fact, electrons are being transferred from the zinc atoms to the hydrogen atoms (which ultimately make a molecule of diatomic hydrogen), changing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

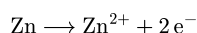
To understand electron-transfer reactions like the one between zinc metal and hydrogen ions, chemists separate them into two parts: one part focuses on the loss of electrons, and one part focuses on the gain of electrons. The loss of electrons is called **oxidation**. The gain of electrons is called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

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

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

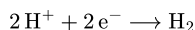


zinc atoms are oxidized to Zn^{2+} . The **half reaction for the oxidation** reaction, omitting phase labels, is as follows:



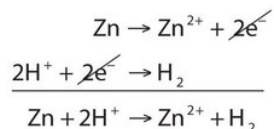
This half reaction is balanced in terms of the number of zinc atoms, and it also shows the two electrons that are needed as products to account for the zinc atom losing two negative charges to become a $2+$ ion. With half reactions, there is one more item to balance: the overall charge on each side of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



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.



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.)

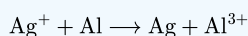
Redox reactions are often balanced by balancing each individual half reaction and then combining the two balanced half reactions. **Sometimes a half reaction must have all of its coefficients multiplied by some integer for all the electrons to cancel.** The following example demonstrates this process.

✓ Example 10.1.1: Reducing Silver Ions

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

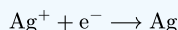
Solution

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



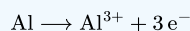
The equation looks balanced as it is written. However, when we compare the overall charges on each side of the equation, we find a charge of +1 on the left but a charge of +3 on the right. This equation is not properly balanced. To balance it, let us write the two half reactions. Silver ions are reduced,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

Reduction half-reaction:

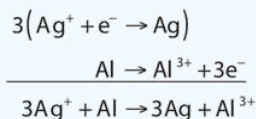


Aluminum is oxidized, losing three electrons to change from Al to Al^{3+} :

Oxidation half-reaction:



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



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

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

? Exercise 10.1.1

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

Answer

Reduction: $\text{Ca}^{2+} + 2\text{e}^- \rightarrow \text{Ca}$

Oxidation: $2\text{K} \rightarrow 2\text{K}^+ + 2\text{e}^-$

Combined: $\text{Ca}^{2+} + 2\text{K} \rightarrow \text{Ca} + 2\text{K}^+$

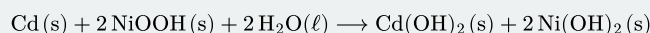
- The **substance oxidized** is the reactant that had undergone oxidation: K
- The **substance reduced** is the reactant that had undergone reduction: Ca^{2+}
- The **reducing agent** is the same as the substance oxidized: K
- The **oxidizing agent** is the same as the substance reduced: Ca^{2+}

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

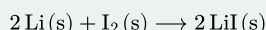
📌 To Your Health: Redox Reactions and Pacemaker Batteries

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

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



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:

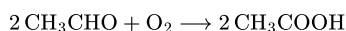


Lithium is oxidized, and iodine is reduced. Although the lithium/iodine battery cannot be recharged, one of its advantages is that it lasts up to 10 years. Thus, a person with a pacemaker does not have to worry about periodic recharging; about once per decade a person requires minor surgery to replace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



Figure 10.1.1: A small button battery like this is used to power a watch, pacemaker, or calculator. (CC BY-SA; Gerhard H Wrodnigg via Wikipedia)

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



Thus, acetaldehyde is being oxidized.

Similarly, **reduction and oxidation can be defined in terms of the gain or loss of hydrogen atoms**. If a molecule adds hydrogen atoms, it is being reduced. If a molecule loses hydrogen atoms, the molecule is being oxidized. For example, in the conversion of acetaldehyde into ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), hydrogen atoms are added to acetaldehyde, so the acetaldehyde is being reduced:

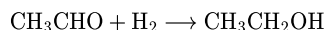


Table shows how each process affects the change in oxygen and change in hydrogen.

Process	Change in oxygen (some reactions)	Change in hydrogen (some reactions)
Oxidation	gain	lose
Reduction	lose	gain

✓ Example 10.1.2

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

- $\text{N}_2 \rightarrow \text{NH}_3$
- $\text{CH}_3\text{CH}_2\text{OHCH}_3 \rightarrow \text{CH}_3\text{COCH}_3$
- $\text{HCHO} \rightarrow \text{HCOOH}$

Solution

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

? Exercise 10.1.2

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

- $\text{CH}_4 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$
- $\text{NO}_2 \rightarrow \text{N}_2$
- $\text{CH}_2=\text{CH}_2 \rightarrow \text{CH}_3\text{CH}_3$

Answer a:

Oxygen is being added. Oxidation is occurring.

Answer b:

Oxygen is being removed. Reduction is occurring.

Answer a:

Hydrogen is being added. Reduction is occurring.

10.1.1 Key Takeaway

Chemical reactions in which electrons are transferred are called oxidation-reduction, or redox, reactions. Oxidation is the loss of electrons. Reduction is the gain of electrons. Oxidation and reduction always occur together, even though they can be written as separate chemical equations.

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10.2: Redox Reactions in Organic Chemistry

Learning Objectives

- To identify oxidation-reduction reactions with organic compounds.

Oxidation-reduction reactions are of central importance in organic chemistry and biochemistry. The burning of fuels that provides the energy to maintain our civilization and the metabolism of foods that furnish the energy that keeps us alive both involve redox reactions.



Figure 10.2.1: The Burning of Natural Gas. The burning of natural gas is not only a combustion reaction but also a redox reaction. Similar reactions include the burning of gasoline and coal. These are also redox reactions. (CC BY-SA 2.0 Generic; [Simon Law](#) via [Flickr](#)).

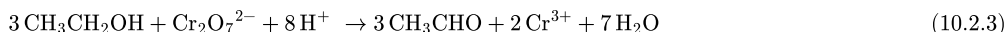
All combustion reactions are also redox reactions. A typical combustion reaction is the burning of methane, the principal component of natural gas (Figure 10.2.1).



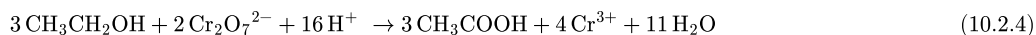
In respiration, the biochemical process by which the oxygen we inhale in air oxidizes foodstuffs to carbon dioxide and water, redox reactions provide energy to living cells. A typical respiratory reaction is the oxidation of [glucose](#) ($\text{C}_6\text{H}_{12}\text{O}_6$), the simple sugar we encountered in the chapter-opening essay that makes up the diet of yeast:



Organic chemists use a variety of redox reactions. For example, potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) 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* ($\text{C}=\text{O}$) and is often written as RCHO . One example is the reaction used by the Breathalyzer to detect ethyl alcohol ($\text{CH}_3\text{CH}_2\text{OH}$) in a person's breath:



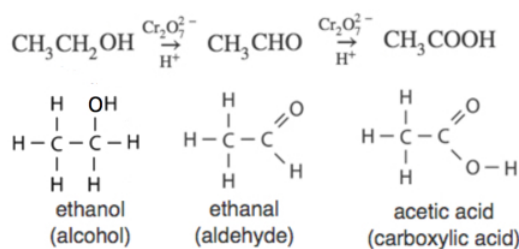
If the product acetaldehyde (CH_3CHO) is not removed as it forms, it is further oxidized to acetic acid (CH_3COOH). In this case, the overall reaction is as follows:



In this reaction, the chromium atom is reduced because it lost oxygen atoms from $\text{Cr}_2\text{O}_7^{2-}$ to Cr^{3+} . On the other hand, the carbon atom in ethanol is oxidized. In the **oxidation** of ethyl alcohol ($\text{CH}_3\text{CH}_2\text{OH}$, a.k.a. ethanol) to form acetaldehyde (CH_3CHO , a.k.a. ethanal), the **number of bonds to oxygen has increased and the number of hydrogen atoms has decreased** from six to four. Either or both of these indicate that an oxidation has occurred.



In the oxidation of acetaldehyde to acetic acid (a.k.a. ethanoic acid), the carbon atom that gained an additional oxygen is the element oxidized.



When the OH group of the alcohol is bonded to an interior carbon atom, the oxidation of an alcohol will produce a **ketone** (the formulas of ketones are often written as RCOR , and the carbon–oxygen bond is a double bond). The simplest ketone is derived from 2-propanol ($\text{CH}_3\text{CHOHCH}_3$). It is the common solvent acetone [$(\text{CH}_3)_2\text{CO}$], which is used in varnishes, lacquers, rubber cement, and nail polish remover. Acetone can be formed by the following redox reaction:

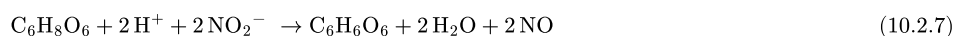


As we have just seen, aldehydes and ketones can be formed by the oxidation of alcohols. Conversely, aldehydes and ketones can be reduced to alcohols. Reduction of the carbonyl group is important in living organisms. For example, in anaerobic metabolism, in which biochemical processes take place in the absence of oxygen, pyruvic acid (CH_3COCOOH) is reduced to lactic acid ($\text{CH}_3\text{CHOHCOOH}$) in the muscles.



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

In food chemistry, the substances known as antioxidants are reducing agents. Ascorbic acid (**vitamin C**; $\text{C}_6\text{H}_8\text{O}_6$) is thought to retard potentially damaging oxidation of living cells. In the process, it is oxidized to dehydroascorbic acid ($\text{C}_6\text{H}_6\text{O}_6$). In the stomach, ascorbic acid reduces the nitrite ion (NO_2^-) to nitric oxide (NO):



If reaction in Equation 10.2.7 did not occur, nitrite ions from foods would oxidize the iron in hemoglobin, destroying its ability to carry oxygen.

Tocopherol (**vitamin E**) is also an antioxidant. In the body, **vitamin E** is thought to act by scavenging harmful by-products of metabolism, such as the highly reactive molecular fragments called free radicals. In foods, vitamin E acts to prevent fats from being oxidized and thus becoming rancid. **Vitamin C** is also a good antioxidant (Figure 10.2.2).



Figure 10.2.2: Citrus Fruits. Citrus fruits, such as oranges, lemons, and limes, are good sources of vitamin C, which is an antioxidant. (Pexels License; Scott Webb via [Pexels](#))

Finally, and of greatest importance, green plants carry out the redox reaction that makes possible almost all life on Earth. They do this through a process called photosynthesis, in which carbon dioxide and water are converted to glucose ($\text{C}_6\text{H}_{12}\text{O}_6$). The synthesis of glucose requires a variety of proteins called enzymes and a green pigment called chlorophyll that converts sunlight into chemical energy (Figure 10.2.3). The overall change that occurs is as follows:



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 10.2.3: Life on Earth. Photosynthesis is the fundamental process by which plants use sunlight to convert carbon dioxide and water into glucose and oxygen. Then plants make more complex carbohydrates. It is the ultimate source of all food on Earth, and it is a redox reaction. (Public Domain; Wikipedia).

Summary

Redox reactions are common in organic and biological chemistry, including the combustion of organic chemicals, respiration, and photosynthesis.

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10.3: Reactions that Form Alcohols

Learning Objectives

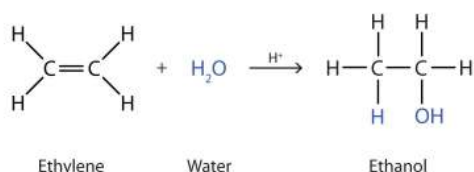
- To describe how to prepare alcohols from alkenes

Methanol is prepared by combining hydrogen gas and carbon monoxide at high temperatures and pressures in the presence of a catalyst composed of zinc oxide (ZnO) and chromium oxide (Cr₂O₃) catalyst.

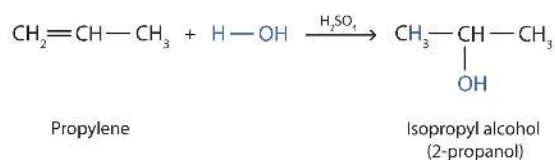
Methanol is an important solvent and is used as an automotive fuel, either as the pure liquid—as in some racing cars—or as an additive in gasoline.

Nearly 2 billion gallons of methanol are produced each year in the United States by the catalytic reduction of carbon monoxide with hydrogen gas.

Many simple alcohols are made by the hydration of alkenes. Ethanol is made by the hydration of ethylene in the presence of a catalyst such as sulfuric acid (H₂SO₄).



In a similar manner, isopropyl alcohol is produced by the addition of water to propene (propylene).

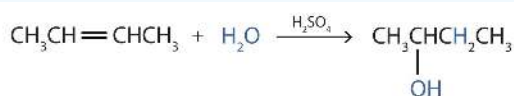


Additional Exercise 13.4.113.4.1 describes how to use a generalization called [Markovnikov's rule](#) to predict the results when the addition of water to an alcohol has two possible products.

✓ Example 10.3.1

Write the equation for the reaction of 2-butene with water to form 2-butanol. Indicate that sulfuric acid is used as a catalyst.

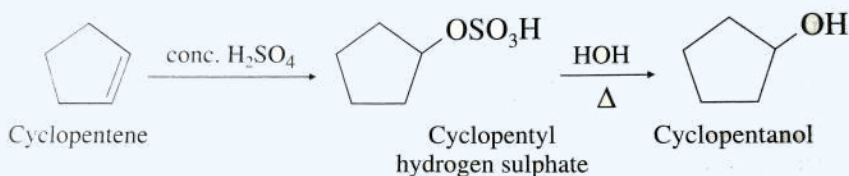
First write the condensed structural formula of 2-butene and indicate that it reacts with water. Then write the condensed structural formula of 2-butanol after the reaction arrow to indicate that it is the product. Finally, write the formula for the catalyst above the arrow.



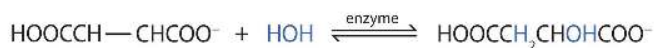
? Exercise 10.3.1

Write the equation for the reaction of cyclopentene with water to form cyclopentanol. Indicate that sulfuric acid (H₂SO₄) is used as a catalyst.

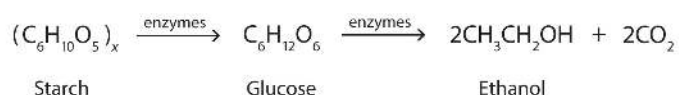
Answer



Many OH compounds in living systems are formed by alkene hydration. Here is an example that occurs in the [Krebs cycle](#): fumarate is hydrated to form malate.

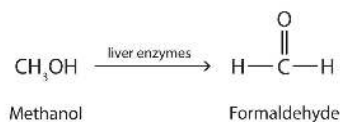


In addition to its preparation from ethylene, ethanol is made by the fermentation of sugars or starch from various sources (potatoes, corn, wheat, rice, etc.). Fermentation is catalyzed by enzymes found in yeast and proceeds by an elaborate multistep mechanism. We can represent the overall process as follows:



To Your Health: The Physiological Effects of Alcohols

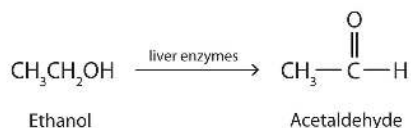
Methanol is quite poisonous to humans. Ingestion of as little as 15 mL of methanol can cause blindness, and 30 mL (1 oz) can cause death. However, the usual fatal dose is 100 to 150 mL. The main reason for methanol's toxicity is that we have liver enzymes that catalyze its oxidation to formaldehyde, the simplest member of the [aldehyde family](#):



Formaldehyde reacts rapidly with the components of cells, coagulating proteins in much the same way that cooking coagulates an egg. This property of formaldehyde accounts for much of the toxicity of methanol.

Organic and biochemical equations are frequently written showing only the organic reactants and products. In this way, we focus attention on the organic starting material and product, rather than on balancing complicated equations.

Ethanol is oxidized in the liver to acetaldehyde:



The acetaldehyde is in turn oxidized to acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$), a normal constituent of cells, which is then oxidized to carbon dioxide and water. Even so, ethanol is potentially toxic to humans. The rapid ingestion of 1 pt (about 500 mL) of pure ethanol would kill most people, and acute ethanol poisoning kills several hundred people each year—often those engaged in some sort of drinking contest. Ethanol freely crosses into the brain, where it depresses the respiratory control center, resulting in failure of the respiratory muscles in the lungs and hence suffocation. Ethanol is believed to act on nerve cell membranes, causing a diminution in speech, thought, cognition, and judgment.

Rubbing alcohol is usually a 70% aqueous solution of isopropyl alcohol. It has a high vapor pressure, and its rapid evaporation from the skin produces a cooling effect. It is toxic when ingested but, compared to methanol, is less readily absorbed through the skin.

10.3.1 Summary

Many alcohols are made by the hydration of alkenes. Ethanol can be made by the fermentation of sugars or starch from various sources.

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10.4: Reactions of Alcohols

Learning Objectives

1. Give two major types of reactions of alcohols.
2. Describe the result of the oxidation of a primary alcohol.
3. Describe the result of the oxidation of a secondary alcohol.

Chemical reactions in alcohols occur mainly at the functional group, but some involve hydrogen atoms attached to the OH-bearing carbon atom or to an adjacent carbon atom. Of the three major kinds of alcohol reactions, which are summarized in Figure 10.4.1, two—dehydration and oxidation—are considered here. The third reaction type—[esterification](#)—is covered elsewhere.

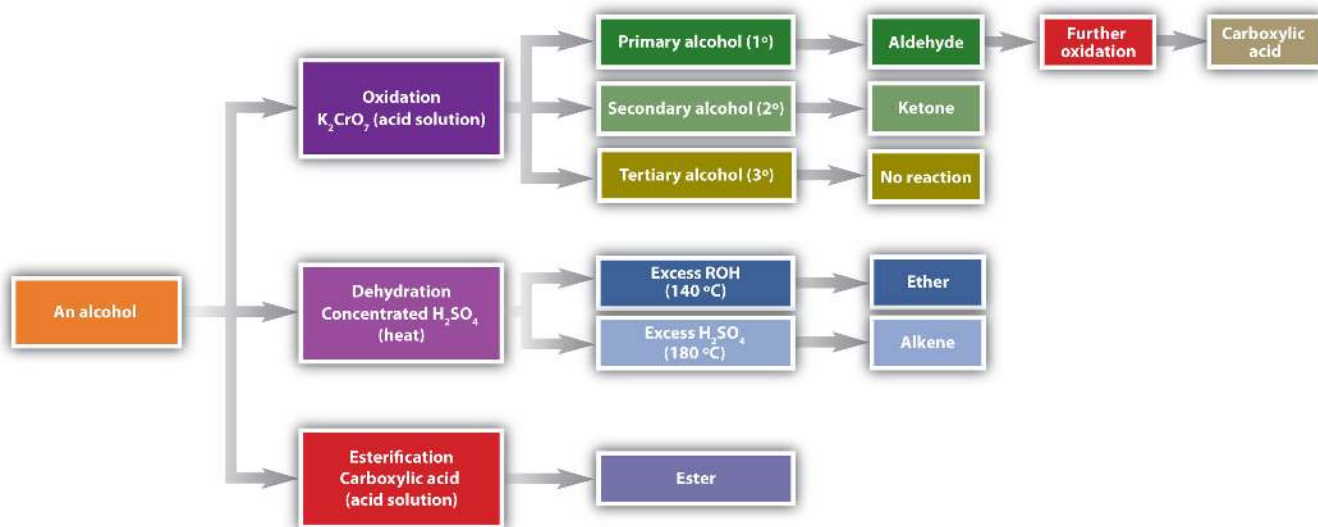
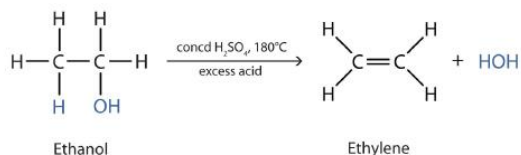


Figure 10.4.1: Reactions of Alcohols. Oxidation and dehydration of alcohols are considered here. A flow diagram of three possible reactions of an alcohol. The final products of the reactions are also shown at the end of the flow diagram.

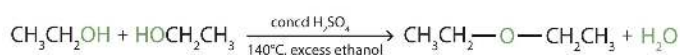
10.4.1 Dehydration

As noted in Figure 10.4.1, an alcohol undergoes dehydration in the presence of a catalyst to form an alkene and water. The reaction removes the OH group from the alcohol carbon atom and a hydrogen atom from an adjacent carbon atom in the same molecule:



Structural formula of ethanol dehydrating under excess concentrated sulfuric acid at 180 degrees celsius. The products are ethylene and a side product of a water molecule.

Under the proper conditions, it is possible for the dehydration to occur between *two* alcohol molecules. The entire OH group of one molecule and only the hydrogen atom of the OH group of the second molecule are removed. The two ethyl groups attached to an oxygen atom form an ether molecule.



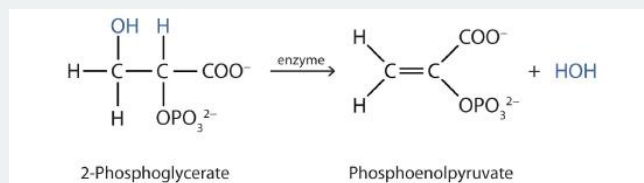
Two molecules of ethanol

Diethyl ether

Two molecules of ethanol are dehydrated under concentrated sulfuric acid at 140 degrees celsius and excess ethanol to give a diethyl ether and a water molecule.

(Ethers are discussed in elsewhere) Thus, depending on conditions, one can prepare either alkenes or ethers by the dehydration of alcohols.

Both dehydration and hydration reactions occur continuously in cellular metabolism, with enzymes serving as catalysts and at a temperature of about 37°C. The following reaction occurs in the "Embden–Meyerhof" pathway

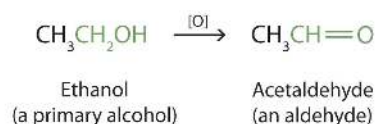


Structural formula of 2 phosphoglycerate forming phosphoenolpyruvate and a water molecule with the aid of enzymes.

Although the participating compounds are complex, the reaction is the same: elimination of water from the starting material. The idea is that if you know the chemistry of a particular functional group, you know the chemistry of hundreds of different compounds.

10.4.2 Oxidation

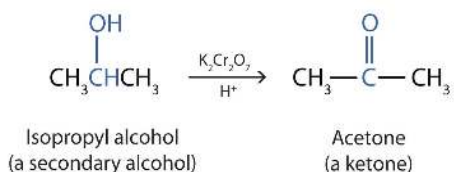
Primary and secondary alcohols are readily oxidized. We saw earlier how methanol and ethanol are oxidized by liver enzymes to form aldehydes. Because a variety of oxidizing agents can bring about oxidation, we can indicate an oxidizing agent without specifying a particular one by writing an equation with the symbol [O] above the arrow. For example, we write the oxidation of ethanol—a primary alcohol—to form acetaldehyde—an aldehyde—as follows:



Formula of ethanol reacting to form acetaldehyde with

an O in a bracket above the right pointing arrow.

We shall see that aldehydes are even more easily oxidized than alcohols and yield carboxylic acids. Secondary alcohols are oxidized to ketones. The oxidation of isopropyl alcohol by potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) gives acetone, the simplest ketone:

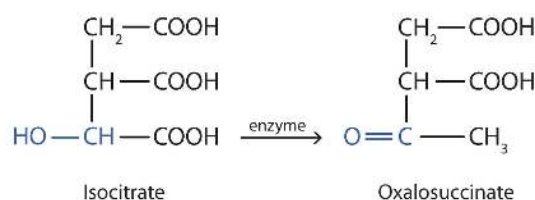


Unlike aldehydes, ketones are relatively resistant to further oxidation, so no special precautions are required to isolate them as they form. Note that in oxidation of both primary (RCH_2OH) and secondary (R_2CHOH) alcohols, two hydrogen atoms are removed from the alcohol molecule, one from the OH group and other from the carbon atom that bears the OH group.

These reactions can also be carried out in the laboratory with chemical oxidizing agents. One such oxidizing agent is potassium dichromate. The balanced equation (showing only the species involved in the reaction) in this case is as follows:



Alcohol oxidation is important in living organisms. Enzyme-controlled oxidation reactions provide the energy cells need to do useful work. One step in the metabolism of carbohydrates involves the oxidation of the secondary alcohol group in isocitric acid to a ketone group:



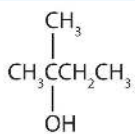
The overall type of reaction is the same as that in the conversion of isopropyl alcohol to acetone.

Tertiary alcohols (R_3COH) are resistant to oxidation because the carbon atom that carries the OH group does not have a hydrogen atom attached but is instead bonded to other carbon atoms. The oxidation reactions we have described involve the formation of a carbon-to-oxygen double bond. Thus, the carbon atom bearing the OH group must be able to release one of its attached atoms to form the double bond. The carbon-to-hydrogen bonding is easily broken under oxidative conditions, but carbon-to-carbon bonds are not. Therefore tertiary alcohols are not easily oxidized.

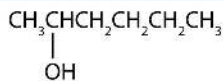
✓ Example 10.4.1

Write an equation for the oxidation of each alcohol. Use [O] above the arrow to indicate an oxidizing agent. If no reaction occurs, write "no reaction" after the arrow.

- a. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$



- b. From left to right, there are four carbons on the alkane straight chain with a methyl and hydroxyl group on carbon 2.

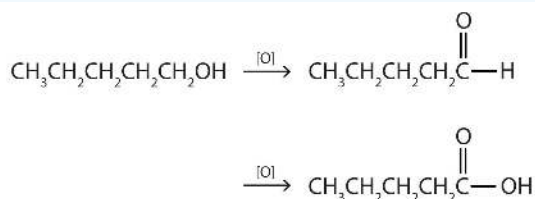


- c. From left to right, there are six carbons on the alkane straight chain with a hydroxyl group on carbon 2.

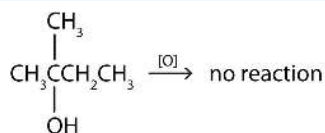
Solution

The first step is to recognize the class of each alcohol as primary, secondary, or tertiary.

- a. This alcohol has the OH group on a carbon atom that is attached to only *one* other carbon atom, so it is a primary alcohol. Oxidation forms first an aldehyde and further oxidation forms a carboxylic acid.

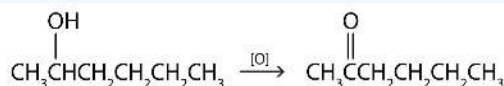


- b. This alcohol has the OH group on a carbon atom that is attached to three other carbon atoms, so it is a tertiary alcohol. No



reaction occurs.

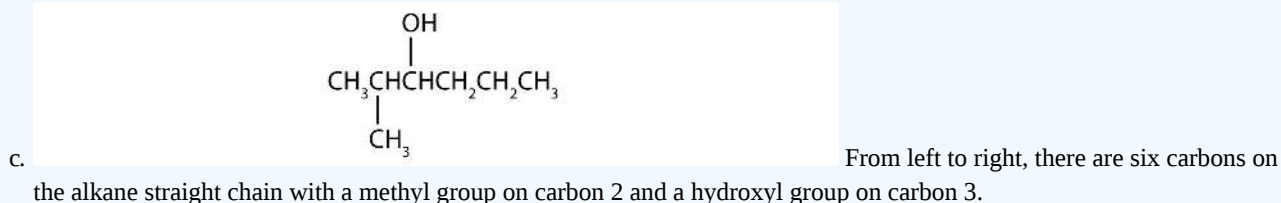
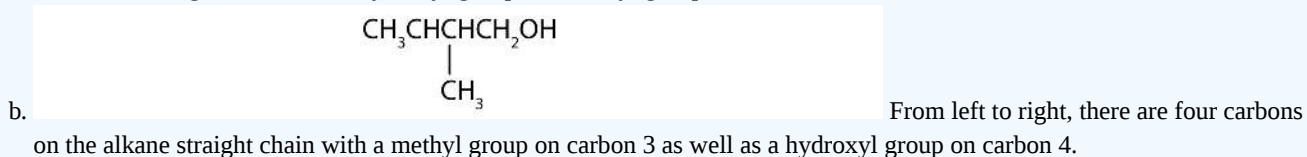
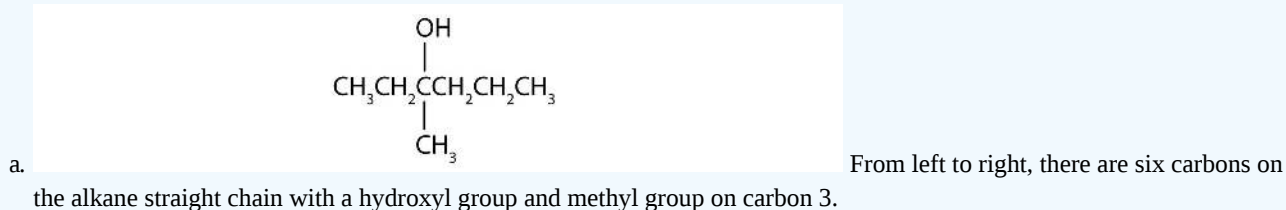
- c. This alcohol has the OH group on a carbon atom that is attached to two other carbon atoms, so it is a secondary alcohol;



oxidation gives a ketone.

? Exercise 10.4.1

Write an equation for the oxidation of each alcohol. Use [O] above the arrow to indicate an oxidizing agent. If no reaction occurs, write "no reaction" after the arrow.



10.4.3 Summary

Alcohols can be dehydrated to form either alkenes (higher temperature, excess acid) or ethers (lower temperature, excess alcohol). Primary alcohols are oxidized to form aldehydes. Secondary alcohols are oxidized to form ketones. Tertiary alcohols are not readily oxidized.

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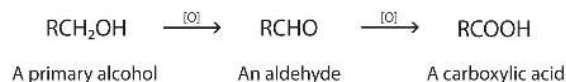
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10.5: The Formation of Carboxylic Acids

Learning Objectives

- To describe the preparation of carboxylic acids.

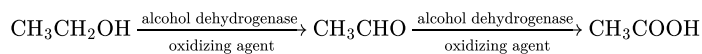
As we noted previously, the oxidation of aldehydes or primary alcohols forms carboxylic acids:



In the presence of an oxidizing agent, ethanol is oxidized to acetaldehyde, which is then oxidized to acetic acid.



This process also occurs in the liver, where enzymes catalyze the oxidation of ethanol to acetic acid.



Acetic acid can be further oxidized to carbon dioxide and water.

Summary

Whether in the laboratory or in the body, the oxidation of aldehydes or primary alcohols forms carboxylic acids.

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10.6: Properties of Esters

Learning Objectives

- Compare the boiling points of esters with alcohols of similar molar mass.
- Compare the solubilities of esters in water with the solubilities of comparable alkanes and alcohols in water.

Ester molecules are polar but have no hydrogen atom attached directly to an oxygen atom. They are therefore incapable of engaging in intermolecular hydrogen bonding with one another and thus have considerably lower boiling points than their isomeric carboxylic acids counterparts. Because ester molecules can engage in hydrogen bonding with water molecules, however, esters of low molar mass are somewhat soluble in water. Borderline solubility occurs in those molecules that have three to five carbon atoms. Table 10.6.1 lists the physical properties of some common esters.

Esters are common solvents. Ethyl acetate is used to extract organic solutes from aqueous solutions—for example, to remove caffeine from coffee. It also is used to remove nail polish and paint. Cellulose nitrate is dissolved in ethyl acetate and butyl acetate to form lacquers. The solvent evaporates as the lacquer “dries,” leaving a thin film on the surface. High boiling esters are used as softeners (plasticizers) for brittle plastics.

Table 10.6.1: Physical Properties of Some Esters

Condensed Structural Formula	Name	Molar Mass	Melting Point (°C)	Boiling Point (°C)	Aroma
HCOOCH_3	methyl formate	60	−99	32	
$\text{HCOOCH}_2\text{CH}_3$	ethyl formate	74	−80	54	rum
$\text{CH}_3\text{COOCH}_3$	methyl acetate	74	−98	57	
$\text{CH}_3\text{COOCH}_2\text{CH}_3$	ethyl acetate	88	−84	77	
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_3$	methyl butyrate	102	−85	102	apple
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3$	ethyl butyrate	116	−101	121	pineapple
$\text{CH}_3\text{COO}(\text{CH}_2)_4\text{CH}_3$	pentyl acetate	130	−71	148	pear
$\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$	isopentyl acetate	130	−79	142	banana
$\text{CH}_3\text{COOCH}_2\text{C}_6\text{H}_5$	benzyl acetate	150	−51	215	jasmine
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COO}(\text{CH}_2)_4\text{CH}_3$	pentyl butyrate	158	−73	185	apricot
$\text{CH}_3\text{COO}(\text{CH}_2)_7\text{CH}_3$	octyl acetate	172	−39	210	orange

Summary

Esters have polar bonds but do not engage in hydrogen bonding and are therefore intermediate in boiling points between the nonpolar alkanes and the alcohols, which engage in hydrogen bonding. Ester molecules can engage in hydrogen bonding with water, so esters of low molar mass are therefore somewhat soluble in water.

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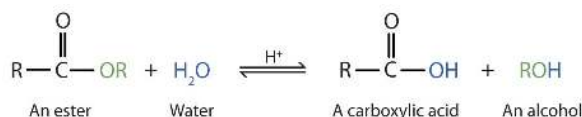
10.7: Hydrolysis of Esters

Learning Objectives

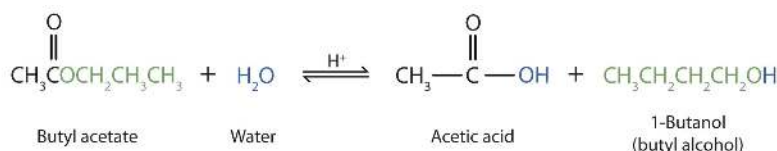
- Describe the typical reaction that takes place with esters.
- Identify the products of an acidic hydrolysis of an ester.
- Identify the products of a basic hydrolysis of an ester.

Esters are neutral compounds, unlike the acids from which they are formed. In typical reactions, the alkoxy (OR') group of an ester is replaced by another group. One such reaction is hydrolysis, literally “splitting with water.” The hydrolysis of esters is catalyzed by either an acid or a base.

Acidic hydrolysis is simply the reverse of [esterification](#). The ester is heated with a large excess of water containing a strong-acid catalyst. Like esterification, the reaction is reversible and does not go to completion.



As a specific example, butyl acetate and water react to form acetic acid and 1-butanol. The reaction is reversible and does not go to completion.

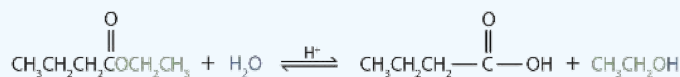


✓ Example 10.7.1

Write an equation for the acidic hydrolysis of ethyl butyrate ($\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3$) and name the products.

Solution

Remember that in acidic hydrolysis, water (HOH) splits the ester bond. The H of HOH joins to the oxygen atom in the OR part of the original ester, and the OH of HOH joins to the carbonyl carbon atom:

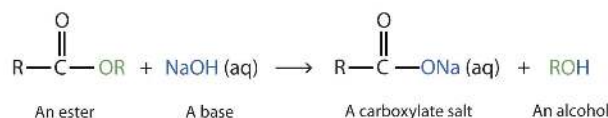


The products are butyric acid (butanoic acid) and ethanol.

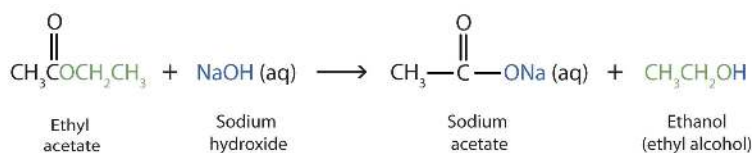
? Exercise 10.7.1

Write an equation for the acidic hydrolysis of methyl butanoate and name the products.

When a base (such as sodium hydroxide [NaOH] or potassium hydroxide [KOH]) is used to hydrolyze an ester, the products are a carboxylate salt and an alcohol. Because soaps are prepared by the alkaline hydrolysis of fats and oils, alkaline hydrolysis of esters is called saponification (Latin *sapon*, meaning “soap,” and *facere*, meaning “to make”). In a saponification reaction, the base is a reactant, not simply a catalyst. The reaction goes to completion:



As a specific example, ethyl acetate and NaOH react to form sodium acetate and ethanol:

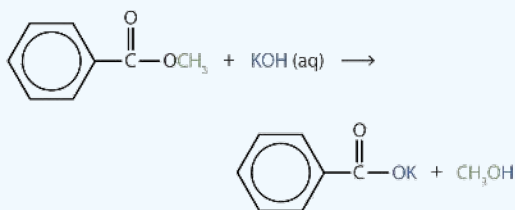


✓ Example 10.7.2

Write an equation for the hydrolysis of methyl benzoate in a potassium hydroxide solution.

Solution

In basic hydrolysis, the molecule of the base splits the ester linkage. The acid portion of the ester ends up as the *salt* of the acid (in this case, the potassium salt). The alcohol portion of the ester ends up as the free alcohol.



? Exercise 10.7.2

Write the equation for the hydrolysis of ethyl propanoate in a sodium hydroxide solution.

Summary

Hydrolysis is a most important reaction of esters. Acidic hydrolysis of an ester gives a carboxylic acid and an alcohol. Basic hydrolysis of an ester gives a carboxylate salt and an alcohol.

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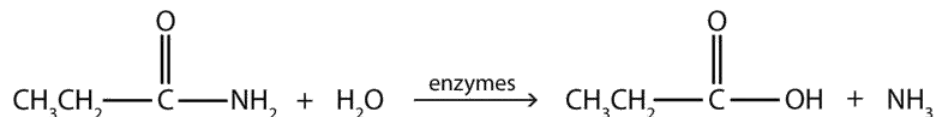
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10.8: Hydrolysis of Amides

Learning Objectives

- To identify the typical reaction that amides undergo.

Generally, amides resist hydrolysis in plain water, even after prolonged heating. In the presence of added acid or base, however, hydrolysis proceeds at a moderate rate. In living cells, amide hydrolysis is catalyzed by enzymes. Amide hydrolysis is illustrated in the following example:



Hydrolysis of an amide in acid solution actually gives a carboxylic acid and the salt of ammonia or an amine (the ammonia or amine initially formed is neutralized by the acid). Basic hydrolysis gives a salt of the carboxylic acid and ammonia or an amine.

✓ Example 10.8.1

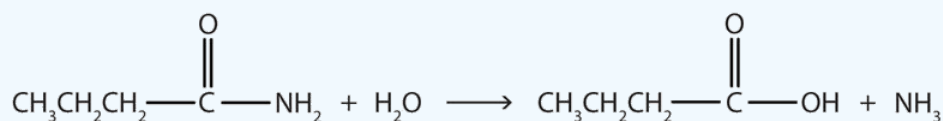
Write the equation for the hydrolysis of each compound.

- butyramide
- benzamide

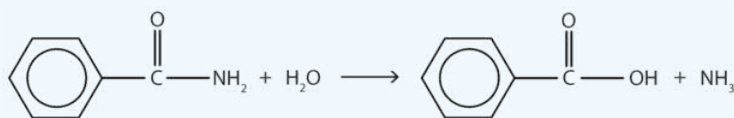
Solution

Solution

- The hydrolysis of a simple amide produces an organic acid and ammonia. Butyramide thus yields butyric acid and ammonia.



- The hydrolysis of an amide produces an organic acid and ammonia. Benzamide thus yields benzoic acid and ammonia.



? Exercise 10.8.1

What are the parent compounds of each amide

- propionamide (propanamide)
- hexanamide

Answer

- propanoic acid and ammonia
- hexanoic acid and ammonia

Exercise 13.9.113.9.1

Career Focus: Athletic Trainer

Athletic training is an allied health-care profession recognized by the American Medical Association. The athletic trainer's role is to recognize, evaluate, and provide immediate care for athletic injuries; prevent athletic injuries by taping, bandaging, and bracing vulnerable body parts; make referrals to medical doctors when necessary; and rehabilitate injured athletes. Athletic trainers work in high schools, colleges, and other organizations where athletics programs are found. Athletic trainers usually have a degree from an accredited athletic training program whose curriculum includes such basic science courses as biology, chemistry, and physics. These studies provide the necessary background for more applied courses, such as anatomy and physiology, exercise physiology, kinesiology, and nutrition. Knowledge of chemistry is necessary for understanding pharmacological and medical terminology. For example, athletic trainers must understand the action of numerous drugs, many of which are esters, amines, or amides like those mentioned in this chapter.

Athletic trainers may have administrative duties, such as the responsibility for ordering supplies. They also need to be able to evaluate nutritional supplements because providing the wrong one can get an athlete banned from competition and may bring sanctions against a school. In short, the athletic trainer is responsible for the overall health and well-being of the athletes in his or her charge.

10.8.1 Key Takeaway

- The hydrolysis of an amide produces a carboxylic acid and ammonia or an amine.

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10.9: Summary

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

A **carboxylic acid** (RCOOH) contains the functional group COOH , called the **carboxyl group**, which has an OH group attached to a carbonyl carbon atom. An **ester** (RCOOR') has an OR' group attached to a carbonyl carbon atom. An **amine** is derived from ammonia (NH_3), with one, two, or all three of the hydrogen atoms of NH_3 replaced by an alkyl (or an aryl) group. The **amide** functional group has a carbonyl group joined to a nitrogen atom from NH_3 or an amine.

There are many familiar carboxylic acids. The R group may be a hydrogen atom (as in formic acid, HCOOH), an alkyl group (as in acetic acid, CH_3COOH), or an aryl group (as in benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$). The location of substituents along the carbon chain is indicated by a Greek letter (for common names) or a number (for names from the International Union of Pure and Applied Chemistry).

A carboxylic acid is formed by the oxidation of an aldehyde with the same number of carbon atoms. Because aldehydes are formed from primary alcohols, these alcohols are also a starting material for carboxylic acids.

Carboxylic acids have strong, often disagreeable, odors. They are highly polar molecules and readily engage in hydrogen bonding, so they have relatively high boiling points.

Carboxylic acids are weak acids. They react with bases to form salts and with carbonates and bicarbonates to form carbon dioxide gas and the salt of the acid.

Esters are pleasant-smelling compounds that are responsible for the fragrances of flowers and fruits. They have lower boiling points than comparable carboxylic acids because, even though ester molecules are somewhat polar, they cannot engage in hydrogen bonding. However, with water, esters can engage in hydrogen bonding; consequently, the low molar mass esters are soluble in water. Esters can be synthesized by **esterification**, in which a carboxylic acid and an alcohol are combined under acidic conditions. Esters are neutral compounds that undergo **hydrolysis**, a reaction with water. Under acidic conditions, hydrolysis is essentially the reverse of esterification. When carried out under basic conditions, the process is called **saponification**.

Inorganic acids also react with alcohols to form esters. Some of the most important esters in biochemistry are those formed from phosphoric acid.

Amines are nitrogen-containing organic molecules derived from ammonia (NH_3). A **primary (1°) amine** (RNH_2) has one organic group bonded to the nitrogen atom, a **secondary (2°) amine** (R_2NH) has two organic groups bonded to the nitrogen atom, and a **tertiary (3°) amine** (R_3N) has three organic groups bonded to the nitrogen atom. Amines are basic compounds that react with strong acids to produce ammonium (NH_4^+) salts. A cyclic compound in which the ring contains one or more noncarbon atoms is called a **heterocyclic compound**. There are many heterocyclic amines, including many physiologically important ones. **Alkaloids** are heterocyclic amines found in many plants. Caffeine, nicotine, and cocaine are familiar alkaloids.

Organic compounds containing a carbonyl group bonded to a nitrogen atom are amides, and the carbon-to-nitrogen bond is an amide linkage (or a peptide linkage). Most amides are colorless and odorless, and the lighter ones are soluble in water. Because they are polar molecules, amides have comparatively high boiling points and melting points. Amides are synthesized from carboxylic acids and NH_3 or amines. Amides are neutral compounds. They resist hydrolysis in water, but acids, bases, and enzymes catalyze the reaction.

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CHAPTER OVERVIEW

11: 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.

- [11.1: Prelude to Carbohydrates](#)
- [11.2: Carbohydrates](#)
- [11.3: Classes of Monosaccharides](#)
- [11.4: Important Hexoses](#)
- [11.5: Cyclic Structures of Monosaccharides](#)
- [11.6: Properties of Monosaccharides](#)
- [11.7: Disaccharides](#)
- [11.8: Polysaccharides](#)
- [11.S: Carbohydrates \(Summary\)](#)

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11.1: Prelude to Carbohydrates

In the United States, 17.9 million people have been diagnosed with diabetes, and experts estimate that at least another 5.7 million people have the disease but have not been diagnosed. In 2006, diabetes was the seventh leading cause of death, listed on 72,507 death certificates. Moreover, it was a contributing factor in over 200,000 deaths in which the cause was listed as something else, such as heart or kidney disease.

People with diabetes are impaired in their ability to metabolize glucose, a sugar needed by the body for energy; as a result, excessive quantities of glucose accumulate in the blood and the urine. The characteristic symptoms of diabetes are weight loss, constant hunger, extreme thirst, and frequent urination (the kidneys excrete large amounts of water in an attempt to remove the excess sugar from the blood).

An important diagnostic test for diabetes is the oral glucose tolerance test, which measures the level of glucose in blood plasma. A first measurement is made after a fast of at least 8 h, followed by another measurement 2 h after the person drinks a flavored solution of 75 g of glucose dissolved in water. At the second measurement, the glucose plasma level should be no higher than 139 mg/dL. Individuals with a value between 140 and 199 mg/dL are diagnosed with prediabetes, while those with a value of 200 mg/dL or above are diagnosed with diabetes. Following a diagnosis of diabetes a person will need to monitor his or her blood glucose levels daily (or more often) using a glucose meter.



Figure 11.1.1: Using a Glucose Meter to Test Blood Glucose Level. (Public Domain; Centers for Disease Control and Prevention).

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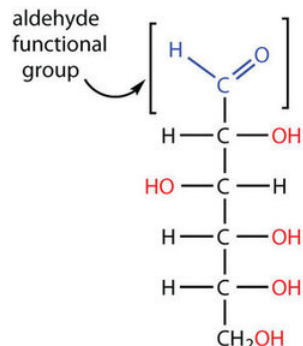
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11.2: Carbohydrates

Learning Objectives

- To recognize carbohydrates and classify them as mono-, di-, or polysaccharides.

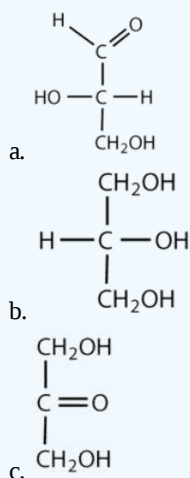
All carbohydrates consist of carbon, hydrogen, and oxygen atoms and are polyhydroxy aldehydes or ketones or are compounds that can be broken down to form such compounds. Examples of carbohydrates include starch, fiber, the sweet-tasting compounds called sugars, and structural materials such as cellulose. The term *carbohydrate* had its origin in a misinterpretation of the molecular formulas of many of these substances. For example, because its formula is $C_6H_{12}O_6$, glucose was once thought to be a “carbon hydrate” with the structure $C_6 \cdot 6H_2O$.



Because glucose has an aldehyde functional group and several $-OH$ (hydroxyl) groups, it is described as a polyhydroxy aldehyde.

Example 11.2.1

Which compounds would be classified as carbohydrates?

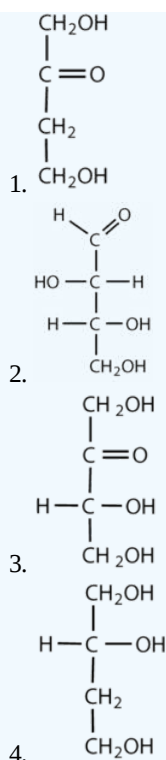


Solution

- This is a carbohydrate because the molecule contains an aldehyde functional group with OH groups on the other two carbon atoms.
- This is not a carbohydrate because the molecule does not contain an aldehyde or a ketone functional group.
- This is a carbohydrate because the molecule contains a ketone functional group with OH groups on the other two carbon atoms.

? Exercise 11.2.1

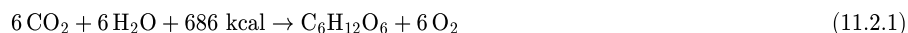
Which compounds would be classified as carbohydrates?



Answer

1. This is a carbohydrate because the molecule contains a ketone functional group with OH groups on the other two carbon atoms.
2. This is a carbohydrate because the molecule contains an aldehyde with OH groups on the other carbon atoms.
3. This is a carbohydrate because the molecule contains a ketone functional group with OH groups on the other two carbon atoms.
4. This is not a carbohydrate because it does not contain a functional ketone or aldehyde.

Green plants are capable of synthesizing glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) from carbon dioxide (CO_2) and water (H_2O) by using solar energy in the process known as photosynthesis:



(The 686 kcal come from solar energy.) Plants can use the glucose for energy or convert it to larger carbohydrates, such as starch or cellulose. Starch provides energy for later use, perhaps as nourishment for a plant's seeds, while cellulose is the structural material of plants. We can gather and eat the parts of a plant that store energy—seeds, roots, tubers, and fruits—and use some of that energy ourselves. Carbohydrates are also needed for the synthesis of nucleic acids and many proteins and lipids.

Animals, including humans, cannot synthesize carbohydrates from carbon dioxide and water and are therefore dependent on the plant kingdom to provide these vital compounds. We use carbohydrates not only for food (about 60%–65% by mass of the average diet) but also for clothing (cotton, linen, rayon), shelter (wood), fuel (wood), and paper (wood).

The simplest carbohydrates—those that cannot be hydrolyzed to produce even smaller carbohydrates—are called monosaccharides. Two or more monosaccharides can link together to form chains that contain from two to several hundred or thousand monosaccharide units. Prefixes are used to indicate the number of such units in the chains. Disaccharide molecules have two monosaccharide units, *trisaccharide* molecules have three units, and so on. Chains with many monosaccharide units joined together are called polysaccharides. All these so-called higher saccharides can be hydrolyzed back to their constituent monosaccharides.

Compounds that cannot be hydrolyzed will not react with water to form two or more smaller compounds.

Summary

Carbohydrates are an important group of biological molecules that includes sugars and starches. Photosynthesis is the process by which plants use energy from sunlight to synthesize carbohydrates. A monosaccharide is the simplest carbohydrate and cannot be hydrolyzed to produce a smaller carbohydrate molecule. Disaccharides contain two monosaccharide units, and polysaccharides contain many monosaccharide units.

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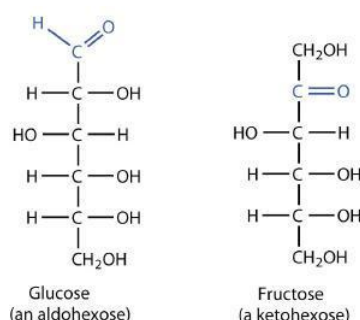
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11.3: Classes of Monosaccharides

Learning Objectives

- Classify monosaccharides as aldoses or ketoses and as trioses, tetroses, pentoses, or hexoses.
- Distinguish between a D sugar and an L sugar.

The naturally occurring monosaccharides contain three to seven carbon atoms per molecule. Monosaccharides of specific sizes may be indicated by names composed of a stem denoting the number of carbon atoms and the suffix *-ose*. For example, the terms *triose*, *tetrose*, *pentose*, and *hexose* signify monosaccharides with, respectively, three, four, five, and six carbon atoms. Monosaccharides are also classified as aldoses or ketoses. Those monosaccharides that contain an aldehyde functional group are called aldoses; those containing a ketone functional group on the second carbon atom are ketoses. Combining these classification systems gives general names that indicate both the type of carbonyl group *and* the number of carbon atoms in a molecule. Thus, monosaccharides are described as aldotetroses, aldopentoses, ketopentoses, ketoheptoses, and so forth. Glucose and fructose are specific examples of an aldohexose and a ketohexose, respectively.



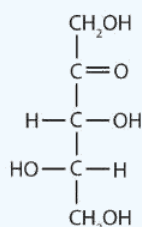
✓ Example 11.3.1

Draw an example of each type of compound.

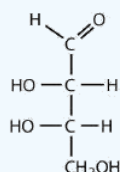
- a ketopentose
- an aldotetrose

Solution

- The structure must have five carbon atoms with the second carbon atom being a carbonyl group and the other four carbon atoms each having an OH group attached. Several structures are possible, but one example is shown.



- The structure must have four carbon atoms with the first carbon atom part of the aldehyde functional group. The other three carbon atoms each have an OH group attached. Several structures are possible, but one example is shown.



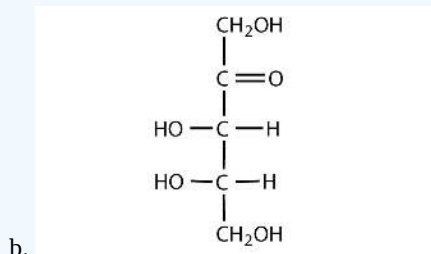
? Exercise 11.3.1

Draw an example of each type of compound.

- an aldohexose
- a ketopentose

Answer

-  Difference Between Aldohexose and Ketohexose | Compare the Difference Between Similar Terms



The simplest sugars are the trioses. The possible trioses are shown in part (a) of Figure 11.3.1; 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 11.3.1. Molecules that are nonsuperimposable (nonidentical) mirror images of each other are a type of stereoisomer called *enantiomers* (Greek *enantios*, meaning “opposite”).

Note

These are another type of stereoisomers than the *cis-trans* (geometric) isomers previously discussed.

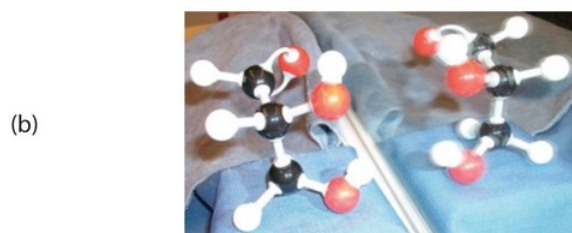
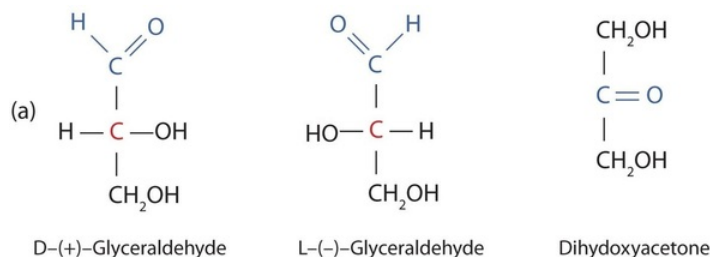


Figure 11.3.1: Structures of the Trioses. (a) D- and L-glyceraldehyde are mirror images of each other and represent a pair of enantiomers. (b) A ball-and-stick model of D-glyceraldehyde is reflected in a mirror. Note that the reflection has the same structure as L-glyceraldehyde.

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 11.3.1). 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 $+8.7^\circ$, while the other has a specific rotation of -8.7° .

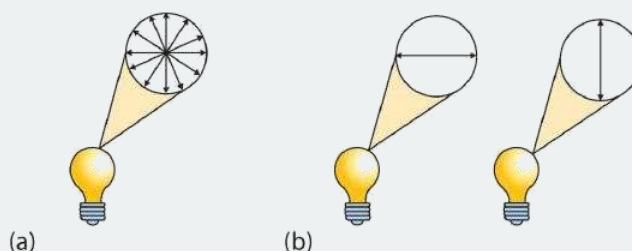
H. Emil Fischer, a German chemist, developed the convention commonly used for writing two-dimensional representations of the monosaccharides, such as those in part (a) of Figure 11.3.1. In these structural formulas, the aldehyde group is written at the top, and the hydrogen atoms and OH groups that are 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.

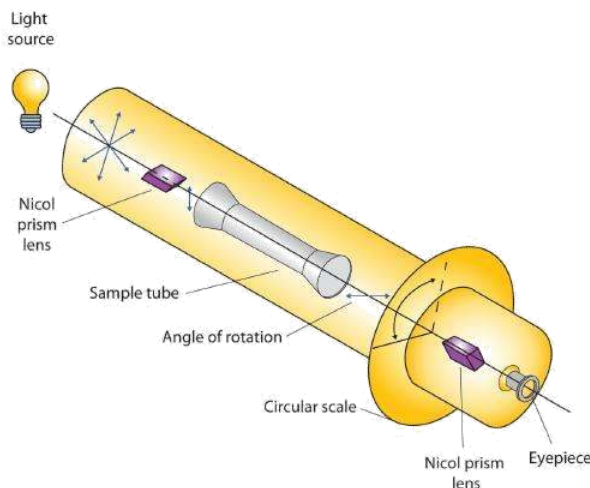


Figure 11.3.2: Diagram of a Polarimeter

Some optically active substances rotate the plane of polarized light to the right (clockwise) from the observer's point of view. These compounds are said to be dextrorotatory; substances that rotate light to the left (counterclockwise) are levorotatory. To denote the direction of rotation, a positive sign (+) is given to dextrorotatory substances, and a negative sign (−) is given to levorotatory substances.

Summary

Monosaccharides can be classified by the number of carbon atoms in the structure and/or the type of carbonyl group they contain (aldose or ketose). Most monosaccharides contain at least one chiral carbon and can form stereoisomers. Enantiomers are a specific type of stereoisomers that are mirror images of each other.

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11.4: Important Hexoses

Learning Objectives

- To identify the structures of D-glucose, D-galactose, and D-fructose and describe how they differ from each other.

Although a variety of monosaccharides are found in living organisms, three hexoses are particularly abundant: D-glucose, D-galactose, and D-fructose (Figure 11.4.1). Glucose and galactose are both aldohexoses, while fructose is a ketohexose.

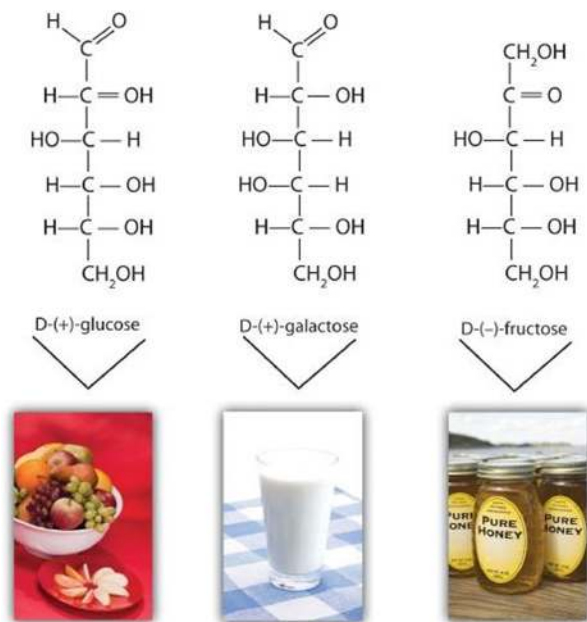


Figure 11.4.1: Structures of Three Important Hexoses. Each hexose is pictured with a food source in which it is commonly found. Source: Photos © Thinkstock.

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.

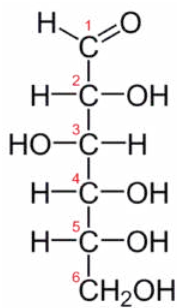


Figure 11.4.2: Fischer projection of D-glucose

The **Fischer projection** of D-glucose is given in Figure 11.4.2. 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 11.4.1. Notice that the configuration differs from that of glucose only at the fourth carbon atom.

Fructose

D-Fructose, also shown in Figure 11.4.1, 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 11.4.1).

Table 11.4.1: The Relative Sweetness of Some Compounds (Sucrose = 100)

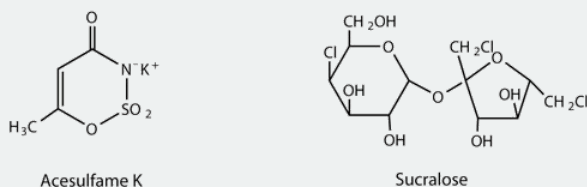
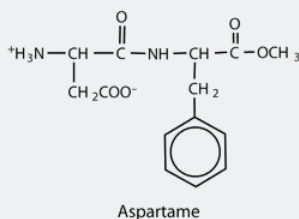
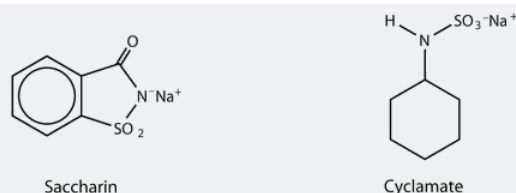
Compound	Relative Sweetness
lactose	16
maltose	32
glucose	74
sucrose	100
fructose	173
aspartame	18,000
acesulfame K	20,000
saccharin	30,000
sucralose	60,000

Looking Closer: Artificial Sweeteners

Although sweetness is commonly associated with mono- and disaccharides, it is not a property found only in sugars. Several other kinds of organic compounds have been synthesized that are far superior as sweetening agents. These so-called high-intensity or artificial sweeteners are useful for people with diabetes or other medical conditions that require them to control their carbohydrate intake. The synthetic compounds are noncaloric or used in such small quantities that they do not add significantly to the caloric value of food.

The first artificial sweetener—saccharin—was discovered by accident in 1879. It is 300 times sweeter than sucrose, but it passes through the body unchanged and thus adds no calories to the diet. After its discovery, saccharin was used until it was banned in the early 1900s. However, during the sugar-short years of World War I, the ban was lifted and was not reinstated at the war’s end. One drawback to the use of saccharin is its bitter, metallic aftertaste. The initial solution to this problem was to combine saccharin with cyclamate, a second artificial sweetener discovered in 1937.

In the 1960s and 1970s, several clinical tests with laboratory animals implicated both cyclamate and saccharin as carcinogenic (cancer-causing) substances. The results from the cyclamate tests were completed first, and cyclamate was banned in the United States in 1969. Then a major study was released in Canada in 1977 indicating that saccharin increased the incidence of bladder cancer in rats. The U.S. 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.

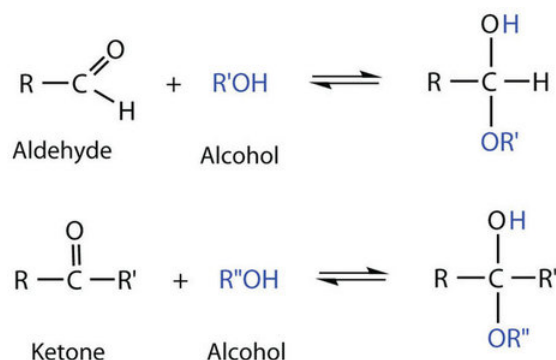
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11.5: Cyclic Structures of Monosaccharides

Learning Objectives

- Define what is meant by anomers and describe how they are formed.
- Explain what is meant by mutarotation.

So far we have represented monosaccharides as linear molecules, but many of them also adopt cyclic structures. This conversion occurs because of the ability of aldehydes and ketones to react with alcohols:



You might wonder why the aldehyde reacts with the OH group on the fifth carbon atom rather than the OH group on the second carbon atom next to it. Recall that cyclic alkanes containing five or six carbon atoms in the ring are the most stable. The same is true for monosaccharides that form cyclic structures: rings consisting of five or six carbon atoms are the most stable.

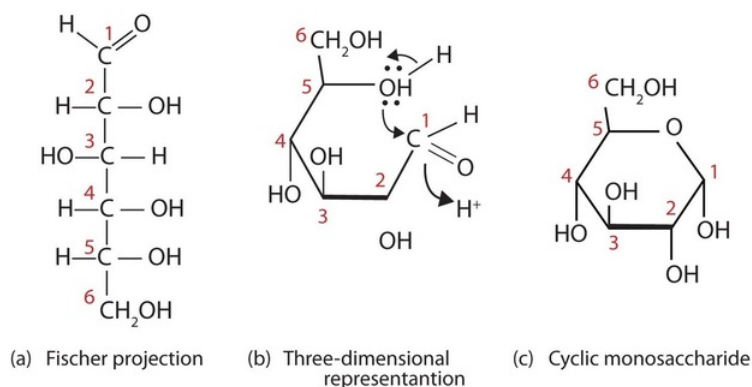


Figure 11.5.1: Cyclization of D-Glucose. D-Glucose can be represented with a Fischer projection (a) or three dimensionally (b). By reacting the OH group on the fifth carbon atom with the aldehyde group, the cyclic monosaccharide (c) is produced.

When a straight-chain monosaccharide, such as any of the structures shown in Figure 11.5.1, forms a cyclic structure, the carbonyl oxygen atom may be pushed either up or down, giving rise to two stereoisomers, as shown in Figure 11.5.2. The structure shown on the left side of Figure 11.5.2, with the OH group on the first carbon atom projected downward, represent what is called the *alpha* (α) form. The structures on the right side, with the OH group on the first carbon atom pointed upward, is the *beta* (β) form. These two stereoisomers of a cyclic monosaccharide are known as anomers; they differ in structure around the anomeric carbon—that is, the carbon atom that was the carbonyl carbon atom in the straight-chain form.

It is possible to obtain a sample of crystalline glucose in which all the molecules have the α structure or all have the β structure. The α form melts at 146°C and has a specific rotation of +112°, while the β form melts at 150°C and has a specific rotation of +18.7°. When the sample is dissolved in water, however, a mixture is soon produced containing both anomers as well as the straight-chain form, in dynamic equilibrium (part (a) of Figure 11.5.2). 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 $+52.7^\circ$.

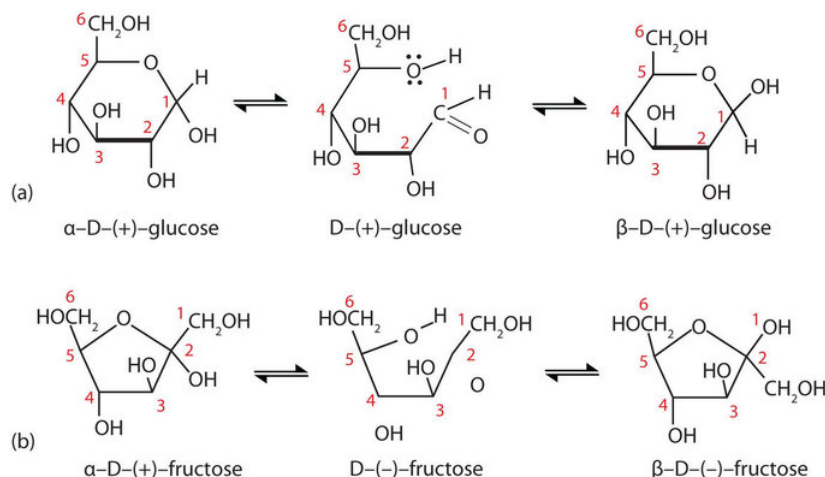


Figure 11.5.2: Monosaccharides. In an aqueous solution, monosaccharides exist as an equilibrium mixture of three forms. The interconversion between the forms is known as *mutarotation*, which is shown for D-glucose (a) and D-fructose (b).

Even though only a small percentage of the molecules are in the open-chain aldehyde form at any time, the solution will nevertheless exhibit the characteristic reactions of an aldehyde. As the small amount of free aldehyde is used up in a reaction, there is a shift in the equilibrium to yield more aldehyde. Thus, *all* the molecules may eventually react, even though very little free aldehyde is present at a time.

Commonly, (e.g., in Figures 11.5.1 and 11.5.2) 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 carbon atoms form cyclic structures in aqueous solution. Two cyclic stereoisomers can form from each straight-chain monosaccharide; these are known as anomers. In an aqueous solution, an equilibrium mixture forms between the two anomers and the straight-chain structure of a monosaccharide in a process known as mutarotation.

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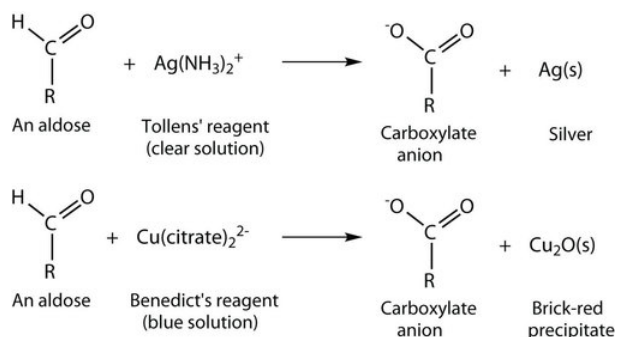
11.6: Properties of Monosaccharides

Learning Objectives

- To identify the physical and chemical properties of monosaccharides.

Monosaccharides such as glucose and fructose are crystalline solids at room temperature, but they are quite soluble in water, each molecule having several OH groups that readily engage in hydrogen bonding. The chemical behavior of these monosaccharides is likewise determined by their functional groups.

An important reaction of monosaccharides is the oxidation of the aldehyde group, one of the most easily oxidized organic functional groups. Aldehyde oxidation can be accomplished with any mild oxidizing agent, such as Tollens' reagent or [Benedict's reagent](#). With the latter, complexed copper(II) ions are reduced to copper(I) ions that form a brick-red precipitate [copper(I) oxide; Figure 11.6.1].



Any carbohydrate capable of reducing either Tollens' or Benedict's reagents without first undergoing hydrolysis is said to be a reducing sugar. Because both the Tollens' and Benedict's reagents are basic solutions, ketoses (such as fructose) also give positive tests due to an equilibrium that exists between ketoses and aldoses in a reaction known as *tautomerism*.

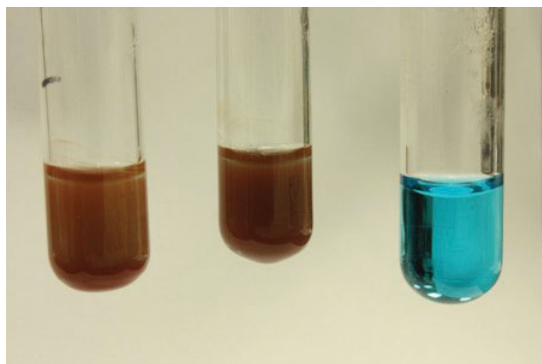


Figure 11.6.1: Benedict's Test. Benedict's test was performed on three carbohydrates, depicted from left to right: fructose, glucose, and sucrose. The solution containing sucrose remains blue because sucrose is a nonreducing sugar.

These reactions have been used as simple and rapid diagnostic tests for the presence of glucose in blood or urine. For example, Clinistest tablets, which are used to test for sugar in the urine, contain copper(II) ions and are based on Benedict's test. A green color indicates very little sugar, whereas a brick-red color indicates sugar in excess of 2 g/100 mL of urine.

Summary

Monosaccharides are crystalline solids at room temperature and quite soluble in water. Monosaccharides are reducing sugars; they reduce mild oxidizing agents, such as Tollens' or Benedict's reagents.

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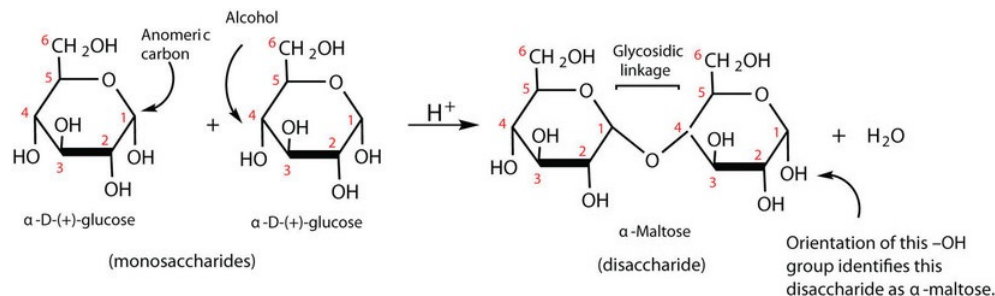
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11.7: Disaccharides

Learning Objectives

- Identify the structures of sucrose, lactose, and maltose.
- Identify the monosaccharides that are needed to form sucrose, lactose, and maltose

Previously, you learned that monosaccharides can form cyclic structures by the reaction of the carbonyl group with an OH group. These cyclic molecules can in turn react with another alcohol. Disaccharides ($C_{12}H_{22}O_{11}$) are sugars composed of two monosaccharide units that are joined by a carbon–oxygen–carbon linkage known as a glycosidic linkage. This linkage is formed from the reaction of the anomeric carbon of one cyclic monosaccharide with the OH group of a second monosaccharide.

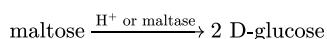


The disaccharides differ from one another in their monosaccharide constituents and in the specific type of glycosidic linkage connecting them. There are three common disaccharides: maltose, lactose, and sucrose. All three are white crystalline solids at room temperature and are soluble in water. We'll consider each sugar in more detail.

Maltose

Maltose occurs to a limited extent in sprouting grain. It is formed most often by the partial hydrolysis of starch and glycogen. In the manufacture of beer, maltose is liberated by the action of malt (germinating barley) on starch; for this reason, it is often referred to as *malt sugar*. Maltose is about 30% as sweet as sucrose. The human body is unable to metabolize maltose or any other disaccharide directly from the diet because the molecules are too large to pass through the cell membranes of the intestinal wall. Therefore, an ingested disaccharide must first be broken down by hydrolysis into its two constituent monosaccharide units.

In the body, such hydrolysis reactions are catalyzed by enzymes such as *maltase*. The same reactions can be carried out in the laboratory with dilute acid as a catalyst, although in that case the rate is much slower, and high temperatures are required. Whether it occurs in the body or a glass beaker, the hydrolysis of maltose produces two molecules of D-glucose.



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 11.7.1). 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 11.7.1.

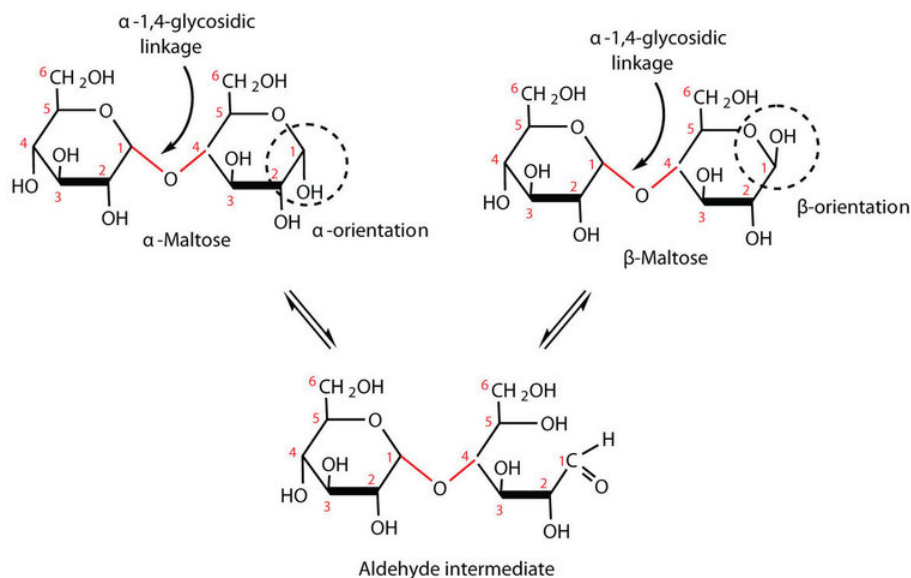
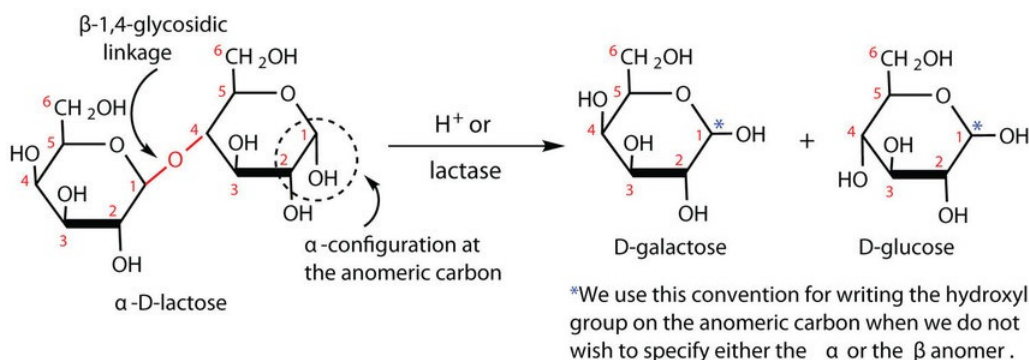


Figure 11.7.1: An Equilibrium Mixture of Maltose Isomers

Lactose

Lactose is known as *milk sugar* because it occurs in the milk of humans, cows, and other mammals. In fact, the natural synthesis of lactose occurs only in mammary tissue, whereas most other carbohydrates are plant products. Human milk contains about 7.5% lactose, and cow's milk contains about 4.5%. This sugar is one of the lowest ranking in terms of sweetness, being about one-sixth as sweet as sucrose. Lactose is produced commercially from whey, a by-product in the manufacture of cheese. It is important as an infant food and in the production of penicillin.

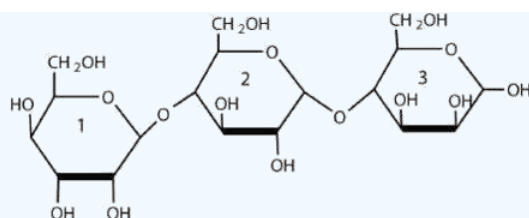
Lactose is a reducing sugar composed of one molecule of D-galactose and one molecule of D-glucose joined by a β -1,4-glycosidic bond (the bond from the anomeric carbon of the first monosaccharide unit being directed upward). The two monosaccharides are obtained from lactose by acid hydrolysis or the catalytic action of the enzyme *lactase*:



Many adults and some children suffer from a deficiency of lactase. These individuals are said to be lactose intolerant because they cannot digest the lactose found in milk. A more serious problem is the genetic disease galactosemia, which results from the absence of an enzyme needed to convert galactose to glucose. Certain bacteria can metabolize lactose, forming lactic acid as one of the products. This reaction is responsible for the "souring" of milk.

✓ Example 11.7.1

For this trisaccharide, indicate whether each glycosidic linkage is α or β .

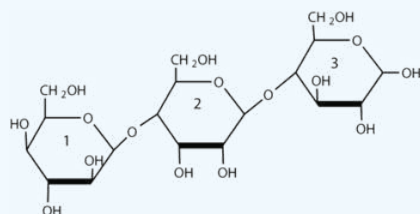


Solution

The glycosidic linkage between sugars 1 and 2 is β because the bond is directed up from the anomeric carbon. The glycosidic linkage between sugars 2 and 3 is α because the bond is directed down from the anomeric carbon.

? Exercise 11.7.1

For this trisaccharide, indicate whether each glycosidic linkage is α or β .



Answer

The glycosidic linkages are in the β orientation between carbons 1 and carbon 4. This is true for the linkage between sugars 1 and 2 and sugars 2 and 3.

📌 To Your Health: Lactose Intolerance and Galactosemia

Lactose makes up about 40% of an infant's diet during the first year of life. Infants and small children have one form of the enzyme lactase in their small intestines and can digest the sugar easily; however, adults usually have a less active form of the enzyme, and about 70% of the world's adult population has some deficiency in its production. As a result, many adults experience a reduction in the ability to hydrolyze lactose to galactose and glucose in their small intestine. For some people the inability to synthesize sufficient enzyme increases with age. Up to 20% of the US population suffers some degree of lactose intolerance.

In people with lactose intolerance, some of the unhydrolyzed lactose passes into the colon, where it tends to draw water from the interstitial fluid into the intestinal lumen by osmosis. At the same time, intestinal bacteria may act on the lactose to produce organic acids and gases. The buildup of water and bacterial decay products leads to abdominal distention, cramps, and diarrhea, which are symptoms of the condition.

The symptoms disappear if milk or other sources of lactose are excluded from the diet or consumed only sparingly. Alternatively, many food stores now carry special brands of milk that have been pretreated with lactase to hydrolyze the lactose. Cooking or fermenting milk causes at least partial hydrolysis of the lactose, so some people with lactose intolerance are still able to enjoy cheese, yogurt, or cooked foods containing milk. The most common treatment for lactose intolerance, however, is the use of lactase preparations (e.g., Lactaid), which are available in liquid and tablet form at drugstores and grocery stores. These are taken orally with dairy foods—or may be added to them directly—to assist in their digestion.

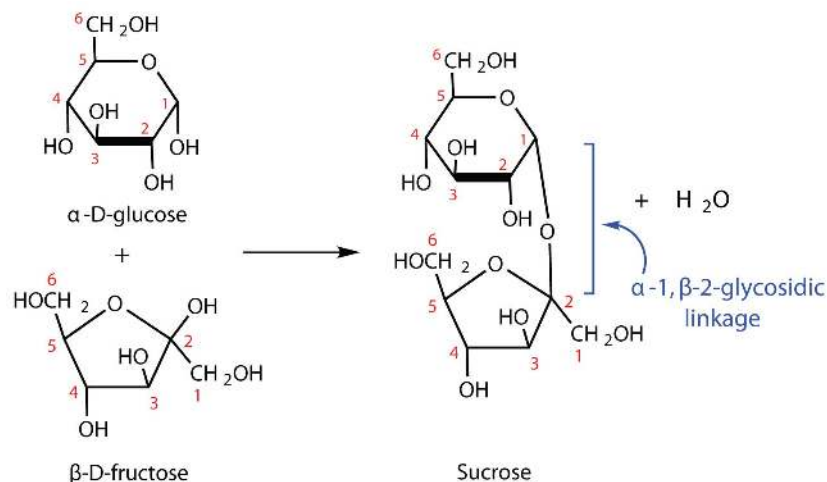
Galactosemia is a condition in which one of the enzymes needed to convert galactose to glucose is missing. Consequently, the blood galactose level is markedly elevated, and galactose is found in the urine. An infant with galactosemia experiences a lack of appetite, weight loss, diarrhea, and jaundice. The disease may result in impaired liver function, cataracts, mental retardation, and even death. If galactosemia is recognized in early infancy, its effects can be prevented by the exclusion of milk and all other sources of galactose from the diet. As a child with galactosemia grows older, he or she usually develops an alternate

pathway for metabolizing galactose, so the need to restrict milk is not permanent. The incidence of galactosemia in the United States is 1 in every 65,000 newborn babies.

Sucrose

Sucrose, probably the largest-selling pure organic compound in the world, is known as *beet sugar*, *cane sugar*, *table sugar*, or simply *sugar*. Most of the sucrose sold commercially is obtained from sugar cane and sugar beets (whose juices are 14%–20% sucrose) by evaporation of the water and recrystallization. The dark brown liquid that remains after the recrystallization of sugar is sold as molasses.

The sucrose molecule is unique among the common disaccharides in having an α -1, β -2-glycosidic (head-to-head) linkage. Because this glycosidic linkage is formed by the OH group on the anomeric carbon of α -D-glucose and the OH group on the anomeric carbon of β -D-fructose, it ties up the anomeric carbons of both glucose and fructose.



This linkage gives sucrose certain properties that are quite different from those of maltose and lactose. As long as the sucrose molecule remains intact, neither monosaccharide “uncyclizes” to form an open-chain structure. Thus, sucrose is incapable of mutarotation and exists in only one form both in the solid state and in solution. In addition, sucrose does not undergo reactions that are typical of aldehydes and ketones. Therefore, sucrose is a nonreducing sugar.

The hydrolysis of sucrose in dilute acid or through the action of the enzyme *sucrase* (also known as invertase) gives an equimolar mixture of glucose and fructose. This 1:1 mixture is referred to as *invert sugar* because it rotates plane-polarized light in the opposite direction than sucrose. The hydrolysis reaction has several practical applications. Sucrose readily recrystallizes from a solution, but invert sugar has a much greater tendency to remain in solution. In the manufacture of jelly and candy and in the canning of fruit, the recrystallization of sugar is undesirable. Therefore, conditions leading to the hydrolysis of sucrose are employed in these processes. Moreover, because fructose is sweeter than sucrose, the hydrolysis adds to the sweetening effect. Bees carry out this reaction when they make honey.

The average American consumes more than 100 lb of sucrose every year. About two-thirds of this amount is ingested in soft drinks, presweetened cereals, and other highly processed foods. The widespread use of sucrose is a contributing factor to obesity and tooth decay. Carbohydrates such as sucrose, are converted to fat when the caloric intake exceeds the body’s requirements, and sucrose causes tooth decay by promoting the formation of plaque that sticks to teeth.

Summary

Maltose is composed of two molecules of glucose joined by an α -1,4-glycosidic linkage. It is a reducing sugar that is found in sprouting grain. Lactose is composed of a molecule of galactose joined to a molecule of glucose by a β -1,4-glycosidic linkage. It is a reducing sugar that is found in milk. Sucrose is composed of a molecule of glucose joined to a molecule of fructose by an α -1, β -2-glycosidic linkage. It is a nonreducing sugar that is found in sugar cane and sugar beets

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11.8: Polysaccharides

Learning Objectives

- To compare and contrast the structures and uses of starch, glycogen, and cellulose.

The polysaccharides are the most abundant carbohydrates in nature and serve a variety of functions, such as energy storage or as components of plant cell walls. Polysaccharides are very large polymers composed of tens to thousands of monosaccharides joined together by glycosidic linkages. The three most abundant polysaccharides are starch, glycogen, and cellulose. These three are referred to as *homopolymers* because each yields only one type of monosaccharide (glucose) after complete hydrolysis. *Heteropolymers* may contain sugar acids, amino sugars, or noncarbohydrate substances in addition to monosaccharides. Heteropolymers are common in nature (gums, pectins, and other substances) but will not be discussed further in this textbook. The polysaccharides are nonreducing carbohydrates, are not sweet tasting, and do not undergo mutarotation.

Starch

Starch is the most important source of carbohydrates in the human diet and accounts for more than 50% of our carbohydrate intake. It occurs in plants in the form of granules, and these are particularly abundant in seeds (especially the cereal grains) and tubers, where they serve as a storage form of carbohydrates. The breakdown of starch to glucose nourishes the plant during periods of reduced photosynthetic activity. We often think of potatoes as a “starchy” food, yet other plants contain a much greater percentage of starch (potatoes 15%, wheat 55%, corn 65%, and rice 75%). Commercial starch is a white powder.

Starch is a mixture of two polymers: amylose and amylopectin. Natural starches consist of about 10%–30% amylose and 70%–90% amylopectin. Amylose is a linear polysaccharide composed entirely of D-glucose units joined by the α -1,4-glycosidic linkages we saw in maltose (part (a) of Figure 11.8.1). 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 11.8.1). 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.

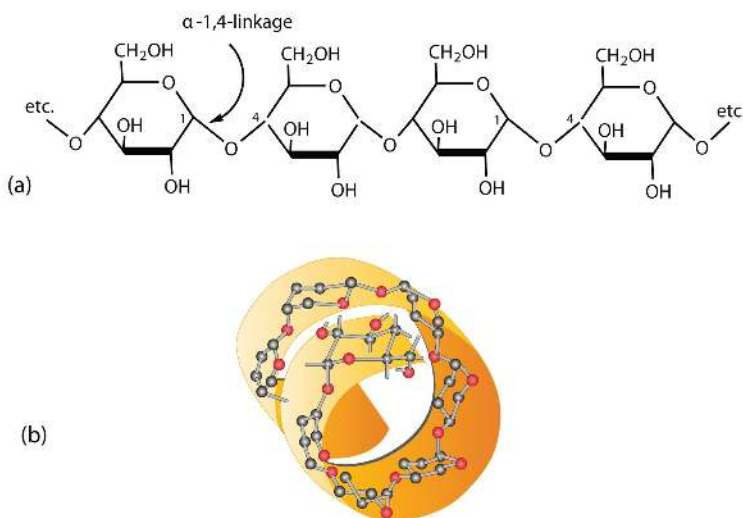


Figure 11.8.1: Amylose. (a) Amylose is a linear chain of α -D-glucose units joined together by α -1,4-glycosidic bonds. (b) Because of hydrogen bonding, amylose acquires a spiral structure that contains six glucose units per turn.

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 11.8.2). 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.

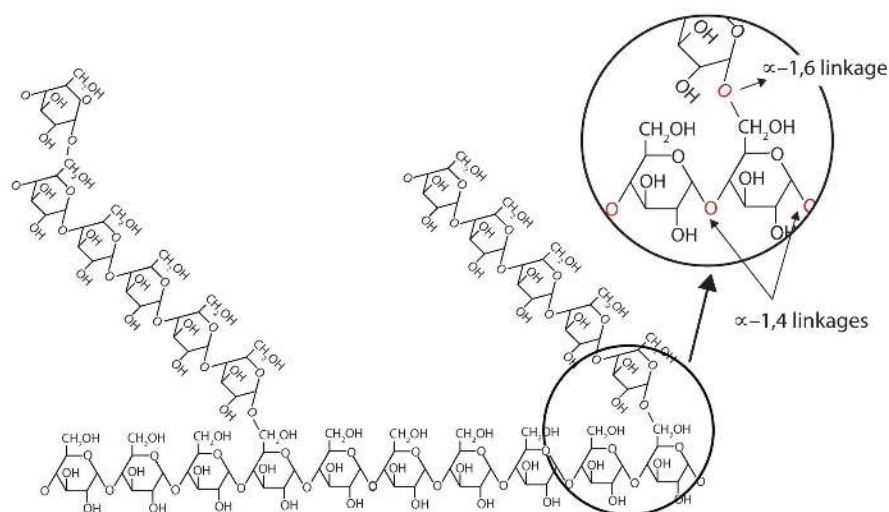
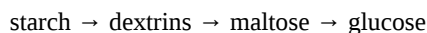


Figure 11.8.2: Representation of the Branching in Amylopectin and Glycogen. Both amylopectin and glycogen contain branch points that are linked through α -1,6-linkages. These branch points occur more often in glycogen.

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:



In the human body, several enzymes known collectively as amylases degrade starch sequentially into usable glucose units.

Glycogen

Glycogen is the energy reserve carbohydrate of animals. Practically all mammalian cells contain some stored carbohydrates in the form of glycogen, but it is especially abundant in the liver (4%–8% by weight of tissue) and in skeletal muscle cells (0.5%–1.0%). Like starch in plants, glycogen is found as granules in liver and muscle cells. When fasting, animals draw on these glycogen reserves during the first day without food to obtain the glucose needed to maintain metabolic balance.

Glycogen is structurally quite similar to amylopectin, although glycogen is more highly branched (8–12 glucose units between branches) and the branches are shorter. When treated with iodine, glycogen gives a reddish brown color. Glycogen can be broken down into its D-glucose subunits by acid hydrolysis or by the same enzymes that catalyze the breakdown of starch. In animals, the enzyme phosphorylase catalyzes the breakdown of glycogen to phosphate esters of glucose.

About 70% of the total glycogen in the body is stored in muscle cells. Although the percentage of glycogen (by weight) is higher in the liver, the much greater mass of skeletal muscle stores a greater total amount of glycogen.

Cellulose

Cellulose, a fibrous carbohydrate found in all plants, is the structural component of plant cell walls. Because the earth is covered with vegetation, cellulose is the most abundant of all carbohydrates, accounting for over 50% of all the carbon found in the vegetable kingdom. Cotton fibrils and filter paper are almost entirely cellulose (about 95%), wood is about 50% cellulose, and the dry weight of leaves is about 10%–20% cellulose. The largest use of cellulose is in the manufacture of paper and paper products. Although the use of noncellulose synthetic fibers is increasing, rayon (made from cellulose) and cotton still account for over 70% of textile production.

Like amylose, cellulose is a linear polymer of glucose. It differs, however, in that the glucose units are joined by β -1,4-glycosidic linkages, producing a more extended structure than amylose (part (a) of Figure 11.8.3). 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 11.8.3). 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.

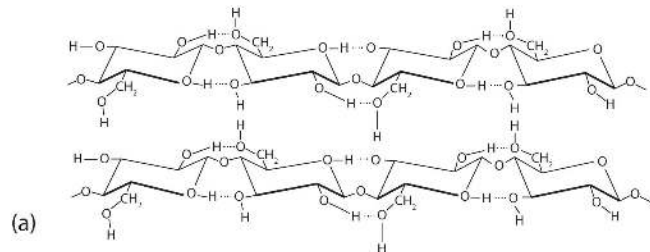


Figure 11.8.3: Cellulose. (a) There is extensive hydrogen bonding in the structure of cellulose. (b) In this electron micrograph of the cell wall of an alga, the wall consists of successive layers of cellulose fibers in parallel arrangement.

Cellulose yields D-glucose after complete acid hydrolysis, yet humans are unable to metabolize cellulose as a source of glucose. Our digestive juices lack enzymes that can hydrolyze the β -glycosidic linkages found in cellulose, so although we can eat potatoes, we cannot eat grass. However, certain microorganisms can digest cellulose because they make the enzyme cellulase, which catalyzes the hydrolysis of cellulose. The presence of these microorganisms in the digestive tracts of herbivorous animals (such as cows, horses, and sheep) allows these animals to degrade the cellulose from plant material into glucose for energy. Termites also contain cellulase-secreting microorganisms and thus can subsist on a wood diet. This example once again demonstrates the extreme stereospecificity of biochemical processes.

📌 Career Focus: Certified Diabetes Educator

Certified diabetes educators come from a variety of health professions, such as nursing and dietetics, and specialize in the education and treatment of patients with diabetes. A diabetes educator will work with patients to manage their diabetes. This involves teaching the patient to monitor blood sugar levels, make good food choices, develop and maintain an exercise program, and take medication, if required.



A certified diabetes educator at Naval Medical Center Portsmouth (left) and a registered dietician at the medical center (center), provide nutritional information to a diabetes patient and her mother at the Diabetes Boot Camp.

Diabetes educators also work with hospital or nursing home staff to improve the care of diabetic patients. Educators must be willing to spend time attending meetings and reading the current literature to maintain their knowledge of diabetes medications, nutrition, and blood monitoring devices so that they can pass this information to their patients.

Summary

Starch is a storage form of energy in plants. It contains two polymers composed of glucose units: amylose (linear) and amylopectin (branched). Glycogen is a storage form of energy in animals. It is a branched polymer composed of glucose units. It is more highly branched than amylopectin. Cellulose is a structural polymer of glucose units found in plants. It is a linear polymer with the glucose units linked through β -1,4-glycosidic bonds.

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11.S: Carbohydrates (Summary)

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

Carbohydrates, a large group of biological compounds containing carbon, hydrogen, and oxygen atoms, include sugars, starch, glycogen, and cellulose. All carbohydrates contain alcohol functional groups, and either an aldehyde or a ketone group (or a functional group that can be converted to an aldehyde or ketone). The simplest carbohydrates are **monosaccharides**. Those with two monosaccharide units are **disaccharides**, and those with many monosaccharide units are **polysaccharides**. Most sugars are either monosaccharides or disaccharides. Cellulose, glycogen, and starch are polysaccharides.

Many carbohydrates exist as **stereoisomers**, in which the three-dimensional spatial arrangement of the atoms in space is the only difference between the isomers. These particular stereoisomers contain at least one **chiral carbon**, a carbon atom that has four different groups bonded to it. A molecule containing a chiral carbon is nonsuperimposable on its mirror image, and two molecules that are nonsuperimposable mirror images of each other are a special type of stereoisomer called **enantiomers**. Enantiomers have the same physical properties, such as melting point, but differ in the direction they rotate polarized light.

A sugar is designated as being a D sugar or an L sugar according to how, in a Fischer projection of the molecule, the hydrogen atom and OH group are attached to the *penultimate* carbon atom, which is the carbon atom immediately before the terminal alcohol carbon atom. If the structure at this carbon atom is the same as that of D-glyceraldehyde (OH to the right), the sugar is a **D sugar**; if the configuration is the same as that of L-glyceraldehyde (OH to the left), the sugar is an **L sugar**.

Monosaccharides of five or more carbons atoms readily form cyclic structures when the carbonyl carbon atom reacts with an OH group on a carbon atom three or four carbon atoms distant. Consequently, glucose in solution exists as an equilibrium mixture of three forms, two of them cyclic (α - and β -) and one open chain. In Haworth projections, the *alpha* form is drawn with the OH group on the “former” carbonyl carbon atom (**anomeric carbon**) pointing downward; the *beta* form, with the OH group pointing upward; these two compounds are stereoisomers and are given the more specific term of **anomers**. Any solid sugar can be all alpha or all beta. Once the sample is dissolved in water, however, the ring opens up into the open-chain structure and then closes to form either the α - or the β -anomer. These interconversions occur back and forth until a dynamic equilibrium mixture is achieved in a process called **mutarotation**.

The carbonyl group present in monosaccharides is easily oxidized by Tollens’ or Benedict’s reagents (as well as others). Any mono- or disaccharide containing a free anomeric carbon is a **reducing sugar**. The disaccharide *maltose* contains two glucose units joined in an α -1,4-glycosidic linkage. The disaccharide *lactose* contains a galactose unit and a glucose unit joined by a β -1,4-glycosidic linkage. Both maltose and lactose contain a free anomeric carbon that can convert to an aldehyde functional group, so they are reducing sugars; they also undergo mutarotation. Many adults, and some children, have a deficiency of the enzyme lactase (which is needed to break down lactose) and are said to be **lactose intolerant**. A more serious problem is the genetic disease **galactosemia**, which results from the absence of an enzyme needed to convert galactose to glucose.

The disaccharide *sucrose* (table sugar) consists of a glucose unit and a fructose unit joined by a glycosidic linkage. The linkage is designated as an α -1, β -2-glycosidic linkage because it involves the OH group on the first carbon atom of glucose and the OH group on the second carbon atom of fructose. Sucrose is not a reducing sugar because it has no anomeric carbon that can reform a carbonyl group, and it cannot undergo mutarotation because of the restrictions imposed by this linkage.

Starch, the principal carbohydrate of plants, is composed of the polysaccharides **amylose** (10%–30%) and **amylopectin** (70%–90%). When ingested by humans and other animals, starch is hydrolyzed to glucose and becomes the body’s energy source. *Glycogen* is the polysaccharide animals use to store excess carbohydrates from their diets. Similar in structure to amylopectin, glycogen is hydrolyzed to glucose whenever an animal needs energy for a metabolic process. The polysaccharide *cellulose* provides structure for plant cells. It is a linear polymer of glucose units joined by β -1,4-glycosidic linkages. It is indigestible in the human body but digestible by many microorganisms, including microorganisms found in the digestive tracts of many herbivores.

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CHAPTER OVERVIEW

12: 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.

[12.1: Prelude to Lipids](#)

[12.2: Fatty Acids](#)

[12.3: Fats and Oils](#)

[12.4: Membranes and Membrane Lipids](#)

[12.5: Steroids](#)

[12.S: Lipids \(Summary\)](#)

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12.1: Prelude to Lipids

On July 11, 2003, the Food and Drug Administration amended its food labeling regulations to require that manufacturers list the amount of *trans* fatty acids on Nutrition Facts labels of foods and dietary supplements, effective January 1, 2006. This amendment was a response to published studies demonstrating a link between the consumption of *trans* fatty acids and an increased risk of heart disease. *Trans* fatty acids are produced in the conversion of liquid oils to solid fats, as in the creation of many commercial margarines and shortenings. They have been shown to increase the levels of low-density lipoproteins (LDLs)—complexes that are often referred to as bad cholesterol—in the blood. In this chapter, you will learn about fatty acids and what is meant by a *trans* fatty acid, as well as the difference between fats and oils. You will also learn what cholesterol is and why it is an important molecule in the human body.

Fats and oils, found in many of the foods we eat, belong to a class of biomolecules known as lipids. Gram for gram, they pack more than twice the caloric content of carbohydrates: the oxidation of fats and oils supplies about 9 kcal of energy for every gram oxidized, whereas the oxidation of carbohydrates supplies only 4 kcal/g. Although the high caloric content of fats may be bad news for the dieter, it says something about the efficiency of nature's designs. Our bodies use carbohydrates, primarily in the form of glucose, for our *immediate* energy needs. Our capacity for storing carbohydrates for later use is limited to tucking away a bit of glycogen in the liver or in muscle tissue. We store our *reserve* energy in lipid form, which requires far less space than the same amount of energy stored in carbohydrate form. Lipids have other biological functions besides energy storage. They are a major component of the membranes of the 10 trillion cells in our bodies. They serve as protective padding and insulation for vital organs. Furthermore, without lipids in our diets, we would be deficient in the fat-soluble vitamins A, D, E, and K.

Lipids are not defined by the presence of specific functional groups, as carbohydrates are, but by a physical property—solubility. Compounds isolated from body tissues are classified as lipids if they are more soluble in organic solvents, such as dichloromethane, than in water. By this criterion, the lipid category includes not only fats and oils, which are esters of the trihydroxy alcohol glycerol and fatty acids, but also compounds that incorporate functional groups derived from phosphoric acid, carbohydrates, or amino alcohols, as well as steroid compounds such as cholesterol (Figure 12.1.1 presents one scheme for classifying the various kinds of lipids). We will discuss the various kinds of lipids by considering one subclass at a time and pointing out structural similarities and differences as we go.

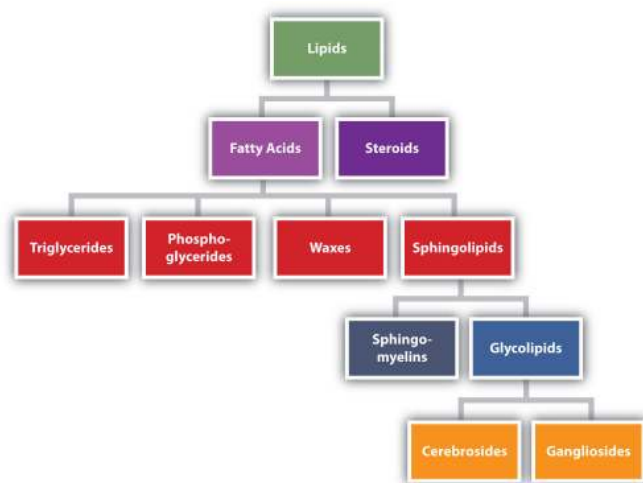


Figure 12.1.1: Lipid Organization Based on Structural

Relationships Lipid categorized into fatty acids and steroids. Fatty acids are further separated into triglycerides, phospho-glycerides, waxes, and sphingolipids. Sphingolipids are separated into sphingo-myelins and glycolipids. Glycolipids are separated into cerebrosides and gangliosides.

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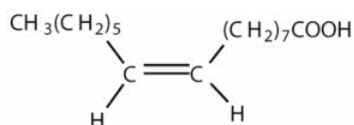
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12.2: Fatty Acids

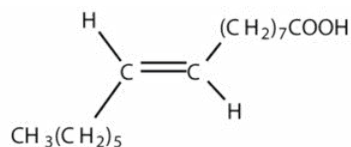
Learning Objectives

- To recognize the structures of common fatty acids and classify them as saturated, monounsaturated, or polyunsaturated.

Fatty acids are carboxylic acids that are structural components of fats, oils, and all other categories of lipids, except steroids. More than 70 have been identified in nature. They usually contain an even number of carbon atoms (typically 12–20), are generally unbranched, and can be classified by the presence and number of carbon-to-carbon double bonds. Thus, saturated fatty acids contain no carbon-to-carbon double bonds, monounsaturated fatty acids contain one carbon-to-carbon double bond, and polyunsaturated fatty acids contain two or more carbon-to-carbon double bonds.



cis fatty acid



trans fatty acid

Cis fatty acids have two H atoms on the same side of the plane of the fatty acid while trans has the two H atoms on opposite sides.

Table 12.2.1 lists some common fatty acids and one important source for each. The atoms or groups around the double bonds in unsaturated fatty acids can be arranged in either the cis or trans isomeric form. Naturally occurring fatty acids are generally in the cis configuration.

Table 12.2.1: Some Common Fatty Acids Found in Natural Fats

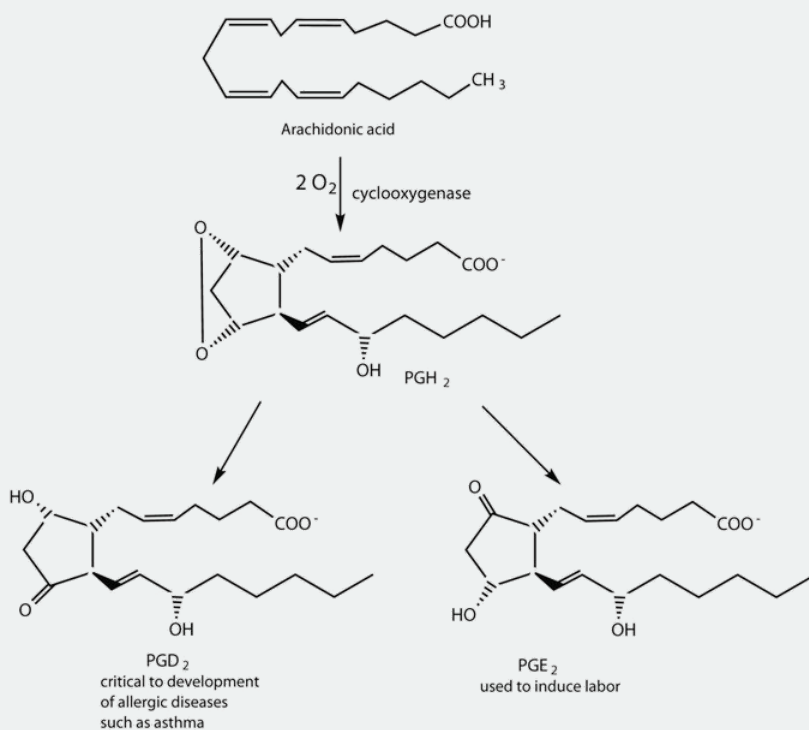
Name	Abbreviated Structural Formula	Condensed Structural Formula	Melting Point (°C)	Source
lauric acid	C ₁₁ H ₂₃ COOH	CH ₃ (CH ₂) ₁₀ COOH	44	palm kernel oil
myristic acid	C ₁₃ H ₂₇ COOH	CH ₃ (CH ₂) ₁₂ COOH	58	oil of nutmeg
palmitic acid	C ₁₅ H ₃₁ COOH	CH ₃ (CH ₂) ₁₄ COOH	63	palm oil
palmitoleic acid	C ₁₅ H ₂₉ COOH	CH ₃ (CH ₂) ₅ CH=CH(CH ₂) ₇ COOH	0.5	macadamia oil
stearic acid	C ₁₇ H ₃₅ COOH	CH ₃ (CH ₂) ₁₆ COOH	70	cocoa butter
oleic acid	C ₁₇ H ₃₃ COOH	CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₇ COOH	16	olive oil
linoleic acid	C ₁₇ H ₃₁ COOH	CH ₃ (CH ₂) ₃ (CH ₂ CH=CH) ₂ (CH ₂) ₇ COOH	−5	canola oil
α-linolenic acid	C ₁₇ H ₂₉ COOH	CH ₃ (CH ₂ CH=CH) ₃ (CH ₂) ₇ COOH	−11	flaxseed
arachidonic acid	C ₁₉ H ₃₁ COOH	CH ₃ (CH ₂) ₄ (CH ₂ CH=CH) ₄ (CH ₂) ₂ COOH	−50	liver

Two polyunsaturated fatty acids—linoleic and α-linolenic acids—are termed essential fatty acids because humans must obtain them from their diets. Both substances are required for normal growth and development, but the human body does not synthesize them. The body uses linoleic acid to synthesize many of the other unsaturated fatty acids, such as arachidonic acid, a precursor for the synthesis of prostaglandins. In addition, the essential fatty acids are necessary for the efficient transport and metabolism of cholesterol. The average daily diet should contain about 4–6 g of the essential fatty acids.

📌 To Your Health: Prostaglandins

Prostaglandins are chemical messengers synthesized in the cells in which their physiological activity is expressed. They are unsaturated fatty acids containing 20 carbon atoms and are synthesized from arachidonic acid—a polyunsaturated fatty acid—when needed by a particular cell. They are called *prostaglandins* because they were originally isolated from semen found in the prostate gland. It is now known that they are synthesized in nearly all mammalian tissues and affect almost all organs in the body. The five major classes of prostaglandins are designated as PGA, PGB, PGE, PGF, and PGI. Subscripts are attached at the end of these abbreviations to denote the number of double bonds outside the five-carbon ring in a given prostaglandin.

The prostaglandins are among the most potent biological substances known. Slight structural differences give them highly distinct biological effects; however, all prostaglandins exhibit some ability to induce smooth muscle contraction, lower blood pressure, and contribute to the inflammatory response. Aspirin and other nonsteroidal anti-inflammatory agents, such as ibuprofen, obstruct the synthesis of prostaglandins by inhibiting cyclooxygenase, the enzyme needed for the initial step in the conversion of arachidonic acid to prostaglandins.

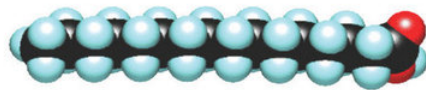


Their wide range of physiological activity has led to the synthesis of hundreds of prostaglandins and their analogs. Derivatives of PGE₂ are now used in the United States to induce labor. Other prostaglandins have been employed clinically to lower or increase blood pressure, inhibit stomach secretions, relieve nasal congestion, relieve asthma, and prevent the formation of blood clots, which are associated with heart attacks and strokes.

Although we often draw the carbon atoms in a straight line, they actually have more of a zigzag configuration (Figure 12.2.2a). Viewed as a whole, however, the saturated fatty acid molecule is relatively straight (Figure 12.2.2b). Such molecules pack closely together into a crystal lattice, maximizing the strength of dispersion forces and causing fatty acids and the fats derived from them to have relatively high melting points. In contrast, each *cis* carbon-to-carbon double bond in an unsaturated fatty acid produces a pronounced bend in the molecule, so that these molecules do not stack neatly. As a result, the intermolecular attractions of unsaturated fatty acids (and unsaturated fats) are weaker, causing these substances to have lower melting points. Most are liquids at room temperature.



(a)

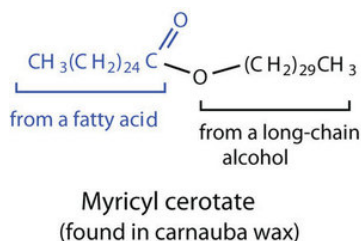


(b)

Figure 12.2.2: The Structure of Saturated Fatty

Acids. (a) There is a zigzag pattern formed by the carbon-to-carbon single bonds in the ball-and-stick model of a palmitic acid molecule. (b) A space-filling model of palmitic acid shows the overall straightness of a saturated fatty acid molecule.

Waxes are esters formed from long-chain fatty acids and long-chain alcohols. Most natural waxes are mixtures of such esters. Plant waxes on the surfaces of leaves, stems, flowers, and fruits protect the plant from dehydration and invasion by harmful microorganisms. Carnauba wax, used extensively in floor waxes, automobile waxes, and furniture polish, is largely myricyl cerotate, obtained from the leaves of certain Brazilian palm trees. Animals also produce waxes that serve as protective coatings, keeping the surfaces of feathers, skin, and hair pliable and water repellent. In fact, if the waxy coating on the feathers of a water bird is dissolved as a result of the bird swimming in an oil slick, the feathers become wet and heavy, and the bird, unable to maintain its buoyancy, drowns.



Summary

Fatty acids are carboxylic acids that are the structural components of many lipids. They may be saturated or unsaturated. Most fatty acids are unbranched and contain an even number of carbon atoms. Unsaturated fatty acids have lower melting points than saturated fatty acids containing the same number of carbon atoms.

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12.3: Fats and Oils

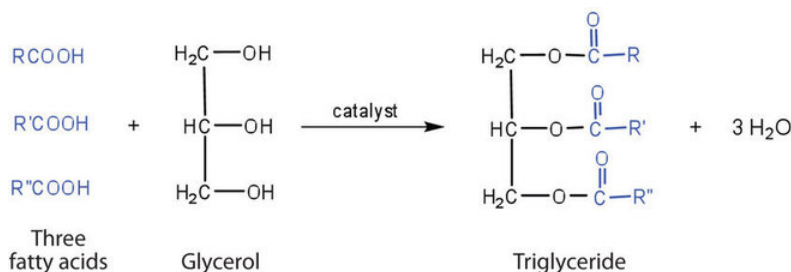
Learning Objectives

- Explain why fats and oils are referred to as triglycerides.
- Explain how the fatty acid composition of the triglycerides determines whether a substance is a fat or oil.
- Describe the importance of key reactions of triglycerides, such as hydrolysis, hydrogenation, and oxidation.

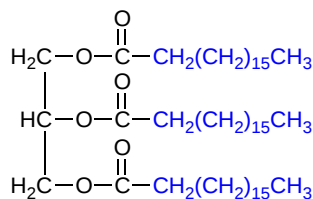
Fats and oils are the most abundant lipids in nature. They provide energy for living organisms, insulate body organs, and transport fat-soluble vitamins through the blood.

Structures of Fats and Oils

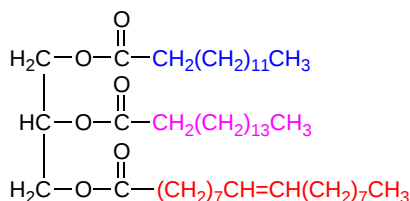
Fats and oils are called triglycerides (or *triacylglycerols*) because they are esters composed of three fatty acid units joined to *glycerol*, a trihydroxy alcohol:



If all three OH groups on the glycerol molecule are esterified with the same fatty acid, the resulting ester is called a *simple triglyceride*. Although simple triglycerides have been synthesized in the laboratory, they rarely occur in nature. Instead, a typical triglyceride obtained from naturally occurring fats and oils contains two or three different fatty acid components and is thus termed a *mixed triglyceride*.



Tristearin
a simple triglyceride



a mixed triglyceride

A triglyceride is called a fat if it is a solid at 25°C; it is called an oil if it is a liquid at that temperature. These differences in melting points reflect differences in the degree of unsaturation and number of carbon atoms in the constituent fatty acids. Triglycerides obtained from animal sources are usually solids, while those of plant origin are generally oils. Therefore, we commonly speak of animal fats and vegetable oils.

No single formula can be written to represent the naturally occurring fats and oils because they are highly complex mixtures of triglycerides in which many different fatty acids are represented. Table 12.3.1 shows the fatty acid compositions of some common fats and oils. The composition of any given fat or oil can vary depending on the plant or animal species it comes from as well as on

dietetic and climatic factors. To cite just one example, lard from corn-fed hogs is more highly saturated than lard from peanut-fed hogs. Palmitic acid is the most abundant of the saturated fatty acids, while oleic acid is the most abundant unsaturated fatty acid.

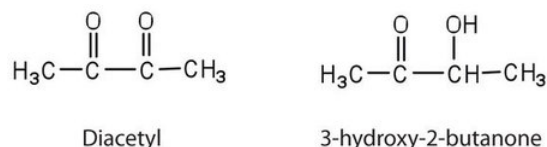
Table 12.3.1: Average Fatty Acid Composition of Some Common Fats and Oils (%)*

	Lauric	Myristic	Palmitic	Stearic	Oleic	Linoleic	Linolenic
Fats							
butter (cow)	3	11	27	12	29	2	1
tallow		3	24	19	43	3	1
lard		2	26	14	44	10	
Oils							
canola oil			4	2	62	22	10
coconut oil [†]	47	18	9	3	6	2	
corn oil			11	2	28	58	1
olive oil			13	3	71	10	1
peanut oil			11	2	48	32	
soybean oil			11	4	24	54	7
*Totals less than 100% indicate the presence of fatty acids with fewer than 12 carbon atoms or more than 18 carbon atoms.							
[†] Coconut oil is highly saturated. It contains an unusually high percentage of the low-melting C ₈ , C ₁₀ , and C ₁₂ saturated fatty acids.							

Terms such as *saturated fat* or *unsaturated oil* are often used to describe the fats or oils obtained from foods. Saturated fats contain a high proportion of saturated fatty acids, while unsaturated oils contain a high proportion of unsaturated fatty acids. The high consumption of saturated fats is a factor, along with the high consumption of cholesterol, in increased risks of heart disease.

Physical Properties of Fats and Oils

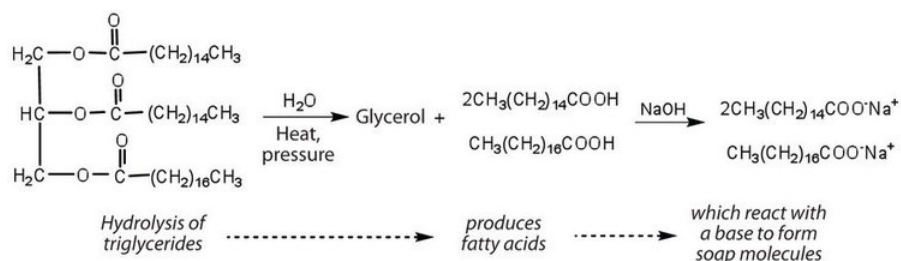
Contrary to what you might expect, *pure* fats and oils are colorless, odorless, and tasteless. The characteristic colors, odors, and flavors that we associate with some of them are imparted by foreign substances that are lipid soluble and have been absorbed by these lipids. For example, the yellow color of butter is due to the presence of the pigment carotene; the taste of butter comes from two compounds—diacetyl and 3-hydroxy-2-butanone—produced by bacteria in the ripening cream from which the butter is made.



Fats and oils are lighter than water, having densities of about 0.8 g/cm³. 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

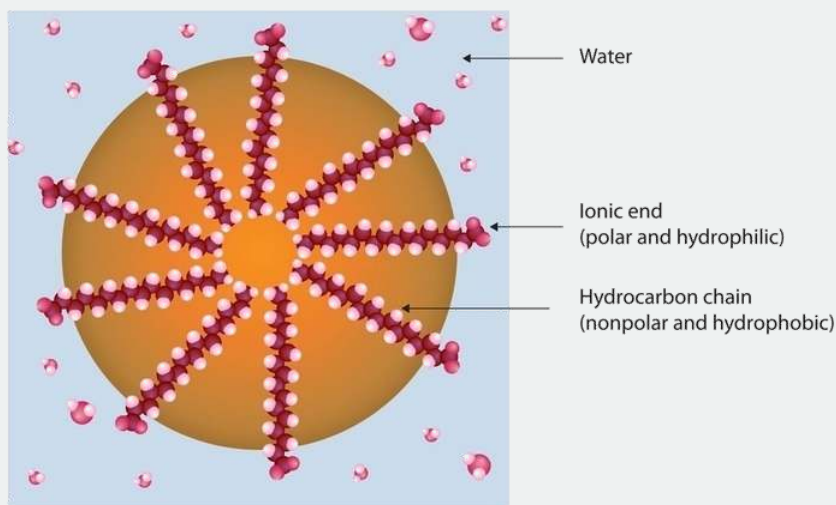
Fats and oils can participate in a variety of chemical reactions—for example, because triglycerides are esters, they can be hydrolyzed in the presence of an acid, a base, or specific enzymes known as lipases. The hydrolysis of fats and oils in the presence of a base is used to make soap and is called [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/in² (~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

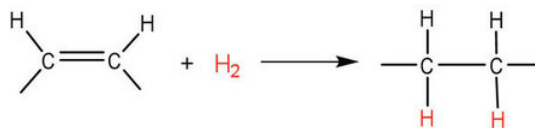
Ordinary soap is a mixture of the sodium salts of various fatty acids, produced in one of the oldest organic syntheses practiced by humans (second only to the fermentation of sugars to produce ethyl alcohol). Both the Phoenicians (600 BCE) and the Romans made soap from animal fat and wood ash. Even so, 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.

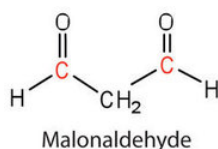
Many people have switched from butter to margarine or vegetable shortening because of concerns that saturated animal fats can raise blood cholesterol levels and result in clogged arteries. However, during the hydrogenation of vegetable oils, an isomerization reaction occurs that produces the *trans* 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*.



Rancidity is a major concern of the food industry, which is why food chemists are always seeking new and better antioxidants, substances added in very small amounts (0.001%–0.01%) to prevent oxidation and thus suppress rancidity. Antioxidants are compounds whose affinity for oxygen is greater than that of the lipids in the food; thus they function by preferentially depleting the supply of oxygen absorbed into the product. Because vitamin E has antioxidant properties, it helps reduce damage to lipids in the body, particularly to unsaturated fatty acids found in cell membrane lipids.

Summary

Fats and oils are composed of molecules known as triglycerides, which are esters composed of three fatty acid units linked to glycerol. An increase in the percentage of shorter-chain fatty acids and/or unsaturated fatty acids lowers the melting point of a fat or oil. The hydrolysis of fats and oils in the presence of a base makes soap and is known as saponification. Double bonds present in unsaturated triglycerides can be hydrogenated to convert oils (liquid) into margarine (solid). The oxidation of fatty acids can form compounds with disagreeable odors. This oxidation can be minimized by the addition of antioxidants.

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12.4: Membranes and Membrane Lipids

Learning Objectives

- Identify the distinguishing characteristics of membrane lipids.
- Describe membrane components and how they are arranged.

All living cells are surrounded by a cell membrane. Plant cells (Figure 12.4.1A) and animal cells (Figure 12.4.1B) contain a cell nucleus that is also surrounded by a membrane and holds the genetic information for the cell. Everything between the cell membrane and the nuclear membrane—including intracellular fluids and various subcellular components such as the mitochondria and ribosomes—is called the cytoplasm. The membranes of all cells have a fundamentally similar structure, but membrane function varies tremendously from one organism to another and even from one cell to another within a single organism. This diversity arises mainly from the presence of different proteins and lipids in the membrane.

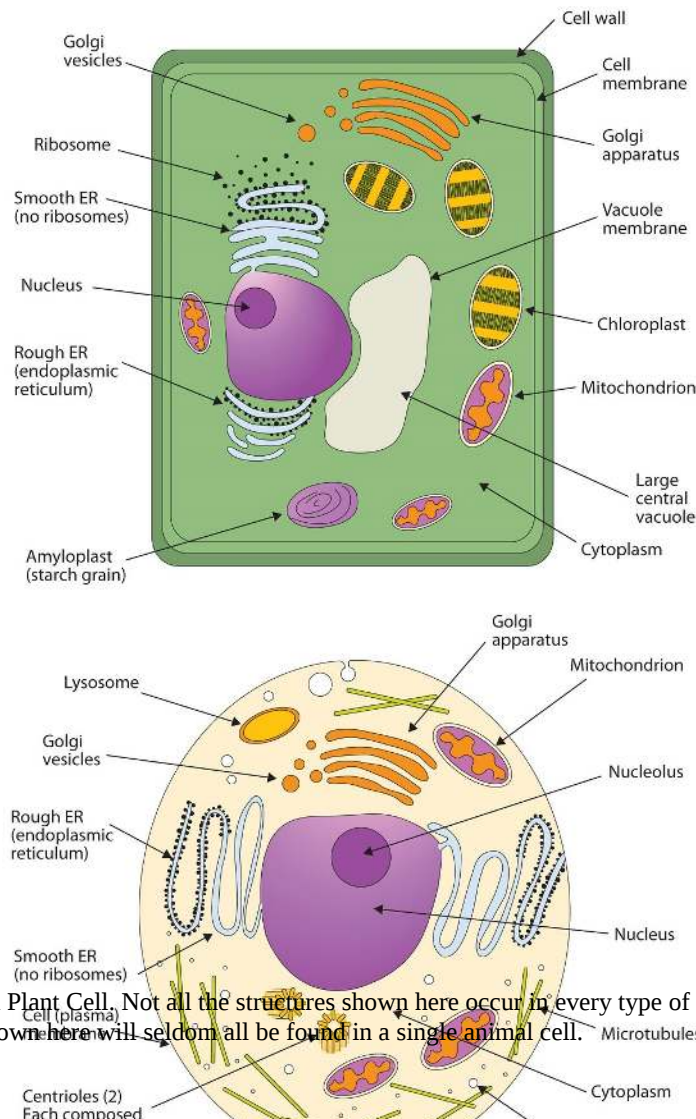


Figure 12.4.1: (A) An Idealized Plant Cell. Not all the structures shown here occur in every type of plant cell. (B) An Idealized Animal Cell. The structures shown here will seldom all be found in a single animal cell.

The lipids in cell membranes are highly polar but have dual characteristics: part of the lipid is ionic and therefore dissolves in water, whereas the rest has a hydrocarbon structure and therefore dissolves in nonpolar substances. Often, the ionic part is referred to as hydrophilic, meaning “water loving,” and the nonpolar part as hydrophobic, meaning “water fearing” (repelled by water). When allowed to float freely in water, polar lipids spontaneously cluster together in any one of three arrangements: micelles, monolayers, and bilayers (Figure 12.4.2).

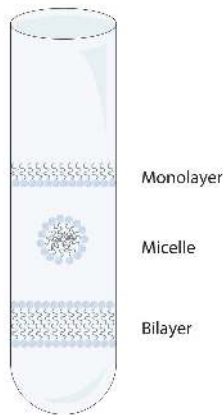


Figure 12.4.2: Spontaneously Formed Polar Lipid Structures in Water: Monolayer, Micelle, and Bilayer

Micelles are aggregations in which the lipids’ hydrocarbon tails—being hydrophobic—are directed toward the center of the assemblage and away from the surrounding water while the hydrophilic heads are directed outward, in contact with the water. Each micelle may contain thousands of lipid molecules. Polar lipids may also form a monolayer, a layer one molecule thick on the surface of the water. The polar heads face into water, and the nonpolar tails stick up into the air. Bilayers are double layers of lipids arranged so that the hydrophobic tails are sandwiched between an inner surface and an outer surface consisting of hydrophilic heads. The hydrophilic heads are in contact with water on either side of the bilayer, whereas the tails, sequestered inside the bilayer, are prevented from having contact with the water. Bilayers like this make up every cell membrane (Figure 12.4.3).

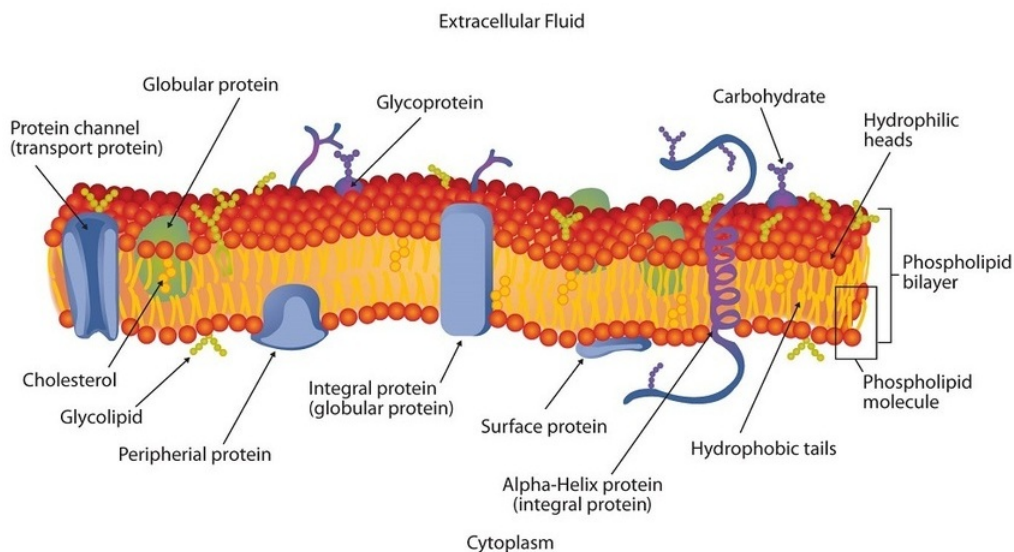


Figure 12.4.3: Schematic

Diagram of a Cell Membrane. The membrane enclosing a typical animal cell is a phospholipid bilayer with embedded cholesterol and protein molecules. Short oligosaccharide chains are attached to the outer surface.

In the bilayer interior, the hydrophobic tails (that is, the fatty acid portions of lipid molecules) interact by means of dispersion forces. The interactions are weakened by the presence of unsaturated fatty acids. As a result, the membrane components are free to mill about to some extent, and the membrane is described as fluid.

The lipids found in cell membranes can be categorized in various ways. Phospholipids are lipids containing phosphorus. Glycolipids are sugar-containing lipids. The latter are found exclusively on the outer surface of the cell membrane, acting as distinguishing surface markers for the cell and thus serving in cellular recognition and cell-to-cell communication. Sphingolipids are phospholipids or glycolipids that contain the unsaturated amino alcohol sphingosine rather than glycerol. Diagrammatic structures of representative membrane lipids are presented in Figure 12.4.4.

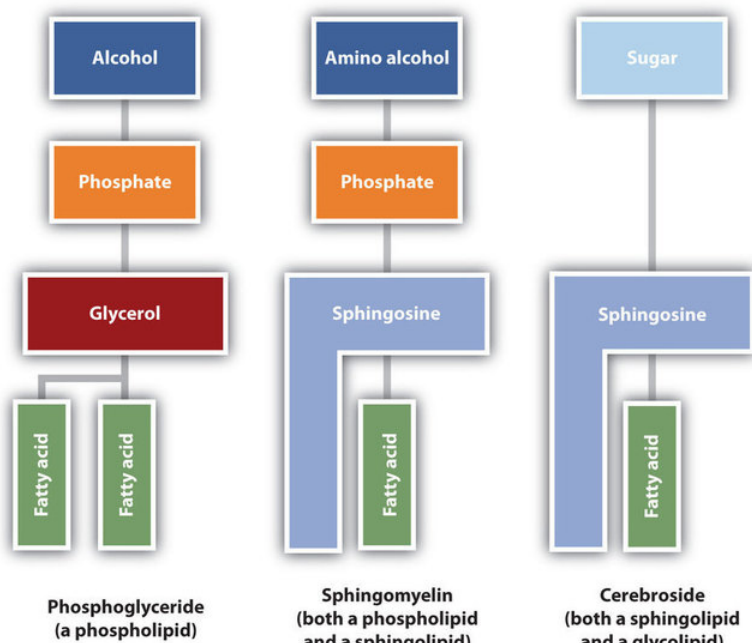


Figure 12.4.4: Component Structures of Some

Important Membrane Lipids Phosphoglyceride are composed of alcohol, phosphate, glycerol and 2 fatty acids. A sphingomyelin contains phosphate, sphingosine, and a fatty acid. A cerebroside contains sugar, sphingosine and a fatty acid.

Phosphoglycerides (also known as glycerophospholipids) are the most abundant phospholipids in cell membranes. They consist of a glycerol unit with fatty acids attached to the first two carbon atoms, while a phosphoric acid unit, esterified with an amino alcohol molecule (usually an amino alcohol, as in part (a) of Figure 12.4.5) is attached to the third carbon atom of glycerol (part (b) of Figure 12.4.5). Notice that the phosphoglyceride molecule is identical to a triglyceride up to the phosphoric acid unit (part (b) of Figure 12.4.5).

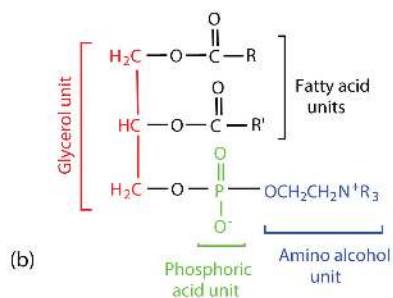
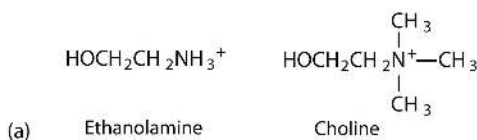
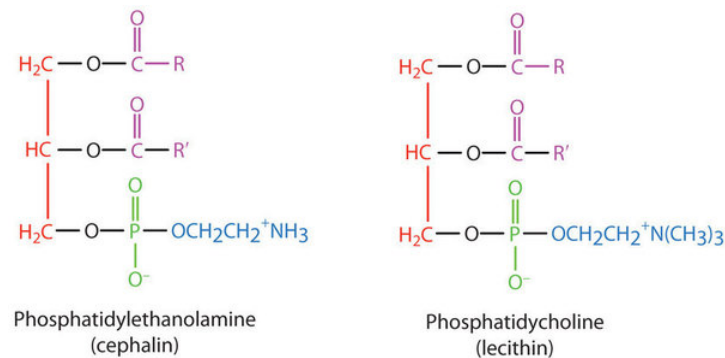


Figure 12.4.5: Phosphoglycerides. (a) Amino alcohols are

commonly found in phosphoglycerides, which are evident in its structural formula (b). Structural formula of ethanolamine and choline are shown. The structural formula of a phosphoglyceride is shown with the glycerol unit, phosphoric unit, and amino alcohol unit highlighted in different colors.

There are two common types of phosphoglycerides. Phosphoglycerides containing ethanolamine as the amino alcohol are called *phosphatidylethanolamines* or *cephalins*. Cephalins are found in brain tissue and nerves and also have a role in blood clotting. Phosphoglycerides containing choline as the amino alcohol unit are called *phosphatidylcholines* or *lecithins*. Lecithins occur in all living organisms. Like cephalins, they are important constituents of nerve and brain tissue. Egg yolks are especially rich in lecithins. Commercial-grade lecithins isolated from soybeans are widely used in foods as emulsifying agents. An emulsifying agent is used to stabilize an emulsion—a dispersion of two liquids that do not normally mix, such as oil and water. Many foods are

emulsions. Milk is an emulsion of butterfat in water. The emulsifying agent in milk is a protein called *casein*. Mayonnaise is an emulsion of salad oil in water, stabilized by lecithins present in egg yolk.



Sphingomyelins, the simplest sphingolipids, each contain a fatty acid, a phosphoric acid, sphingosine, and choline (Figure 12.4.6). Because they contain phosphoric acid, they are also classified as phospholipids. Sphingomyelins are important constituents of the myelin sheath surrounding the axon of a nerve cell. Multiple sclerosis is one of several diseases resulting from damage to the myelin sheath.

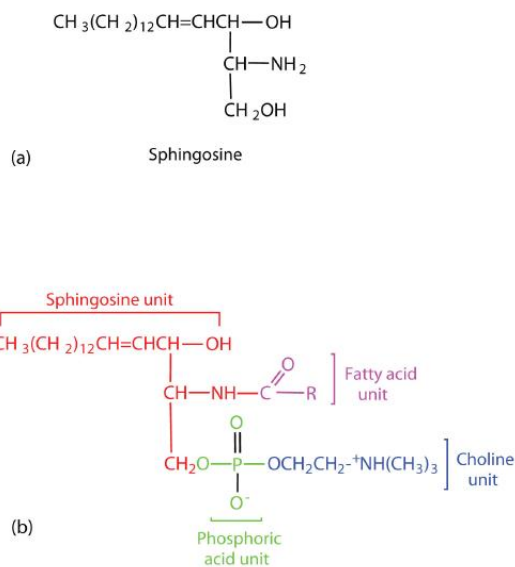


Figure 12.4.6: Sphingolipids. (a) Sphingosine, an amino alcohol, is found in all sphingolipids. (b) A sphingomyelin is also known as a phospholipid, as evidenced by the phosphoric acid unit in its structure. Structural formula of sphingosine is shown. The general structure of a sphingolipid is shown with the sphingosine unit, fatty acid unit, phosphoric acid unit, and choline unit highlighted in different colors.

Most animal cells contain sphingolipids called cerebrosides (Figure 12.4.7). 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.

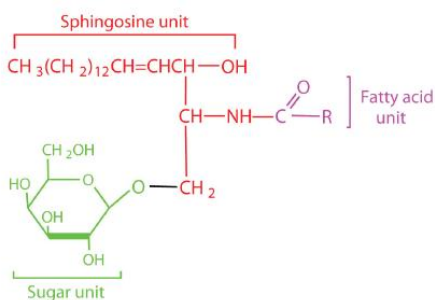


Figure 12.4.7: Cerebrosides. Cerebrosides are sphingolipids that contain a sugar unit. General structure of a cerebroside with its sugar unit, sphingosine unit, and fatty acid unit highlighted in different colors.

The sphingolipids called gangliosides are more complex, usually containing a branched chain of three to eight monosaccharides and/or substituted sugars. Because of considerable variation in their sugar components, about 130 varieties of gangliosides have been identified. Most cell-to-cell recognition and communication processes (e.g., blood group antigens) depend on differences in the sequences of sugars in these compounds. Gangliosides are most prevalent in the outer membranes of nerve cells, although they also occur in smaller quantities in the outer membranes of most other cells. Because cerebrosides and gangliosides contain sugar groups, they are also classified as glycolipids.

Membrane Proteins

If membranes were composed only of lipids, very few ions or polar molecules could pass through their hydrophobic “sandwich filling” to enter or leave any cell. However, certain charged and polar species do cross the membrane, aided by proteins that move about in the lipid bilayer. The two major classes of proteins in the cell membrane are integral proteins, which span the hydrophobic interior of the bilayer, and peripheral proteins, which are more loosely associated with the surface of the lipid bilayer (Figure 12.4.3). Peripheral proteins may be attached to integral proteins, to the polar head groups of phospholipids, or to both by hydrogen bonding and electrostatic forces.

Small ions and molecules soluble in water enter and leave the cell by way of channels through the integral proteins. Some proteins, called *carrier proteins*, facilitate the passage of certain molecules, such as hormones and neurotransmitters, by specific interactions between the protein and the molecule being transported.

Summary

Lipids are important components of biological membranes. These lipids have dual characteristics: part of the molecule is hydrophilic, and part of the molecule is hydrophobic. Membrane lipids may be classified as phospholipids, glycolipids, and/or sphingolipids. Proteins are another important component of biological membranes. Integral proteins span the lipid bilayer, while peripheral proteins are more loosely associated with the surface of the membrane.

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12.5: Steroids

Learning Objectives

- To identify the functions of steroids produced in mammals.

All the lipids discussed so far are *saponifiable*, reacting with aqueous alkali to yield simpler components, such as glycerol, fatty acids, amino alcohols, and sugars. Lipid samples extracted from cellular material, however, also contain a small but important fraction that does not react with alkali. The most important nonsaponifiable lipids are the steroids. These compounds include the *bile salts*, *cholesterol* and related compounds, and certain *hormones* (such as cortisone and the sex hormones).

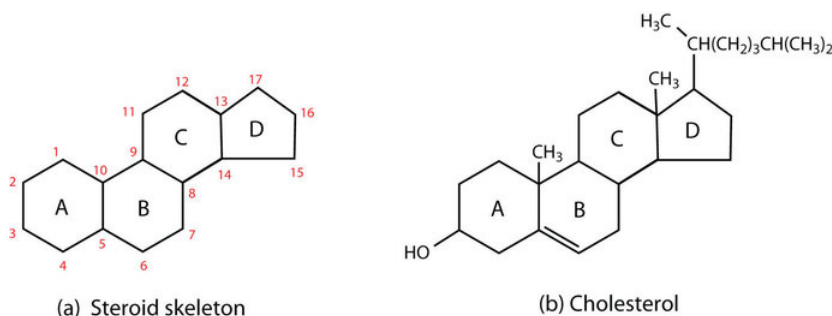


Figure 12.5.1 Steroids. (a) The four-fused-ring

steroid skeleton uses letter designations for each ring and the numbering of the carbon atoms. (b) The cholesterol molecule follows this pattern.

Steroids occur in plants, animals, yeasts, and molds but not in bacteria. They may exist in free form or combined with fatty acids or carbohydrates. All steroids have a characteristic structural component consisting of four fused rings. Chemists identify the rings by capital letters and number the carbon atoms as shown in Figure 12.5.1a. Slight variations in this structure or in the atoms or groups attached to it produce profound differences in biological activity.

Cholesterol

Cholesterol (Figure 12.5.1b) does not occur in plants, but it is the most abundant steroid in the human body (240 g is a typical amount). Excess cholesterol is believed to be a primary factor in the development of atherosclerosis and heart disease, which are major health problems in the United States today. About half of the body's cholesterol is interspersed in the lipid bilayer of cell membranes. Much of the rest is converted to cholic acid, which is used in the formation of bile salts. Cholesterol is also a precursor in the synthesis of sex hormones, adrenal hormones, and vitamin D.

Excess cholesterol not metabolized by the body is released from the liver and transported by the blood to the gallbladder. Normally, it stays in solution there until being secreted into the intestine (as a component of bile) to be eliminated. Sometimes, however, cholesterol in the gallbladder precipitates in the form of gallstones (Figure 12.5.2). Indeed, the name *cholesterol* is derived from the Greek *chole*, meaning "bile," and *stereos*, meaning "solid."



Figure 12.5.2: Numerous small gallstones made up largely of

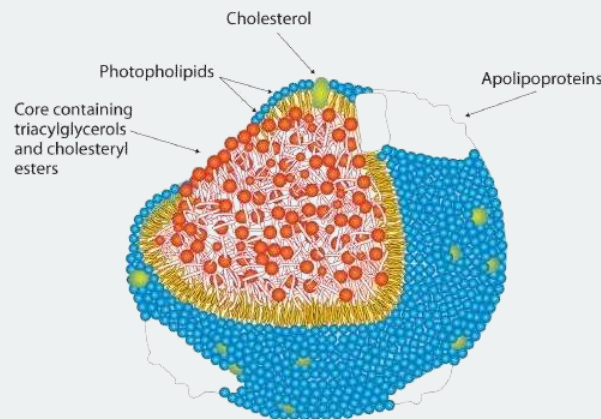
cholesterol, all removed in one patient. Grid scale 1 mm

To Your Health: Cholesterol and Heart Disease

Heart disease is the leading cause of death in the United States for both men and women. The Centers for Disease Control and Prevention reported that heart disease claimed 631,636 lives in the United States (26% of all reported deaths) in 2006.

Scientists agree that elevated cholesterol levels in the blood, as well as high blood pressure, obesity, diabetes, and cigarette smoking, are associated with an increased risk of heart disease. A long-term investigation by the National Institutes of Health showed that among men ages 30 to 49, the incidence of heart disease was five times greater for those whose cholesterol levels were above 260 mg/100 mL of serum than for those with cholesterol levels of 200 mg/100 mL or less. The cholesterol content of blood varies considerably with age, diet, and sex. Young adults average about 170 mg of cholesterol per 100 mL of blood, whereas males at age 55 may have cholesterol levels at 250 mg/100 mL or higher because the rate of cholesterol breakdown decreases with age. Females tend to have lower blood cholesterol levels than males.

To understand the link between heart disease and cholesterol levels, it is important to understand how cholesterol and other lipids are transported in the body. Lipids, such as cholesterol, are not soluble in water and therefore cannot be transported in the blood (an aqueous medium) unless they are complexed with proteins that are soluble in water, forming assemblages called *lipoproteins*. Lipoproteins are classified according to their density, which is dependent on the relative amounts of protein and lipid they contain. Lipids are less dense than proteins, so lipoproteins containing a greater proportion of lipid are less dense than those containing a greater proportion of protein.



Research on cholesterol and its role in heart disease has focused on serum levels of low-density lipoproteins (LDLs) and high-density lipoproteins (HDLs). One of the most fascinating discoveries is that high levels of HDLs reduce a person's risk of developing heart disease, whereas high levels of LDLs increase that risk. Thus the serum LDL:HDL ratio is a better predictor of heart disease risk than the overall level of serum cholesterol. Persons who, because of hereditary or dietary factors, have high LDL:HDL ratios in their blood have a higher incidence of heart disease.

How do HDLs reduce the risk of developing heart disease? No one knows for sure, but one role of HDLs appears to be the transport of excess cholesterol to the liver, where it can be metabolized. Therefore, HDLs aid in removing cholesterol from blood and from the smooth muscle cells of the arterial wall.

Dietary modifications and increased physical activity can help lower total cholesterol and improve the LDL:HDL ratio. The average American consumes about 600 mg of cholesterol from animal products each day and also synthesizes approximately 1 g of cholesterol each day, mostly in the liver. The amount of cholesterol synthesized is controlled by the cholesterol level in the blood; when the blood cholesterol level exceeds 150 mg/100 mL, the rate of cholesterol biosynthesis is halved. Hence, if cholesterol is present in the diet, a feedback mechanism suppresses its synthesis in the liver. However, the ratio of suppression is not a 1:1 ratio; the reduction in biosynthesis does not equal the amount of cholesterol ingested. Thus, dietary substitutions of unsaturated fat for saturated fat, as well as a reduction in consumption of *trans* fatty acids, is recommended to help lower serum cholesterol and the risk of heart disease.

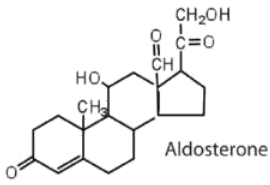
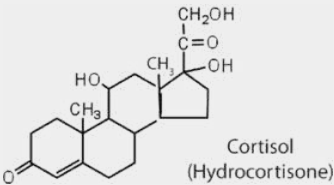
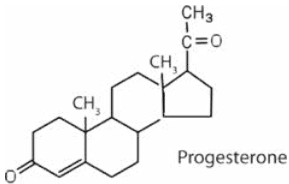
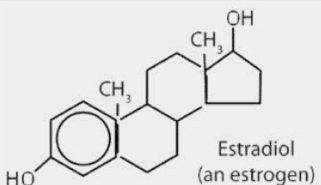
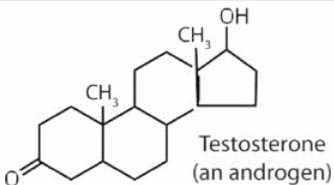
Steroid Hormones

Hormones are chemical messengers that are released in one tissue and transported through the circulatory system to one or more other tissues. One group of hormones is known as steroid hormones because these hormones are synthesized from cholesterol, which is also a steroid. There are two main groups of steroid hormones: adrenocortical hormones and sex hormones.

The adrenocortical hormones, such as aldosterone and cortisol (Table 12.5.1), are produced by the adrenal gland, which is located adjacent to each kidney. Aldosterone acts on most cells in the body, but it is particularly effective at enhancing the rate of reabsorption of sodium ions in the kidney tubules and increasing the secretion of potassium ions and/or hydrogen ions by the

tubules. Because the concentration of sodium ions is the major factor influencing water retention in tissues, aldosterone promotes water retention and reduces urine output. Cortisol regulates several key metabolic reactions (for example, increasing glucose production and mobilizing fatty acids and amino acids). It also inhibits the inflammatory response of tissue to injury or stress. Cortisol and its analogs are therefore used pharmacologically as immunosuppressants after transplant operations and in the treatment of severe skin allergies and autoimmune diseases, such as rheumatoid arthritis.

Table 12.5.1: Representative Steroid Hormones and Their Physiological Effects

Hormone	Effect
 Aldosterone	regulates salt metabolism; stimulates kidneys to retain sodium and excrete potassium
 Cortisol (Hydrocortisone)	stimulates the conversion of proteins to carbohydrates
 Progesterone	regulates the menstrual cycle; maintains pregnancy
 Estradiol (an estrogen)	stimulates female sex characteristics; regulates changes during the menstrual cycle
 Testosterone (an androgen)	stimulates and maintains male sex characteristics

The sex hormones are a class of steroid hormones secreted by the gonads (ovaries or testes), the placenta, and the adrenal glands. Testosterone and androstenedione are the primary male sex hormones, or *androgens*, controlling the primary sexual characteristics of males, or the development of the male genital organs and the continuous production of sperm. Androgens are also responsible for the development of secondary male characteristics, such as facial hair, deep voice, and muscle strength. Two kinds of sex hormones are of particular importance in females: progesterone, which prepares the uterus for pregnancy and prevents the further release of eggs from the ovaries during pregnancy, and the estrogens, which are mainly responsible for the development of female secondary sexual characteristics, such as breast development and increased deposition of fat tissue in the breasts, the buttocks, and the thighs. Both males and females produce androgens and estrogens, differing in the amounts of secreted hormones rather than in the presence or absence of one or the other.

Sex hormones, both natural and synthetic, are sometimes used therapeutically. For example, a woman who has had her ovaries removed may be given female hormones to compensate. Some of the earliest chemical compounds employed in cancer chemotherapy were sex hormones. For example, estrogens are one treatment option for prostate cancer because they block the release and activity of testosterone. Testosterone enhances prostate cancer growth. Sex hormones are also administered in

preparation for sex-change operations, to promote the development of the proper secondary sexual characteristics. Oral contraceptives are synthetic derivatives of the female sex hormones; they work by preventing ovulation.

Bile Salts

Bile is a yellowish green liquid (pH 7.8–8.6) produced in the liver. The most important constituents of bile are bile salts, which are sodium salts of amidelike combinations of bile acids, such as cholic acid (part (a) of Figure 12.5.3) and an amine such as the amino acid glycine (part (b) of Figure 12.5.3). They are synthesized from cholesterol in the liver, stored in the gallbladder, and then secreted in bile into the small intestine. In the gallbladder, the composition of bile gradually changes as water is absorbed and the other components become more concentrated.

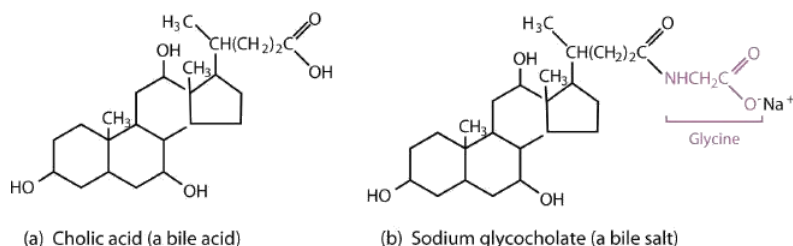


Figure 12.5.3 Bile Acids. (a) Cholic acid is an example of a bile acid. (b) Sodium glycocholate is a bile salt synthesized from cholic acid and glycine.

Because they contain both hydrophobic and hydrophilic groups, bile salts are highly effective detergents and emulsifying agents; they break down large fat globules into smaller ones and keep those smaller globules suspended in the aqueous digestive environment. Enzymes can then hydrolyze fat molecules more efficiently. Thus, the major function of bile salts is to aid in the digestion of dietary lipids.

Surgical removal is often advised for a gallbladder that becomes infected, inflamed, or perforated. This surgery does not seriously affect digestion because bile is still produced by the liver, but the liver's bile is more dilute and its secretion into the small intestine is not as closely tied to the arrival of food.

Summary

Steroids have a four-fused-ring structure and have a variety of functions. Cholesterol is a steroid found in mammals that is needed for the formation of cell membranes, bile acids, and several hormones. Bile salts are secreted into the small intestine to aid in the digestion of fats.

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12.S: Lipids (Summary)

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

Lipids, found in the body tissues of all organisms, are compounds that are more soluble in organic solvents than in water. Many of them contain **fatty acids**, which are carboxylic acids that generally contain an even number of 4–20 carbon atoms in an unbranched chain. **Saturated fatty acids** have no carbon-to-carbon double bonds. **Monounsaturated fatty acids** have a single carbon-to-carbon double bond, while **polyunsaturated fatty acids** have more than one carbon-to-carbon double bond. Linoleic and linolenic acid are known as **essential fatty acids** because the human body cannot synthesize these polyunsaturated fatty acids. The lipids known as **fats** and **oils** are triacylglycerols, more commonly called **triglycerides**—esters composed of three fatty acids joined to the trihydroxy alcohol glycerol. Fats are triglycerides that are solid at room temperature, and oils are triglycerides that are liquid at room temperature. Fats are found mainly in animals, and oils found mainly in plants. *Saturated triglycerides* are those containing a higher proportion of saturated fatty acid chains (fewer carbon-to-carbon double bonds); *unsaturated triglycerides* contain a higher proportion of unsaturated fatty acid chains.

Saponification is the hydrolysis of a triglyceride in a basic solution to form glycerol and three carboxylate anions or soap molecules. Other important reactions are the hydrogenation and oxidation of double bonds in unsaturated fats and oils.

Phospholipids are lipids containing phosphorus. In **phosphoglycerides**, the phosphorus is joined to an amino alcohol unit. Some phosphoglycerides, like lecithins, are used to stabilize an **emulsion**—a dispersion of two liquids that do not normally mix, such as oil and water. **Sphingolipids** are lipids for which the precursor is the amino alcohol sphingosine, rather than glycerol. A **glycolipid** has a sugar substituted at one of the OH groups of either glycerol or sphingosine. All are highly polar lipids found in cell membranes.

Polar lipids have dual characteristics: one part of the molecule is ionic and dissolves in water; the rest has a hydrocarbon structure and dissolves in nonpolar substances. Often, the ionic part is referred to as **hydrophilic** (literally, “water loving”) and the nonpolar part as **hydrophobic** (“water fearing”). When placed in water, polar lipids disperse into any one of three arrangements: *micelles*, *monolayers*, and *bilayers*. **Micelles** are aggregations of molecules in which the hydrocarbon tails of the lipids, being hydrophobic, are directed inward (away from the surrounding water), and the hydrophilic heads that are directed outward into the water. **Bilayers** are double layers arranged so that the hydrophobic tails are sandwiched between the two layers of hydrophilic heads, which remain in contact with the water.

Every living cell is enclosed by a *cell membrane* composed of a lipid bilayer. In animal cells, the bilayer consists mainly of phospholipids, glycolipids, and the steroid cholesterol. Embedded in the bilayer are **integral proteins**, and **peripheral proteins** are loosely associated with the surface of the bilayer. Everything between the cell membrane and the membrane of the cell nucleus is called the **cytoplasm**.

Most lipids can be saponified, but some, such as **steroids**, cannot be saponified. The steroid **cholesterol** is found in animal cells but never in plant cells. It is a main component of all cell membranes and a precursor for hormones, vitamin D, and bile salts. Bile salts are the most important constituents of **bile**, which is a yellowish-green liquid secreted by the gallbladder into the small intestine and is needed for the proper digestion of lipids.

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CHAPTER OVERVIEW

13: Proteins and Enzymes

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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.

- [13.1: Properties of Amino Acids](#)
- [13.2: Reactions of Amino Acids](#)
- [13.3: Organic Sulfur Compounds](#)
- [13.4: Amines - Structures and Names](#)
- [13.5: Physical Properties of Amines](#)
- [13.6: Amines as Bases](#)
- [13.7: Amides- Structures and Names](#)
- [13.8: Physical Properties of Amides](#)
- [13.9: Formation of Amides](#)
- [13.10: Chemical Properties of Amides- Hydrolysis](#)
- [13.11: Peptides](#)
- [13.12: Proteins](#)
- [13.13: Enzymes](#)
- [13.14: Enzymatic Catalysis](#)
- [13.15: Enzyme Activity](#)
- [13.16: Enzyme Regulation](#)
- [13.17: Enzyme Cofactors and Vitamins](#)
- [13.18: Chapter Summary](#)

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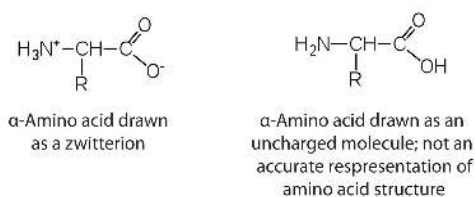
13.1: Properties of Amino Acids

Learning Objectives

- To recognize amino acids and classify them based on the characteristics of their side chains.

The proteins in all living species, from bacteria to humans, are constructed from the same set of 20 amino acids, so called because each contains an amino group attached to a carboxylic acid. The amino acids in proteins are α -amino acids, which means the amino group is attached to the α -carbon of the carboxylic acid. Humans can synthesize only about half of the needed amino acids; the remainder must be obtained from the diet and are known as essential amino acids. However, two additional amino acids have been found in limited quantities in proteins: Selenocysteine was discovered in 1986, while pyrrolysine was discovered in 2002.

The amino acids are colorless, nonvolatile, crystalline solids, melting and decomposing at temperatures above 200°C. These melting temperatures are more like those of inorganic salts than those of amines or organic acids and indicate that the structures of the amino acids in the solid state and in neutral solution are best represented as having both a negatively charged group and a positively charged group. Such a species is known as a zwitterion.

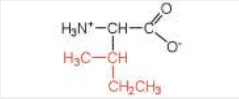
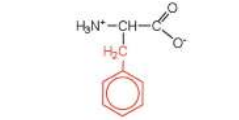
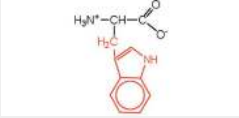
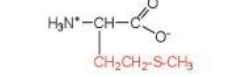
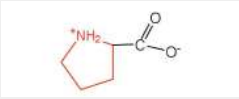
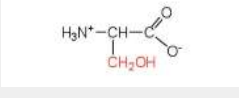
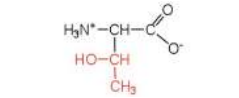
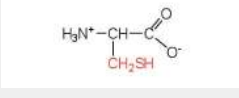
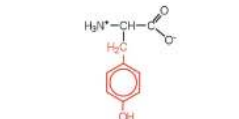
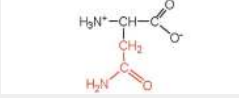
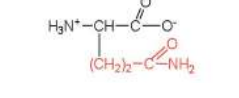


13.1.1 Classification

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 13.1.1.

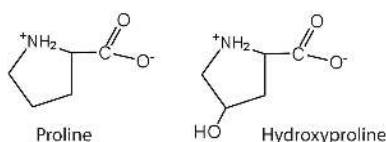
Table 13.1.1: Common Amino Acids Found in Proteins

Common Name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
Amino acids with a nonpolar R group				
glycine	gly (G)	$\text{H}_3\text{N}^+-\text{CH}(\text{H})-\text{COO}^-$	75	the only amino acid lacking a chiral carbon
alanine	ala (A)	$\text{H}_3\text{N}^+-\text{CH}(\text{CH}_3)-\text{COO}^-$	89	—
valine	val (V)	$\text{H}_3\text{N}^+-\text{CH}(\text{CH}(\text{CH}_3)_2)-\text{COO}^-$	117	a branched-chain amino acid
leucine	leu (L)	$\text{H}_3\text{N}^+-\text{CH}(\text{CH}_2\text{CH}(\text{CH}_3)_2)-\text{COO}^-$	131	a branched-chain amino acid

Common Name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
isoleucine	ile (I)		131	an essential amino acid because most animals cannot synthesize branched-chain amino acids
phenylalanine	phe (F)		165	also classified as an aromatic amino acid
tryptophan	trp (W)		204	also classified as an aromatic amino acid
methionine	met (M)		149	side chain functions as a methyl group donor
proline	pro (P)		115	contains a secondary amine group; referred to as an α -imino acid
Amino acids with a polar but neutral R group				
serine	ser (S)		105	found at the active site of many enzymes
threonine	thr (T)		119	named for its similarity to the sugar threose
cysteine	cys (C)		121	oxidation of two cysteine molecules yields <i>cystine</i>
tyrosine	tyr (Y)		181	also classified as an aromatic amino acid
asparagine	asn (N)		132	the amide of aspartic acid
glutamine	gln (Q)		146	the amide of glutamic acid
Amino acids with a negatively charged R group				

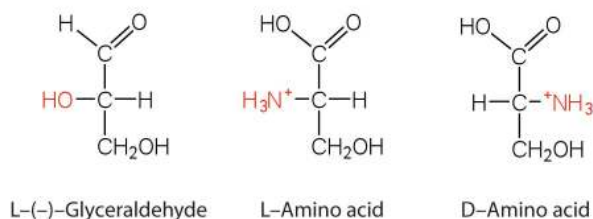
Common Name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
aspartic acid	asp (D)		132	carboxyl groups are ionized at physiological pH; also known as aspartate
glutamic acid	glu (E)		146	carboxyl groups are ionized at physiological pH; also known as glutamate
Amino acids with a positively charged R group				
histidine	his (H)		155	the only amino acid whose R group has a pK _a (6.0) near physiological pH
lysine	lys (K)		147	—
arginine	arg (R)		175	almost as strong a base as sodium hydroxide

The first amino acid to be isolated was asparagine in 1806. It was obtained from protein found in asparagus juice (hence the name). Glycine, the major amino acid found in gelatin, was named for its sweet taste (Greek *glykys*, meaning “sweet”). In some cases an amino acid found in a protein is actually a derivative of one of the common 20 amino acids (one such derivative is hydroxyproline). The modification occurs *after* the amino acid has been assembled into a protein.



13.1.2 Configuration

Notice in Table 13.1.1 that glycine is the only amino acid whose α -carbon is *not* chiral. Therefore, with the exception of glycine, the amino acids could theoretically exist in either the D- or the L-enantiomeric form and rotate plane-polarized light. As with sugars, chemists used L-glyceraldehyde as the reference compound for the assignment of absolute configuration to amino acids. Its structure closely resembles an amino acid structure except that in the latter, an amino group takes the place of the OH group on the chiral carbon of the L-glyceraldehyde and a carboxylic acid replaces the aldehyde. Modern stereochemistry assignments using the Cahn-Ingold-Prelog priority rules used ubiquitously in chemistry show that all of the naturally occurring chiral amino acids are S except Cys which is R.



We learned that all naturally occurring sugars belong to the D series. It is interesting, therefore, that nearly all known plant and animal proteins are composed entirely of L-amino acids. However, certain bacteria contain D-amino acids in their cell walls, and several antibiotics (e.g., actinomycin D and the gramicidins) contain varying amounts of D-leucine, D-phenylalanine, and D-valine.

Summary

Amino acids can be classified based on the characteristics of their distinctive side chains as nonpolar, polar but uncharged, negatively charged, or positively charged. The amino acids found in proteins are L-amino acids.

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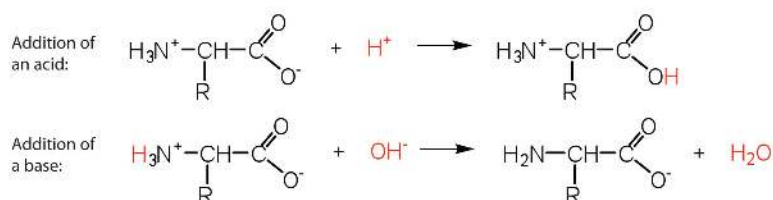
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13.2: Reactions of Amino Acids

Learning Objectives

- To explain how an amino acid can act as both an acid and a base.
- Define zwitterion

The structure of an amino acid allows it to act as both an acid and a base. An amino acid has this ability because at a certain pH value (different for each amino acid) nearly all the amino acid molecules exist as zwitterions. If acid is added to a solution containing the zwitterion, the carboxylate group captures a hydrogen (H^+) ion, and the amino acid becomes positively charged. If base is added, ion removal of the H^+ ion from the amino group of the zwitterion produces a negatively charged amino acid. In both circumstances, the amino acid acts to maintain the pH of the system—that is, to remove the added acid (H^+) or base (OH^-) from solution.



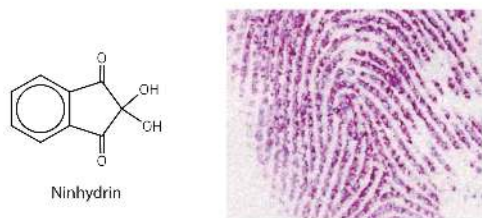
The particular pH at which a given amino acid exists in solution as a zwitterion is called the **isoelectric point** (pI). At its pI, the positive and negative charges on the amino acid balance, and the molecule as a whole is electrically neutral. The amino acids whose side chains are always neutral 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 13.2.1).

Table 13.2.1: Examples of Some Representative Amino Acids (* you do not need to know pI values)

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.



13.2.1 Summary

Amino acids can act as both an acid and a base due to the presence of the amino and carboxyl functional groups. The pH at which a given amino acid exists in solution as a zwitterion is called the *isoelectric point* (pI).

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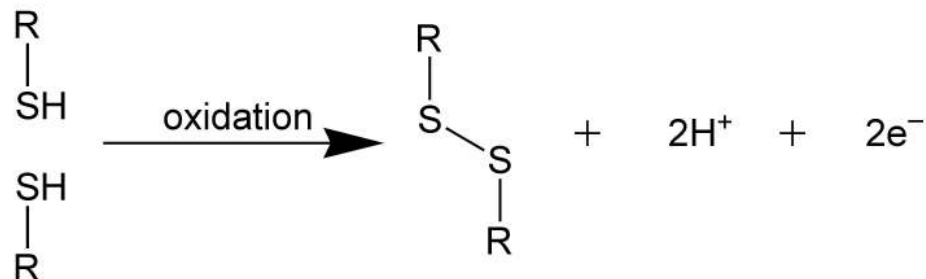
13.3: Organic Sulfur Compounds

Learning Objectives

- Describe how the mild oxidation of thiols gives disulfide.

Because sulfur is in the same group (6A) of the periodic table as oxygen, the two elements have some similar properties. We might expect sulfur to form organic compounds related to those of oxygen, and indeed it does. **Thiols** (also called mercaptans), which are sulfur analogs of alcohols, have the general formula RSH. Methanethiol (also called methyl mercaptan), has the formula CH₃SH. Ethanethiol (ethyl mercaptan) is the most common odorant for liquid propane (LP) gas.

The mild oxidation of thiols gives compounds called **disulfides**.



The amino acids cysteine [HSCH₂CH(NH₂)COOH] and methionine [CH₃SCH₂CH₂CH(NH₂)COOH] contain sulfur atoms, as do all proteins that contain these amino acids.

Disulfide linkages (–S–S–) between protein chains are extremely important in protein structure.

Thioethers, which are sulfur analogs of ethers, have the form general formula RSR'. An example is dimethylsulfide (CH₃SCH₃), which is responsible for the sometimes unpleasant odor of cooking cabbage and related vegetables. Note that methionine has a thioether functional group.

Career focus

Paramedics are highly trained experts at providing emergency medical treatment. Their critical duties often include rescue work and emergency medical procedures in a wide variety of settings, sometimes under extremely harsh and difficult conditions. Like other science-based professions, their work requires knowledge, ingenuity, and complex thinking, as well as a great deal of technical skill. The recommended courses for preparation in this field include anatomy, physiology, medical terminology, and—not surprisingly—chemistry. An understanding of basic principles of organic chemistry, for example, is useful when paramedics have to deal with such traumas as burns from fuel (hydrocarbons) or solvent (alcohols, ethers, esters, and so on) fires and alcohol and drug overdoses.

To become a paramedic requires 2–4 y of training and usually includes a stint as an emergency medical technician (EMT). An EMT provides basic care, can administer certain medications and treatments, such as oxygen for respiratory problems and epinephrine (adrenalin) for allergic reactions, and has some knowledge of common medical conditions. A paramedic, in contrast, must have extensive knowledge of common medical problems and be trained to administer a wide variety of emergency drugs.

Paramedics usually work under the direction of a medical doctor with a title such as “medical director.” Some paramedics are employed by fire departments and may work from a fire engine that carries medical equipment as well as fire-fighting gear. Some work from hospital-sponsored ambulances and continue to care for their patients after reaching the hospital emergency room. Still other paramedics work for a government department responsible for emergency health care in a specific geographical area. Finally, some work for private companies that contract to provide service for a government body.

An experienced paramedic has a broad range of employment options, including training for mountain or ocean rescue, working with police department special weapons and tactics (SWAT) teams, or working in isolated settings such as on oil rigs. With their expertise at treating and stabilizing patients before quickly moving them to a hospital, paramedics often provide the first

critical steps in saving an endangered life. The following quotation, inscribed on the Arlington National Cemetery headstone of Army Lieutenant R. Adams Cowley, who is often called the “father” of shock trauma medicine, serves as the motto for many paramedic units: “Next to creating a life the finest thing a man can do is save one.” —Abraham Lincoln

13.3.1 Summary

Thiols, thioethers, and disulfides are common in biological compounds.

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13.4: Amines - Structures and Names

Learning Objectives

- Identify the general structure for an amine.
- Identify the functional group for amines.
- Determine the structural feature that classifies amines as primary, secondary, or tertiary.
- Use nomenclature systems to name amines.

Amines are classified according to the number of carbon atoms bonded directly to the nitrogen atom. A primary (1°) amine has one alkyl (or aryl) group on the nitrogen atom, a secondary (2°) amine has two, and a tertiary (3°) amine has three (Figure 13.4.1).

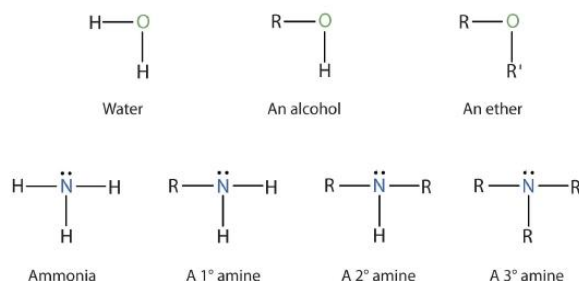
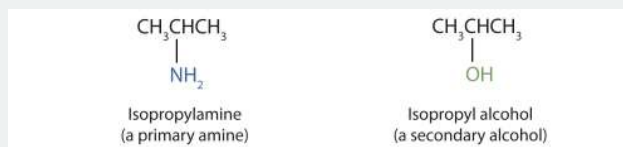


Figure 13.4.1: The Structure of Amines Compared to Water, an Alcohol, and an Ether

To classify alcohols, we look at the number of carbon atoms bonded to the *carbon atom* bearing the OH group, not the oxygen atom itself. Thus, although isopropylamine looks similar to isopropyl alcohol, the former is a *primary* amine, while the latter is a *secondary* alcohol.

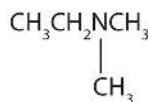


The common names for simple aliphatic amines consist of an alphabetic list of alkyl groups attached to the nitrogen atom, followed by the suffix *-amine*. (Systematic names are often used by some chemists.) The amino group (NH_2) is named as a substituent in more complicated amines, such as those that incorporate other functional groups or in which the alkyl groups cannot be simply named.

✓ Example 13.4.1

Name and classify each compound.

a. $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$



b.

c. $\text{CH}_3\text{CH}_2\text{NHCH}_2\text{CH}_3$

d. $\text{CH}_3\text{CH}_2\text{CH}_2\text{NHCH}_3$

Solution

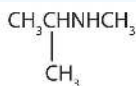
- There is only one alkyl group attached to the nitrogen atom, so the amine is primary. A group of three carbon atoms (a propyl group) is attached to the NH_2 group through an end carbon atom, so the name is propylamine.
- There are two methyl groups and one ethyl group on the nitrogen atom. The compound is ethyldimethylamine, a tertiary amine.
- There are two ethyl groups attached to the nitrogen atom; the amine is secondary, so the compound is diethylamine.

d. The nitrogen atom has a methyl group and a propyl group, so the compound is methylpropylamine, a secondary amine.

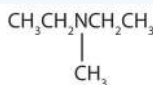
? Exercise 13.4.1

Name and classify each compound.

a.



b.



c. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$

d. $\text{CH}_3\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_3$

Answer

a. There are two alkyl groups attached to the amine, the the amine is secondary. Alkyl groups: Isopropyl and methyl; name: Isopropylmethylamine.

b. There are three alkyl groups attached to the amine, the amine is tertiary. Alkyl groups: two ethyl (diethyl) and one methyl; name: diethylmethylamine.

c. There is one alkyl group attached to the amine, the amine is primary. Alkyl groups: butyl; name: butylamine.

d. There are two alkyl groups attached to the amine, the amine is secondary. Alkyl groups: two propyl (dipropyl); name: dipropylamine.

✓ Example 13.4.2

Draw the structure for each compound and classify.

a. isopropyl dimethylamine

b. dipropylamine

Solution

a. The name indicates that there are an isopropyl group (in red) and two methyl groups (in green) attached to the nitrogen atom; the amine is tertiary.



b. The name indicates that there are two propyl groups attached to the nitrogen atom; the amine is secondary. (The third bond on the nitrogen atom goes to a hydrogen atom.) $\text{CH}_3\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_3$

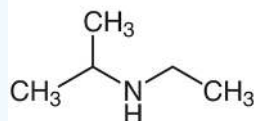
? Exercise 13.4.1

Draw the structure for each compound and classify.

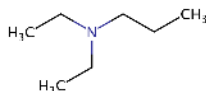
a. ethylisopropylamine

b. diethylpropylamine

Answer

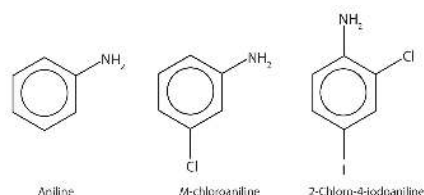


a. secondary;



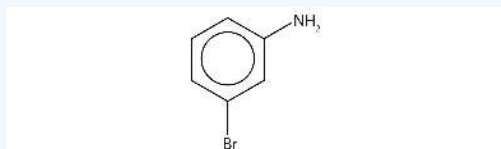
b. tertiary;

The primary amine in which the nitrogen atom is attached directly to a benzene ring has a special name—**aniline**. Aryl amines are named as derivatives of aniline.



✓ Example 13.4.3

Name this compound.



Solution

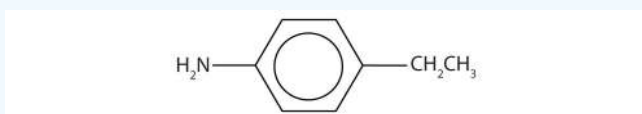
The benzene ring with an amino (NH_2) group is aniline. The compound is named as a derivative of aniline: 3-bromoaniline or *m*-bromoaniline.

✓ Example 13.4.4

Draw the structure for *para*-ethylaniline or 3-ethylaniline and classify.

Solution

The compound is a derivative of aniline. It is a primary amine having an ethyl group located *para* to the amino (NH_2) group.

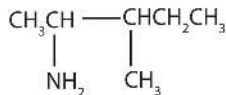


✓ Example 13.4.5

Draw the structure for 2-amino-3-methylpentane.

Solution

Always start with the parent compound: draw the pentane chain. Then attach a methyl group at the third carbon atom and an amino group at the second carbon atom.

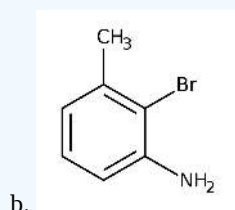


? Exercise 13.4.1

- Draw the structure for dimethylpropylamine.
- Draw the structure for 2-bromo-3-methylaniline

Answer

a.  DIMETHYLPROPYLAMINE | C5H13N | ChemSpider



Ammonium (NH_4^+) ions, in which one or more hydrogen atoms are replaced with alkyl groups, are named in a manner analogous to that used for simple amines. The alkyl groups are named as substituents, and the parent species is regarded as the NH_4^+ ion. For example, CH_3NH_3^+ is the methylammonium ion. The ion formed from aniline ($\text{C}_6\text{H}_5\text{NH}_3^+$) is called the anilinium ion.

✓ Example 13.4.6

Name each ion.

- CH_3NH_3^+
- $(\text{CH}_3)_2\text{NH}_2^+$
- $(\text{CH}_3)_3\text{NH}^+$
- $(\text{CH}_3)_4\text{N}^+$

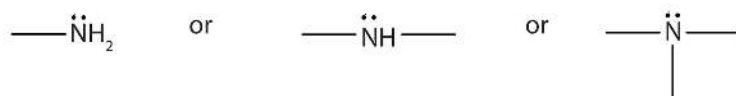
Solution

The ions have one, two, three, and four methyl (CH_3) groups attached to a nitrogen atom. Their names are as follows:

- methylammonium ion
- dimethylammonium ion
- trimethylammonium ion
- tetramethylammonium ion

Summary

An amine is a derivative of ammonia in which one, two, or all three hydrogen atoms are replaced by hydrocarbon groups. The amine functional group is as follows:



Amines are classified as primary, secondary, or tertiary by the number of hydrocarbon groups attached to the nitrogen atom. Amines are named by naming the alkyl groups attached to the nitrogen atom, followed by the suffix *-amine*.

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13.5: Physical Properties of Amines

Learning Objectives

- Explain why the boiling points of primary and secondary amines are higher than those of alkanes or ethers of similar molar mass but are lower than those of alcohols.
- Compare the boiling points of tertiary amines with alcohols, alkanes, and ethers of similar molar mass.
- Compare the solubilities in water of amines of five or fewer carbon atoms with the solubilities of comparable alkanes and alcohols in water.

Primary and secondary amines have hydrogen atoms bonded to a nitrogen atom and are therefore capable of hydrogen bonding (part (a) of Figure 13.5.1), although not as strongly as alcohol molecules (which have hydrogen atoms bonded to an oxygen atom, which is more electronegative than nitrogen). These amines boil at higher temperatures than alkanes but at lower temperatures than alcohols of comparable molar mass. For example, compare the boiling point of methylamine (CH_3NH_2 ; -6°C) with those of ethane (CH_3CH_3 ; -89°C) and methanol (CH_3OH ; 65°C). Tertiary amines have no hydrogen atom bonded to the nitrogen atom and so cannot participate in intermolecular hydrogen bonding. They have boiling points comparable to those of ethers (Table 13.5.1).

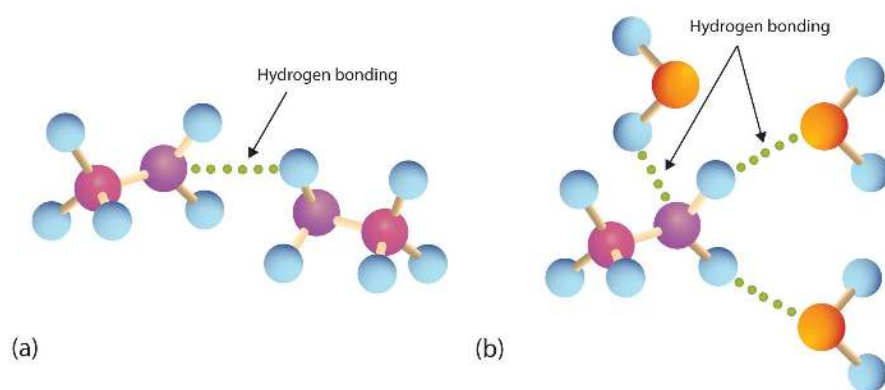


Figure 13.5.1: Hydrogen Bonding. (a)

Amine molecules are associated through hydrogen bonding. (b) An amine molecule can form a hydrogen bond with water molecules.

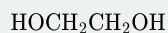
Table 13.5.1: Physical Properties of Some Amines and Comparable Oxygen-Containing Compounds

Name	Condensed Structural Formula	Class	Molar Mass	Boiling Point ($^\circ\text{C}$)	Solubility at 25°C (g/100 g Water)
butylamine	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$ H_2	1°	73	78	miscible
diethylamine	$(\text{CH}_3\text{CH}_2)_2\text{NH}$	2°	73	55	miscible
butyl alcohol	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$ H	—	74	118	8
dipropylamine	$(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{NH}$	2°	101	111	4
triethylamine	$(\text{CH}_3\text{CH}_2)_3\text{N}$	3°	101	90	14
dipropyl ether	$(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{O}$	—	102	91	0.25

All three classes of amines can engage in hydrogen bonding with water (Figure 13.5.1b). Amines of low molar mass are quite soluble in water; the borderline of solubility in water is at five or six carbon atoms.

To Your Health: Amines in Death and Life

Amines have “interesting” odors. The simple ones smell very much like ammonia. Higher aliphatic amines smell like decaying fish. Or perhaps we should put it the other way around: Decaying fish give off odorous amines. The stench of rotting fish is due in part to two diamines: putrescine and cadaverine. They arise from the decarboxylation of ornithine and lysine, respectively, amino acids that are found in animal cells.



Aromatic amines generally are quite toxic. They are readily absorbed through the skin, and workers must exercise caution when handling these compounds. Several aromatic amines, including β -naphthylamine, are potent carcinogens.



13.5.1 Key Takeaways

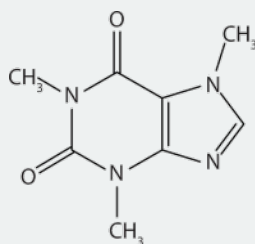
- Primary and secondary amines have higher boiling points than those of alkanes or ethers of similar molar mass because they can engage in intermolecular hydrogen bonding. Their boiling points are lower than those of alcohols because alcohol molecules have hydrogen atoms bonded to an oxygen atom, which is more electronegative.
- The boiling points of tertiary amines, which cannot engage in hydrogen bonding because they have no hydrogen atom on the nitrogen atom, are comparable to those of alkanes and ethers of similar molar mass.
- Because all three classes of amines can engage in hydrogen bonding with water, amines of low molar mass are quite soluble in water.

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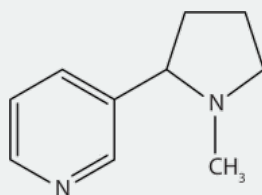
📌 To Your Health: Three Well-Known Alkaloids

Caffeine is a stimulant found in coffee, tea, and some soft drinks. Its mechanism of action is not well understood, but it is thought to block the activity of adenosine, a heterocyclic base that acts as a neurotransmitter, a substance that carries messages across a tiny gap (synapse) from one nerve cell (neuron) to another cell. The effective dose of caffeine is about 200 mg, corresponding to about two cups of strong coffee or tea.



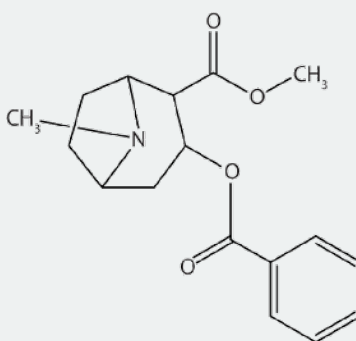
Caffeine

Nicotine acts as a stimulant by a different mechanism; it probably mimics the action of the neurotransmitter acetylcholine. People ingest this drug by smoking or chewing tobacco. Its stimulant effect seems transient, as this initial response is followed by depression. Nicotine is highly toxic to animals. It is especially deadly when injected; the lethal dose for a human is estimated to be about 50 mg. Nicotine has also been used in agriculture as a contact insecticide.



Nicotine

Cocaine acts as a stimulant by preventing nerve cells from taking up dopamine, another neurotransmitter, from the synapse. High levels of dopamine are therefore available to stimulate the pleasure centers of the brain. The enhancement of dopamine action is thought to be responsible for cocaine's "high" and its addictive properties. After the binge, dopamine is depleted in less than an hour. This leaves the user in a pleasureless state and (often) craving more cocaine.



Cocaine

Cocaine is used as the salt cocaine hydrochloride and in the form of broken lumps of the free (unneutralized) base, which is called *crack cocaine*.



Because it is soluble in water, cocaine hydrochloride is readily absorbed through the watery mucous membranes of the nose when it is snorted. Crack cocaine is more volatile than cocaine hydrochloride. It vaporizes at the temperature of a burning cigarette. When smoked, cocaine reaches the brain in 15 s.

Summary

Amines are bases; they react with acids to form salts. Salts of aniline are properly named as *anilinium* compounds, but an older system is used to name drugs: the salts of amine drugs and hydrochloric acid are called “hydrochlorides.” Heterocyclic amines are cyclic compounds with one or more nitrogen atoms in the ring.

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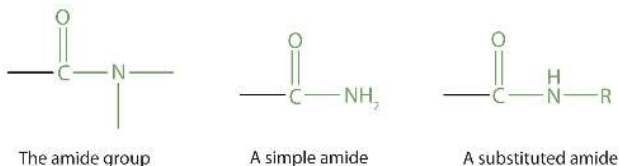
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13.7: Amides- Structures and Names

Learning Objectives

- Identify the general structure for an amide.
- Identify the functional group for an amide.
- Name amides with common names.
- Name amides according to the IUPAC system.

The amide functional group has an nitrogen atom attached to a carbonyl carbon atom. If the two remaining bonds on the nitrogen atom are attached to hydrogen atoms, the compound is a *simple amide*. If one or both of the two remaining bonds on the atom are attached to alkyl or aryl groups, the compound is a *substituted amide*.



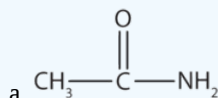
The carbonyl carbon-to-nitrogen bond is called an *amide linkage*. This bond is quite stable and is found in the repeating units of protein molecules, where it is called a *peptide linkage*.

Simple amides are named as derivatives of carboxylic acids. The *-ic* ending of the common name or the *-oic* ending of the International Union of Pure and Applied Chemistry (IUPAC) name of the carboxylic acid is replaced with the suffix *-amide*.



✓ Example 13.7.1

Name each compound with the the IUPAC name.



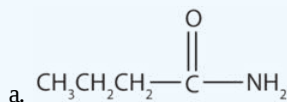
b. NN-Diethylbutyramide | C8H17NO | ChemSpider

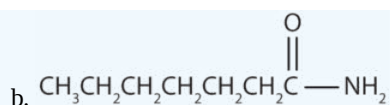
Solution

- This amide has two carbon atoms and is thus derived from acetic acid. The OH of acetic acid is replaced by an NH₂ group. The *-ic* from *acetic* (or *-oic* from ethanoic) is dropped, and *-amide* is added to give *acetamide* (or ethanamide in the IUPAC system).
- This amide is derived from butanoic acid. The *-oic* is dropped, and *-amide* is added to give us butanamide. There are two ethyl groups off the N - dimethyl. Putting this together we have N,N-diethylbutanamide.

? Exercise 13.7.1

Name each compound with the common name, the IUPAC name, or both.



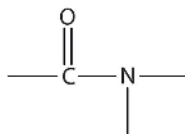


Answer

- a. Butanamide. Parent compounds: butanoic acid and ammonia.
- b. Heptamide. Parent compounds: heptanoic acid and ammonia.

13.7.1 Key Takeaways

- Amides have a general structure in which a nitrogen atom is bonded to a carbonyl carbon atom.
- The functional group for an amide is as follows:



- In names for amides, the *-ic acid* of the common name or the *-oic* ending of the IUPAC for the corresponding carboxylic acid is replaced by *-amide*.

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13.8: Physical Properties of Amides

Learning Objectives

- Compare the boiling points of amides with alcohols of similar molar mass.
- Compare the solubilities in water of amides of five or fewer carbon atoms with the solubilities of comparable alkanes and alcohols in water.

With the exception of formamide (HCONH_2), which is a liquid, all simple amides are solids (Table 13.8.1). The lower members of the series are soluble in water, with borderline solubility occurring in those that have five or six carbon atoms. Like the esters, solutions of amides in water usually are neutral—neither acidic nor basic.

Table 13.8.1: *Physical Constants of Some Unsubstituted Amides*

Condensed Structural Formula	Name	Melting Point ($^{\circ}\text{C}$)	Boiling Point ($^{\circ}\text{C}$)	Solubility in Water
HCONH_2	formamide	2	193	soluble
CH_3CONH_2	acetamide	82	222	soluble
$\text{CH}_3\text{CH}_2\text{CONH}_2$	propionamide	81	213	soluble
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CONH}_2$	butyramide	115	216	soluble
$\text{C}_6\text{H}_5\text{CONH}_2$	benzamide	132	290	slightly soluble

The amides generally have high boiling points and melting points. These characteristics and their solubility in water result from the polar nature of the amide group and hydrogen bonding (Figure 13.8.1). (Similar hydrogen bonding plays a critical role in determining the structure and properties of proteins, deoxyribonucleic acid [DNA], ribonucleic acid [RNA], and other giant molecules so important to life processes.

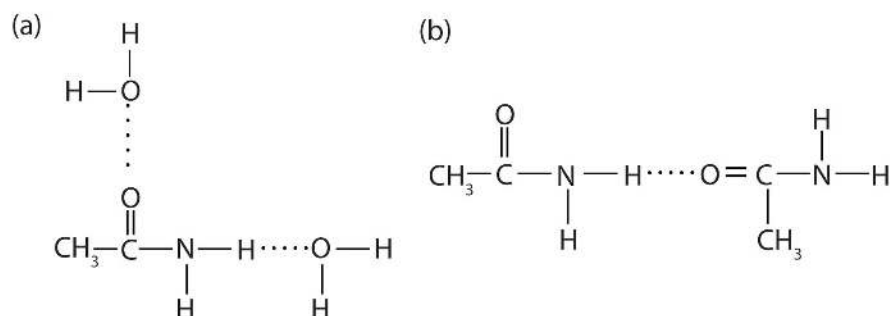


Figure 13.8.1: Hydrogen Bonding in

Amides. Amide molecules can engage in hydrogen bonding with water molecules (a). Those amides with a hydrogen atom on the nitrogen atom can also engage in hydrogen bonding (b). Both hydrogen bonding networks extend in all directions.

13.8.1 Key Takeaways

- Most amides are solids at room temperature; the boiling points of amides are much higher than those of alcohols of similar molar mass.
- Amides of five or fewer carbon atoms are soluble in water?

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13.9: Formation of Amides

Learning Objectives

- To describe the preparation procedure for amides.

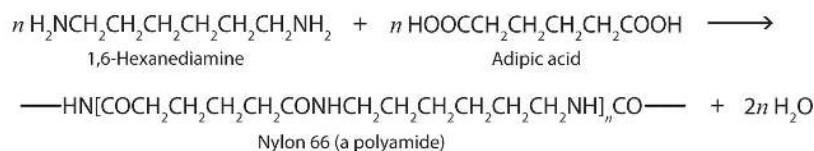
The addition of ammonia (NH_3) to a carboxylic acid forms an amide, but the reaction is very slow in the laboratory at room temperature. Water molecules are split out, and a bond is formed between the nitrogen atom and the carbonyl carbon atom.



In living cells, amide formation is catalyzed by enzymes. Proteins are polyamides; they are formed by joining amino acids into long chains. In proteins, the amide functional group is called a *peptide bond*.

13.9.1 Polyamides

Just as the reaction of a diol and a diacid forms a polyester, the reaction of a diacid and a diamine yields a polyamide. The two difunctional monomers often employed are adipic acid and 1,6-hexanediamine. The monomers condense by splitting out water to form a new product, which is still difunctional and thus can react further to yield a polyamide polymer.



Some polyamides are known as *nylons*. Nylons are among the most widely used synthetic fibers—for example, they are used in ropes, sails, carpets, clothing, tires, brushes, and parachutes. They also can be molded into blocks for use in electrical equipment, gears, bearings, and valves.

13.9.2 Key Takeaway

- Amides are prepared by the reaction of a carboxylic acid with ammonia or an amine.

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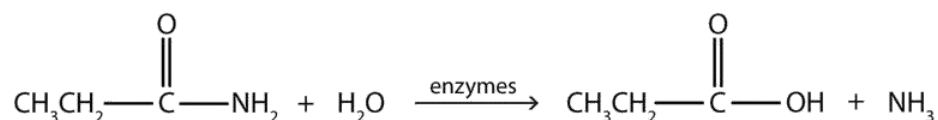
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13.10: Chemical Properties of Amides- Hydrolysis

Learning Objectives

- To identify the typical reaction that amides undergo.

Generally, amides resist hydrolysis in plain water, even after prolonged heating. In the presence of added acid or base, however, hydrolysis proceeds at a moderate rate. In living cells, amide hydrolysis is catalyzed by enzymes. Amide hydrolysis is illustrated in the following example:



Hydrolysis of an amide in acid solution actually gives a carboxylic acid and the salt of ammonia or an amine (the ammonia or amine initially formed is neutralized by the acid). Basic hydrolysis gives a salt of the carboxylic acid and ammonia or an amine.

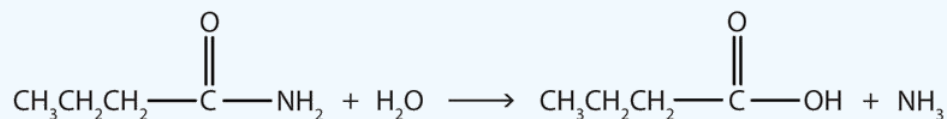
✓ Example 13.10.1

Write the equation for the hydrolysis of each compound.

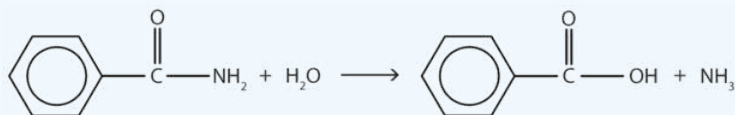
- butyramide (common name) or butanamide.
- benzamide

Solution

- The hydrolysis of a simple amide produces an organic acid and ammonia. Butyramide thus yields butyric (common name) acid and ammonia.



- The hydrolysis of an amide produces an organic acid and ammonia. Benzamide thus yields benzoic acid and ammonia.

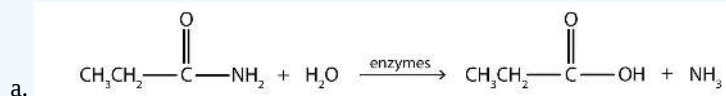


? Exercise 13.10.1

Write the equation for the hydrolysis of each compound.

- propionamide (propanamide)
- hexanamide

Answer



- Reaction for hexanamide would be similar but yield hexanoic acid and ammonia.

Career Focus: Athletic Trainer

Athletic training is an allied health-care profession recognized by the American Medical Association. The athletic trainer's role is to recognize, evaluate, and provide immediate care for athletic injuries; prevent athletic injuries by taping, bandaging, and bracing vulnerable body parts; make referrals to medical doctors when necessary; and rehabilitate injured athletes. Athletic trainers work in high schools, colleges, and other organizations where athletics programs are found. Athletic trainers usually have a degree from an accredited athletic training program whose curriculum includes such basic science courses as biology, chemistry, and physics. These studies provide the necessary background for more applied courses, such as anatomy and physiology, exercise physiology, kinesiology, and nutrition. Knowledge of chemistry is necessary for understanding pharmacological and medical terminology. For example, athletic trainers must understand the action of numerous drugs, many of which are esters, amines, or amides like those mentioned in this chapter.

Athletic trainers may have administrative duties, such as the responsibility for ordering supplies. They also need to be able to evaluate nutritional supplements because providing the wrong one can get an athlete banned from competition and may bring sanctions against a school. In short, the athletic trainer is responsible for the overall health and well-being of the athletes in his or her charge.

13.10.1 Key Takeaway

- The hydrolysis of an amide produces a carboxylic acid and ammonia or an amine.

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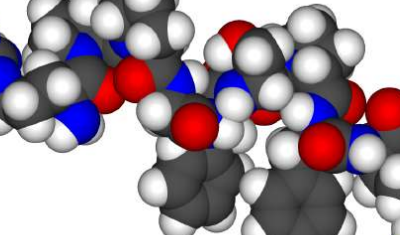
- Explain how a peptide is formed from individual amino acids.
- Explain why the sequence of amino acids in a protein is essential.

$$\text{H}_3\text{N}^+-\underset{\text{R}}{\text{CH}}-\overset{\text{O}}{\parallel}{\text{C}}\text{O}^- + \text{H}_3\text{N}^+-\underset{\text{R}'}{\text{CH}}-\overset{\text{O}}{\parallel}{\text{C}}\text{O}^- \longrightarrow \text{H}_3\text{N}^+-\underset{\text{R}}{\text{CH}}-\overset{\text{O}}{\parallel}{\text{C}}\text{O}-\underset{\text{R}'}{\text{NH}}-\underset{\text{R}'}{\text{CH}}-\overset{\text{O}}{\parallel}{\text{C}}\text{O}^- + \text{H}_2\text{O}$$

Peptide bond

[illegible]

$$\text{H}_3\text{N}^+ - \underset{\text{CH}_2\text{OH}}{\text{CH}} - \text{C}(=\text{O}) - \text{NH} - \underset{\text{CH}_3}{\text{CH}} - \text{C}(=\text{O}) - \text{NH} - \underset{\text{CH}_2\text{SH}}{\text{CH}} - \text{C}(=\text{O}) - \text{O}^-$$
 N-terminal end Ser-ala-cys C-terminal end
 Tripeptide



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.

13.11.1 Summary

The **amino group of one amino acid** can react with the **carboxyl group on another amino acid** to form a **peptide bond** that links the two amino acids together. Additional amino acids can be added on through the formation of addition peptide (amide) bonds. A sequence of amino acids in a peptide or protein is written with the N-terminal amino acid first and the C-terminal amino acid at the end (writing left to right).

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13.12: Proteins

Learning Objectives

- Describe the four levels of protein structure.
- Identify the types of attractive interactions that hold proteins in their most stable three-dimensional structure.
- Explain what happens when proteins are denatured.
- Identify how a protein can be denatured.

Each of the thousands of naturally occurring proteins has its own characteristic amino acid composition and sequence that result in a unique three-dimensional shape. Since the 1950s, scientists have determined the amino acid sequences and three-dimensional conformation of numerous proteins and thus obtained important clues on how each protein performs its specific function in the body.

Proteins are compounds of high molar mass consisting largely or entirely of chains of amino acids. Because of their great complexity, protein molecules cannot be classified on the basis of specific structural similarities, as carbohydrates and lipids are categorized. The two major structural classifications of proteins are based on far more general qualities: whether the protein is (1) fiberlike and insoluble or (2) globular and soluble. Some proteins, such as those that compose hair, skin, muscles, and connective tissue, are fiberlike. These fibrous proteins are insoluble in water and usually serve structural, connective, and protective functions. Examples of fibrous proteins are keratins, collagens, myosins, and elastins. Hair and the outer layer of skin are composed of keratin. Connective tissues contain collagen. Myosins are muscle proteins and are capable of contraction and extension. Elastins are found in ligaments and the elastic tissue of artery walls.

Globular proteins, the other major class, are soluble in aqueous media. In these proteins, the chains are folded so that the molecule as a whole is roughly spherical. Familiar examples include egg albumin from egg whites and serum albumin in blood. Serum albumin plays a major role in transporting fatty acids and maintaining a proper balance of osmotic pressures in the body. Hemoglobin and myoglobin, which are important for binding oxygen, are also globular proteins.

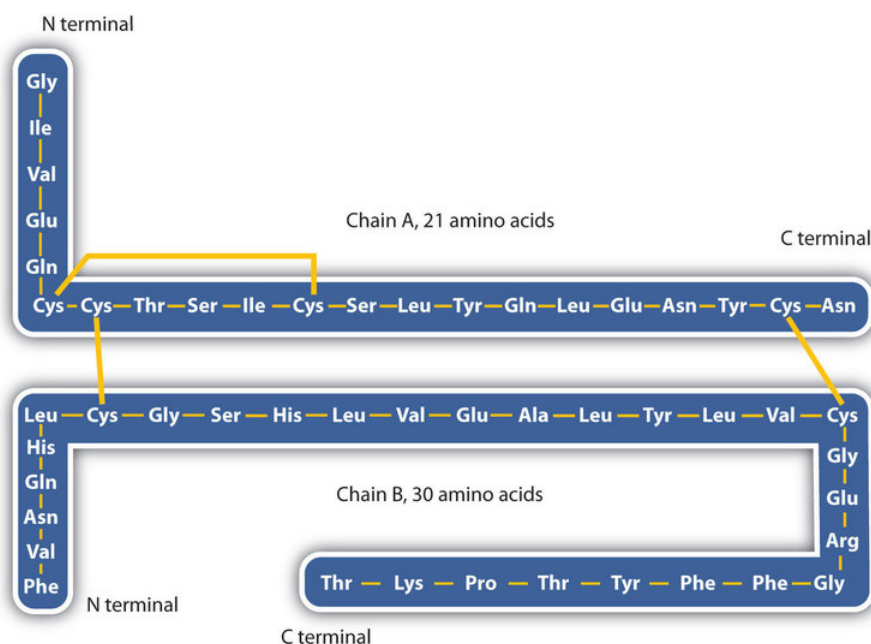


Figure 13.12.1: Primary Structure of

Human Insulin. Human insulin, whose amino acid sequence is shown here, is a hormone that is required for the proper metabolism of glucose.

13.12.1 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 13.12.1.

A protein molecule is not a random tangle of polypeptide chains. Instead, the chains are arranged in unique but specific conformations. The term secondary structure refers to the fixed arrangement of the polypeptide backbone. On the basis of X ray studies, Linus Pauling and Robert Corey postulated that certain proteins or portions of proteins twist into a spiral or a helix. This helix is stabilized by *intrachain* hydrogen bonding between the carbonyl oxygen atom of one amino acid and the amide hydrogen atom four amino acids up the chain (located on the next turn of the helix) and is known as a right-handed α -helix. X ray data indicate that this helix makes one turn for every 3.6 amino acids, and the side chains of these amino acids project outward from the coiled backbone (Figure 13.12.2). 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.

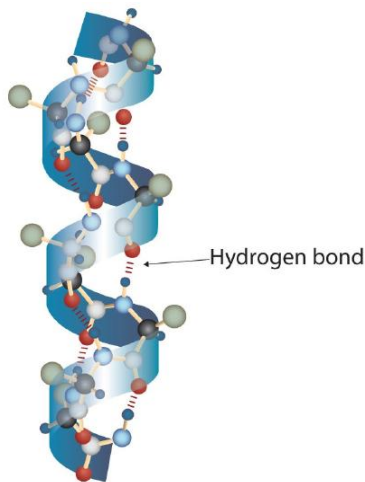


Figure 13.12.2 A Ball-and-Stick Model of an α -Helix. This ball-and-stick model shows the intrachain hydrogen bonding between carbonyl oxygen atoms and amide hydrogen atoms. Each turn of the helix spans 3.6 amino acids. Note that the side chains (represented as green spheres) point out from the helix.

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 13.12.3). 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.

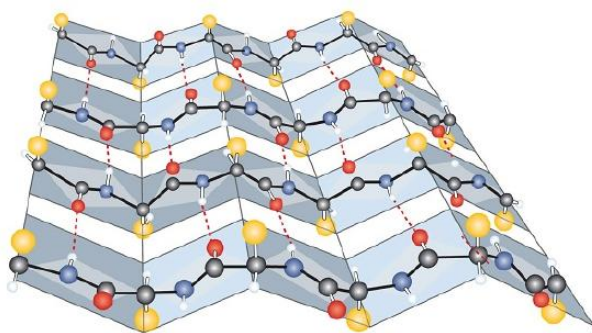


Figure 13.12.3: A Ball-and-Stick Model of the β -Pleated Sheet Structure in Proteins. The side chains extend above or below the sheet and alternate along the chain. The protein chains are held together by interchain hydrogen bonding.

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 13.12.4 shows a depiction of the three-dimensional structure of insulin.

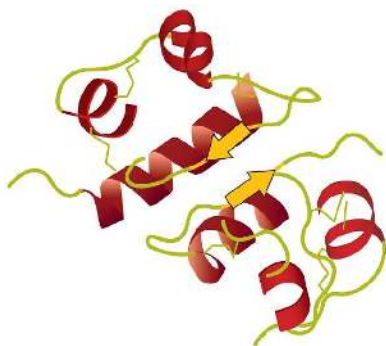
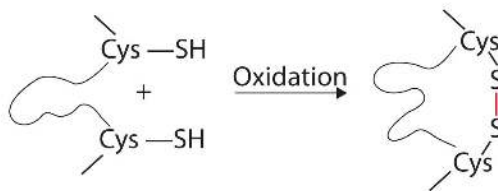


Figure 13.12.4: A Ribbon Model of the Three-Dimensional Structure of Insulin. The spiral regions represent sections of the polypeptide chain that have an α -helical structure, while the broad arrows represent β -pleated sheet structures.

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 13.12.5).
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 13.12.5).
3. **Disulfide linkages.** Two cysteine amino acid units may be brought close together as the protein molecule folds. Subsequent oxidation and linkage of the sulfur atoms in the highly reactive sulfhydryl (SH) groups leads to the formation of cystine (part (c) of Figure 13.12.5). Intrachain disulfide linkages are found in many proteins, including insulin (yellow bars in Figure 13.12.1) and have a strong stabilizing effect on the tertiary structure.



4. **Dispersion forces.** Dispersion forces arise when a normally nonpolar atom becomes momentarily polar due to an uneven distribution of electrons, leading to an instantaneous dipole that induces a shift of electrons in a neighboring nonpolar atom. Dispersion forces are weak but can be important when other types of interactions are either missing or minimal (part (d) of Figure 13.12.5). 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.

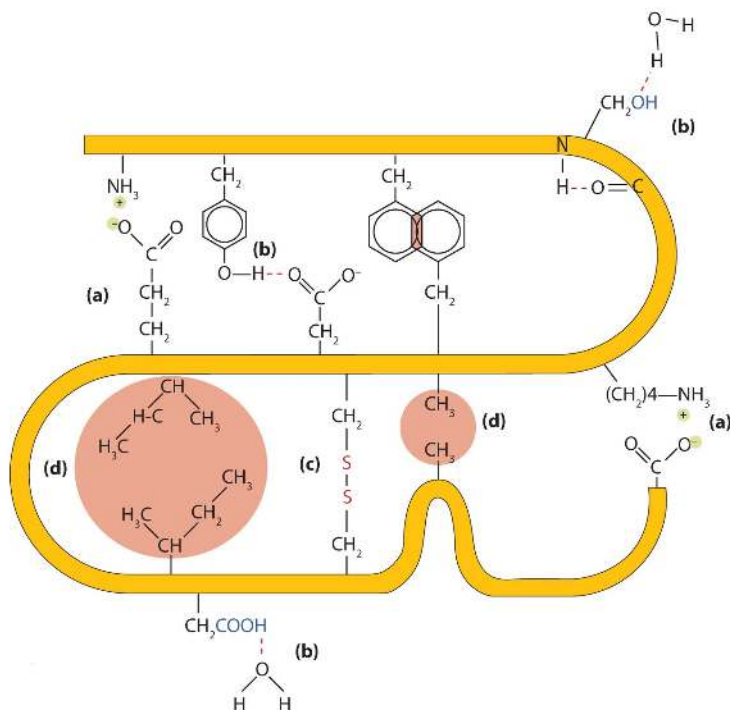


Figure 13.12.5: Tertiary Protein Structure Interactions.

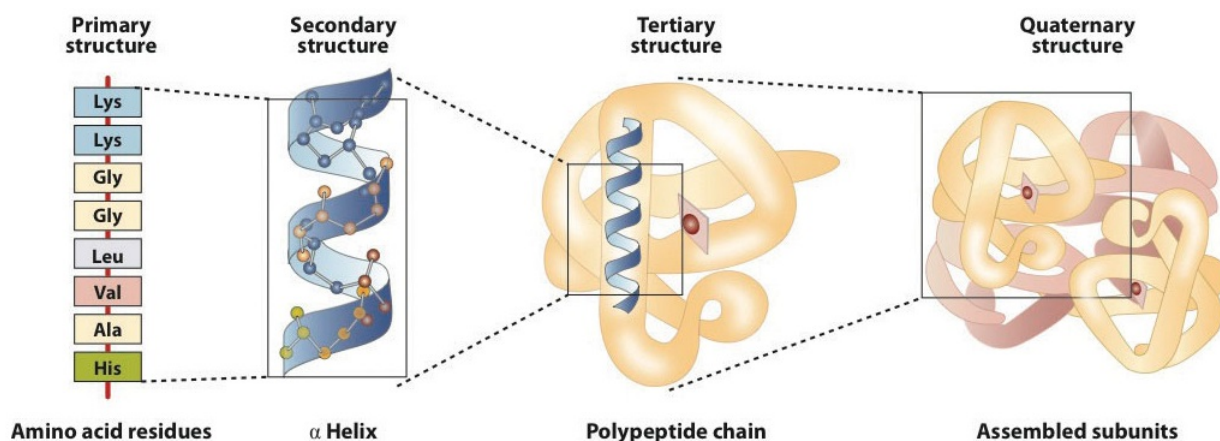
Four interactions stabilize the tertiary structure of a protein: (a) ionic bonding, (b) hydrogen bonding, (c) disulfide linkages, and (d) dispersion forces.

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 13.12.6). 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 13.12.7.



Figure 13.12.6 The Quaternary Structure of Hemoglobin. Hemoglobin is a protein that transports oxygen throughout the body.

Source: Image from the RCSB PDB ([www.pdb.org/opens in new window](http://www.pdb.org/opens%20in%20new%20window)) 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

13.12.7: 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.

13.12.2 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 13.12.1).

Figure 13.12.1: 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 13.12.8). 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.

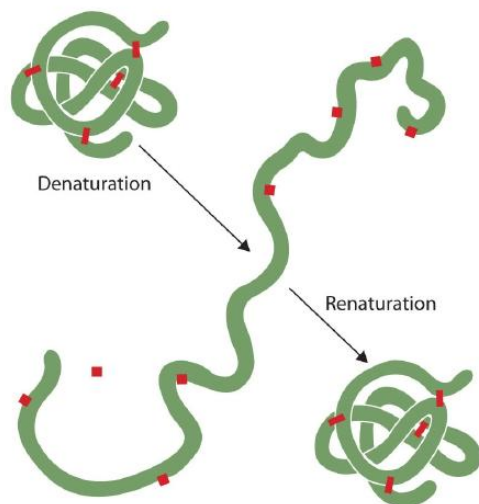


Figure 13.12.8: Denaturation and Renaturation of a Protein. The

denaturation (unfolding) and renaturation (refolding) of a protein is depicted. The red boxes represent stabilizing interactions, such as disulfide linkages, hydrogen bonding, and/or ionic bonds.

The primary structures of proteins are quite sturdy. In general, fairly vigorous conditions are needed to hydrolyze peptide bonds. At the secondary through quaternary levels, however, proteins are quite vulnerable to attack, though they vary in their vulnerability to denaturation. The delicately folded globular proteins are much easier to denature than are the tough, fibrous proteins of hair and skin.

Summary

Proteins can be divided into two categories: fibrous, which tend to be insoluble in water, and globular, which are more soluble in water. A protein may have up to four levels of structure. The primary structure consists of the specific amino acid sequence. The resulting peptide chain can form an α -helix or β -pleated sheet (or local structures not as easily categorized), which is known as secondary structure. These segments of secondary structure are incorporated into the tertiary structure of the folded polypeptide chain. The quaternary structure describes the arrangements of subunits in a protein that contains more than one subunit. Four major types of attractive interactions determine the shape and stability of the folded protein: ionic bonding, hydrogen bonding, disulfide linkages, and dispersion forces. A wide variety of reagents and conditions can cause a protein to unfold or denature.

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13.13: Enzymes

Learning Objectives

- Explain the functions of enzymes.
- Explain how enzymes are classified and named.

A catalyst is any substance that increases the *rate* or speed of a chemical reaction without being changed or consumed in the reaction. Enzymes are biological catalysts, and nearly all of them are proteins. The reaction rates attained by enzymes are truly amazing. In their presence, reactions occur at rates that are a million (10^6) or more times faster than would be attainable in their absence. What is even more amazing is that enzymes perform this function at body temperature ($\sim 37^\circ\text{C}$) 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 13.13.1: 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 13.13.1), with subgroups and secondary subgroups that specify the reaction more precisely.

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 13.13.2 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. Understanding this code will be helpful in biochemistry.

Table 13.13.2: Assignment of an Enzyme Classification Number

Example: 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 <i>alcohol:NAD⁺ oxidoreductase</i> , while the recommended or common name is alcohol dehydrogenase.	
Reaction catalyzed:	$\text{RCH}_2\text{—OH} + \text{NAD}^+ \rightleftharpoons \text{R—}\overset{\text{O}}{\underset{\text{ }}{\text{C}}}\text{—H} + \text{NADH} + \text{H}^+$

Summary

An enzyme is a biological catalyst, a substance that increases the rate of a chemical reaction without being changed or consumed in the reaction. A systematic process is used to name and classify enzymes.

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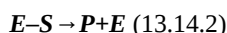
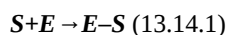
13.14: Enzymatic Catalysis

Learning Objectives

- To describe the interaction between an enzyme and its substrate.

Enzyme-catalyzed reactions occur in at least two steps. In the first step, an enzyme molecule (E) and the substrate molecule or molecules (S) collide and react to form an intermediate compound called the *enzyme-substrate* (E-S) *complex*. (This step is reversible because the complex can break apart into the original substrate or substrates and the free enzyme.) Once the E-S complex forms, the enzyme is able to catalyze the formation of product (P), which is then released from the enzyme surface:

13.14.0.0.1



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 13.14.3).

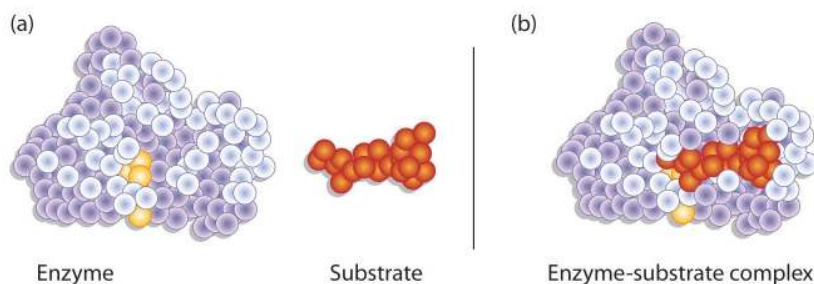


Figure 13.14.3: Substrate Binding to the Active Site of an Enzyme. The enzyme dihydrofolate reductase is shown with one of its substrates: NADP^+ (a) unbound and (b) bound. The NADP^+ (shown in red) binds to a pocket that is complementary to it in shape and ionic properties.

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 13.14.4). This model portrayed the enzyme as conformationally rigid and able to bond only to substrates that exactly fit the active site.

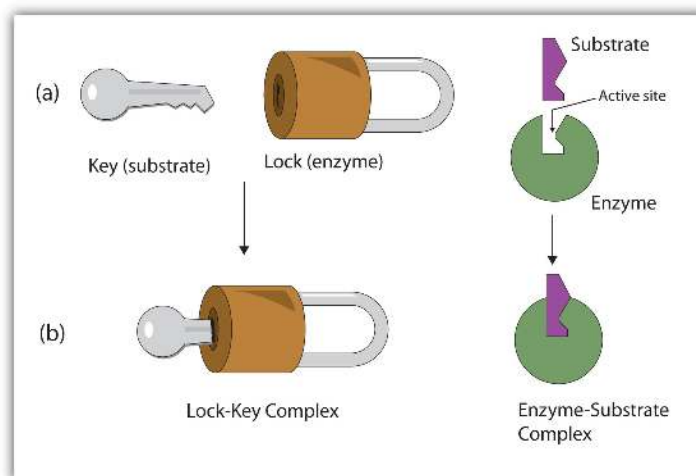


Figure 13.14.4: The Lock-and-Key Model of Enzyme Action. (a) Because the substrate and the active site of the enzyme have complementary structures and bonding groups, they fit together as a key fits a lock. (b) The catalytic reaction occurs while the two are bonded together in the enzyme-substrate complex.

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 13.14.5. After catalysis, the enzyme resumes its original structure.

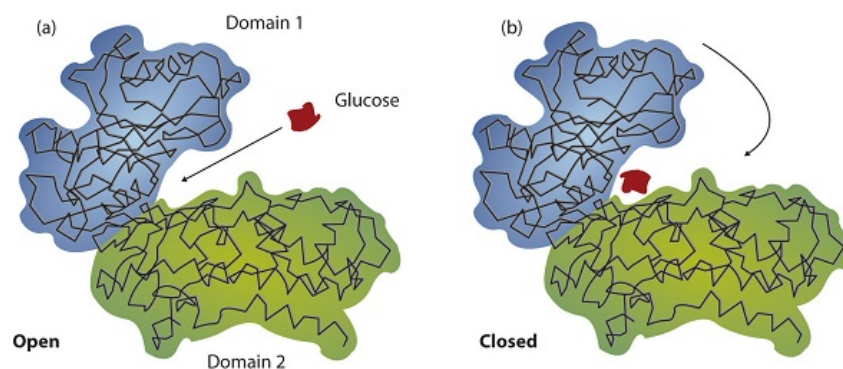


Figure 13.14.5: The Induced-Fit Model of Enzyme Action. (a) The enzyme hexokinase without its substrate (glucose, shown in red) is bound to the active site. (b) The enzyme conformation changes dramatically when the substrate binds to it, resulting in additional interactions between hexokinase and glucose.

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 13.14.1

1. 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?
2. 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

1. An OH group would most likely engage in hydrogen bonding with an appropriate functional group present in the active site of an enzyme.
2. Several amino acid side chains would be able to engage in hydrogen bonding with an OH group. One example would be asparagine, which has an amide functional group.

? Exercise 13.14.1

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?
 1. COOH
 2. NH_3^+
 3. OH
 4. $\text{CH}(\text{CH}_3)_2$
2. What type of interaction would occur between each group present on a substrate molecule and a functional group of the active site in an enzyme?
 1. SH
 2. NH_2
 3. C_6H_5
 4. COO^-
3. For each functional group in Exercise 1, suggest an amino acid whose side chain might be in the active site of an enzyme and form the type of interaction you identified.

Answer

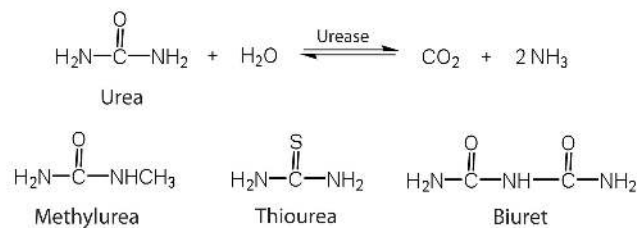
Question 1: 1. hydrogen bonding 2. ionic bonding 3. hydrogen bonding 4. dispersion forces

Question 2: 1. disulfide bonding 2. ionic bonding 3. dispersion forces 4. hydrogen bonding

Question 3:

1. The amino acid has a polar side chain capable of engaging in hydrogen bonding; serine (answers will vary).
2. The amino acid has a negatively charged side chain; aspartic acid (answers will vary).
3. The amino acid has a polar side chain capable of engaging in hydrogen bonding; asparagine (answers will vary).
4. The amino acid has a nonpolar side chain; isoleucine (answers will vary)

One characteristic that distinguishes an enzyme from all other types of catalysts is its *substrate specificity*. An inorganic acid such as sulfuric acid can be used to increase the reaction rates of many different reactions, such as the hydrolysis of disaccharides, polysaccharides, lipids, and proteins, with complete impartiality. In contrast, enzymes are much more specific. Some enzymes act on a single substrate, while other enzymes act on any of a group of related molecules containing a similar functional group or chemical bond. Some enzymes even distinguish between D- and L-stereoisomers, binding one stereoisomer but not the other. Urease, for example, is an enzyme that catalyzes the hydrolysis of a single substrate—urea—but not the closely related compounds methyl urea, thiourea, or biuret. The enzyme carboxypeptidase, on the other hand, is far less specific. It catalyzes the removal of nearly any amino acid from the carboxyl end of any peptide or protein.



Enzyme specificity results from the uniqueness of the active site in each different enzyme because of the identity, charge, and spatial orientation of the functional groups located there. It regulates cell chemistry so that the proper reactions occur in the proper place at the proper time. Clearly, it is crucial to the proper functioning of the living cell.

13.14.1 Summary

A substrate binds to a specific region on an enzyme known as the active site, where the substrate can be converted to product. The substrate binds to the enzyme primarily through **hydrogen bonding and other electrostatic interactions**. The induced-fit model says that an enzyme can undergo a conformational change when binding a substrate. *Enzymes exhibit varying degrees of substrate specificity.*

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13.15: Enzyme Activity

Learning Objectives

- To describe how pH, temperature, and the concentration of an enzyme and its substrate influence enzyme activity.

The single most important property of enzymes is the ability to increase the rates of reactions occurring in living organisms, a property known as *catalytic activity*. Because most enzymes are proteins, their activity is affected by factors that disrupt protein structure, as well as by factors that affect catalysts in general. Factors that disrupt protein structure include temperature and pH; factors that affect catalysts in general include reactant or substrate concentration and catalyst or enzyme concentration. The activity of an enzyme can be measured by monitoring either the rate at which a substrate disappears or the rate at which a product forms.

Concentration of Substrate

In the presence of a given amount of enzyme, the rate of an enzymatic reaction increases as the substrate concentration increases until a limiting rate is reached, after which further increase in the substrate concentration produces no significant change in the reaction rate (part (a) of Figure 13.15.1). 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).

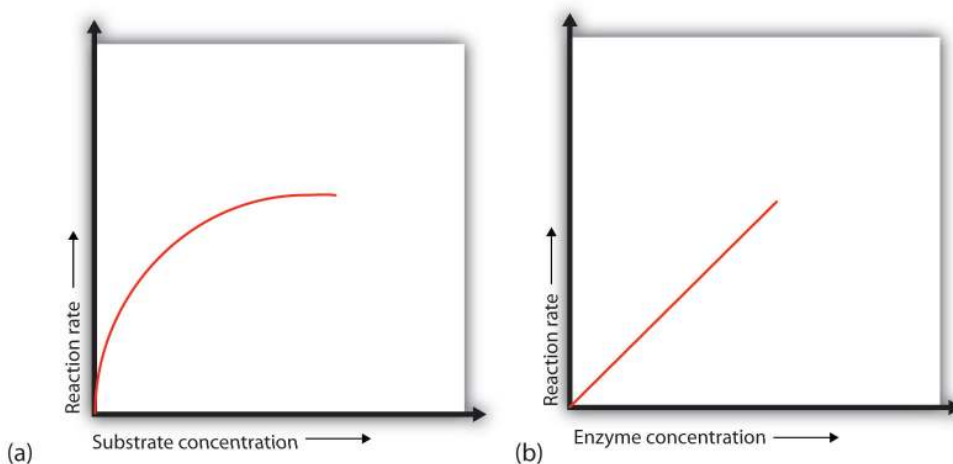


Figure 13.15.1: Concentration

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 13.15.1). 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 13.15.2). 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.

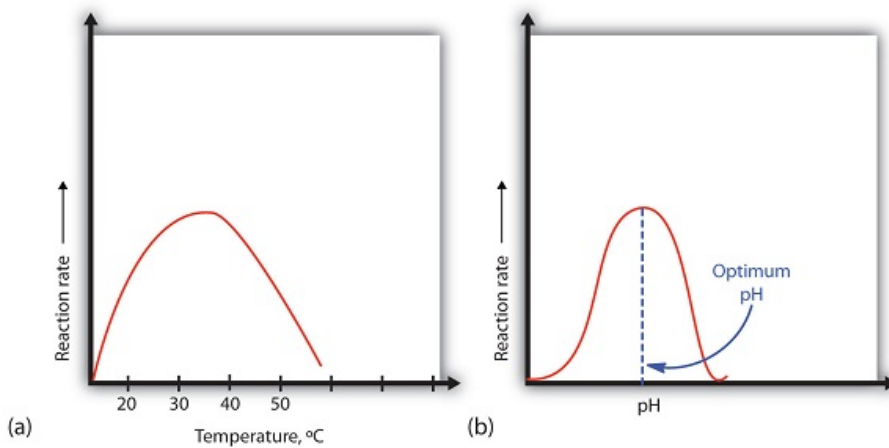


Figure 13.15.2: Temperature and pH

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 13.15.2). With the notable exception of gastric juice (the fluids secreted in the stomach), most body fluids have pH values between 6 and 8. Not surprisingly, most enzymes exhibit optimal activity in this pH range. However, a few enzymes have optimum pH values outside this range. For example, the optimum pH for pepsin, an enzyme that is active in the stomach, is 2.0.

Summary

Initially, an increase in substrate concentration leads to an increase in the rate of an enzyme-catalyzed reaction. As the enzyme molecules become saturated with substrate, this increase in reaction rate levels off. The rate of an enzyme-catalyzed reaction increases with an increase in the concentration of an enzyme. At low temperatures, an increase in temperature increases the rate of an enzyme-catalyzed reaction. At higher temperatures, the protein is denatured, and the rate of the reaction dramatically decreases. An enzyme has an optimum pH range in which it exhibits maximum activity.

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13.16: Enzyme Regulation

Learning Objectives

- Explain what an enzyme inhibitor is.
- Distinguish between reversible and irreversible inhibitors.
- Distinguish between competitive and noncompetitive inhibitors.
- Describe ways in which enzymes are regulated.

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.

13.16.1 Regulation of enzyme activity

Apart from their ability to greatly speed the rates of chemical reactions in cells, enzymes have another property that makes them valuable. This property is that their activity can be regulated, allowing them to be activated and inactivated, as necessary. This is tremendously important in maintaining homeostasis, permitting cells to respond in controlled ways to changes in both internal and external conditions.

Inhibition of specific enzymes by drugs can also be medically useful. Understanding the mechanisms that control enzyme activity is, therefore, of considerable importance.

Inhibition

We will first discuss four types of enzyme inhibition – competitive, non-competitive, uncompetitive, and suicide inhibition. Of these, the first three types are reversible. The last one, suicide inhibition, is not.

13.16.2 Competitive inhibition

Probably the easiest type of enzyme inhibition to understand is competitive inhibition and it is the one most commonly exploited pharmaceutically. Molecules that are competitive inhibitors of enzymes resemble one of the normal substrates of an enzyme. An example is methotrexate, which resembles the folate substrate of the enzyme dihydrofolate reductase (DHFR). This enzyme normally catalyzes the reduction of folate, an important reaction in the metabolism of nucleotides.

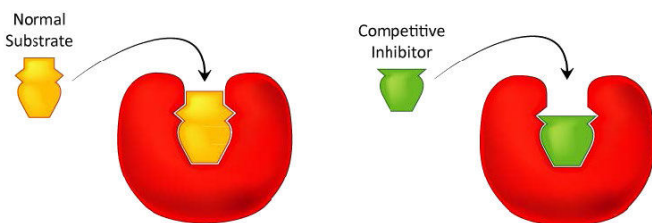


Figure 13.16.1 - Competitive inhibitors resemble the normal substrate and compete for binding at the active site. Image by Aleia Kim

Inhibitor binding

When the drug methotrexate is present, some of the DHFR enzyme binds to it, instead of to folate, and during the time methotrexate is bound, the enzyme is inactive and unable to bind folate. Thus, the enzyme is inhibited. Notably, the binding site on DHFR for methotrexate is the active site, the same place that folate would normally bind. As a result, methotrexate ‘competes’ with folate for binding to the enzyme. The more methotrexate there is, the more effectively it competes with folate for the enzyme’s active site. Conversely, the more folate there is, the less of an effect methotrexate has on the enzyme because folate outcompetes it.

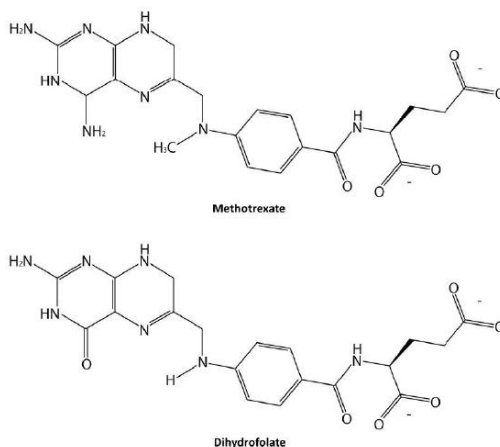


Figure 13.16.2 - Methotrexate and dihydrofolate. Image by Ben Carson

No effect on V_{max}

How do we study competitive inhibition? It is typically done as follows. First, one performs a set of V_0 vs. $[S]$ reactions without inhibitor (20 or so tubes, with buffer and constant amounts of enzyme, varying amounts of substrate, equal reaction times). V_0 vs. $[S]$ is plotted (Figure 13.16.3 red line), as well as $1/V_0$ vs. $1/[S]$ (Figure 13.16.4 green line). Next, a second set of reactions is performed in the same manner as before, except that a fixed amount of the methotrexate inhibitor is added to each tube. At low concentrations of substrate, the methotrexate competes for the enzyme effectively, but at high concentrations of substrate, the inhibitor will have a much reduced effect, since the substrate outcompetes it, due to its higher concentration (remember that the inhibitor is at fixed concentration).

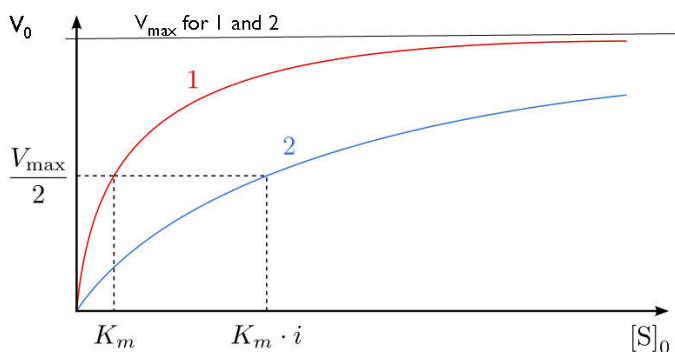


Figure 13.16.3 V_0 vs $[S]$ Plots for uninhibited reactions (red) and competitively inhibited reactions (blue). Both ultimately have same V_{max}

Graphically, the results of these inhibitor experiments are shown in Figure 13.16.3 (blue line) and Figure 13.16.4 (orange line). Notice that at high substrate concentrations, the competitive inhibitor has essentially no effect, causing the V_{max} for the enzyme to remain unchanged. To reiterate, this is due to the fact that at high substrate concentrations, the inhibitor doesn't compete well. However, at lower substrate concentrations, it does.

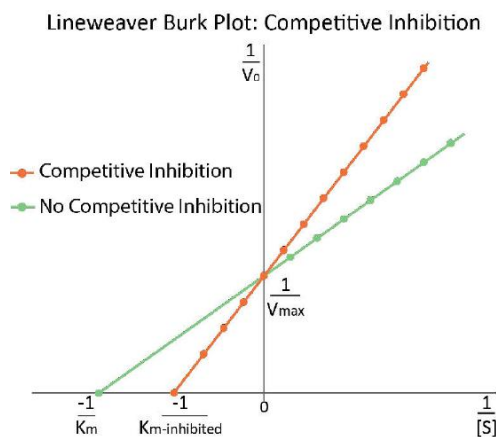


Figure 13.16.4 - Lineweaver-Burk plots - uninhibited reactions (green). Competitively inhibited reactions (orange). Lines cross on Y-axis at $1/V_{max}$ Since V_{max} is the same for both reactions. Image by Aleia Kim

Increased K_m

In competitively inhibited reactions, the apparent K_m of the enzyme for the substrate increases ($-1/K_m - 1/K_m$ gets closer to zero - red line in Figure 13.16.3) when the inhibitor is present compared to when the inhibitor is absent, thus illustrating the better competition of the inhibitor at lower substrate concentrations. It may not be obvious why we call the changed K_m the apparent K_m of the enzyme. The reason is that the inhibitor doesn't actually change the enzyme's affinity for the folate substrate. It only appears to do so. This is because of the way that competitive inhibition works. When the competitive inhibitor binds the enzyme, it is effectively 'taken out of action.' Inactive enzymes have NO affinity for substrate and no activity either. We can't measure K_m for an inactive enzyme.

The enzyme molecules that are not bound by methotrexate can, in fact, bind folate and are active. Methotrexate has no effect on them and their K_m values are unchanged. Why then, does K_m appear higher in the presence of a competitive inhibitor? The reason is that the competitive inhibitor is having a greater effect of reducing the amount of active enzyme at lower concentrations of substrate than it does at higher concentrations of substrate. When the amount of enzyme is reduced, one must have more substrate to supply the reduced amount of enzyme sufficiently to get to $V_{max}/2$.

It is worth noting that in competitive inhibition, the percentage of inactive enzyme changes drastically over the range of $[S]$ values used. To start, at low $[S]$ values, the greatest percentage of the enzyme is inhibited. At high $[S]$, no significant percentage of enzyme is inhibited. This is not always the case, as we shall see in non-competitive inhibition.

13.16.3 Non-competitive inhibition

A second type of inhibition employs inhibitors that do not resemble the substrate and bind not to the active site, but rather to a separate site on the enzyme (Figure 13.16.5). The effect of binding a non-competitive inhibitor is significantly different from binding a competitive inhibitor because there is no competition. In the case of competitive inhibition, the effect of the inhibitor could be reduced and eventually overwhelmed with increasing amounts of substrate. This was because increasing substrate made increasing percentages of the enzyme active. With non-competitive inhibition, increasing the amount of substrate has no effect on the percentage of enzyme that is active. Indeed, in non-competitive inhibition, the percentage of enzyme inhibited remains the same through all ranges of $[S]$.

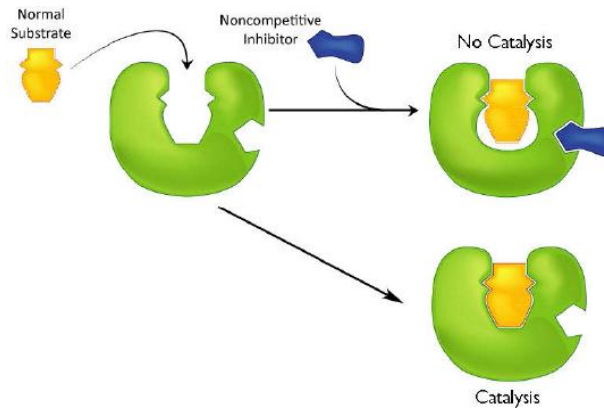


Figure 13.16.5 - Non-competitive inhibition - inhibitor does not resemble the substrate and binds to a site other than the active site. Image by Aleia Kim

This means, then, that non-competitive inhibition effectively reduces the amount of enzyme by the same fixed amount in a typical experiment at every substrate concentration used. The effect of this inhibition is shown in Figure 13.16.6 & 13.16.7. As you can see, V_{max} is reduced in non-competitive inhibition compared to uninhibited reactions.

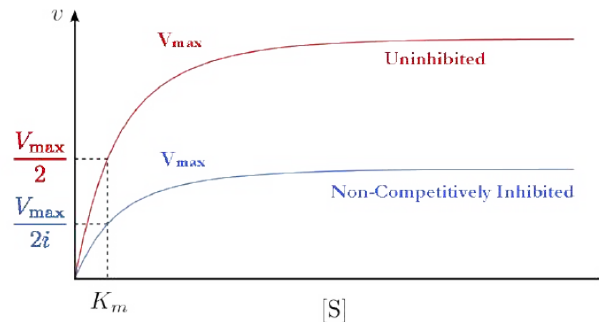


Figure 13.16.6 - V_0 vs $[S]$ plots of uninhibited reactions (red) and non-competitively inhibited reactions (blue). V_{max} is reduced, but K_m values are unchanged in non-competitively inhibited reactions

This makes sense if we remember that V_{max} is dependent on the amount of enzyme present. Reducing the amount of enzyme present reduces V_{max} . In competitive inhibition, this doesn't occur detectably, because at high substrate concentrations, there is essentially 100% of the enzyme active and the V_{max} appears not to change. Additionally, K_m for non-competitively inhibited reactions does not change from that of uninhibited reactions. This is because, as noted previously, one can only measure the K_m of active enzymes and K_m is a constant for a given enzyme.

Lineweaver Burk Plot: Noncompetitive Inhibition

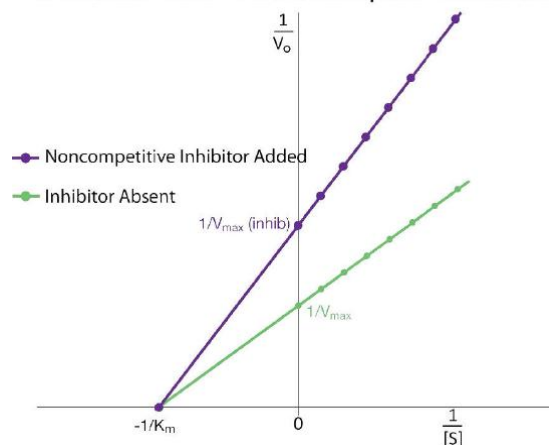


Figure 13.16.7 - Lineweaver Burk plots of uninhibited reactions (green) and non-competitively inhibited reactions (purple). Image by Aleia Kim

13.16.4 Uncompetitive inhibition

A third type of enzymatic inhibition is that of uncompetitive inhibition, which has the odd property of a reduced V_{max} as well as a reduced K_m . The explanation for these seemingly odd results is rooted in the fact that the uncompetitive inhibitor binds only to the enzyme-substrate (ES) complex (Figure 13.16.8). The inhibitor-bound complex forms mostly under concentrations of high substrate and the ES-I complex cannot release product while the inhibitor is bound, thus explaining the reduced V_{max} .

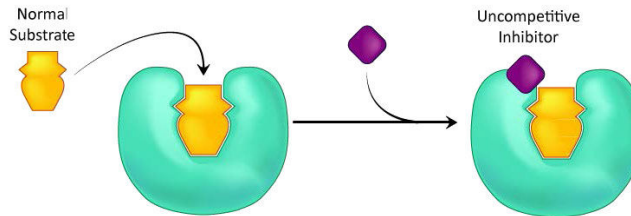


Figure 13.16.8 - Uncompetitive inhibition. Image by Aleia Kim

The reduced K_m is a bit harder to conceptualize. The reason is that the inhibitor-bound complex effectively reduces the concentration of the ES complex. By Le Chatelier's Principle, a shift occurs to form additional ES complex, resulting in less free enzyme and more enzyme in the forms ES and ESI (ES with inhibitor). Decreases in free enzyme correspond to an enzyme with greater affinity for its substrate. Thus, paradoxically, uncompetitive inhibition both decreases V_{max} and increases an enzyme's affinity for its substrate (K_m - Figures 13.16.9 & 13.16.10).

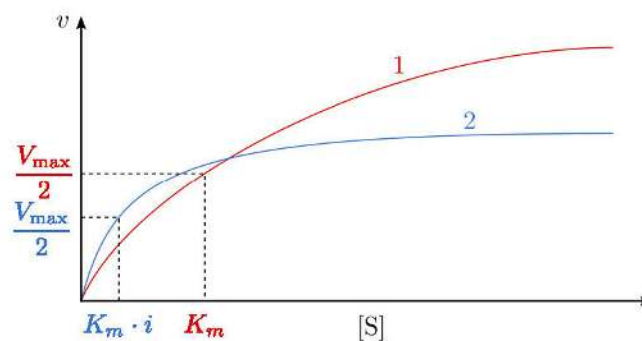


Figure 13.16.9 - V_0 vs $[S]$ plot for uncompetitive inhibition (blue) and uninhibited reactions (red)

Lineweaver Burk Plot: Uncompetitive Inhibition

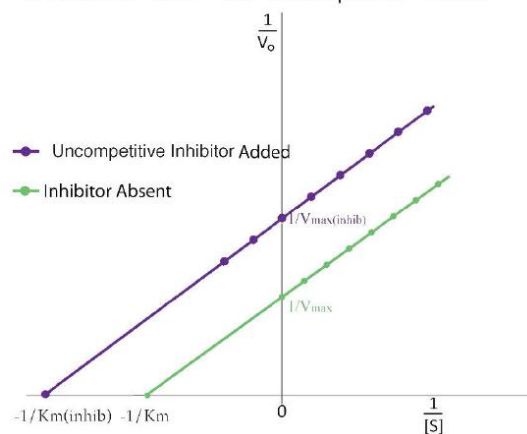


Figure 13.16.10 - Uncompetitive inhibition (purple) and uninhibited reactions (green). Image by Aleia Kim

13.16.5 Irreversible (Suicide) inhibition

In contrast to the first three types of inhibition, which involve reversible binding of the inhibitor to the enzyme, suicide inhibition is irreversible, because the inhibitor becomes covalently bound to the enzyme during the inhibition. Suicide inhibition rather closely resembles competitive inhibition because the inhibitor generally resembles the substrate and binds to the active site of the enzyme. The primary difference is that the suicide inhibitor is chemically reactive in the active site and makes a bond with it that precludes its removal. Such a mechanism is that employed by penicillin (Figure 13.16.11), which covalently links to the bacterial enzyme, DD transpeptidase and stops it from functioning. Since the normal function of the enzyme is to make a bond necessary for the peptidoglycan complex of the bacterial cell wall, the cell wall cannot properly form and bacteria cannot reproduce.

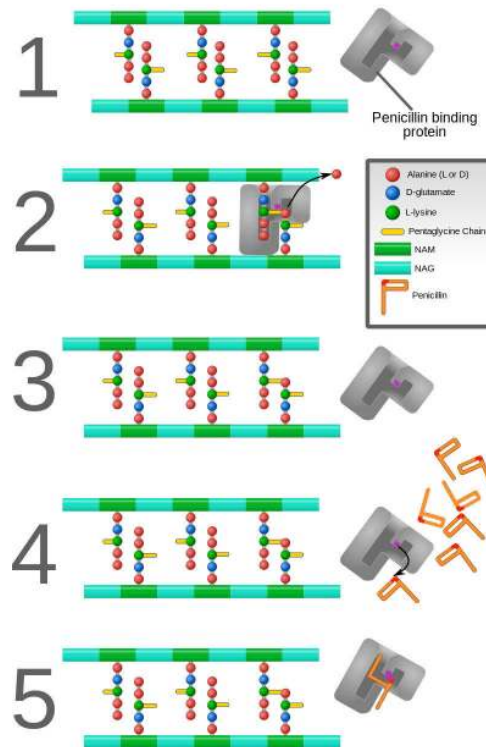


Figure 13.16.11 - Action of penicillin. DD-transpeptidase builds peptidoglycan layer of bacterial cell wall (1-3). Binding of penicillin by DD-transpeptidase stops peptidoglycan synthesis (4-5). Wikipedia

13.16.6 Control of enzymes

It is appropriate to talk at this point about mechanisms cells use to control enzymes. There are four general methods that are employed:

1. allosteric regulation,
2. covalent modification,
3. access to substrate, and
4. control of enzyme level via synthesis or breakdown.

Some enzymes are controlled by more than one of these methods.

13.16.7 Allosteric regulation

The term allosteric regulation, or allostery, refers to the fact that the activity of certain enzymes can be affected by the binding of small molecules. Molecules causing allosteric effects come in two classifications. A substrate for an enzyme can also regulate that same enzyme. These allosteric regulators are generally called **homotropic effectors**. Regulators that are not substrates are called **heterotropic effectors**.

The homotropic effectors usually are activators of the enzymes they bind to and the results of their action can be seen in the conversion of the hyperbolic curve typical of a V_0 vs. $[S]$ plot for an enzyme, being converted to a sigmoidal plot (Figure 13.16.12). This is due to the conversion of the enzyme from the T-state to the R-state on binding the substrate/homotropic effector.

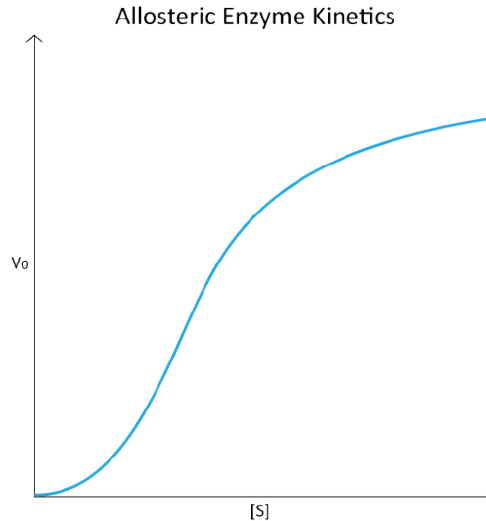


Figure 13.16.12 - Kinetic profile of an allosteric enzyme whose activity is controlled by a homotropic effector. Image by Aleia Kim

The V_0 vs. $[S]$ plot of allosteric enzyme reactions resembles the oxygen binding curve of hemoglobin. Even though hemoglobin is not an enzyme and is thus not catalyzing a reaction, the similarity of the plots is not coincidental. In both cases, the binding of an external molecule is being measured – directly, in the hemoglobin plot, and indirectly by the V_0 vs. $[S]$ plot, since substrate binding is a factor in enzyme reaction velocity.

Allosteric inhibition

Allosterically, regulation of these enzymes works by inducing different physical states (shapes, as it were) that affect their ability to bind to substrate. When an enzyme is inhibited by binding an effector, it is converted to the T-state (T=tight), it has a reduced affinity for substrate and it is through this means that the reaction is slowed.

Allosteric activation

On the other hand, when an enzyme is activated by effector binding, it converts to the R-state (R=relaxed) and binds substrate much more readily. When no effector is present, the enzyme may be in a mixture of T- and R-states.

Feedback inhibition

An interesting kind of allosteric control is exhibited by HMG-CoA reductase, which catalyzes an important reaction in the pathway leading to the synthesis of cholesterol. Binding of cholesterol to the enzyme reduces the enzyme's activity significantly. Cholesterol is not a substrate for the enzyme, so it is therefore a heterotropic effector.

Notably, though, cholesterol is the end-product of the pathway that HMG-CoA reductase catalyzes a reaction in. When enzymes are inhibited by an end-product of the pathway in which they participate, they are said to exhibit feedback inhibition.

Feedback inhibition always operates by allosterism and further, provides important and efficient control of an entire pathway. By inhibiting an early enzyme in a pathway, the flow of materials (and ATP hydrolysis required for their processing) for the entire pathway is stopped or reduced, assuming there are not alternate supply methods.

Pathway control

In the cholesterol biosynthesis pathway, stopping this one enzyme has the effect of shutting off (or at least slowing down) the entire pathway. This is significant because after catalysis by HMG-CoA reductase, there are over 20 further reactions necessary to make cholesterol, many of them requiring ATP energy. Shutting down one reactions stops all of them. Another excellent example of allosteric control and feedback inhibition is the enzyme ATCase, discussed below.

ATCase

Another interesting example of allosteric control and feedback inhibition is associated with the enzyme Aspartate Transcarbamoylase (ATCase). This enzyme, which catalyzes a step in the synthesis of pyrimidine nucleotides, has 12 subunits (Figure 13.16.13). These include six identical catalytic subunits and six identical regulatory subunits. The catalytic subunits bind to substrate and catalyze a reaction. The regulatory subunits bind to either ATP or CTP. If they bind to ATP, the enzyme subunits arrange themselves in the R-state.

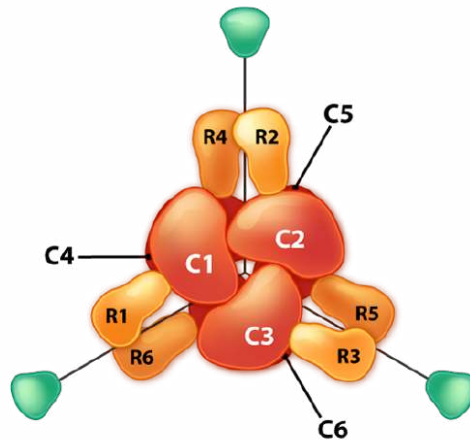


Figure 13.16.13- Schematic structure of ATCase. Regulatory Units = R, Catalytic Units = C. Image by Aleia Kim

R-state

The R-state of ATCase allows the substrate to have easier access to the six active sites and the reaction occurs more rapidly. For the same amount of substrate, an enzyme in the R-state will have a higher velocity than the same enzyme that is not in the R-state. By contrast, if the enzyme binds to CTP on one of its regulatory subunits, the subunits will arrange in the T-state and in this form, the substrate will not have easy access to the active sites, resulting in a slower velocity for the same concentration of substrate compared to the R-state. ATCase is interesting in that it can also flip into the R-state when one of the substrates (aspartate) binds to an active site within one of the catalytic subunits.

Aspartate has the effect of activating the catalytic action of the enzyme by favoring the R-state. Thus, aspartate, which is a substrate of the enzyme is a homotropic effector and ATP and CTP, which are not substrates of the enzyme are heterotropic effectors of ATCase.

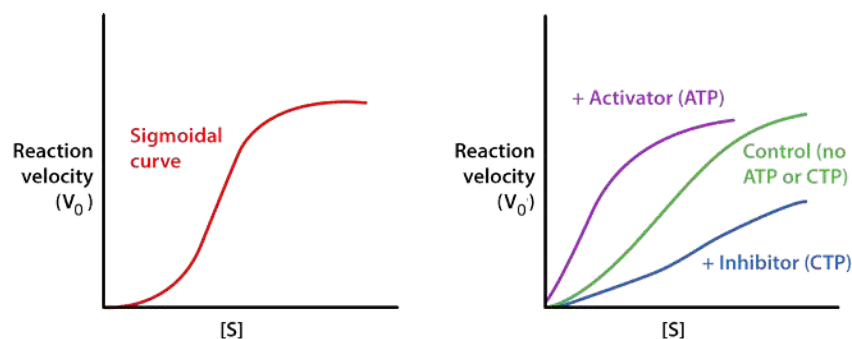


Figure Figure 13.16.14 - Plots of V_0 vs. $[S]$ for ATCase. Left - Allosteric effect of aspartate. Right - Allosteric effects of ATP (activator) and CTP (inhibitor). Image by Pehr Jacobson

13.16.8 Covalent control of enzymes

Some enzymes are synthesized in a completely inactive form and their activation requires covalent bonds in them to be cleaved. Such inactive forms of enzymes are called zymogens. Examples include the proteins involved in blood clotting and proteolytic enzymes of the digestive system, such as trypsin, chymotrypsin, pepsin, and others.

Synthesizing some enzymes in an inactive form makes very good sense when an enzyme's activity might be harmful to the tissue where it is being made. For example, the painful condition known as pancreatitis arises when digestive enzymes made in the

pancreas are activated too soon and end up attacking the pancreas.

Cascades

For both the blood clotting enzymes and the digestive enzymes, the zymogens are activated in a protease cascade. This occurs when activation of one enzyme activates others in a sort of chain reaction. In such a scheme the first enzyme activated proteolytically cleaves the second zymogen, causing it to be activated, which in turn activates a third and this may proceed through several levels of enzymatic action (Figure 13.16.15).

The advantage of cascades is that they allow a large amount of zymogens to become activated fairly quickly, since there is an amplification of the signal at each level of catalysis.

Zymogens are also abundant in blood. Blood clotting involves polymerization of a protein known as fibrin. Since random formation of fibrin is extremely hazardous because it can block the flow of blood, potentially causing heart attack/stroke, the body synthesizes fibrin as a zymogen (fibrinogen) and its activation results from a “cascade” of activations of proteases that arise when a signal is received from a wound. Similarly, the enzyme catalyzing removal of fibrin clots (plasmin) is also synthesized as a zymogen (plasminogen), since random clot removal would also be hazardous (see below also).

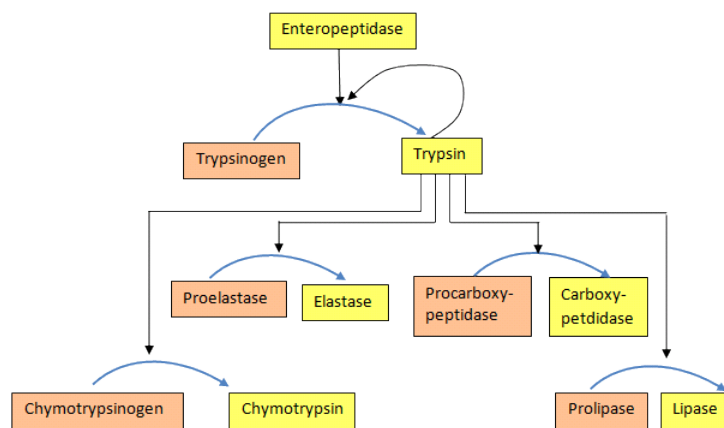


Figure 13.16.15 - Protease activation scheme. Wikipedia

Phosphorylation/dephosphorylation

Another common mechanism for control of enzyme activity by covalent modification is phosphorylation. The phosphorylation of enzymes (on the side chains of serine, threonine or tyrosine residues) is carried out by protein kinases. Enzymes activated by phosphorylation can be regulated by the addition of phosphate groups by kinases or their removal by phosphatases. Thus, this type of covalent modification is readily reversible, in contrast to proteolytic cleavage.

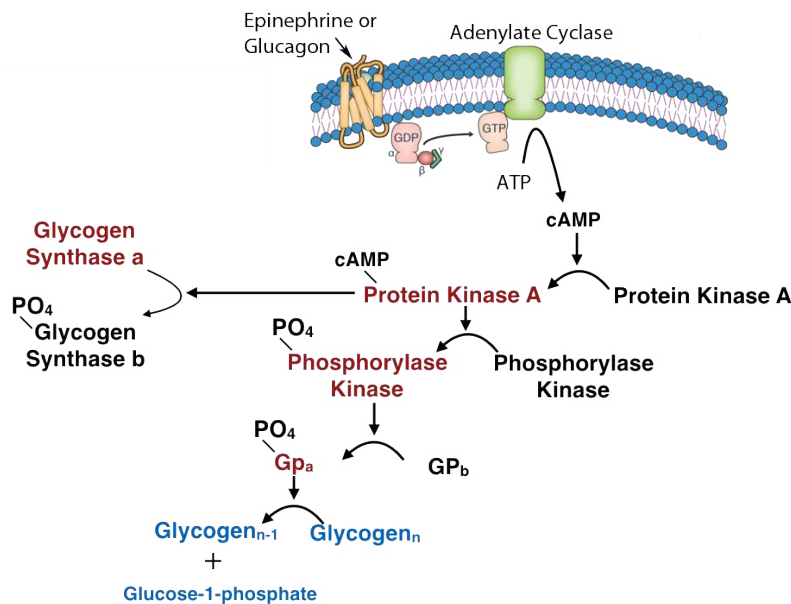


Figure Figure 13.16.16 - Regulation by covalent modification of glycogen catabolism enzymes

Reduction/oxidation

An interesting covalent control of enzymes using reduction/oxidation is exhibited in photosynthetic plants. In the light phase of photosynthesis, electrons are excited by light and flow through carriers to NADP⁺, forming NADPH. Thus, in the light, the NADPH concentration is high. When NADPH concentration is high, the concentration of reduced ferredoxin (a molecule donating electrons to NADP⁺) is also high.

Reduced ferredoxin can transfer electrons to thioredoxin, reducing it. Reduced thioredoxin can, in turn, transfer electrons to proteins to reduce their disulfide bonds. Four enzymes related to the Calvin cycle can receive electrons from thioredoxin and become activated, as a result.

These include sedoheptulose 1,7-bisphosphatase, ribulose-5-phosphate kinase, fructose 1,6-bisphosphatase, and glyceraldehyde 3-phosphate dehydrogenase. Thus, in the light, electrons flow, causing NADPH to accumulate and ferredoxin to push electrons in the direction of these enzymes above, activating them and favoring the Calvin cycle. In the dark, the concentration of reduced NADPH, reduced ferredoxin, and reduced thioredoxin fall, resulting in loss of electrons by the Calvin cycle enzymes (oxidations that re-form disulfide bonds) and the Calvin cycle inactivates.

Other enzyme control mechanisms

Other means of controlling enzymes relate to access to the substrate (substrate-level control) and control of enzyme synthesis. Hexokinase is an enzyme that is largely regulated by the availability of its substrate, glucose. When glucose concentration is low, the product of the enzyme's catalysis, glucose-6-phosphate, inhibits the enzyme's function.

Regulation of enzymes by controlling their synthesis is covered later in the book in the discussion relating to control of gene expression.

✓ Example 13.16.1

1. What are the characteristics of an irreversible inhibitor?
2. In what ways does a competitive inhibitor differ from a noncompetitive inhibitor?

Solution

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.

? Exercise 13.16.1

Oxaloacetate ($\text{OOCCH}_2\text{COCOO}$) inhibits succinate dehydrogenase (Enzyme in the TCA cycle). Would you expect oxaloacetate to be a competitive or noncompetitive inhibitor? Explain. Hint: look at a picture of the TCA cycle. Oxaloacetate is a product of this process.

Answer

Oxaloacetate is a competitive inhibitor. Oxaloacetate accumulates and is **a more potent competitive inhibitor** of succinate dehydrogenase than malonate even at small concentration.

Summary

An irreversible inhibitor inactivates an enzyme by bonding covalently to a particular group at the active site. A reversible inhibitor inactivates an enzyme through noncovalent, reversible interactions. A competitive inhibitor competes with the substrate for binding at the active site of the enzyme. A noncompetitive inhibitor binds at a site distinct from the active site.

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13.17: Enzyme Cofactors and Vitamins

Learning Objectives

- To explain why vitamins are necessary in the diet.

Many enzymes are simple proteins consisting entirely of one or more amino acid chains. Other enzymes contain a nonprotein component called a **cofactor** that is necessary for the enzyme's proper functioning. There are two types of cofactors: inorganic ions [e.g., zinc or Cu(I) ions] and organic molecules known as coenzymes. Most **coenzymes** are vitamins or are derived from vitamins.

Vitamins are organic compounds that are essential in very small (trace) amounts for the maintenance of normal metabolism. They generally cannot be synthesized at adequate levels by the body and must be obtained from the diet. The absence or shortage of a vitamin may result in a vitamin-deficiency disease. In the first half of the 20th century, a major focus of biochemistry was the identification, isolation, and characterization of vitamins. Despite accumulating evidence that people needed more than just carbohydrates, fats, and proteins in their diets for normal growth and health, it was not until the early 1900s that research established the need for trace nutrients in the diet.

Table 13.17.1: Fat-Soluble Vitamins and Physiological Functions

Vitamin	Physiological Function	Effect of Deficiency
vitamin A (retinol)	formation of vision pigments; differentiation of epithelial cells	night blindness; continued deficiency leads to total blindness
vitamin D (cholecalciferol)	increases the body's ability to absorb calcium and phosphorus	osteomalacia (softening of the bones); known as rickets in children
vitamin E (tocopherol)	fat-soluble antioxidant	damage to cell membranes
vitamin K (phylloquinone)	formation of prothrombin, a key enzyme in the blood-clotting process	increases the time required for blood to clot

Because organisms differ in their synthetic abilities, a substance that is a vitamin for one species may not be so for another. Over the past 100 years, scientists have identified and isolated 13 vitamins required in the human diet and have divided them into two broad categories: the *fat-soluble vitamins*, which include vitamins A, D, E, and K, and the *water-soluble vitamins*, which are the B complex vitamins and vitamin C. All fat-soluble vitamins contain a high proportion of hydrocarbon structural components. There are one or two oxygen atoms present, but the compounds as a whole are nonpolar. In contrast, water-soluble vitamins contain large numbers of electronegative oxygen and nitrogen atoms, which can engage in hydrogen bonding with water. Most water-soluble vitamins act as coenzymes or are required for the synthesis of coenzymes. The fat-soluble vitamins are important for a variety of physiological functions. The key vitamins and their functions are found in Tables 13.17.1 and 13.17.2.

Table 13.17.2: 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 deoxyadenosylcobalamin	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.

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13.18: 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.

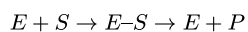
Protein molecules can have as many as four levels of structure. The **primary structure** is the sequence of amino acids in the chain. The **secondary structure** is the arrangement of adjacent atoms in the peptide chain; the most common arrangements are α -helices or β -pleated sheets. The **tertiary 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:



The original **lock-and-key model** of enzyme and substrate binding pictured a rigid enzyme of unchanging configuration binding to the appropriate substrate. The newer **induced-fit model** describes the enzyme active site as changing its conformation after binding to the substrate.

Most enzymes have maximal activity in a narrow pH range centered on an **optimum pH**. In this pH range, the enzyme is correctly folded, and catalytic groups in the active site have the correct charge (positive, negative, or neutral). For most enzymes, the optimum pH is between 6 and 8.

Substances that interfere with enzyme function are called inhibitors. An **irreversible inhibitor** inactivates enzymes by forming covalent bonds to the enzyme, while a **reversible inhibitor** inactivates an enzyme by a weaker, noncovalent interaction that is easier to disrupt. A **competitive inhibitor** is a reversible inhibitor that is structurally similar to the substrate and binds to the active site. When the inhibitor is bound, the substrate is blocked from the active site and no reaction occurs. Because the binding of such an inhibitor is reversible, a high substrate concentration will overcome the inhibition because it increases the likelihood of the substrate binding. A **noncompetitive inhibitor** binds reversibly at a site distinct from the active site. Thus, it can bind to either the enzyme or the enzyme-substrate complex. The inhibitor changes the conformation of the active site so that the enzyme cannot

function properly. Noncompetitive inhibitors are important in **feedback inhibition**, in which the amount of product produced by a series of reactions is carefully controlled. The final product in a series of reactions acts as a noncompetitive inhibitor of the initial enzyme.

Simple enzymes consist entirely of one or more amino acid chains. Complex enzymes are composed of one or more amino acid chains joined to **cofactors**—inorganic ions or organic **coenzymes**. **Vitamins** are organic compounds that are essential in very small amounts for the maintenance of normal metabolism and generally cannot be synthesized at adequate levels by the body. Vitamins are divided into two broad categories: *fat-soluble* vitamins and *water-soluble* vitamins. Many of the water-soluble vitamins are used for the synthesis of coenzymes.

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CHAPTER OVERVIEW

14: Nucleic Acids

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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.

[14.1: Nucleotides](#)

[14.2: Nucleic Acid Structure](#)

[14.3: Chapter Summary](#)

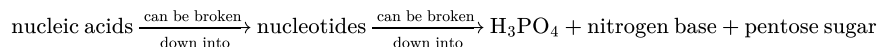
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14.1: Nucleotides

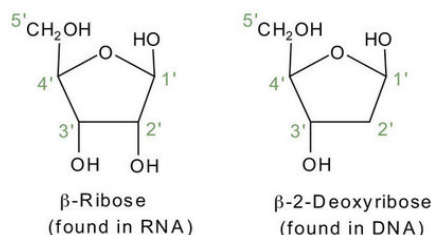
Learning Objectives

- To identify the different molecules that combine to form nucleotides.

The repeating, or monomer, units that are linked together to form nucleic acids are known as nucleotides. The deoxyribonucleic acid (DNA) of a typical mammalian cell contains about 3×10^9 nucleotides. Nucleotides can be further broken down to phosphoric acid (H_3PO_4), a pentose sugar (a sugar with five carbon atoms), and a nitrogenous base (a base containing nitrogen atoms).



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-membered ring and include uracil, thymine, and cytosine. Purines are heterocyclic amines consisting of a pyrimidine ring fused to a five-membered ring with two nitrogen atoms. Adenine and guanine are the major purines found in nucleic acids (Figure 14.1.1).

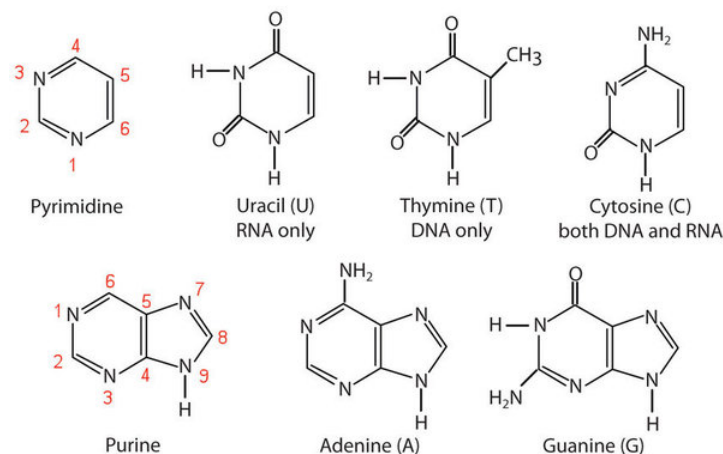


Figure 14.1.1: The Nitrogenous Bases Found in DNA and RNA

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 14.1.1 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.

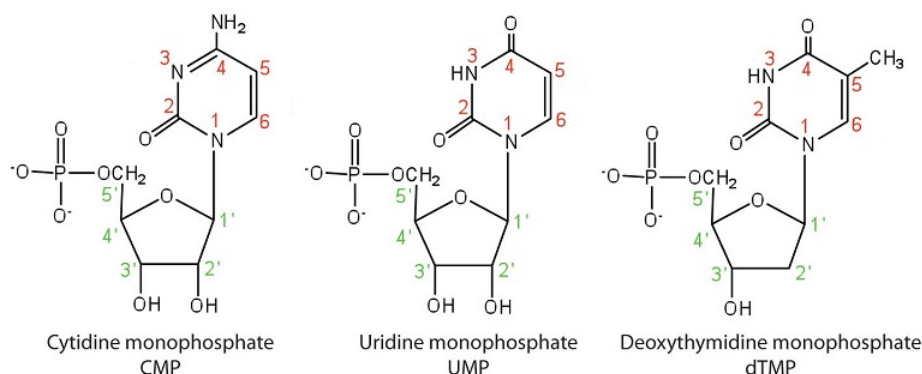
Table 14.1.1: Composition of Nucleotides in DNA and RNA

Composition	DNA	RNA
purine bases	adenine and guanine	adenine and guanine

Composition	DNA	RNA
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 14.1.2.

Pyrimidine Nucleotides



Purine Nucleotides

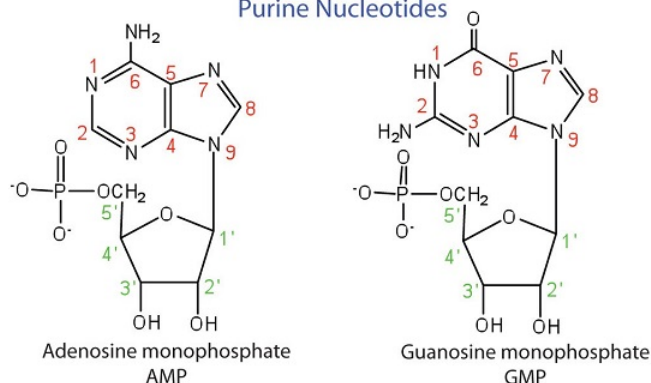


Figure 14.1.2: The Pyrimidine and Purine

Nucleotides

Apart from being the monomer units of DNA and RNA, the nucleotides and some of their derivatives have other functions as well. Adenosine diphosphate (ADP) and adenosine triphosphate (ATP), shown in Figure 14.1.3, 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.

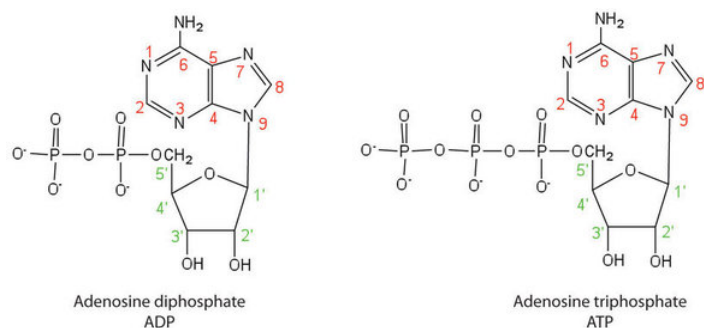


Figure 14.1.3: Structures of Two Important Adenine-

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.

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14.2: Nucleic Acid Structure

Learning Objectives

- 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.

14.2.1 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 14.2.1). 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.*

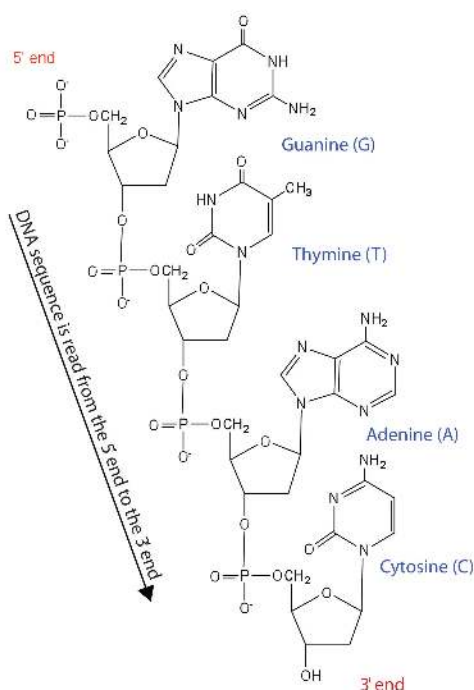


Figure 14.2.1 Structure of a Segment of DNA. A similar segment of RNA would have OH groups on each C2', and uracil would replace thymine.

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 14.2.1) starting with the nucleotide having a free phosphate group, which is known as the 5' end, and indicate the

nucleotides in order. For DNA, a lowercase *d* is often written in front of the sequence to indicate that the monomers are deoxyribonucleotides. The final nucleotide has a free OH group on the 3' carbon atom and is called the 3' *end*. The sequence of nucleotides in the DNA segment shown in Figure 19.2.119.2.1 would be written 5'-dG-dT-dA-dC-3', which is often further abbreviated to dGTAC or just GTAC.

14.2.2 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 14.2.2).

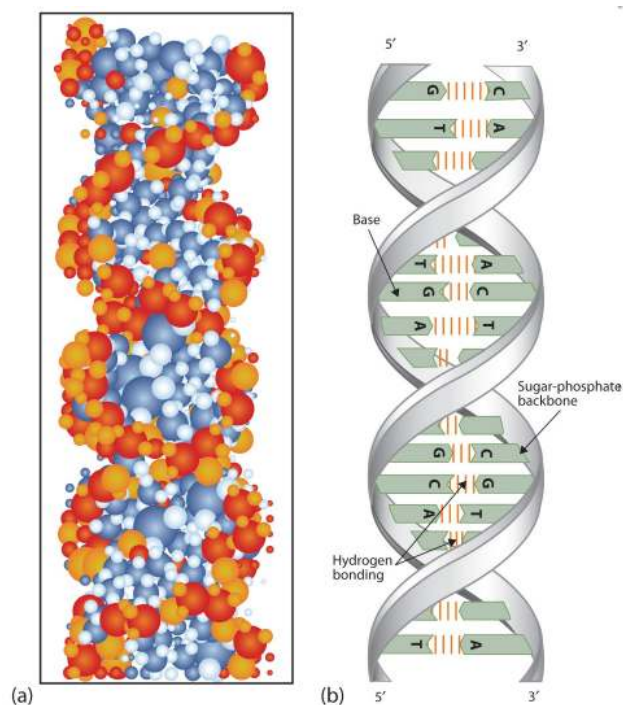


Figure 14.2.2 DNA Double Helix. (a) This represents a computer-generated model of the DNA double helix. (b) This represents a schematic representation of the double helix, showing the complementary bases.

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 14.2.3 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).

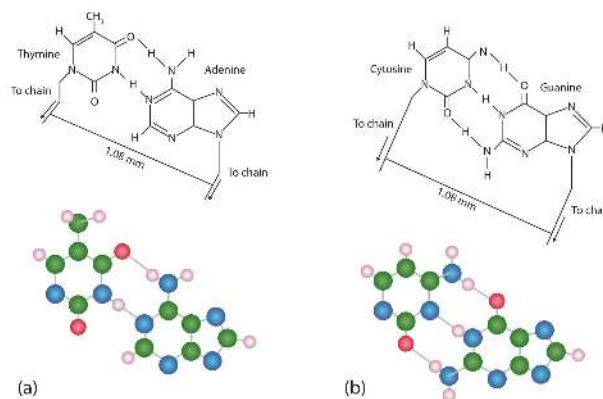


Figure 14.2.3 Complementary Base Pairing. Complementary bases engage in hydrogen bonding with one another: (a) thymine and adenine; (b) cytosine and guanine.

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 14.2.4. 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 14.2.3 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.

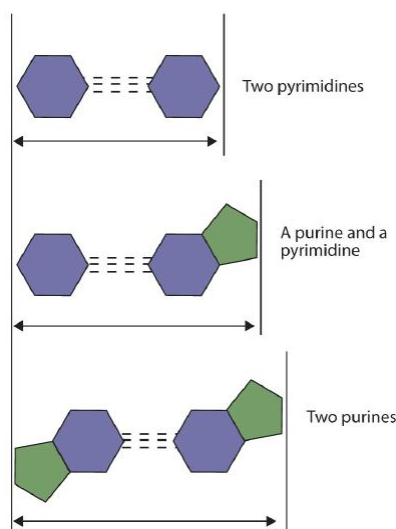


Figure 14.2.3 Difference in Widths of Possible Base Pairs

✓ Example 14.2.1

1. Name the two kinds of nucleic acids.
2. Which type of nucleic acid stores genetic information in the cell?
3. What are complementary bases?
4. Why is it structurally important that a purine base always pair with a pyrimidine base in the DNA double helix?

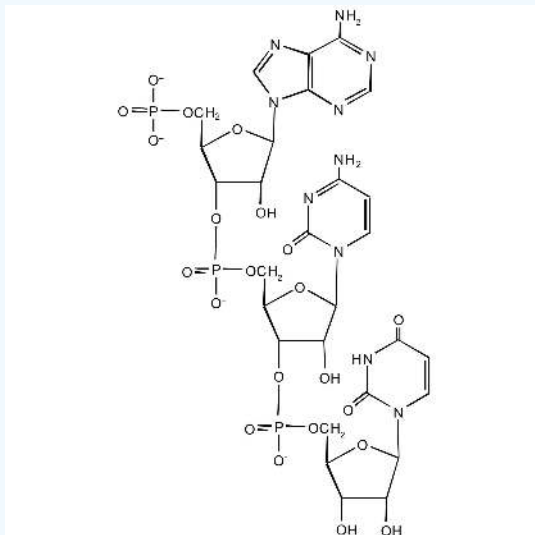
Solution

1. deoxyribonucleic acid (DNA) and ribonucleic acid (RNA)
2. DNA
3. the specific base pairings in the DNA double helix in which guanine is paired with cytosine and adenine is paired with thymine

4. 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).

? Exercise 14.2.1

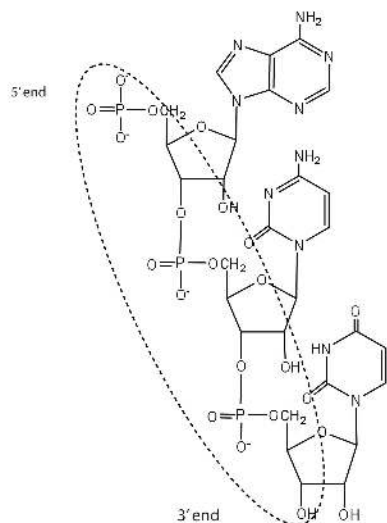
1. For this short RNA segment,
 - a) identify the 5' end and the 3' end of the molecule.
 - b) circle the atoms that comprise the backbone of the nucleic acid chain.
 - c) write the nucleotide sequence of this RNA segment.



2. Which nitrogenous base in DNA pairs with each nitrogenous base?
 1. cytosine
 2. adenine
 3. guanine
 4. thymine
3. How many hydrogen bonds can form between the two strands in the short DNA segment shown below?

5' ATGCGACTA 3' 3' TACGCTGAT 5'

Answer



c. ACU

Question 2:

1. guanine
2. thymine
3. cytosine
4. adenine

Question 3:

22 (2 between each AT base pair and 3 between each GC base pair)

14.2.3 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.

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14.3: Chapter Summary

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**.

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CHAPTER OVERVIEW

15: Flow of Genetic Information

As the cell's so-called blueprint, DNA must be copied to pass on to new cells and its integrity safeguarded. The information in the DNA must also be accessed and transcribed to make the RNA instructions that direct the synthesis of proteins.

[15.1: Replication and Expression of Genetic Information](#)

[15.2: Translation](#)

[15.3: Mutations and Genetic Diseases](#)

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15.1: Replication and Expression of Genetic Information

Learning Objectives

- Describe how a new copy of DNA is synthesized.
- Describe how RNA is synthesized from DNA.
- Identify the different types of RNA and the function of each type of RNA

We previously stated that deoxyribonucleic acid (DNA) stores genetic information, while ribonucleic acid (RNA) is responsible for transmitting or expressing genetic information by directing the synthesis of thousands of proteins found in living organisms. But how do the nucleic acids perform these functions? Three processes are required: (1) *replication*, in which new copies of DNA are made; (2) *transcription*, in which a segment of DNA is used to produce RNA; and (3) *translation*, in which the information in RNA is translated into a protein sequence.

15.1.1 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 15.1.1). 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.

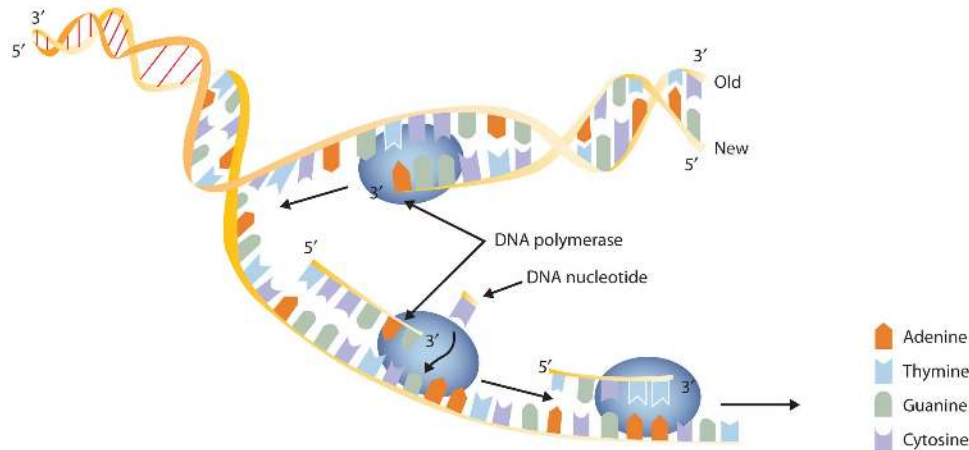


Figure 15.1.1: A Schematic Diagram of DNA Replication. DNA replication occurs by the sequential unzipping of segments of the double helix. Each new nucleotide is brought into position by DNA polymerase and is added to the growing strand by the formation of a phosphate ester bond. Thus, two double helices 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 15.1.1

A segment of one strand from a DNA molecule has the sequence 5'TCCATGAGTTGA3'. What is the sequence of nucleotides in the opposite, or complementary, DNA chain?

Solution

Knowing that the two strands are antiparallel and that T basepairs with A, while C base pairs with G, the sequence of the complementary strand will be 3'AGGTACTCAACT5' (can also be written as TCAACTCATGGA).

? Exercise 15.1.1

A segment of one strand from a DNA molecule has the sequence 5'CCAGTGAATTGCCTAT3'. What is the sequence of nucleotides in the opposite, or complementary, DNA chain? What do we mean when we say information is encoded in the DNA molecule?

Answer

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'GGTCACTTAACGGATA5'. The sequence of nucleotides is a code that is used to define gene regions.

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.

15.1.2 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 15.1.2). 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.

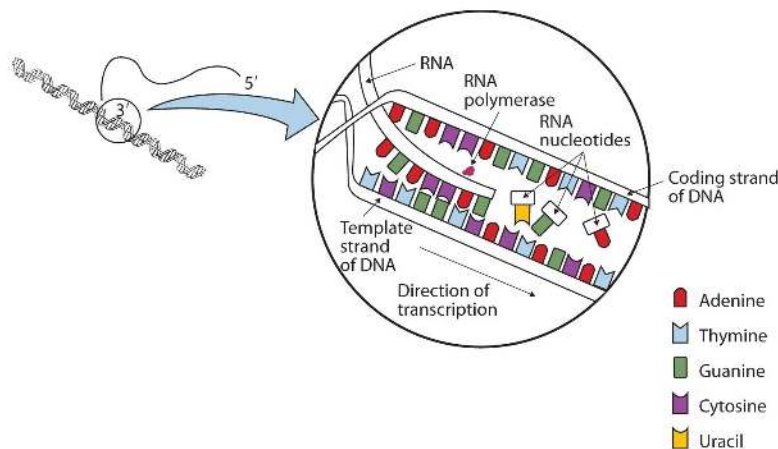


Figure 15.1.2: A Schematic Diagram of RNA Transcription from a DNA Template. The representation of RNA polymerase is proportionately much smaller than the actual molecule, which encompasses about 50 nucleotides at a time.

✓ Example 15.1.1

A portion of the template strand of a gene has the sequence 5'TCCATGAGTTGA3'. 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'AGGUACUCAACU5' (can also be written as 5'UCAACUCAUGGA3').

? Exercise 15.1.1

A portion of the template strand of a gene has the sequence 5'CCAGTGAATTGCCTAT3'. What is the sequence of nucleotides in the RNA that is formed from this template?

Answer

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'GGUCACUUAACGGAUA5'

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 15.1.1). 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 15.1.1: Properties of Cellular
in *Escherichia coli*

RNA

Type	Function	Approximate Number of Nucleotides	Percentage of Total Cell RNA
mRNA	codes for proteins	100–6,000	~3
rRNA	component of ribosomes	120–2900	83
tRNA	adapter molecule that brings the amino acid to the ribosome	75–90	14

Ribosomes are cellular substructures where proteins are synthesized. They contain about 65% rRNA and 35% protein, held together by numerous noncovalent interactions, such as hydrogen bonding, in an overall structure consisting of two globular particles of unequal size. Molecules of tRNA, which bring amino acids (one at a time) to the ribosomes for the construction of proteins, differ from one another in the kinds of amino acid each is specifically designed to carry. A set of three nucleotides, known as a codon, on the mRNA determines which kind of tRNA will add its amino acid to the growing chain. Each of the 20 amino acids found in proteins has at least one corresponding kind of tRNA, and most amino acids have more than one.

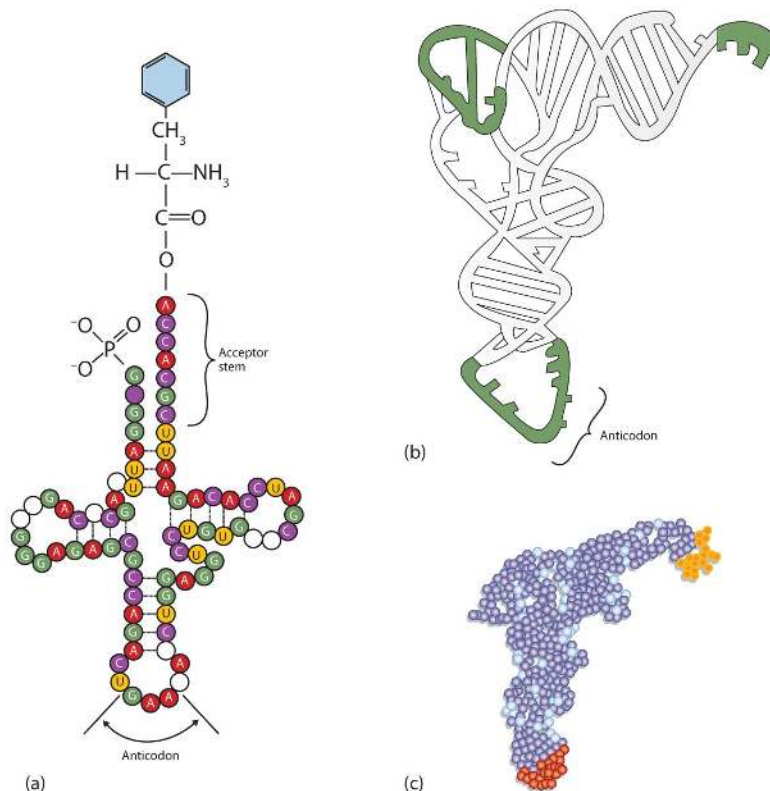


Figure 15.1.3: Transfer RNA. (a) In the two-dimensional structure of a yeast tRNA molecule for phenylalanine, the amino acid binds to the acceptor stem located at the 3' end of the tRNA primary sequence. (The nucleotides that are not specifically identified here are slightly altered analogs of the four 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 15.1.3). 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.

15.1.3 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.

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15.2: Translation

Translation is the process by which information in mRNAs is used to direct the synthesis of proteins. As you have learned in introductory biology, in eukaryotic cells, this process is carried out in the cytoplasm of the cell, by large RNA-protein machines called **ribosomes**. Ribosomes contain ribosomal RNAs (rRNAs) and proteins. The proteins and rRNAs are organized into two subunits, a large and a small. The large subunit has an enzymatic activity, known as a peptidyl transferase, that makes the peptide bonds that join amino acids to make a polypeptide. The small and large subunits assemble on the mRNA at its 5' end to initiate translation. Ribosomes function by binding to mRNAs and holding them in a way that allows the amino acids encoded by the RNA to be joined sequentially to form a polypeptide.

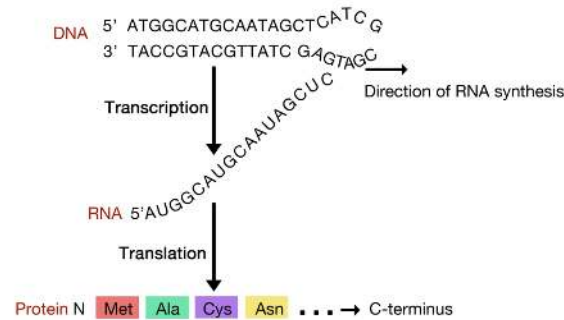


Figure 15.2.1: Coupled transcription and translation in prokaryotes

The sequence of an mRNA directly specifies the sequence of amino acids in the protein it encodes. Each amino acid in the protein is specified by a sequence of 3 bases called a **codon** in the mRNA. For example, the amino acid tryptophan is encoded by the sequence 5'UGG3' on an mRNA. Given that there are 4 bases in RNA, the number of different 3-base combinations that are possible is 4^3 , or 64. There are, however, only 20 amino acids that are used in building proteins. This discrepancy in the number of possible codons and the actual number of amino acids they specify is explained by the fact that the same amino acid may be specified by more than one codon. In fact, with the exception of the amino acids methionine and tryptophan, all the other amino acids are encoded by multiple codons. The figure above shows the codons that are used for each of the twenty amino acids.

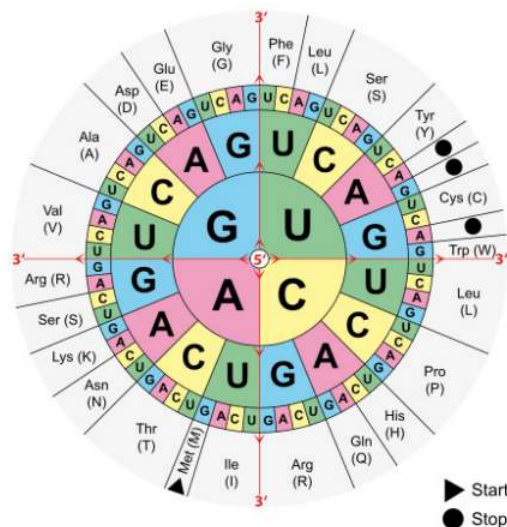


Figure 15.2.2: The genetic code

Three of the 64 codons are known as termination or **stop codons** and as their name suggests, indicate the end of a protein coding sequence. The codon for methionine, AUG, is used as the start, or initiation, codon.

This ingenious system is used to direct the assembly of a protein in the same way that you might string together colored beads in a particular order using instructions that used symbols like 111 for a red bead, followed by 222 for a green bead, 333 for yellow, and so on, till you came to 000, indicating that you should stop stringing beads.

While the ribosomes are literally the protein factories that join amino acids together using the instructions in mRNAs, another class of RNA molecules, the transfer RNAs (tRNAs) are also needed for translation. Transfer RNAs (see figure, left) are small RNA molecules, about 75-80 nucleotides long, that function to 'interpret' the instructions in the mRNA during protein synthesis. In terms of the bead analogy above, someone, or something, has to be able to bring a red bead in when the instructions indicate 111, and a green bead when the instructions say 222. Unlike a human, who can choose a red bead when 111 is present in the instructions, neither ribosomes nor tRNAs can think. The system, therefore, relies, like so many processes in cells, solely on molecular recognition.

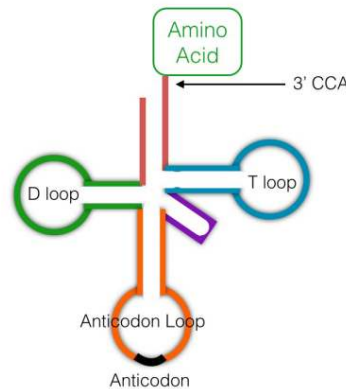


Figure 15.2.3: tRNA structure

A given transfer RNA is specific for a particular amino acid. It is linked covalently to this amino acid at its 3' end by an enzyme called aminoacyl tRNA synthetase. There is an aminoacyl tRNA synthetase specific for each amino acid. A tRNA with an amino acid attached to it is said to be charged. Another region of the tRNA has a sequence of 3 bases, the anticodon, that is complementary to the codon for the amino acid it is carrying. When the tRNA encounters the codon for its amino acid on the messenger RNA, the anticodon will base-pair with the codon, and the amino acid attached to it will be brought in to the ribosome to be added on to the growing protein chain.

With an idea of the various components necessary for translation we can now take a look at the process of protein synthesis. The main steps in the process are similar in prokaryotes and eukaryotes. As we already noted, ribosomes bind to mRNAs and facilitate the interaction between the codons in the mRNA and the anticodons on charged tRNAs.

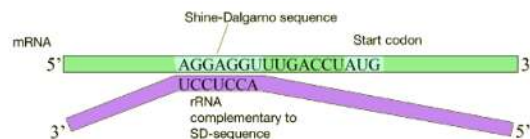


Figure 15.2.4: mRNA alignment by Shine-Dalgarno sequence

In bacterial cells, translation is coupled with transcription and begins even before the mRNA has been completely synthesized. How does the ribosome recognize and bind to the mRNA. Many bacterial mRNAs carry a short purine-rich sequence known as the Shine-Dalgarno site upstream of the AUG start codon, as shown in the figure below. This sequence is recognized and bound by a complementary sequence in the 16S rRNA that is part of the small ribosomal subunit as shown above. Because the Shine-Dalgarno site serves to recruit and bind the ribosome, it is also referred to as the Ribosome Binding Site or RBS.

<i>araB</i>	UUUGGAU	GGAG	UGAAACG	AUGGCG
<i>galE</i>	AGCCUAA	UGGAG	CGAAUUA	AUGAGA
<i>lacI</i>	CAAUUCA	GGGUGG	UGAUUG	UGAAAA
<i>lacZ</i>	UUCACAC	AGGAA	ACAGCU	AUGACC
<i>trpE</i>	CAAAAUU	AGAGAA	UAACA	AUGCAA
<i>trpL leader</i>	GUAAA	AGGG	UAUCGACA	AUGAAA

Figure 15.2.5: Shine-Dalgarno sequences

A variation of this process of ribosome assembly operates in eukaryotic cells. We already know that in eukaryotic cells, processed mRNAs are sent from the nucleus to the cytoplasm.

The small and large subunits of ribosomes, each composed of characteristic rRNAs and proteins are found in the cytoplasm and assemble on mRNAs to form complete ribosomes that carry out translation.

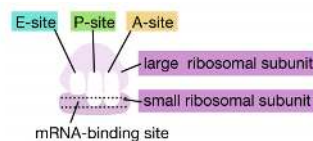


Figure 15.2.6: A, P, and E sites of the ribosome

Protein synthesis in eukaryotes starts with the binding of the small subunit of the ribosome to the 5' end of the mRNA. The assembly of the translation machinery begins with the binding of the small ribosomal subunit to the 7-methyl guanosine cap on the 5' end of an mRNA. Meanwhile, the initiator tRNA pairs with the start codon. (Recall that the start codon is AUG, and codes for methionine. The initiator tRNA carries the amino acid methionine). The large subunit of the ribosome then joins the complex, which is now ready to start protein synthesis.

Ribosomes have two sites for binding charged tRNAs, each of which is positioned to make two adjacent codons on the mRNA available for binding by tRNAs. The initiation codon occupies the first of these ribosomal sites, the P-site. The anticodon complementary to this is on the initiator tRNA, which brings in the first amino acid of the protein. This initial phase of translation is called initiation and requires the help of protein factors called initiation factors.

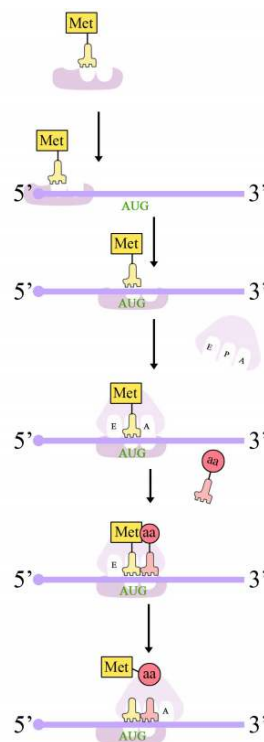


Figure 15.2.7: Initiation of translation

The second codon of the mRNA is positioned adjacent to the second site on the ribosome, the A site. This is where the tRNA carrying the amino acid specified by the second codon binds. The binding of aminoacyl tRNA to the A-site is mediated by proteins called elongation factors and requires the input of energy. Once the appropriate charged tRNAs have "docked" on the codons by base-pairing between the anticodon on the tRNA and the codon on the mRNA, the ribosome joins the amino acids carried by the two tRNAs by making a peptide bond (see figure at right).

Interestingly, the formation of the peptide bond is catalyzed by a catalytic RNA (the 23S rRNA in prokaryotes) rather than by a protein enzyme.

This and subsequent steps in the synthesis of the polypeptide are called the elongation phase of translation. Once the first two amino acids are linked, the first tRNA dissociates, and moves out of the P-site and into the E, or Exit site. The second tRNA then moves into the P-site, vacating the A-site for the tRNA corresponding to the next codon.

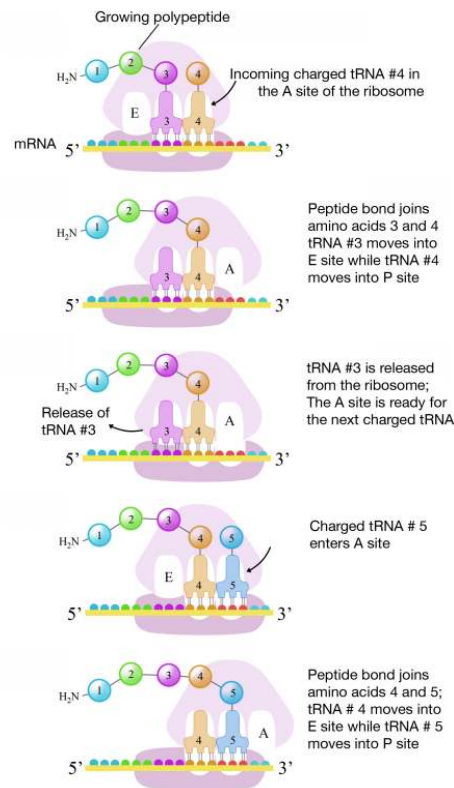


Figure 15.2.8: *Elongation of translation*

The process repeats till the stop codon is in the A-site. At this point, a release factor binds at the A-site, adds a water molecule to the polypeptide at the P-site, and releases the completed polypeptide from the ribosome, which itself, then dissociates into subunits.

As described previously, polypeptides made in this way are then folded into their three dimensional shapes, post-translationally modified and delivered to the appropriate cellular compartments to carry out their functions.

Contributors

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15.3: Mutations and Genetic Diseases

Learning Objectives

- To describe the causes of genetic mutations and how they lead to genetic diseases.

We have seen that the sequence of nucleotides in a cell's deoxyribonucleic acid (DNA) is what ultimately determines the sequence of amino acids in proteins made by the cell and thus is critical for the proper functioning of the cell. On rare occasions, however, the nucleotide sequence in DNA may be modified either spontaneously (by errors during replication, occurring approximately once for every 10 billion nucleotides) or from exposure to heat, radiation, or certain chemicals. Any chemical or physical change that alters the nucleotide sequence in DNA is called a mutation. When a mutation occurs in an egg or sperm cell that then produces a living organism, it will be inherited by all the offspring of that organism.

Common types of mutations include **substitution** (a different nucleotide is substituted), **insertion** (the addition of a new nucleotide), and **deletion** (the loss of a nucleotide). These changes within DNA are called point mutations because only one nucleotide is substituted, added, or deleted (Figure 15.3.1). 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.

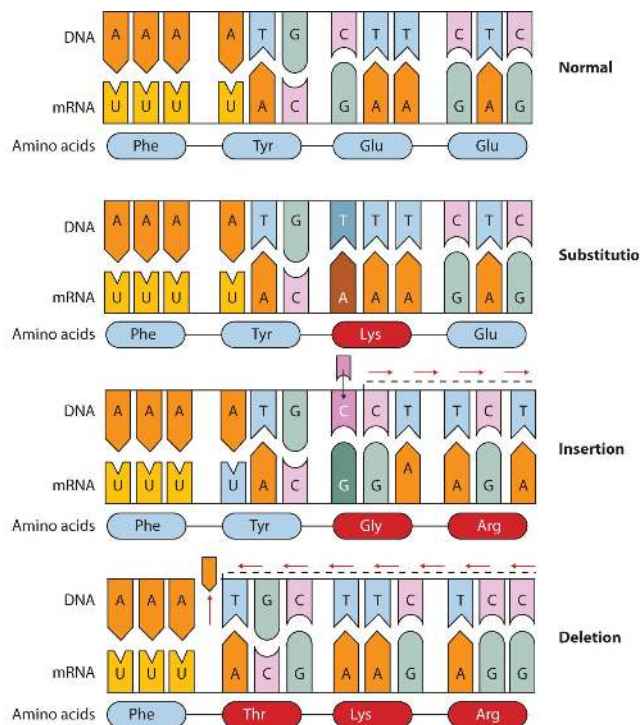


Figure 15.3.1: Three Types of Point Mutations

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 15.3.2). 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.

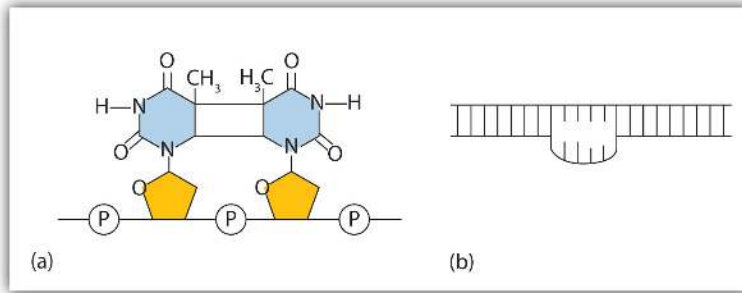


Figure 15.3.2: An Example of Radiation Damage to

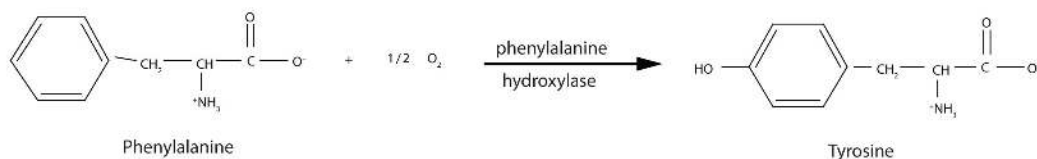
DNA. (a) The thymine dimer is formed by the action of UV light. (b) When a defect in the double strand is produced by the thymine dimer, this defect temporarily stops DNA replication, but the dimer can be removed, and the region can be repaired by an enzyme repair system.

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 15.3.1, 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.

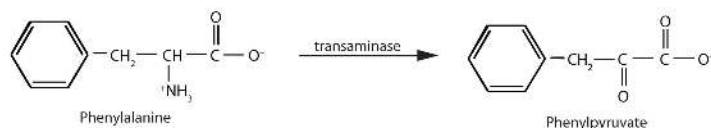
Figure 15.3.1: Some Representative Genetic Diseases in Humans and the Protein or Enzyme Responsible

Disease	Responsible Protein or Enzyme
alkaptonuria	homogentisic acid oxidase
galactosemia	galactose 1-phosphate uridyl transferase, galactokinase, or UDP galactose epimerase
Gaucher disease	glucocerebrosidase
gout and Lesch-Nyhan syndrome	hypoxanthine-guanine phosphoribosyl transferase
hemophilia	antihemophilic factor (factor VIII) or Christmas factor (factor IX)
homocystinuria	cystathionine synthetase
maple syrup urine disease	branched chain α -keto acid dehydrogenase complex
McArdle syndrome	muscle phosphorylase
Niemann-Pick disease	sphingomyelinase
phenylketonuria (PKU)	phenylalanine hydroxylase
sickle cell anemia	hemoglobin
Tay-Sachs disease	hexosaminidase A
tyrosinemia	fumarylacetoacetate hydrolase or tyrosine aminotransferase
von Gierke disease	glucose 6-phosphatase
Wilson disease	Wilson disease protein

PKU results from the absence of the enzyme phenylalanine hydroxylase. Without this enzyme, a person cannot convert phenylalanine to tyrosine, which is the precursor of the neurotransmitters dopamine and norepinephrine as well as the skin pigment melanin.



When this reaction cannot occur, phenylalanine accumulates and is then converted to higher than normal quantities of phenylpyruvate. The disease acquired its name from the high levels of phenylpyruvate (a phenyl ketone) in urine. Excessive amounts of phenylpyruvate impair normal brain development, which causes severe mental retardation.



PKU may be diagnosed by assaying a sample of blood or urine for phenylalanine or one of its metabolites. Medical authorities recommend testing every newborn's blood for phenylalanine within 24 h to 3 weeks after birth. If the condition is detected, mental retardation can be prevented by immediately placing the infant on a diet containing little or no phenylalanine. Because phenylalanine is plentiful in naturally produced proteins, the low-phenylalanine diet depends on a synthetic protein substitute plus very small measured amounts of naturally produced foods. Before dietary treatment was introduced in the early 1960s, severe mental retardation was a common outcome for children with PKU. Prior to the 1960s, 85% of patients with PKU had an intelligence quotient (IQ) less than 40, and 37% had IQ scores below 10. Since the introduction of dietary treatments, however, over 95% of children with PKU have developed normal or near-normal intelligence. The incidence of PKU in newborns is about 1 in 12,000 in North America.

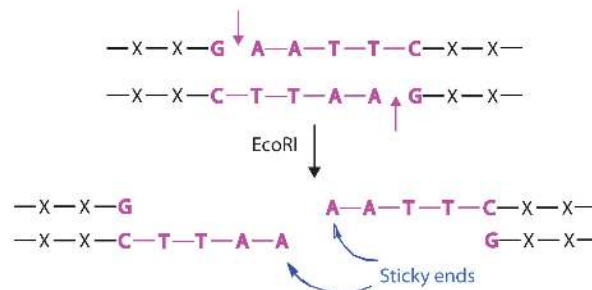
Every state in the United States has mandated that screening for PKU be provided to all newborns.

Several genetic diseases are collectively categorized as *lipid-storage diseases*. Lipids are constantly being synthesized and broken down in the body, so if the enzymes that catalyze lipid degradation are missing, the lipids tend to accumulate and cause a variety of medical problems. When a genetic mutation occurs in the gene for the enzyme hexosaminidase A, for example, gangliosides cannot be degraded but accumulate in brain tissue, causing the ganglion cells of the brain to become greatly enlarged and nonfunctional. This genetic disease, known as *Tay-Sachs disease*, leads to a regression in development, dementia, paralysis, and blindness, with death usually occurring before the age of three. There is currently no treatment, but Tay-Sachs disease can be diagnosed in a fetus by assaying the amniotic fluid (amniocentesis) for hexosaminidase A. A blood test can identify Tay-Sachs carriers—people who inherit a defective gene from only one rather than both parents—because they produce only half the normal amount of hexosaminidase A, although they do not exhibit symptoms of the disease.

15.3.1 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.

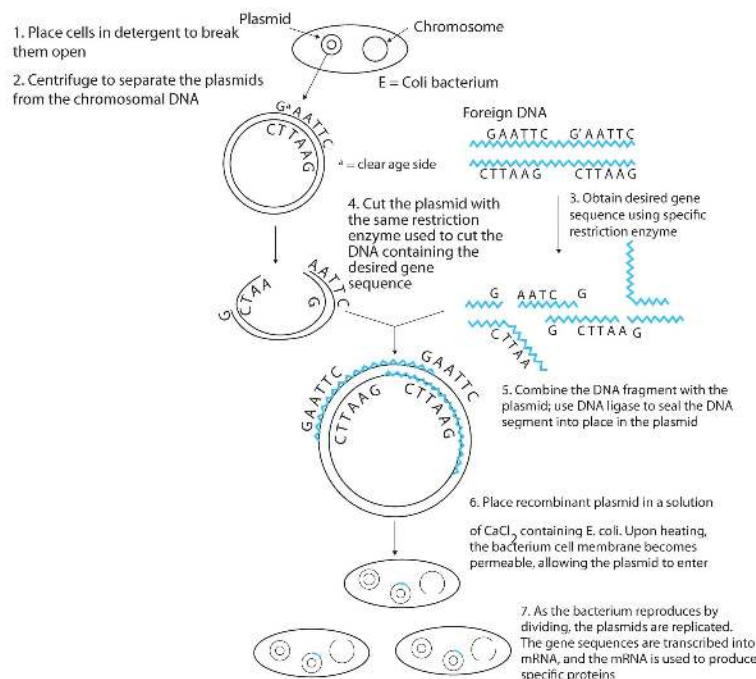
Isolating the specific gene or genes that cause a particular genetic disease is a monumental task. One reason for the difficulty is the enormous amount of a cell's DNA, only a minute portion of which contains the gene sequence. Thus, the first task is to obtain smaller pieces of DNA that can be more 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 recombinant 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.

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CHAPTER OVERVIEW

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.

[16.1: Prelude to Energy Metabolism](#)

[16.2: ATP- the Universal Energy Currency](#)

[16.3: Stage I of Catabolism](#)

[16.4: Overview of Stage II of Catabolism](#)

[16.5: Stage III of Catabolism](#)

[16.6: Stage II of Carbohydrate Catabolism](#)

[16.7: Stage II of Lipid Catabolism](#)

[16.8: Stage II of Protein Catabolism](#)

[16.S: Energy Metabolism \(Summary\)](#)

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16.1: Prelude to Energy Metabolism

The discovery of the link between insulin and diabetes led to a period of intense research aimed at understanding exactly how insulin works in the body to regulate glucose levels. Hormones in general act by binding to some protein, known as the hormone's receptor, thus initiating a series of events that lead to a desired outcome. In the early 1970s, the insulin receptor was purified, and researchers began to study what happens after insulin binds to its receptor and how those events are linked to the uptake and metabolism of glucose in cells.

The insulin receptor is located in the cell membrane and consists of four polypeptide chains: two identical chains called α chains and two identical chains called β chains. The α chains, positioned on the outer surface of the membrane, consist of 735 amino acids each and contain the binding site for insulin. The β chains are integral membrane proteins, each composed of 620 amino acids. The binding of insulin to its receptor stimulates the β chains to catalyze the addition of phosphate groups to the specific side chains of tyrosine (referred to as phosphorylation) in the β chains and other cell proteins, leading to the activation of reactions that metabolize glucose. In this chapter we will look at the pathway that breaks down glucose—in response to activation by insulin—for the purpose of providing energy for the cell.

Figure 16.1.1: Model of the Structure of the Insulin Receptor (PDB code 4ZXB).

Life requires energy. Animals, for example, require heat energy to maintain body temperature, mechanical energy to move their limbs, and chemical energy to synthesize the compounds needed by their cells. Living cells remain organized and functioning properly only through a continual supply of energy. But only specific forms of energy can be used. Supplying a plant with energy by holding it in a flame will not prolong its life. On the other hand, a green plant is able to absorb radiant energy from the sun, the most abundant source of energy for life on the earth. Plants use this energy first to form glucose and then to make other carbohydrates, as well as lipids and proteins. Unlike plants, animals cannot directly use the sun's energy to synthesize new compounds. They must eat plants or other animals to get carbohydrates, fats, and proteins and the chemical energy stored in them. Once digested and transported to the cells, the nutrient molecules can be used in either of two ways: as building blocks for making new cell parts or repairing old ones or "burned" for energy.

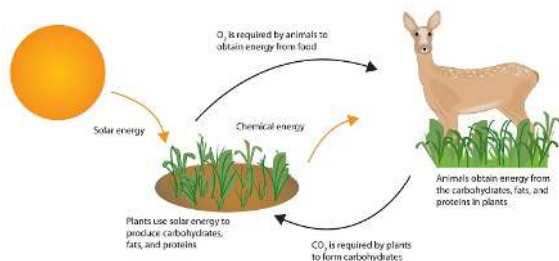


Figure 16.1.2: Some Energy Transformations in Living Systems. Plants and animals exist in a cycle; each requires

products of the other.

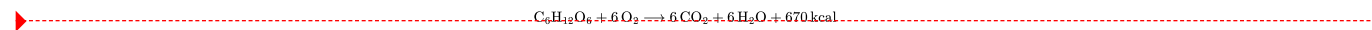
The thousands of coordinated chemical reactions that keep cells alive are referred to collectively as **metabolism**. In general, metabolic reactions are divided into two classes: the breaking down of molecules to obtain energy is **catabolism**, and the building of new molecules needed by living systems is **anabolism**.

Definition: Metabolite

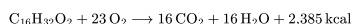
Any chemical compound that participates in a metabolic reaction is a *metabolite*.

Most of the energy required by animals is generated from lipids and carbohydrates. These fuels must be oxidized, or "burned," for the energy to be released. The oxidation process ultimately converts the lipid or carbohydrate to carbon dioxide (CO_2) and water (H_2O).

Carbohydrate:



Lipid:



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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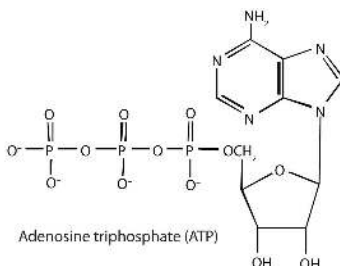
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16.2: ATP- the Universal Energy Currency

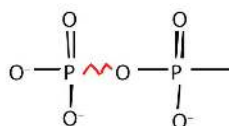
Learning Objectives

- To describe the importance of ATP as a source of energy in living organisms.

Adenosine triphosphate (ATP), a nucleotide composed of adenine, ribose, and three phosphate groups, is perhaps the most important of the so-called energy-rich compounds in a cell. Its concentration in the cell varies from 0.5 to 2.5 mg/mL of cell fluid.



Energy-rich compounds are substances having particular structural features that lead to a release of energy after hydrolysis. As a result, these compounds are able to supply energy for biochemical processes that require energy. The structural feature important in ATP is the phosphoric acid anhydride, or pyrophosphate, linkage:



The pyrophosphate bond, symbolized by a squiggle (~), is hydrolyzed when ATP is converted to adenosine diphosphate (ADP). In this hydrolysis reaction, the products contain less energy than the reactants; there is a release of energy (> 7 kcal/mol). One reason for the amount of energy released is that hydrolysis relieves the electron-electron repulsions experienced by the negatively charged phosphate groups when they are bonded to each other (Figure 20.1.1).

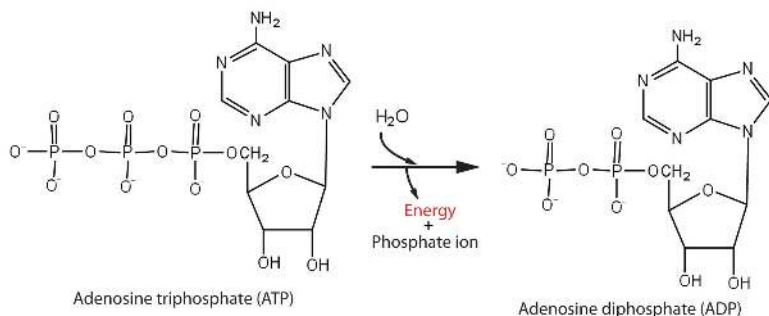


Figure 16.2.1: Hydrolysis of ATP to Form ADP

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:

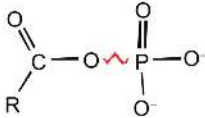
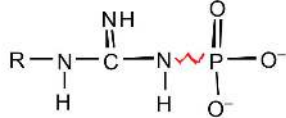
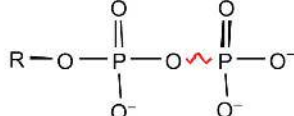


If the hydrolysis of ATP releases energy, its synthesis (from ADP) requires energy. In the cell, ATP is produced by those processes that supply energy to the organism (absorption of radiant energy from the sun in green plants and breakdown of food in animals), and it is hydrolyzed by those processes 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 16.2.1. 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 16.2.1: Energy Released by Hydrolysis of Some Phosphate Compounds

Type	Example	Energy Released (kcal/mol)
acyl phosphate 	1,3-bisphosphoglycerate (BPG)	-11.8
	acetyl phosphate	-11.3
guanidine phosphates 	creatine phosphate	-10.3
	arginine phosphate	-9.1
pyrophosphates 	$PP_i^* \rightarrow 2P_i$	-7.8
	$ATP \rightarrow AMP + PP_i$	-7.7
	$ATP \rightarrow ADP + P_i$	-7.5
	$ADP \rightarrow AMP + P_i$	-7.5
sugar phosphates 	glucose 1-phosphate	-5.0
	fructose 6-phosphate	-3.8
	$AMP \rightarrow adenosine + P_i$	-3.4
	glucose 6-phosphate	-3.3
	glycerol 3-phosphate	-2.2
*PP _i is the pyrophosphate ion.		

Summary

The hydrolysis of ATP releases energy that can be used for cellular processes that require energy.

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16.3: Stage I of Catabolism

Learning Objectives

- To describe how carbohydrates, fats, and proteins are broken down during digestion.

We have said that animals obtain chemical energy from the food—carbohydrates, fats, and proteins—they eat through reactions defined collectively as *catabolism*. We can think of catabolism as occurring in three stages (Figure 16.3.1). 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.

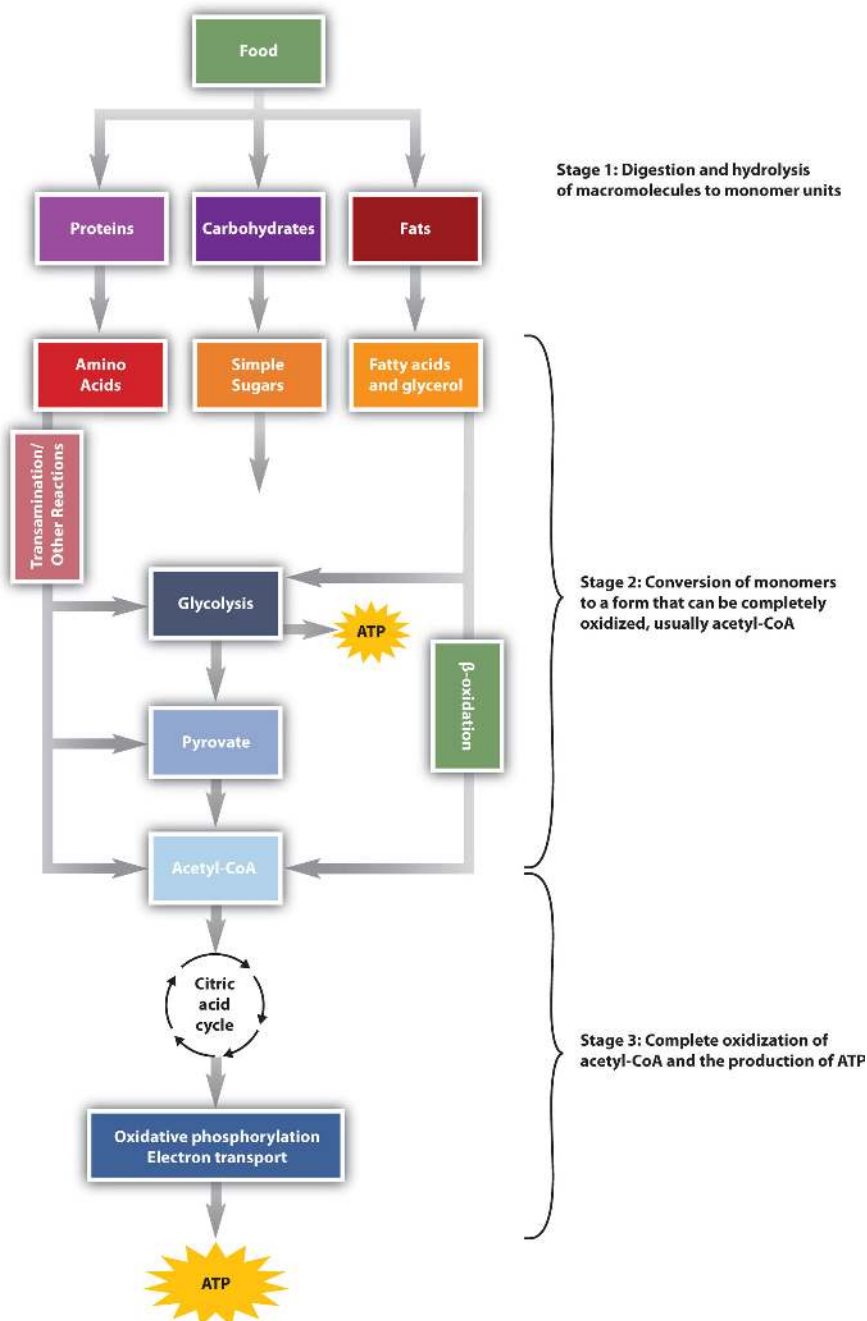


Figure 16.3.1: Energy Conversions

The conversion of food into cellular energy (as ATP) occurs in three stages.

Digestion of Carbohydrates

Carbohydrate digestion begins in the mouth (Figure 16.3.2) 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 dextrans, 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.

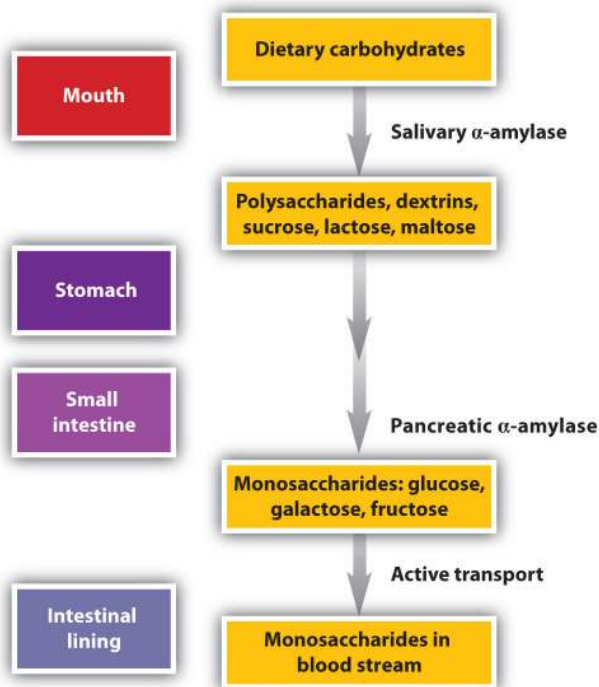


Figure 16.3.2: The Principal Events and Sites of Carbohydrate

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 16.3.3), 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.

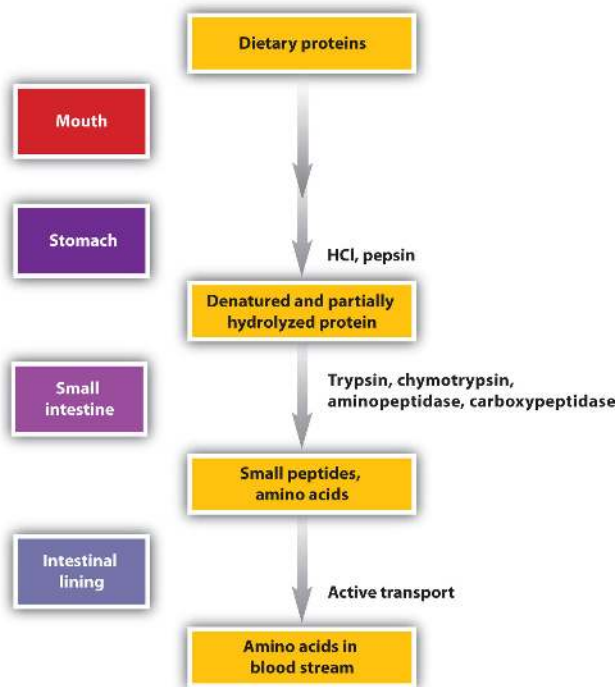


Figure 16.3.3: The Principal Events and Sites of Protein Digestion

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 16.3.4): 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.

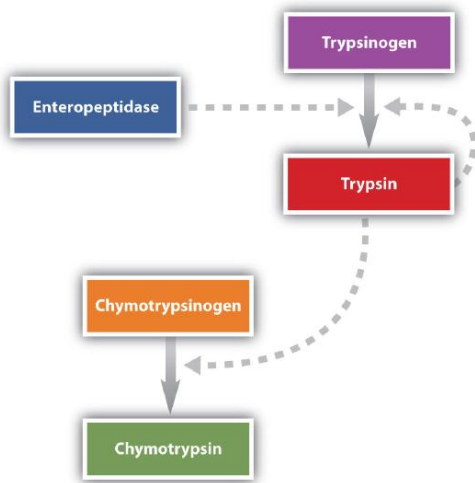


Figure 16.3.4: Activation of Some Pancreatic Enzymes in the Small Intestine

Aminopeptidases in the intestinal juice remove amino acids from the N-terminal end of peptides and proteins possessing a free amino group. Figure 16.3.5 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.

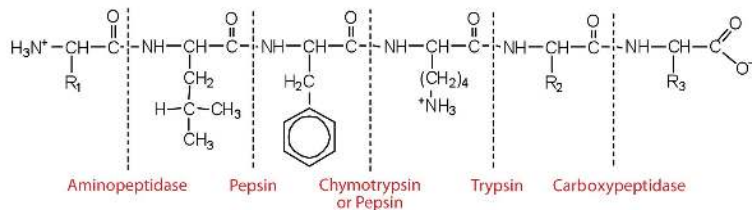


Figure 16.3.5: Hydrolysis of a Peptide by Several

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 16.3.6). 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.

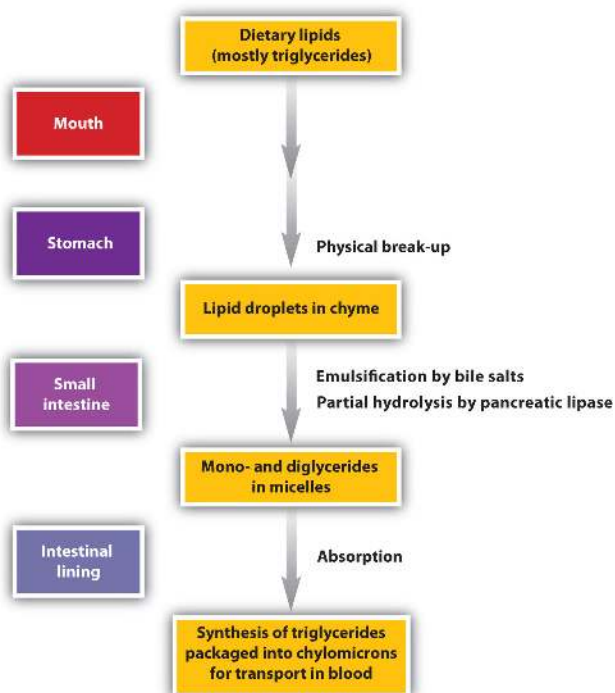
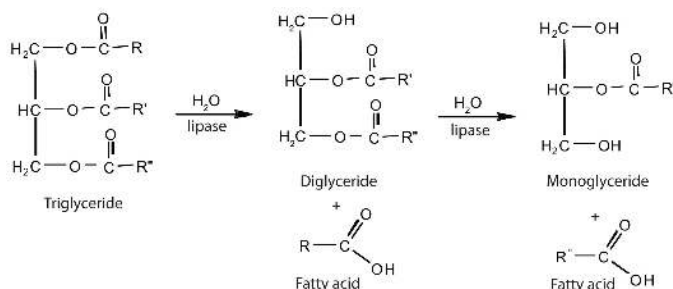


Figure 16.3.6: The Principal Events and Sites of Lipid (Primarily

Triglyceride) Digestion

The lipases in pancreatic juice catalyze the digestion of triglycerides first to diglycerides and then to 2-monoglycerides and fatty acids:



The monoglycerides and fatty acids cross the intestinal lining into the bloodstream, where they are resynthesized into triglycerides and transported as lipoprotein complexes known as chylomicrons. Phospholipids and cholesteryl esters undergo similar hydrolysis in the small intestine, and their component molecules are also absorbed through the intestinal lining.

The further metabolism of monosaccharides, fatty acids, and amino acids released in stage I of catabolism occurs in stages II and III of catabolism.

Summary

During digestion, carbohydrates are broken down into monosaccharides, proteins are broken down into amino acids, and triglycerides are broken down into glycerol and fatty acids. Most of the digestion reactions occur in the small intestine.

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16.4: Overview of Stage II of Catabolism

Learning Objectives

- To describe the role of acetyl-CoA in metabolism.

A metabolic pathway is a series of biochemical reactions by which an organism converts a given reactant to a specific end product. There are specific metabolic pathways—which are different for carbohydrates, triglycerides, and proteins—that break down the products of stage I of catabolism (monosaccharides, fatty acids, and amino acids) to produce a common end product, acetyl-coenzyme A (acetyl-CoA) in stage II of catabolism.

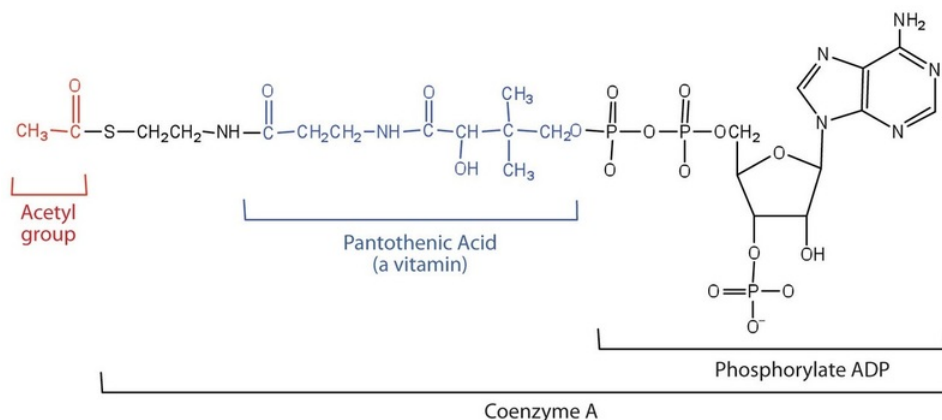


Figure 16.4.1: The Structure of

Acetyl-Coenzyme A (Acetyl-CoA)

Acetyl-CoA is shown in Figure 16.4.1. 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 16.4.1.

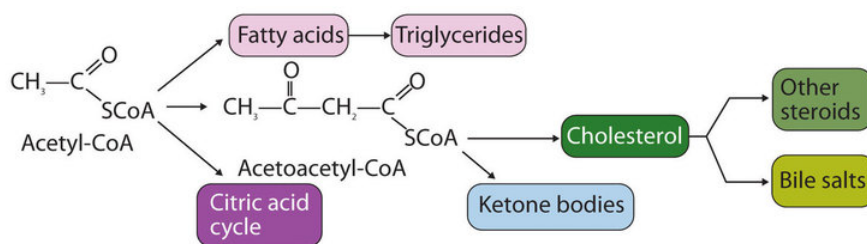


Figure 16.4.2: Cell Chemistry. Acetyl-CoA

plays a variety of roles in cell chemistry.

Glycolysis

Glycolysis is the **catabolic** process in which **glucose** is converted into pyruvate via ten enzymatic steps. There are three regulatory steps, each of which is highly regulated that are separated into two phases:

- the "priming phase" because it requires an input of energy in the form of 2 ATPs per glucose molecule and
- 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 oxygen using a process known as **fermentation**.



Video 16.4.1: Glycolysis: An Overview. Glycolysis is a series of 10 reactions that converts sugars, like glucose, into 3-carbon molecules called pyruvate. This animation provides an overview of the energy consumed and produced by the pathway. NDSU VCell Production's animation; for more information please see [Vcell](https://vcell.ndsu.edu), [NDSU](https://vcell.ndsu.edu)(opens in new window) [vcell.ndsu.edu].

Glycolysis occurs within almost all living cells and is the primary source of Acetyl-CoA, which is the molecule responsible for the majority of energy output under [aerobic](#) conditions. The structures of Glycolysis intermediates can be found in Figure 16.4.3.

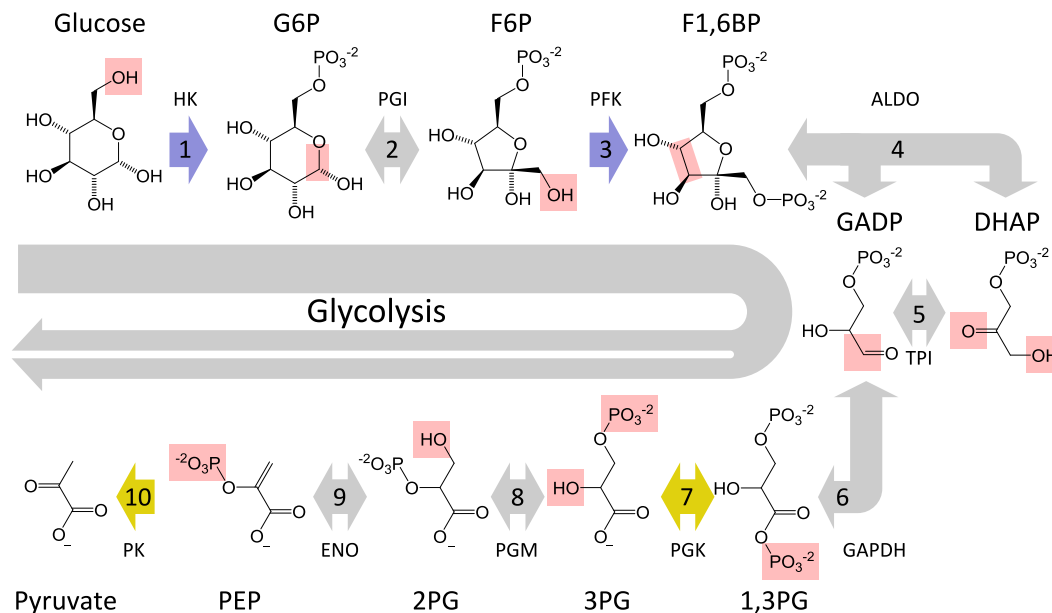


Figure 16.4.3: Glycolysis

pathway. (CC BY-SA 4.0; International; [Thomas Shafee](#) via [Wikipedia](#))

Phase 1: The "Priming Step"

The first phase of Glycolysis requires an input of energy in the form of ATP (adenosine triphosphate).

1. alpha-D-[Glucose](#) is phosphorylated 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 Phosphoglucosomerase (Class: Isomerase)
3. D-Fructose-6-phosphate is once again phosphorylated 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 bisphosphatase 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 phosphorylated at the 1 carbon by the enzyme Glyceraldehyde-3-phosphate dehydrogenase to yield the high energy molecule 1,3-Bisphosphoglycerate (BPG)
2. ADP is then phosphorylated 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 phosphorylated, this time at the expense of PEP by the enzyme pyruvate kinase to yield another molecule of ATP and pyruvate. This step is regulated by the energy in the cell. The higher the energy of the cell the more inhibited pyruvate kinase becomes. Indicators of high energy levels within the cell are high concentrations of ATP, Acetyl-CoA, Alanine, and cAMP.

Because Glucose is split to yield two molecules of D-Glyceraldehyde-3-phosphate, each step in the "Pay Off" phase occurs twice per molecule of glucose.

Beta-Oxidation

The best source of energy for eukaryotic organisms are fats. Glucose offers a ratio 6.3 moles of ATP per carbon while saturated fatty acids offer 8.1 ATP per carbon. Also the complete oxidation of fats yields enormous amounts of water for those organisms that do not have adequate access to drinkable water. Camels and killer whales are good example of this, they obtain their water requirements from the complete oxidation of fats.



Video 16.4.2: Fatty acid metabolism / beta oxidation / β -Oxidation

There are four distinct stages in the oxidation of fatty acids. Fatty acid degradation takes place within the mitochondria and requires the help of several different enzymes. In order for fatty acids to enter the mitochondria the assistance of two carrier proteins is required, Carnitine acyltransferase I and II. It is also interesting to note the similarities between the four steps of beta-oxidation and the later four steps of the [TCA cycle](#).

Entry into Beta-oxidation

Most fats stored in eukaryotic organisms are stored as triglycerides as seen below. In order to enter into beta-oxidation bonds must be broken usually with the use of a Lipase. The end result of these broken bonds are a glycerol molecule and three fatty acids in the case of triglycerides. Other lipids are capable of being degraded as well.

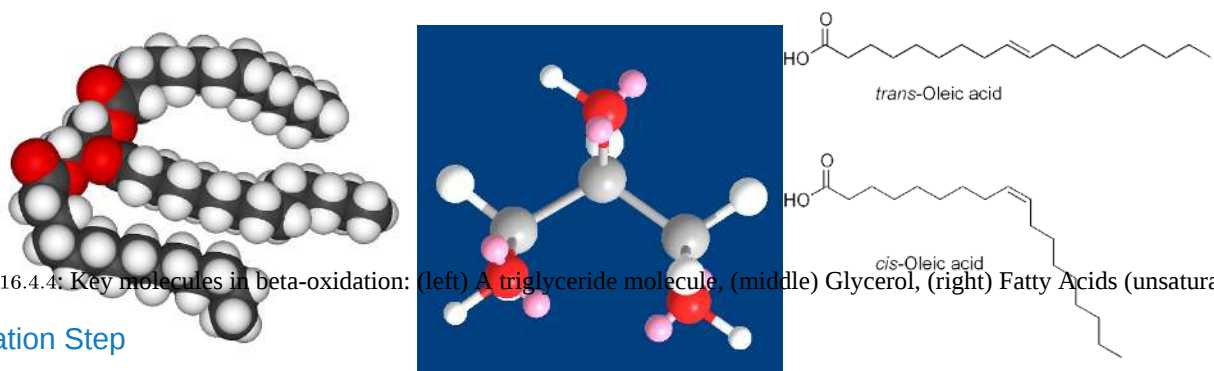


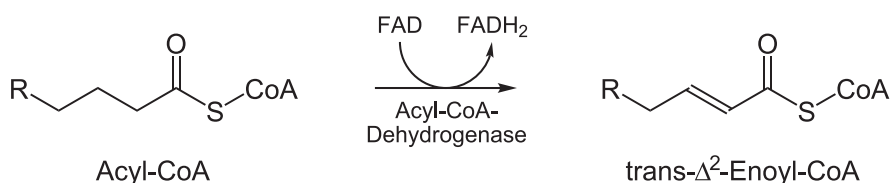
Figure 16.4.4: Key molecules in beta-oxidation: (left) A triglyceride molecule, (middle) Glycerol, (right) Fatty Acids (unsaturated)

Activation Step

- Once the triglycerides are broken down into glycerol and fatty acids they must be activated before they can enter into the mitochondria and proceed on with beta-oxidation. This is done by Acyl-CoA synthetase to yield fatty acyl-CoA.
- After the fatty acid has been acylated it is now ready to enter into the mitochondria.
- There are two carrier proteins (Carnitine acyltransferase I and II), one located on the outer membrane and one on the inner membrane of the mitochondria. Both are required for entry of the Acyl-CoA into the mitochondria.
- Once inside the mitochondria the fatty acyl-CoA can enter into beta-oxidation.

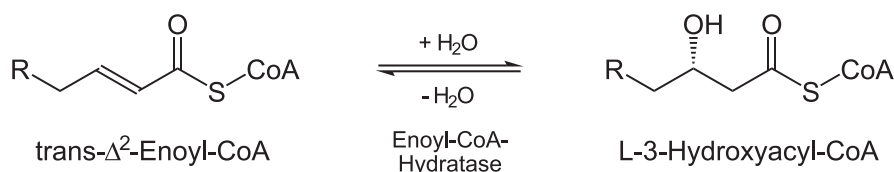
Oxidation Step

A fatty acyl-CoA is oxidized by Acyl-CoA dehydrogenase to yield a trans alkene. This is done with the aid of an [FAD] prosthetic group.



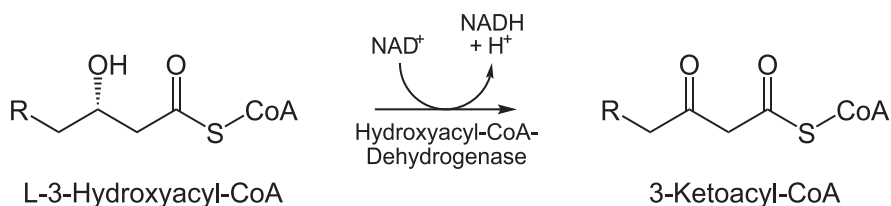
Hydration Step

The trans alkene is then **hydrated** with the help of Enoyl-CoA hydratase



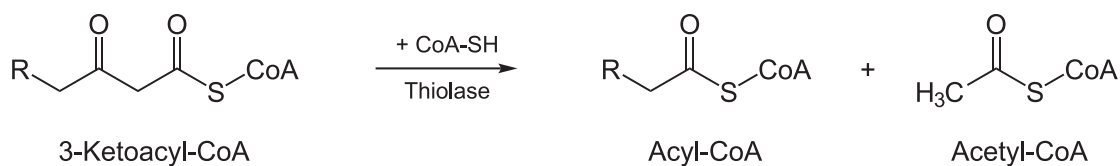
Oxidation Step

The alcohol of the hydroxyacyl-CoA is then **oxidized** by NAD^+ to a carbonyl with the help of Hydroxyacyl-CoA dehydrogenase. NAD^+ is used to oxidize the alcohol rather than [FAD] because NAD^+ is capable of the alcohol while [FAD] is not.



Cleavage

Finally acetyl-CoA is cleaved off with the help of Thiolase to yield an Acyl-CoA that is two carbons shorter than before. The cleaved acetyl-CoA can then enter into the TCA and ETC because it is already within the mitochondria.



Summary

Acetyl-CoA is formed from the breakdown of carbohydrates, lipids, and proteins. It is used in many biochemical pathways.

References

1. Garrett, H., Reginald and Charles Grisham. Biochemistry. Boston: Twayne Publishers, 2008.
2. Raven, Peter. Biology. Boston: Twayne Publishers, 2005.

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16.5: Stage III of Catabolism

Learning Objectives

- Describe the reactions of the citric acid cycle.
- Describe the function of the citric acid cycle and identify the products produced.
- Describe the role of the electron transport chain in energy metabolism.
- Describe the role of oxidative phosphorylation in energy metabolism.

The acetyl group enters a cyclic sequence of reactions known collectively as the **citric acid cycle (or Krebs cycle or tricarboxylic acid [TCA] cycle)**. The cyclical design of this complex series of reactions, which bring about the oxidation of the acetyl group of acetyl-CoA to carbon dioxide and water, was first proposed by Hans Krebs in 1937. (He was awarded the 1953 Nobel Prize in Physiology or Medicine.) Acetyl-CoA's entrance into the citric acid cycle is the beginning of stage III of catabolism. The citric acid cycle produces adenosine triphosphate (ATP), reduced nicotinamide adenine dinucleotide (NADH), reduced flavin adenine dinucleotide (FADH₂), 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 16.5.1). 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 16.5.1, 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.

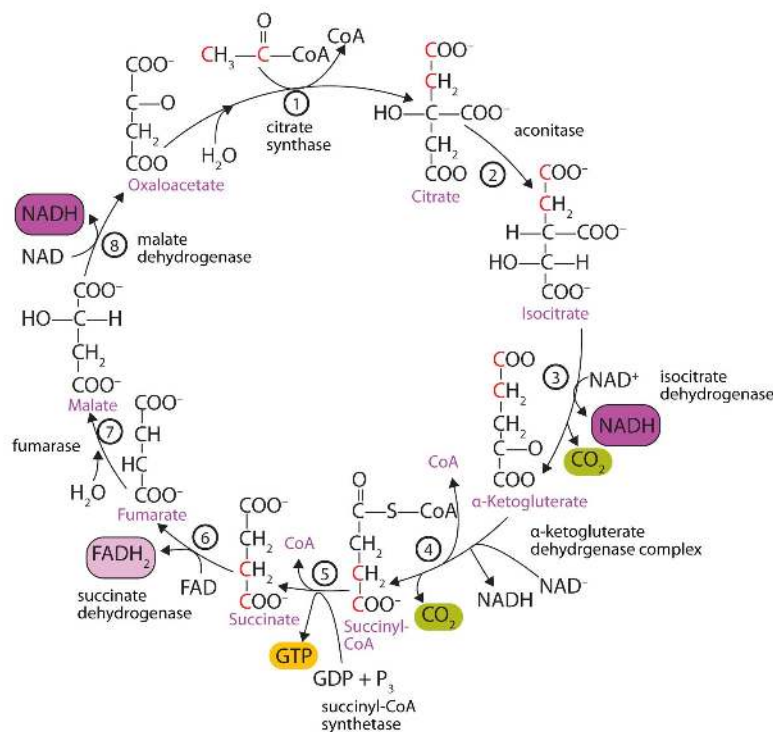


Figure 16.5.1: Reactions of the Citric Acid Cycle

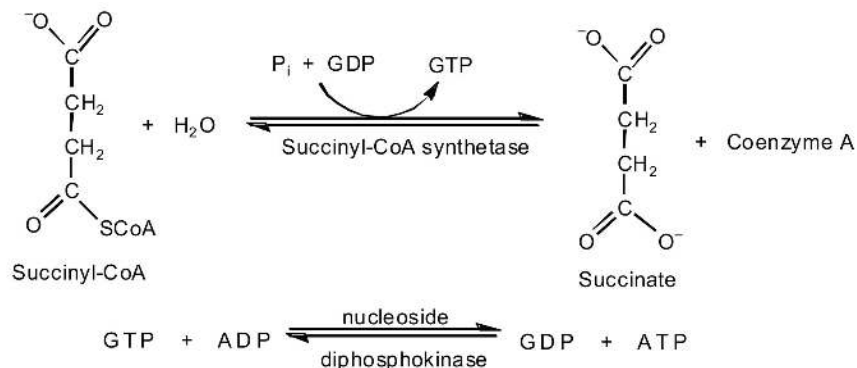
- In the first step, acetyl-CoA enters the citric acid cycle, and the acetyl group is transferred onto oxaloacetate, yielding citrate. Note that this step releases coenzyme A. The reaction is catalyzed by *citrate synthase*.
- In the next step, *aconitase* catalyzes the isomerization of citrate to isocitrate. In this reaction, a tertiary alcohol, which cannot be oxidized, is converted to a secondary alcohol, which can be oxidized in the next step.
- 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.

- The fourth step is another oxidative decarboxylation. This time α -ketoglutarate is converted to succinyl-CoA, and another molecule of NAD^+ is reduced to NADH. The *α -ketoglutarate dehydrogenase complex* catalyzes this reaction. This is the only irreversible reaction in the citric acid cycle. As such, it prevents the cycle from operating in the reverse direction, in which acetyl-CoA would be synthesized from carbon dioxide.

So far, in the first four steps, two carbon atoms have entered the cycle as an acetyl group, and two carbon atoms have been released as molecules of carbon dioxide. The remaining reactions of the citric acid cycle use the four carbon atoms of the succinyl group to resynthesize a molecule of oxaloacetate, which is the compound needed to combine with an incoming acetyl group and begin another round of the cycle.

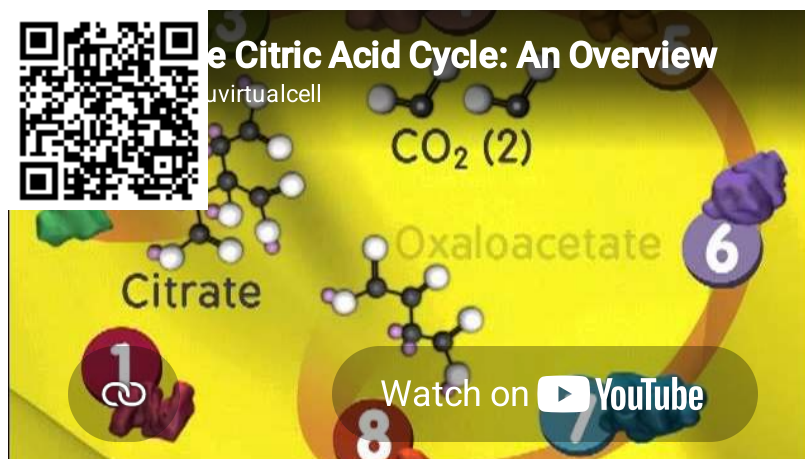
In the fifth reaction, the energy released by the hydrolysis of the high-energy thioester bond of succinyl-CoA is used to form guanosine triphosphate (GTP) from guanosine diphosphate (GDP) and inorganic phosphate in a reaction catalyzed by *succinyl-CoA synthetase*. This step is the only reaction in the citric acid cycle that directly forms a high-energy phosphate compound. GTP can readily transfer its terminal phosphate group to adenosine diphosphate (ADP) to generate ATP in the presence of *nucleoside diphosphokinase*.



Succinate dehydrogenase then catalyzes the removal of two hydrogen atoms from succinate, forming fumarate. This oxidation-reduction reaction uses flavin adenine dinucleotide (FAD), rather than NAD^+ , as the oxidizing agent. Succinate dehydrogenase is the only enzyme of the citric acid cycle located within the inner mitochondrial membrane. We will see soon the importance of this.

In the following step, a molecule of water is added to the double bond of fumarate to form L-malate in a reaction catalyzed by *fumarase*.

One revolution of the cycle is completed with the oxidation of L-malate to oxaloacetate, brought about by *malate dehydrogenase*. This is the third oxidation-reduction reaction that uses NAD^+ as the oxidizing agent. Oxaloacetate can accept an acetyl group from acetyl-CoA, allowing the cycle to begin again.



Video 16.5.1: "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 16.5.2). 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.

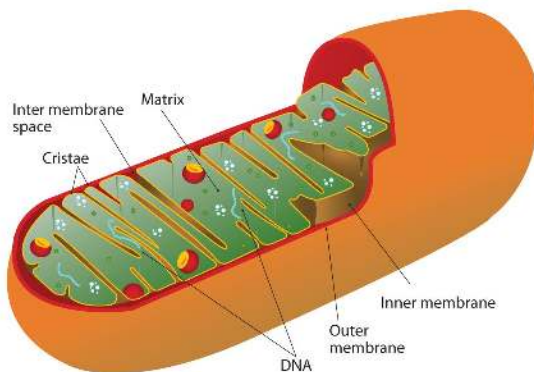


Figure 16.5.2: Respiration

Cellular respiration occurs in the mitochondria

Figure 16.5.2 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 16.5.3 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.

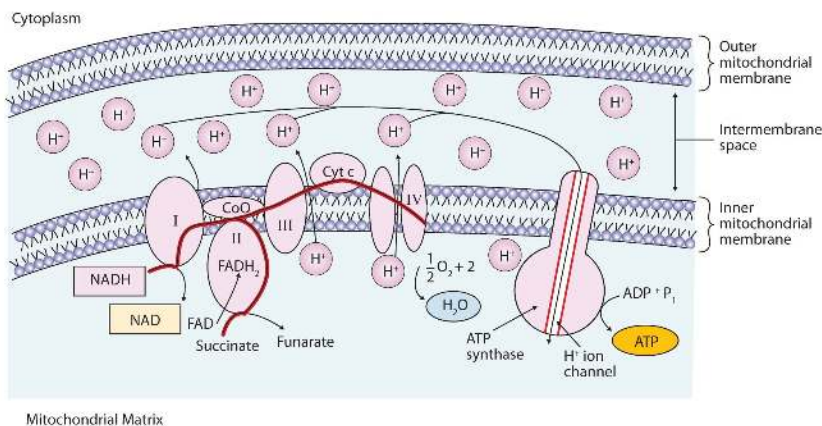
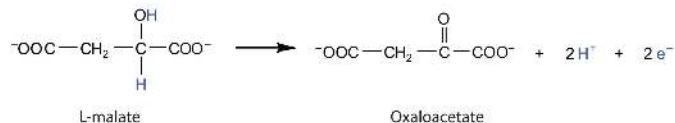


Figure 16.5.3: The Mitochondrial Electron

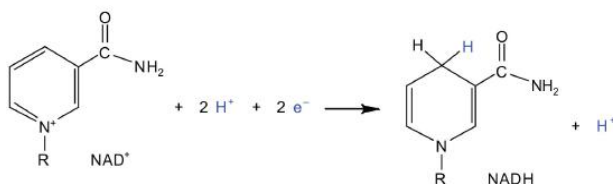
Transport Chain and ATP Synthase. The red line shows the path of electrons.

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:*

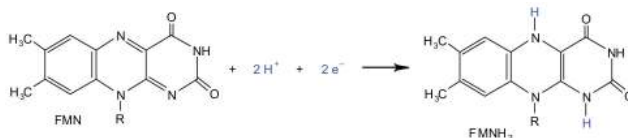


In the oxidation half-reaction, two hydrogen (H^+) ions and two electrons are removed from the substrate. In the reduction half-reaction, the NAD^+ molecule accepts both of those electrons and one of the H^+ ions. The other H^+ ion is transported from the matrix, across the inner mitochondrial membrane, 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:



- Reduction half-reaction:



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:



- Reduction half-reaction:



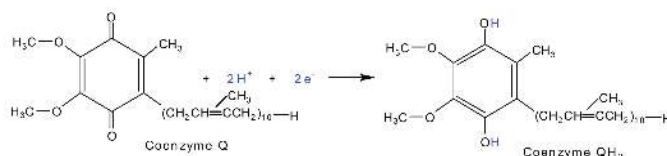
Electrons from complexes I and II are then transferred from the $Fe \cdot S$ protein to coenzyme Q (CoQ), a mobile electron carrier that acts as the electron shuttle between complexes I or II and complex III.

Coenzyme Q is also called ubiquinone because it is ubiquitous in living systems.

- Oxidation half-reaction:



- Reduction half-reaction:

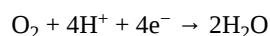


Complexes III and IV include several iron-containing proteins known as **cytochromes**. The iron in these enzymes is located in substructures known as iron porphyrins (Figure 16.5.4). Like the Fe-S centers, the characteristic feature of the cytochromes is the ability of their iron atoms to exist as either 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:



- Reduction half-reaction:



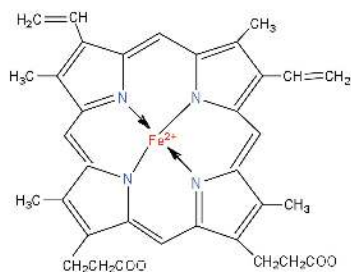


Figure 16.5.4: An Iron Porphyrin. Iron porphyrins are present in cytochromes as well as in myoglobin and hemoglobin.



Video 16.5.2:: 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; for 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 FADH₂ 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 16.5.3, 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 16.5.1 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 16.5.1: Maximum Yield of ATP from the Complete Oxidation of 1 mol of Acetyl-CoA

Reaction	Comments	Yield of ATP (moles)
Isocitrate $\rightarrow$ α -ketoglutarate + CO_2	produces 1 mol NADH	
α -ketoglutarate $\rightarrow$ succinyl-CoA + CO_2	produces 1 mol NADH	
Succinyl-CoA $\rightarrow$ succinate	produces 1 mol GTP	+1
Succinate $\rightarrow$ fumarate	produces 1 mol FADH_2	
Malate $\rightarrow$ oxaloacetate	produces 1 mol NADH	
1 FADH_2 from the citric acid cycle	yields 2 mol ATP	+2
3 NADH from the citric acid cycle	yields 3 mol ATP/NADH	+9
Net yield of ATP:		+12

✓ Example 16.5.1

Two carbon atoms are fed into the citric acid cycle as acetyl-CoA. In what form are two carbon atoms removed from the cycle?

Solution

as carbon dioxide

✓ Example 16.5.2

Replace each question mark with the correct compound.

- ? $\xrightarrow{\text{aconitase}}$ isocitrate
- ? + ? $\xrightarrow{\text{citrate synthase}}$ citrate + coenzyme A
- fumarate $\xrightarrow{\text{fumarase}}$?
- isocitrate + NAD^+ $\rightarrow$ α -ketoglutarate + NADH + CO_2

Solution

- citrate
- oxaloacetate + acetyl-CoA
- malate
- α -ketoglutarate hydrogenase complex

? Exercise 16.5.1

Replace each question mark with the correct compound.

- malate + NAD^+ $\rightarrow$ oxaloacetate + NADH
- ? + ? $\xrightarrow{\text{nucleoside diphosphokinase}}$ GDP + ATP
- succinyl-CoA $\xrightarrow{\text{succinyl-CoA synthetase}}$? + ?
- succinate + FAD $\xrightarrow{\text{succinate dehydrogenase}}$? + FADH_2

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 FADH₂ are produced.
- The reduced coenzymes (NADH and FADH₂) 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 FADH₂ reoxidized, 1.5–2 molecules of ATP are produced.

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16.6: Stage II of Carbohydrate Catabolism

Learning Objectives

- Describe the function of glycolysis and identify its major products.
- Describe how the presence or absence of oxygen determines what happens to the pyruvate and the NADH that are produced in glycolysis.
- Determine the amount of ATP produced by the oxidation of glucose in the presence and absence of oxygen.

In stage II of catabolism, the metabolic pathway known as glycolysis converts glucose into two molecules of pyruvate (a three-carbon compound with three carbon atoms) with the corresponding production of adenosine triphosphate (ATP). The individual reactions in glycolysis were determined during the first part of the 20th century. It was the first metabolic pathway to be elucidated, in part because the participating enzymes are found in soluble form in the cell and are readily isolated and purified. The pathway is structured so that the product of one enzyme-catalyzed reaction becomes the substrate of the next. The transfer of intermediates from one enzyme to the next occurs by diffusion.

Steps in Glycolysis

The 10 reactions of glycolysis, summarized in Figures 16.6.1 and 16.6.2, can be divided into two phases. In the first 5 reactions—phase I—glucose is broken down into two molecules of glyceraldehyde 3-phosphate. In the last five reactions—phase II—each glyceraldehyde 3-phosphate is converted into pyruvate, and ATP is generated. Notice that all the intermediates in glycolysis are phosphorylated and contain either six or three carbon atoms.

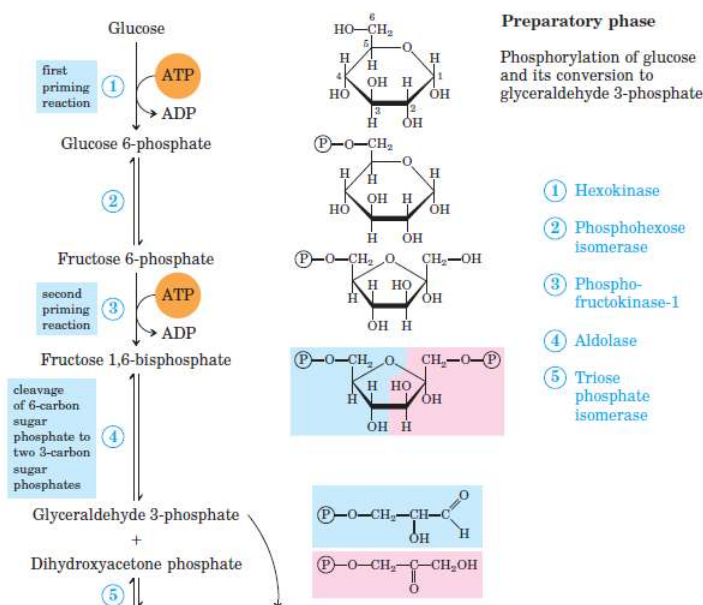


Figure 16.6.1: Phase 1 (preparatory phase) of Glycolysis

- When glucose enters a cell, it is immediately phosphorylated to form glucose 6-phosphate, in the first reaction of phase I. The phosphate donor in this reaction is ATP, and the enzyme—which requires magnesium ions for its activity—is *hexokinase*. In this reaction, ATP is being used rather than being synthesized. The presence of such a reaction in a catabolic pathway that is supposed to *generate* energy may surprise you. However, in addition to activating the glucose molecule, this initial reaction is essentially irreversible, an added benefit that keeps the overall process moving in the right direction. Furthermore, the addition of the negatively charged phosphate group prevents the intermediates formed in glycolysis from diffusing through the cell membrane, as neutral molecules such as glucose can do.
- In the next reaction, *phosphoglucose isomerase* catalyzes the isomerization of glucose 6-phosphate to fructose 6-phosphate. This reaction is important because it creates a primary alcohol, which can be readily phosphorylated.
- The subsequent phosphorylation of fructose 6-phosphate to form fructose 1,6-bisphosphate is catalyzed by *phosphofructokinase*, which requires magnesium ions for activity. ATP is again the phosphate donor.
- Fructose 1,6-bisphosphate is enzymatically cleaved by *aldolase* to form two triose phosphates: dihydroxyacetone phosphate and glyceraldehyde 3-phosphate.

- Isomerization of dihydroxyacetone phosphate into a second molecule of glyceraldehyde 3-phosphate is the final step in phase I. The enzyme catalyzing this reaction is *triose phosphate isomerase*.

When a molecule contains two phosphate groups on different carbon atoms, the convention is to use the prefix *bis*. When the two phosphate groups are bonded to each other on the same carbon atom (for example, adenosine diphosphate [ADP]), the prefix is *di*.

In steps 4 and 5, aldolase and triose phosphate isomerase effectively convert one molecule of fructose 1,6-bisphosphate into two molecules of glyceraldehyde 3-phosphate. Thus, phase I of glycolysis requires energy in the form of two molecules of ATP and releases none of the energy stored in glucose.

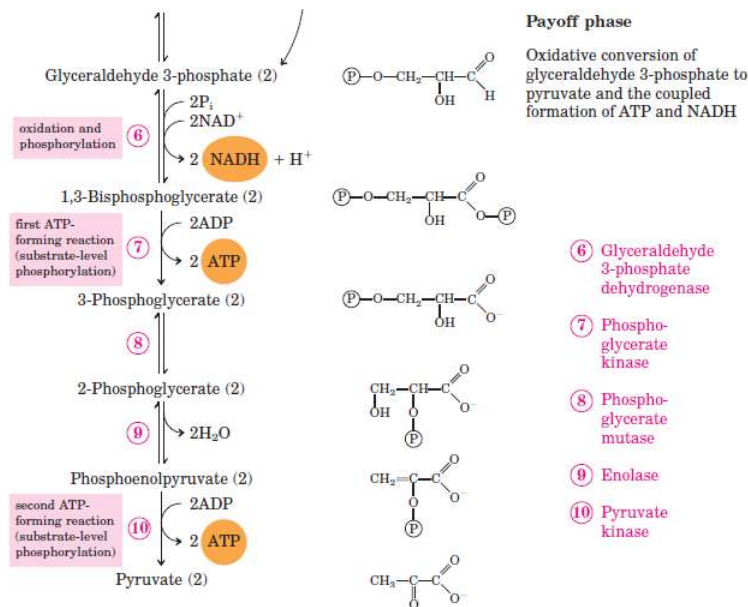


Figure 16.6.2: Phase 2 (payoff phase) of Glycolysis

In the initial step of phase II (Figure 16.6.2), glyceraldehyde 3-phosphate is both oxidized and phosphorylated in a reaction catalyzed by *glyceraldehyde-3-phosphate dehydrogenase*, an enzyme that requires nicotinamide adenine dinucleotide (NAD^+) as the oxidizing agent and inorganic phosphate as the phosphate donor. In the reaction, NAD^+ is reduced to reduced nicotinamide adenine dinucleotide (NADH), and 1,3-bisphosphoglycerate (BPG) is formed.

- BPG has a high-energy phosphate bond (Table 16.6.1) joining a phosphate group to C1. This phosphate group is now transferred directly to a molecule of ADP, thus forming ATP and 3-phosphoglycerate. The enzyme that catalyzes the reaction is **phosphoglycerate kinase**, which, like all other kinases, requires magnesium ions to function. This is the first reaction to produce ATP in the pathway. Because the ATP is formed by a direct transfer of a phosphate group from a metabolite to ADP—that is, from one substrate to another—the process is referred to as substrate-level phosphorylation, to distinguish it from the *oxidative phosphorylation* discussed in Section 20.4.
- In the next reaction, the phosphate group on 3-phosphoglycerate is transferred from the OH group of C3 to the OH group of C2, forming 2-phosphoglycerate in a reaction catalyzed by *phosphoglyceromutase*.
- A dehydration reaction, catalyzed by *enolase*, forms phosphoenolpyruvate (PEP), another compound possessing a high-energy phosphate group.
- The final step is irreversible and is the second reaction in which substrate-level phosphorylation occurs. The phosphate group of PEP is transferred to ADP, with one molecule of ATP being produced per molecule of PEP. The reaction is catalyzed by *pyruvate kinase*, which requires both magnesium and potassium ions to be active.

Table 16.6.1: Maximum Yield of ATP from the Complete Oxidation of 1 Mol of Glucose

Reaction	Comments	Yield of ATP (moles)
glucose $\rightarrow$ glucose 6-phosphate	consumes 1 mol ATP	-1

Reaction	Comments	Yield of ATP (moles)
fructose 6-phosphate → fructose 1,6-bisphosphate	consumes 1 mol ATP	-1
glyceraldehyde 3-phosphate → BPG	produces 2 mol of cytoplasmic NADH	
BPG → 3-phosphoglycerate	produces 2 mol ATP	+2
phosphoenolpyruvate → pyruvate	produces 2 mol ATP	+2
pyruvate → acetyl-CoA + CO ₂	produces 2 mol NADH	
isocitrate → α-ketoglutarate + CO ₂	produces 2 mol NADH	
α-ketoglutarate → succinyl-CoA + CO ₂	produces 2 mol NADH	
succinyl-CoA → succinate	produces 2 mol GTP	+2
succinate → fumarate	produces 2 mol FADH ₂	
malate → oxaloacetate	produces 2 mol NADH	
2 cytoplasmic NADH from glycolysis	yields 2–3 mol ATP per NADH (depending on tissue)	+4 to +6
2 NADH from the oxidation of pyruvate	yields 3 mol ATP per NADH	+6
2 FADH ₂ from the citric acid cycle	yields 2 ATP per FADH ₂	+4
3 NADH from the citric acid cycle	yields 3 ATP per NADH	+18
Net yield of ATP:		+36 to +38

In phase II, two molecules of glyceraldehyde 3-phosphate are converted to two molecules of pyruvate, along with the production of four molecules of ATP and two molecules of NADH.

✓ To Your Health: Diabetes

Although medical science has made significant progress against diabetes, it continues to be a major health threat. Some of the serious complications of diabetes are as follows:

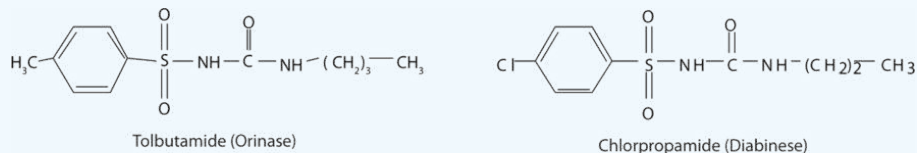
- It is the leading cause of lower limb amputations in the United States.
- It is the leading cause of blindness in adults over age 20.
- It is the leading cause of kidney failure.
- It increases the risk of having a heart attack or stroke by two to four times.

Because a person with diabetes is unable to use glucose properly, excessive quantities accumulate in the blood and the urine. Other characteristic symptoms are constant hunger, weight loss, extreme thirst, and frequent urination because the kidneys excrete large amounts of water in an attempt to remove excess sugar from the blood.

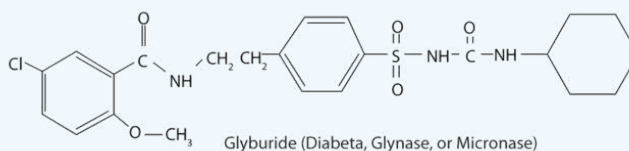
There are two types of diabetes. In immune-mediated diabetes, insufficient amounts of insulin are produced. This type of diabetes develops early in life and is also known as *Type 1 diabetes*, as well as insulin-dependent or juvenile-onset diabetes. Symptoms are rapidly reversed by the administration of insulin, and Type 1 diabetics can lead active lives provided they receive insulin as needed. Because insulin is a protein that is readily digested in the small intestine, it cannot be taken orally and must be injected at least once a day.

In Type 1 diabetes, insulin-producing cells of the pancreas are destroyed by the body's immune system. Researchers are still trying to find out why. Meanwhile, they have developed a simple blood test capable of predicting who will develop Type 1 diabetes several years before the disease becomes apparent. The blood test reveals the presence of antibodies that destroy the body's insulin-producing cells.

Type 2 diabetes, also known as noninsulin-dependent or adult-onset diabetes, is by far the more common, representing about 95% of diagnosed diabetic cases. (This translates to about 16 million Americans.) Type 2 diabetics usually produce sufficient amounts of insulin, but either the insulin-producing cells in the pancreas do not release enough of it, or it is not used properly because of defective insulin receptors or a lack of insulin receptors on the target cells. In many of these people, the disease can be controlled with a combination of diet and exercise alone. For some people who are overweight, losing weight is sufficient to bring their blood sugar level into the normal range, after which medication is not required if they exercise regularly and eat wisely.



First-Generation Antidiabetic Drugs



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 16.6.2. The conversion to lactate or ethanol under anaerobic conditions allows for the reoxidation of NADH to NAD⁺ in the absence of oxygen.

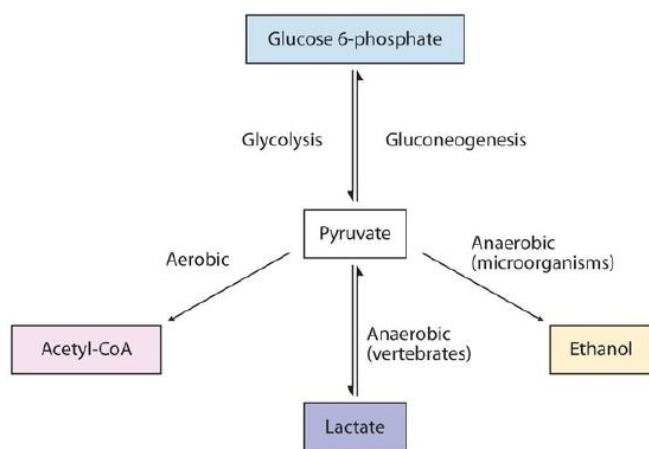


Figure 16.6.2: Metabolic Fates of Pyruvate

ATP Yield from Glycolysis

The net energy yield from anaerobic glucose metabolism can readily be calculated in moles of ATP. In the initial phosphorylation of glucose (step 1), 1 mol of ATP is expended, along with another in the phosphorylation of fructose 6-phosphate (step 3). In step 7, 2 mol of BPG (recall that 2 mol of 1,3-BPG are formed for each mole of glucose) are converted to 2 mol of 3-phosphoglycerate, and 2 mol of ATP are produced. In step 10, 2 mol of pyruvate and 2 mol of ATP are formed per mole of glucose.

For every mole of glucose degraded, 2 mol of ATP are initially consumed and 4 mol of ATP are ultimately produced. The net production of ATP is thus 2 mol for each mole of glucose converted to lactate or ethanol. If 7.4 kcal of energy is conserved per mole of ATP produced, and the total amount of energy that can theoretically be obtained from the complete oxidation of 1 mol of glucose is 670 kcal (as stated in the chapter introduction), the energy conserved in the anaerobic catabolism of glucose to two molecules of lactate (or ethanol) is as follows:

$$\frac{2 \times 7.4 \text{ kcal}}{670 \text{ kcal}} \times 100 = 2.2\%$$

Thus anaerobic cells extract only a very small fraction of the total energy of the glucose molecule.

Contrast this result with the amount of energy obtained when glucose is completely oxidized to carbon dioxide and water through glycolysis, the citric acid cycle, the electron transport chain, and oxidative phosphorylation as summarized in Table 16.6.1. 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 (FADH₂), which then feeds the electrons into the electron transport chain. This route lowers the yield of ATP to 1.5–2 molecules of ATP, rather than the usual 2.5–3 molecules. A more efficient transport system is found in liver, heart, and kidney cells where the formation of one cytoplasmic NADH molecule results in the formation of one mitochondrial NADH molecule, which leads to the formation of 2.5–3 molecules of ATP. The total amount of energy conserved in the aerobic catabolism of glucose in the liver is as follows:

$$\frac{38 \times 7.4 \text{ kcal}}{670 \text{ kcal}} \times 100 = 42\%$$

Conservation of 42% of the total energy released compares favorably with the efficiency of any machine. In comparison, automobiles are only about 20%–25% efficient in using the energy released by the combustion of gasoline.

As indicated earlier, the 58% of released energy that is not conserved enters the surroundings (that is, the cell) as heat that helps to maintain body temperature. If we are exercising strenuously and our metabolism speeds up to provide the energy needed for muscle contraction, more heat is produced. We begin to perspire to dissipate some of that heat. As the perspiration evaporates, the excess heat is carried away from the body by the departing water vapor.

Summary

- The monosaccharide glucose is broken down through a series of enzyme-catalyzed reactions known as glycolysis.
- For each molecule of glucose that is broken down, two molecules of pyruvate, two molecules of ATP, and two molecules of NADH are produced.
- In the absence of oxygen, pyruvate is converted to lactate, and NADH is reoxidized to NAD⁺. In the presence of oxygen, pyruvate is converted to acetyl-CoA and then enters the citric acid cycle.
- More ATP can be formed from the breakdown of glucose when oxygen is present.

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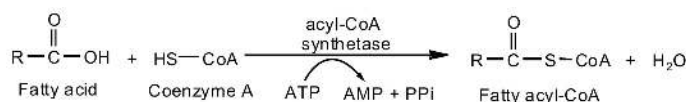
16.7: Stage II of Lipid Catabolism

Learning Objectives

- To describe the reactions needed to completely oxidize a fatty acid to carbon dioxide and water.

Like glucose, the fatty acids released in the digestion of triglycerides and other lipids are broken down in a series of sequential reactions accompanied by the gradual release of usable energy. Some of these reactions are oxidative and require nicotinamide adenine dinucleotide (NAD⁺) and flavin adenine dinucleotide (FAD). The enzymes that participate in fatty acid catabolism are located in the mitochondria, along with the enzymes of the citric acid cycle, the electron transport chain, and oxidative phosphorylation. This localization of enzymes in the mitochondria is of the utmost importance because it facilitates efficient utilization of energy stored in fatty acids and other molecules.

Fatty acid oxidation is initiated on the outer mitochondrial membrane. There the fatty acids, which like carbohydrates are relatively inert, must first be activated by conversion to an energy-rich fatty acid derivative of coenzyme A called *fatty acyl-coenzyme A* (CoA). The activation is catalyzed by *acyl-CoA synthetase*. For each molecule of fatty acid activated, one molecule of coenzyme A and one molecule of adenosine triphosphate (ATP) are used, equaling a net utilization of the two high-energy bonds in one ATP molecule (which is therefore converted to adenosine monophosphate [AMP] rather than adenosine diphosphate [ADP]):



The fatty acyl-CoA diffuses to the inner mitochondrial membrane, where it combines with a carrier molecule known as carnitine in a reaction catalyzed by *carnitine acyltransferase*. The acyl-carnitine derivative is transported into the mitochondrial matrix and converted back to the fatty acyl-CoA.

Steps in the β-Oxidation of Fatty Acids

Further oxidation of the fatty acyl-CoA occurs in the mitochondrial matrix via a sequence of four reactions known collectively as β-oxidation because the β-carbon undergoes successive oxidations in the progressive removal of two carbon atoms from the carboxyl end of the fatty acyl-CoA (Figure 16.7.1).

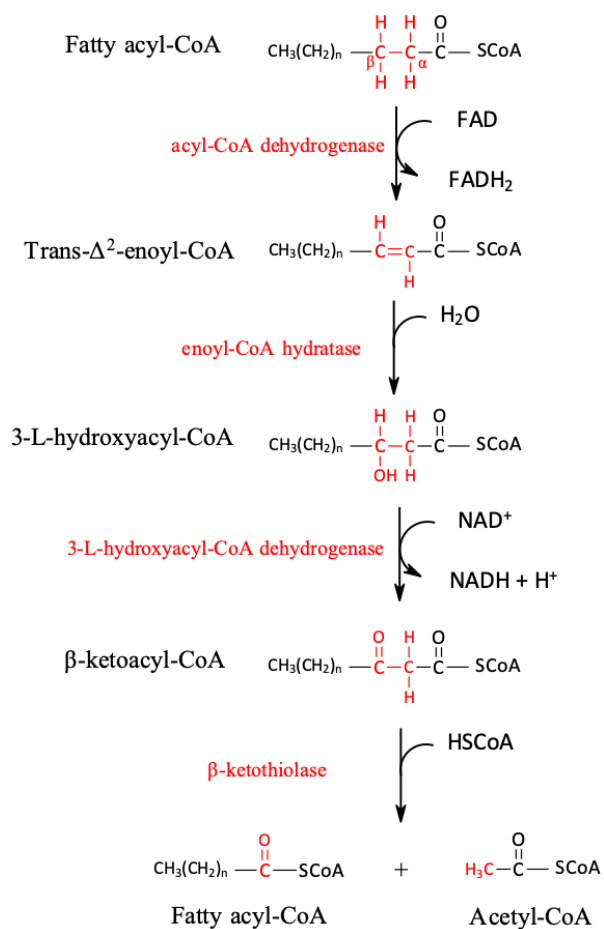


Figure 16.7.1: Fatty Acid Oxidation. The fatty acyl-CoA formed in the final step becomes the substrate for the first step in the next round of β -oxidation. β -oxidation continues until two acetyl-CoA molecules are produced in the final step.

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 (FADH₂).

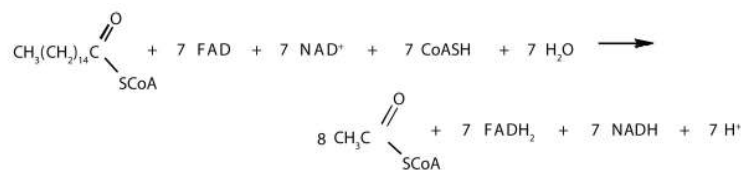
The FADH₂ is reoxidized back to FAD via the [electron transport chain](#) that supplies energy to form 1.5–2 molecules of ATP.

Next, the *trans*-alkene is hydrated to form a secondary alcohol in a reaction catalyzed by *enoyl-CoA hydratase*. The enzyme forms only the L-isomer.

The secondary alcohol is then oxidized to a ketone by *β -hydroxyacyl-CoA dehydrogenase*, with NAD⁺ acting as the oxidizing agent. The reoxidation of each molecule of NADH to NAD⁺ by the electron transport chain furnishes 2.5–3 molecules of ATP.

The final reaction is cleavage of the β -ketoacyl-CoA by a molecule of coenzyme A. The products are acetyl-CoA and a fatty acyl-CoA that has been shortened by two carbon atoms. The reaction is catalyzed by *thiolase*.

The shortened fatty acyl-CoA is then degraded by repetitions of these four steps, each time releasing a molecule of acetyl-CoA. The overall equation for the β -oxidation of palmitoyl-CoA (16 carbon atoms) is as follows:

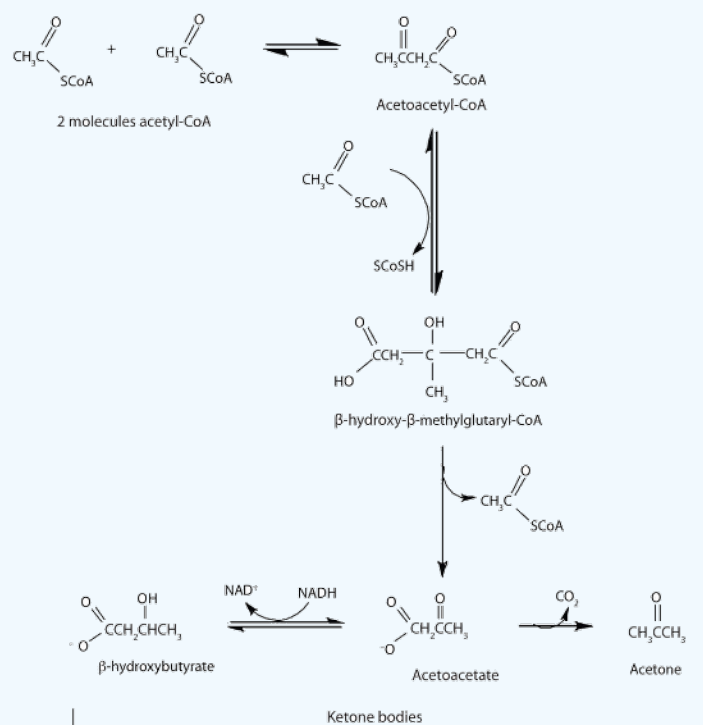


Because each shortened fatty acyl-CoA cycles back to the beginning of the pathway, β -oxidation is sometimes referred to as the fatty acid spiral.

The fate of the acetyl-CoA obtained from fatty acid oxidation depends on the needs of an organism. It may enter the citric acid cycle and be oxidized to produce energy, it may be used for the formation of water-soluble derivatives known as ketone bodies, or it may serve as the starting material for the synthesis of fatty acids. For more information about the citric acid cycle, see [Section 20.4](#).

✓ Looking Closer: Ketone Bodies

In the liver, most of the acetyl-CoA obtained from fatty acid oxidation is oxidized by the citric acid cycle. However, some of the acetyl-CoA is used to synthesize a group of compounds known as *ketone bodies*: acetoacetate, β -hydroxybutyrate, and acetone. Two acetyl-CoA molecules combine, in a reversal of the final step of β -oxidation, to produce acetoacetyl-CoA. The acetoacetyl-CoA reacts with another molecule of acetyl-CoA and water to form β -hydroxy- β -methylglutaryl-CoA, which is then cleaved to acetoacetate and acetyl-CoA. Most of the acetoacetate is reduced to β -hydroxybutyrate, while a small amount is decarboxylated to carbon dioxide and acetone.



The acetoacetate and β -hydroxybutyrate synthesized by the liver are released into the blood for use as a metabolic fuel (to be converted back to acetyl-CoA) by other tissues, particularly the kidney and the heart. Thus, during prolonged starvation, ketone bodies provide about 70% of the energy requirements of the brain. Under normal conditions, the kidneys excrete about 20 mg of ketone bodies each day, and the blood levels are maintained at about 1 mg of ketone bodies per 100 mL of blood.

In starvation, diabetes mellitus, and certain other physiological conditions in which cells do not receive sufficient amounts of carbohydrate, the rate of fatty acid oxidation increases to provide energy. This leads to an increase in the concentration of acetyl-CoA. The increased acetyl-CoA cannot be oxidized by the citric acid cycle because of a decrease in the concentration of oxaloacetate, which is diverted to glucose synthesis. In response, the rate of ketone body formation in the liver increases further, to a level much higher than can be used by other tissues. The excess ketone bodies accumulate in the blood and the urine, a condition referred to as *ketosis*. When the acetone in the blood reaches the lungs, its volatility causes it to be expelled in the breath. The sweet smell of acetone, a characteristic of ketosis, is frequently noticed on the breath of severely diabetic patients.

Because two of the three kinds of ketone bodies are weak acids, their presence in the blood in excessive amounts overwhelms the blood buffers and causes a marked decrease in blood pH (to 6.9 from a normal value of 7.4). This decrease in pH leads to a

serious condition known as *acidosis*. One of the effects of acidosis is a decrease in the ability of hemoglobin to transport oxygen in the blood. In moderate to severe acidosis, breathing becomes labored and very painful. The body also loses fluids and becomes dehydrated as the kidneys attempt to get rid of the acids by eliminating large quantities of water. The lowered oxygen supply and dehydration lead to depression; even mild acidosis leads to lethargy, loss of appetite, and a generally run-down feeling. Untreated patients may go into a coma. At that point, prompt treatment is necessary if the person's life is to be saved.

ATP Yield from Fatty Acid Oxidation

The amount of ATP obtained from fatty acid oxidation depends on the size of the fatty acid being oxidized. For our purposes here, we'll study palmitic acid, a saturated fatty acid with 16 carbon atoms, as a typical fatty acid in the human diet. Calculating its energy yield provides a model for determining the ATP yield of all other fatty acids.

The breakdown by an organism of 1 mol of palmitic acid requires 1 mol of ATP (for activation) and forms 8 mol of acetyl-CoA. Recall from Table 20.4.1 that each mole of acetyl-CoA metabolized by the citric acid cycle yields 10 mol of ATP. The complete degradation of 1 mol of palmitic acid requires the β -oxidation reactions to be repeated seven times. Thus, 7 mol of NADH and 7 mol of FADH_2 are produced. Reoxidation of these compounds through respiration yields 2.5–3 and 1.5–2 mol of ATP, respectively. The energy calculations can be summarized as follows:

ATP Yield from Fatty Acid Oxidation

1 mol of ATP is split to AMP and 2P_i	-2 ATP
8 mol of acetyl-CoA formed (8×12)	96 ATP
7 mol of FADH_2 formed (7×2)	14 ATP
7 mol of NADH formed (7×3)	21 ATP
Total	129 ATP

The number of times β -oxidation is repeated for a fatty acid containing n carbon atoms is $n/2 - 1$ because the final turn yields two acetyl-CoA molecules.

The combustion of 1 mol of palmitic acid releases a considerable amount of energy:



The percentage of this energy that is conserved by the cell in the form of ATP is as follows:

$$\frac{\text{energy conserved}}{\text{total energy available}} \times 100 = \frac{(129 \text{ ATP})(7.4 \text{ kcal/ATP})}{2,340 \text{ kcal}} \times 100 = 41\%$$

The efficiency of fatty acid metabolism is comparable to that of carbohydrate metabolism, which we calculated to be 42%. For more information about the efficiency of fatty acid metabolism, see II of Carbohydrate Catabolism" data-cke-saved-href="/Bookshelves/Introductory_Chemistry/Basics_of_General_Organic_and_Biological_Chemistry_(Ball_et_al.)/20:_Energy_Metabolism/20.05:_Stage_II_of_Carbohydrate_Catabolism" href="/Bookshelves/Introductory_Chemistry/Basics_of_General_Organic_and_Biological_Chemistry_(Ball_et_al.)/20:_Energy_Metabolism/20.05:_Stage_II_of_Carbohydrate_Catabolism" data-quail-id="91">Section 20.5.

The oxidation of fatty acids produces large quantities of water. This water, which sustains migratory birds and animals (such as the camel) for long periods of time.

Summary

- Fatty acids, obtained from the breakdown of triglycerides and other lipids, are oxidized through a series of reactions known as β -oxidation.
- In each round of β -oxidation, 1 molecule of acetyl-CoA, 1 molecule of NADH, and 1 molecule of FADH_2 are produced.
- The acetyl-CoA, NADH, and FADH_2 are used in the citric acid cycle, the electron transport chain, and oxidative phosphorylation to produce ATP.

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16.8: Stage II of Protein Catabolism

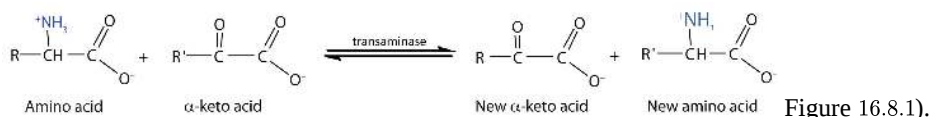
Learning Objectives

- To describe how excess amino acids are degraded.

The liver is the principal site of amino acid metabolism, but other tissues, such as the kidney, the small intestine, muscles, and adipose tissue, take part. Generally, the first step in the breakdown of amino acids is the separation of the amino group from the carbon skeleton, usually by a transamination reaction. The carbon skeletons resulting from the deaminated amino acids are used to form either glucose or fats, or they are converted to a metabolic intermediate that can be oxidized by the [citric acid cycle](#). The latter alternative, amino acid catabolism, is more likely to occur when glucose levels are low—for example, when a person is fasting or starving.

Transamination

Transamination is an exchange of functional groups between any amino acid (except lysine, proline, and threonine) and an α -keto acid. The amino group is usually transferred to the keto carbon atom of pyruvate, oxaloacetate, or α -ketoglutarate, converting the α -keto acid to alanine, aspartate, or glutamate, respectively. Transamination reactions are catalyzed by specific transaminases (also called aminotransferases), which require pyridoxal phosphate as a coenzyme.



In an α -keto acid, the carbonyl or keto group is located on the carbon atom adjacent to the carboxyl group of the acid.

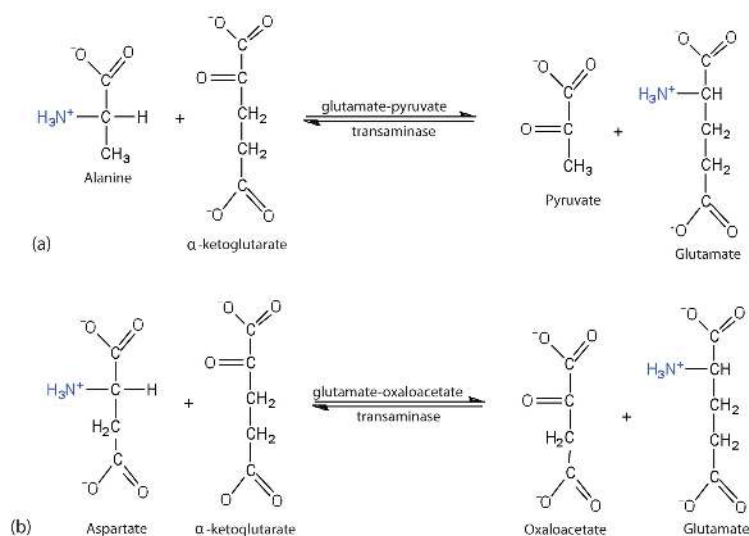
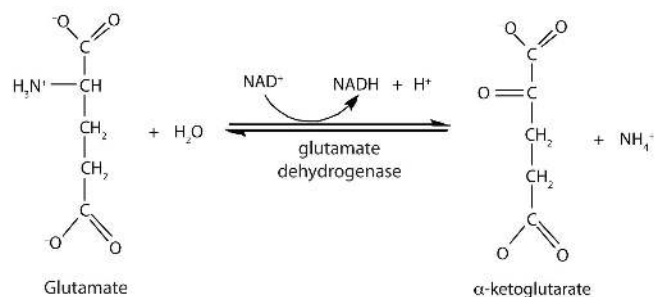


Figure 16.8.1: Two Transamination Reactions.

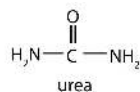
In both reactions, the final acceptor of the amino group is α -ketoglutarate, and the final product is glutamate.

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 undergo oxidative deamination, in which it loses its amino group as an ammonium (NH_4^+) ion and is oxidized back to α -ketoglutarate (ready to accept another amino group):



This reaction occurs primarily in liver mitochondria. Most of the NH_4^+ ion formed by oxidative deamination of glutamate is converted to urea and excreted in the urine in a series of reactions known as the **urea cycle**.



The synthesis of glutamate occurs in animal cells by reversing the reaction catalyzed by glutamate dehydrogenase. For this reaction nicotinamide adenine dinucleotide phosphate (NADPH) acts as the reducing agent. The synthesis of glutamate is significant because it is one of the few reactions in animals that can incorporate inorganic nitrogen (NH_4^+) into an α -keto acid to form an amino acid. The amino group can then be passed on through transamination reactions, to produce other amino acids from the appropriate α -keto acids.

The Fate of the Carbon Skeleton

Any amino acid can be converted into an intermediate of the citric acid cycle. Once the amino group is removed, usually by transamination, the α -keto acid that remains is catabolized by a pathway unique to that acid and consisting of one or more reactions. For example, phenylalanine undergoes a series of six reactions before it splits into fumarate and acetoacetate. Fumarate is an intermediate in the citric acid cycle, while acetoacetate must be converted to acetoacetyl-coenzyme A (CoA) and then to acetyl-CoA before it enters the citric acid cycle.

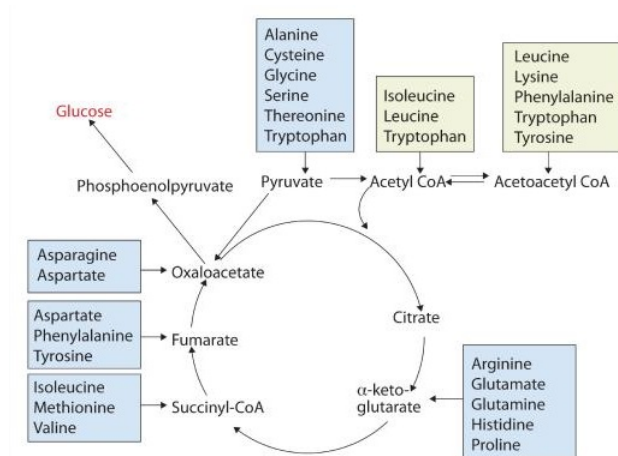


Figure 16.8.2: Fates of the Carbon Skeletons of Amino Acids

Those amino acids that can form any of the intermediates of carbohydrate metabolism can subsequently be converted to glucose via a metabolic pathway known as gluconeogenesis. These amino acids are called glucogenic amino acids. Amino acids that are converted to acetoacetyl-CoA or acetyl-CoA, which can be used for the synthesis of ketone bodies but not glucose, are called ketogenic amino acids. Some amino acids fall into both categories. Leucine and lysine are the only amino acids that are exclusively ketogenic. Figure 16.8.2 summarizes the ultimate fates of the carbon skeletons of the 20 amino acids.

✓ Career Focus: Exercise Physiologist

An exercise physiologist works with individuals who have or wish to prevent developing a wide variety of chronic diseases, such as diabetes, in which exercise has been shown to be beneficial. Each individual must be referred by a licensed physician. An exercise physiologist works in a variety of settings, such as a hospital or in a wellness program at a commercial business, to

design and monitor individual exercise plans. A registered clinical exercise physiologist must have an undergraduate degree in exercise physiology or a related degree. Some job opportunities require a master's degree in exercise physiology or a related degree.



Ergospirometry laboratory for the measurement of metabolic changes during a graded exercise test on a treadmill. from Wikipedia.

Summary

Generally the first step in the breakdown of amino acids is the removal of the amino group, usually through a reaction known as transamination. The carbon skeletons of the amino acids undergo further reactions to form compounds that can either be used for the synthesis of glucose or the synthesis of ketone bodies.

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16.S: Energy Metabolism (Summary)

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

Metabolism is the general term for all chemical reactions in living organisms. The two types of metabolism are **catabolism**—those reactions in which complex molecules (carbohydrates, lipids, and proteins) are broken down to simpler ones with the concomitant release of energy—and **anabolism**—those reactions that consume energy to build complex molecules. Metabolism is studied by looking at individual **metabolic pathways**, which are a series of biochemical reactions in which a given reactant is converted to a desired end product.

The oxidation of fuel molecules (primarily carbohydrates and lipids), a process called **respiration**, is the source of energy used by cells. Catabolic reactions release energy from food molecules and use some of that energy for the synthesis of *adenosine triphosphate* (ATP); anabolic reactions use the energy in ATP to create new compounds. Catabolism can be divided into three stages. In stage I, carbohydrates, lipids, and proteins are broken down into their individual monomer units—simple sugars, fatty acids, and amino acids, respectively. In stage II, these monomer units are broken down by specific metabolic pathways to form a common end product *acetyl-coenzyme A* (CoA). In stage III, acetyl-CoA is completely oxidized to form carbon dioxide and water, and ATP is produced.

The **digestion** of carbohydrates begins in the mouth as α -amylase breaks glycosidic linkages in carbohydrate molecules. Essentially no carbohydrate digestion occurs in the stomach, and food particles pass through to the small intestine, where α -amylase and intestinal enzymes convert complex carbohydrate molecules (starches) to monosaccharides. The monosaccharides then pass through the lining of the small intestine and into the bloodstream for transport to all body cells.

Protein digestion begins in the stomach as pepsinogen in **gastric juice** is converted to pepsin, the enzyme that hydrolyzes peptide bonds. The partially digested protein then passes to the small intestine, where the remainder of protein digestion takes place through the action of several enzymes. The resulting amino acids cross the intestinal wall into the blood and are carried to the liver.

Lipid digestion begins in the small intestine. Bile salts emulsify the lipid molecules, and then lipases hydrolyze them to fatty acids and monoglycerides. The hydrolysis products pass through the intestine and are repackaged for transport in the bloodstream.

In cells that are operating aerobically, acetyl-CoA produced in stage II of catabolism is oxidized to carbon dioxide. The **citric acid cycle** describes this oxidation, which takes place with the formation of the coenzymes reduced nicotinamide adenine dinucleotide (NADH) and reduced flavin adenine dinucleotide (FADH₂). The sequence of reactions needed to oxidize these coenzymes and transfer the resulting electrons to oxygen is called the **electron transport chain**, or the **respiratory chain**. The compounds responsible for this series of oxidation-reduction reactions include proteins known as **cytochromes**, Fe-S proteins, and other molecules that ultimately result in the reduction of molecular oxygen to water. Every time a compound with two carbon atoms is oxidized in the citric acid cycle, a respiratory chain compound accepts the electrons lost in the oxidation (and so is reduced) and then passes them on to the next metabolite in the chain. The energy released by the electron transport chain is used to transport hydrogen (H⁺) ions from the mitochondrial matrix to the intermembrane space. The flow of H⁺ back through ATP synthase leads to the synthesis and release of ATP from adenosine diphosphate (ADP) and inorganic phosphate ions (P_i) in a process known as **oxidative phosphorylation**. Electron transport and oxidative phosphorylation are tightly coupled to each other. The enzymes and intermediates of the citric acid cycle, the electron transport chain, and oxidative phosphorylation are located in organelles called **mitochondria**.

The oxidation of carbohydrates is the source of over 50% of the energy used by cells. Glucose is oxidized to two molecules of pyruvate through a series of reactions known as **glycolysis**. Some of the energy released in these reactions is conserved by the formation of ATP from ADP. Glycolysis can be divided into two phases: phase I consists of the first five reactions and requires energy to “prime” the glucose molecule for phase II, the last five reactions in which ATP is produced through **substrate-level phosphorylation**.

The pyruvate produced by glycolysis has several possible fates, depending on the organism and whether or not oxygen is present. In animal cells, pyruvate can be further oxidized to acetyl-CoA and then to carbon dioxide (through the citric acid cycle) if oxygen supplies are sufficient. When oxygen supplies are insufficient, pyruvate is reduced to lactate. In yeast and other microorganisms, pyruvate is not converted to lactate in the absence of oxygen but instead is converted to ethanol and carbon dioxide.

The amount of ATP formed by the oxidation of glucose depends on whether or not oxygen is present. If oxygen is present, glucose is oxidized to carbon dioxide, and 36–38 ATP molecules are produced for each glucose molecule oxidized, using the combined

pathways of glycolysis, the citric acid cycle, the electron transport chain, and oxidative phosphorylation. Thus, approximately 42% of the energy released by the complete oxidation of glucose is conserved by the synthesis of ATP. In the absence of oxygen, only 2 molecules of ATP are formed for each molecule of glucose converted to lactate (2 molecules), and the amount of energy conserved is much less (2%).

Fatty acids, released by the degradation of triglycerides and other lipids, are converted to fatty acyl-CoA, transported into the mitochondria, and oxidized by repeated cycling through a sequence of four reactions known as **β -oxidation**. In each round of β -oxidation, the fatty acyl-CoA is shortened by two carbon atoms as one molecule of acetyl-CoA is formed. The final round of β -oxidation, once the chain has been shortened to four carbon atoms, forms two molecules of acetyl-CoA. β -oxidation also forms the reduced coenzymes FADH_2 and NADH , whose reoxidation through the electron transport chain and oxidative phosphorylation leads to the synthesis of ATP. The efficiency of fatty acid oxidation in the human body is approximately 41%.

Amino acids from the breakdown of proteins can be catabolized to provide energy. Amino acids whose carbon skeletons are converted to intermediates that can be converted to glucose through gluconeogenesis are known as **glucogenic amino acids**. Amino acids whose carbon skeletons are broken down to compounds used to form ketone bodies are known as **ketogenic amino acids**.

The first step in amino acid catabolism is separation of the amino group from the carbon skeleton. In a **transamination**, the amino acid gives its NH_2 to pyruvate, α -ketoglutarate, or oxaloacetate. The products of this reaction are a new amino acid and an α -keto acid containing the carbon skeleton of the original amino acid. Pyruvate is transaminated to alanine, α -ketoglutarate to glutamate, and oxaloacetate to aspartate. The amino groups used to form alanine and aspartate are ultimately transferred to α -ketoglutarate, forming glutamate. The glutamate then undergoes **oxidative deamination** to yield α -ketoglutarate and ammonia.

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Index

1 A

atomic mass

[2.4: Nuclei of Atoms](#)

ATP

[16.5: Stage III of Catabolism](#)

2 B

bile

[12.5: Steroids](#)

3 C

catabolism

[16.5: Stage III of Catabolism](#)

cholesterol

[12.5: Steroids](#)

citric acid cycle

[16.5: Stage III of Catabolism](#)

4 D

dispersion

[1.5: Intermolecular Forces](#)

dissociation

[1.4: The Dissolution Process](#)

5 E

electron transport chain

[16.5: Stage III of Catabolism](#)

energy metabolism

[16: Energy Metabolism](#)

Enzyme Classification Number

[13.13: Enzymes](#)

enzymes

[13.13: Enzymes](#)

6 F

fats

[12.3: Fats and Oils](#)

fatty acids

[12.2: Fatty Acids](#)

fermentation

[16.4: Overview of Stage II of Catabolism](#)

7 G

glycolysis

[16.4: Overview of Stage II of Catabolism](#)

8 H

hydration

[1.4: The Dissolution Process](#)

hydrogen bonding

[1.5: Intermolecular Forces](#)

9 I

induced dipole

[1.5: Intermolecular Forces](#)

instantaneous dipole

[1.5: Intermolecular Forces](#)

intermolecular force

[1.5: Intermolecular Forces](#)

isotopes

[2.4: Nuclei of Atoms](#)

10 M

membrane lipids

[12.4: Membranes and Membrane Lipids](#)

membranes

[12.4: Membranes and Membrane Lipids](#)

11 O

oils

[12.3: Fats and Oils](#)

oxidative phosphorylation

[16.5: Stage III of Catabolism](#)

12 P

polarizability

[1.5: Intermolecular Forces](#)

13 R

respiration

[16.1: Prelude to Energy Metabolism](#)

14 S

solvation

[1.4: The Dissolution Process](#)

steroids

[12.5: Steroids](#)

stop codons

[15.2: Translation](#)

strong electrolytes

[1.4: The Dissolution Process](#)

15 T

triglyceride

[12.3: Fats and Oils](#)

16 V

van der Waals force

[1.5: Intermolecular Forces](#)

17 W

waxes

[12.2: Fatty Acids](#)

weak electrolytes

[1.4: The Dissolution Process](#)

Glossary

Sample Word 1 | Sample Definition 1

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 - [MUIH Organic Chemistry](#) - [Undeclared](#)
 - [InfoPage](#) - [Undeclared](#)
 - [Table of Contents](#) - [Undeclared](#)
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 - [1: Matter and Solutions](#) - [CC BY-NC-SA 4.0](#)
 - [1.1: What is Chemistry?](#) - [CC BY-NC-SA 3.0](#)
 - [1.2: The Classification of Matter](#) - [CC BY-NC-SA 3.0](#)
 - [1.3: Solutions](#) - [CC BY-NC-SA 3.0](#)
 - [1.4: The Dissolution Process](#) - [CC BY-NC-SA 3.0](#)
 - [1.5: Intermolecular Forces](#) - [CC BY 4.0](#)
 - [1.S: Chemistry and Matter \(Summary\)](#) - [CC BY-NC-SA 3.0](#)
 - [2: Elements, Atoms, and the Periodic Table](#) - [CC BY-NC-SA 3.0](#)
 - [2.1: The Elements](#) - [CC BY-NC-SA 3.0](#)
 - [2.2: Atomic Theory](#) - [CC BY-NC-SA 3.0](#)
 - [2.3: The Structure of Atoms](#) - [CC BY-NC-SA 3.0](#)
 - [2.4: Nuclei of Atoms](#) - [CC BY-NC-SA 3.0](#)
 - [2.5: Atomic Masses](#) - [CC BY-NC-SA 3.0](#)
 - [2.6: Arrangements of Electrons](#) - [CC BY-NC-SA 3.0](#)
 - [2.7: The Periodic Table](#) - [CC BY-NC-SA 3.0](#)
 - [2.S: Elements, Atoms, and the Periodic Table \(Summary\)](#) - [CC BY-NC-SA 3.0](#)
 - [3: Ionic Bonding and Simple Ionic Compounds](#) - [CC BY-NC-SA 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.S: Ionic Bonding and Simple Ionic Compounds \(Summary\)](#) - [CC BY-NC-SA 3.0](#)
 - [4: Covalent Bonding and Simple Molecular Compounds](#) - [CC BY-NC-SA 4.0](#)
 - [4.1: Covalent Bonds](#) - [CC BY-NC-SA 4.0](#)
 - [4.2: Covalent Compounds- Formulas and Names](#) - [CC BY-NC-SA 4.0](#)
 - [4.3: Multiple Covalent Bonds](#) - [CC BY-NC-SA 4.0](#)
 - [4.4: Polar Covalent Bonds and Electronegativity](#) - [Undeclared](#)
 - [4.5: Characteristics of Molecules](#) - [CC BY-NC-SA 4.0](#)
 - [4.6: Intermolecular Forces](#) - [CC BY-NC-SA 4.0](#)
 - [4.7: Naming Binary Molecular Compounds](#) - [Undeclared](#)
 - [4.S: Covalent Bonding and Simple Molecular Compounds \(Summary\)](#) - [CC BY-NC-SA 3.0](#)
 - [5: Classification and Balancing of Chemical Reactions](#) - [Undeclared](#)
 - [5.1: Chemical Equations](#) - [Undeclared](#)
 - [5.2: Balancing Chemical Equations](#) - [Undeclared](#)
 - [5.3: Acids, Bases, and Neutralization Reactions](#) - [Undeclared](#)
 - [5.4: Redox Reactions](#) - [Undeclared](#)
 - [5.5: Recognizing Redox Reactions](#) - [Undeclared](#)
 - [5.6: Net Ionic Equations](#) - [Undeclared](#)
 - [5.7: Le Chatelier's Principle](#) - [CC BY-NC-SA 3.0](#)
 - [5.S: Introduction to Chemical Reactions \(Summary\)](#) - [CC BY-NC-SA 3.0](#)
 - [6: Organic Chemistry of Hydrocarbons](#) - [CC BY-NC-SA 4.0](#)
 - [6.1: Introduction to Organic Chemistry](#) - [CC BY-NC-SA 4.0](#)
 - [6.2: Condensed Structural and Line-Angle Formulas](#) - [CC BY-NC-SA 4.0](#)
 - [6.3: Structures and Names of Alkanes](#) - [CC BY-NC-SA 4.0](#)
 - [6.4: Branched-Chain Alkanes](#) - [CC BY-NC-SA 4.0](#)

- 6.5: Cycloalkanes - CC BY-NC-SA 4.0
- 6.6: IUPAC Nomenclature - CC BY-NC-SA 4.0
- 6.7: Alkenes- Structure and Nomenclature - CC BY-NC-SA 4.0
- 6.8: Alkenes- Cis-Trans Isomerization - CC BY-NC-SA 4.0
- 6.9: Alkynes - CC BY-NC-SA 4.0
- 6.10: Aromatic Compounds - CC BY-NC-SA 4.0
- 6.11: Aromatic Compounds- Structure and Nomenclature - CC BY-NC-SA 4.0
- 6.12: Physical Properties of Hydrocarbons - CC BY-NC-SA 4.0
- 6.13: Chapter Summary - CC BY-NC-SA 4.0
- 6.E: Unsaturated and Aromatic Hydrocarbons (Exercises) - CC BY-NC-SA 3.0
- 7: Organic Compounds of Oxygen - CC BY-NC-SA 3.0
 - 7.1: Prelude to Organic Compounds of Oxygen - CC BY-NC-SA 3.0
 - 7.2: Organic Compounds with Functional Groups - CC BY-NC-SA 3.0
 - 7.3: Alcohols - Nomenclature and Classification - CC BY-NC-SA 3.0
 - 7.4: Physical Properties of Alcohols - CC BY-NC-SA 3.0
 - 7.5: Phenols - CC BY-NC-SA 3.0
 - 7.6: Ethers - CC BY-NC-SA 3.0
 - 7.7: Aldehydes and Ketones- Structure and Names - CC BY-NC-SA 3.0
 - 7.8: Properties of Aldehydes and Ketones - CC BY-NC-SA 3.0
 - 7.S: Organic Compounds of Oxygen (Summary) - CC BY-NC-SA 3.0
- 8: Acids and Bases - CC BY-NC-SA 4.0
 - 8.1: Brønsted-Lowry Definition of Acids and Bases - CC BY-NC-SA 4.0
 - 8.2: Water is both an Acid and a Base - CC BY-NC-SA 4.0
 - 8.3: The Strengths of Acids and Bases - CC BY-NC-SA 4.0
 - 8.4: pH and Kw - CC BY-NC-SA 4.0
 - 8.5: Buffers - CC BY-NC-SA 4.0
 - 8.6: Chapter Summary - CC BY-NC-SA 4.0
- 9: Organic Acids and Bases and Some of Their Derivatives - CC BY-NC-SA 3.0
 - 9.1: Prelude to Organic Acids and Bases and Some of Their Derivatives - CC BY-NC-SA 3.0
 - 9.2: Carboxylic Acids - Structures and Names - CC BY-NC-SA 3.0
 - 9.3: The Formation of Carboxylic Acids - CC BY-NC-SA 3.0
 - 9.4: Physical Properties of Carboxylic Acids - CC BY-NC-SA 3.0
 - 9.5: Chemical Properties of Carboxylic Acids- Ionization and Neutralization - CC BY-NC-SA 3.0
 - 9.6: Esters - Structures and Names - CC BY-NC-SA 3.0
 - 9.7: Physical Properties of Esters - CC BY-NC-SA 3.0
 - 9.8: Preparation of Esters - CC BY-NC-SA 3.0
 - 9.9: Hydrolysis of Esters - CC BY-NC-SA 3.0
 - 9.S: Organic Acids and Bases and Some of Their Derivatives (Summary) - CC BY-NC-SA 3.0
- 10: Functional Group Reactions - CC BY-NC-SA 4.0
 - 10.1: Oxidation-Reduction (Redox) Reactions - CC BY-NC-SA 4.0
 - 10.2: Redox Reactions in Organic Chemistry - CC BY-NC-SA 4.0
 - 10.3: Reactions that Form Alcohols - CC BY-NC-SA 4.0
 - 10.4: Reactions of Alcohols - CC BY-NC-SA 4.0
 - 10.5: The Formation of Carboxylic Acids - CC BY-NC-SA 4.0
 - 10.6: Properties of Esters - CC BY-NC-SA 4.0
 - 10.7: Hydrolysis of Esters - CC BY-NC-SA 4.0
 - 10.8: Hydrolysis of Amides - CC BY-NC-SA 4.0
 - 10.9: Summary - CC BY-NC-SA 4.0
- 11: Carbohydrates - CC BY-NC-SA 3.0
 - 11.1: Prelude to Carbohydrates - CC BY-NC-SA 3.0
 - 11.2: Carbohydrates - CC BY-NC-SA 3.0
 - 11.3: Classes of Monosaccharides - CC BY-NC-SA 3.0
 - 11.4: Important Hexoses - CC BY-NC-SA 3.0
 - 11.5: Cyclic Structures of Monosaccharides - CC BY-NC-SA 3.0
 - 11.6: Properties of Monosaccharides - CC BY-NC-SA 3.0
 - 11.7: Disaccharides - CC BY-NC-SA 3.0
 - 11.8: Polysaccharides - CC BY-NC-SA 3.0
 - 11.S: Carbohydrates (Summary) - CC BY-NC-SA 3.0
- 12: Lipids - CC BY-NC-SA 3.0
 - 12.1: Prelude to Lipids - CC BY-NC-SA 3.0
 - 12.2: Fatty Acids - CC BY-NC-SA 3.0
 - 12.3: Fats and Oils - CC BY-NC-SA 3.0
 - 12.4: Membranes and Membrane Lipids - CC BY-NC-SA 3.0
 - 12.5: Steroids - CC BY-NC-SA 3.0
 - 12.S: Lipids (Summary) - CC BY-NC-SA 3.0
- 13: Proteins and Enzymes - CC BY-NC-SA 4.0
 - 13.1: Properties of Amino Acids - CC BY-NC-SA 4.0
 - 13.2: Reactions of Amino Acids - CC BY-NC-SA 4.0
 - 13.3: Organic Sulfur Compounds - CC BY-NC-SA 3.0

- 13.4: Amines - Structures and Names - *CC BY-NC-SA 3.0*
- 13.5: Physical Properties of Amines - *CC BY-NC-SA 3.0*
- 13.6: Amines as Bases - *CC BY-NC-SA 3.0*
- 13.7: Amides- Structures and Names - *CC BY-NC-SA 3.0*
- 13.8: Physical Properties of Amides - *CC BY-NC-SA 3.0*
- 13.9: Formation of Amides - *CC BY-NC-SA 3.0*
- 13.10: Chemical Properties of Amides- Hydrolysis - *CC BY-NC-SA 3.0*
- 13.11: Peptides - *CC BY-NC-SA 4.0*
- 13.12: Proteins - *CC BY-NC-SA 4.0*
- 13.13: Enzymes - *CC BY-NC-SA 3.0*
- 13.14: Enzymatic Catalysis - *CC BY-NC-SA 4.0*
- 13.15: Enzyme Activity - *CC BY-NC-SA 3.0*
- 13.16: Enzyme Regulation - *CC BY-NC-SA 4.0*
- 13.17: Enzyme Cofactors and Vitamins - *CC BY-NC-SA 4.0*
- 13.18: Chapter Summary - *CC BY-NC-SA 4.0*
- 14: Nucleic Acids - *CC BY-NC-SA 4.0*
 - 14.1: Nucleotides - *CC BY-NC-SA 4.0*
 - 14.2: Nucleic Acid Structure - *CC BY-NC-SA 4.0*
 - 14.3: Chapter Summary - *CC BY-NC-SA 4.0*
- 15: Flow of Genetic Information - *CC BY-NC-SA 4.0*
 - 15.1: Replication and Expression of Genetic Information - *CC BY-NC-SA 4.0*
 - 15.2: Translation - *CC BY-NC-SA 4.0*
 - 15.3: Mutations and Genetic Diseases - *CC BY-NC-SA 4.0*
- 16: Energy Metabolism - *CC BY-NC-SA 3.0*
 - 16.1: Prelude to Energy Metabolism - *CC BY-NC-SA 3.0*
 - 16.2: ATP- the Universal Energy Currency - *CC BY-NC-SA 3.0*
 - 16.3: Stage I of Catabolism - *CC BY-NC-SA 3.0*
 - 16.4: Overview of Stage II of Catabolism - *CC BY-NC-SA 3.0*
 - 16.5: Stage III of Catabolism - *CC BY-NC-SA 4.0*
 - 16.6: Stage II of Carbohydrate Catabolism - *CC BY-NC-SA 3.0*
 - 16.7: Stage II of Lipid Catabolism - *CC BY-NC-SA 3.0*
 - 16.8: Stage II of Protein Catabolism - *CC BY-NC-SA 3.0*
 - 16.S: Energy Metabolism (Summary) - *CC BY-NC-SA 3.0*
- Back Matter - *CC BY-NC-SA 4.0*
 - Index - *CC BY-NC-SA 4.0*
 - Glossary - *CC BY-NC-SA 4.0*
 - Detailed Licensing - *CC BY-NC-SA 4.0*