FUNDAMENTALS OF GENERAL ORGANIC AND BIOLOGICAL CHEMISTRY



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TABLE OF CONTENTS

Licensing

1: Matter and Measurements

1.1: Chemistry - The Central Science

1.2: States of Matter

1.3: Classification of Matter

1.4: Chemical Elements and Symbols

1.5: Chemical Reactions - Examples of Chemical Change

1.6: Physical Quantities - Units and Scientific Notation

1.7: Measuring Mass, Length, and Volume

1.8: Measurement and Significant Figures

1.9: Rounding Off Numbers

1.10: Problem Solving - Unit Conversions and Estimating Answers

1.11: Temperature, Heat, and Energy

1.12: Density and Specific Gravity

2: Atoms and the Periodic Table

2.1: Atomic Theory and the Structure of Atoms

2.2: Elements and Atomic Number

2.3: Isotopes and Atomic Weight

2.4: The Periodic Table

2.5: Some Characteristics of Different Groups

2.6: Electronic Structure of Atoms

2.7: Electron Configurations

2.8: Electron Configurations and the Periodic Table

2.9: Electron-Dot Symbols

3: Ionic Compounds

3.1: Ions

3.2: Ions and the Octet Rule

3.3: Ions of Some Common Elements

3.4: Periodic Properties and Ion Formation

3.5: Naming Monoatomic Ions

3.6: Polyatomic Ions

3.7: Ionic Bonds

3.8: Formulas of Ionic Compounds

3.9: Naming Ionic Compounds

3.10: Some Properties of Ionic Compounds

3.11: $H^{\oplus}$ and $OH^{\ominus}$ Ions - An Introduction to Acids and Bases

4: Molecular Compounds

4.1: Covalent Bonds

4.2: Covalent Bonds and the Periodic Table

4.3: Multiple Covalent Bonds

4.4: Coordinate Covalent Bonds

4.5: Characteristics of Molecular Compounds

4.6: Molecular Formulas and Lewis Structures

4.7: Drawing Lewis Structures

4.8: The Shapes of Molecules

4.9: Polar Covalent Bonds and Electronegativity

4.10: Polar Molecules

4.11: Naming Binary Molecular Compounds

5: Classification and Balancing of Chemical Reactions

5.1: Chemical Equations

5.2: Balancing Chemical Equations

5.3: Precipitation Reactions and Solubility Guidelines

5.4: Acids, Bases, and Neutralization Reactions

5.5: Redox Reactions

5.6: Recognizing Redox Reactions

5.7: Net Ionic Equations

6: Chemical Reactions - Mole and Mass Relationships

6.1: The Mole and Avogadro's Number

6.2: Gram-Mole Conversions

6.3: Mole Relationships and Chemical Equations

6.4: Mass Relationships and Chemical Equations

6.5: Limiting Reagent and Percent Yield

7: Chemical Reactions - Energy, Rates, and Equilibrium

7.1: Energy and Chemical Bonds

7.2: Heat Changes during Chemical Reactions

7.3: Exothermic and Endothermic Reactions

7.4: Why Do Chemical Reactions Occur? Free Energy

7.5: How Do Chemical Reactions Occur? Reaction Rates

7.6: Effects of Temperature, Concentration, and Catalysts on Reaction Rates

7.7: Reversible Reactions and Chemical Equilibrium

7.8: Equilibrium Equations and Equilibrium Constants

7.9: Le Chatelier's Principle- The Effect of Changing Conditions on Equilibria

8: Gases, Liquids, and Solids

8.1: States of Matter and Their Changes

8.2: Intermolecular Forces

8.3: Gases and the Kinetic-Molecular Theory
8.4: Pressure
8.5: Boyle's Law - The Relation between Volume and Pressure
8.6: Charles's Law- The Relation between Volume and Temperature
8.7: Gay-Lussac's Law- The Relationship Between Pressure and Temperature
8.8: The Combined Gas Law
8.9: Avogadro's Law - The Relation between Volume and Molar Amount
8.10: The Ideal Gas Law
8.11: Partial Pressure and Dalton's Law
8.12: Liquids
8.13: Solids
8.14: Changes of State Calculations

9: Solutions

9.1: Mixtures and Solutions
9.2: The Solution Process
9.3: Solubility
9.4: The Effect of Temperature on Solubility
9.5: The Effect of Pressure on Solubility - Henry's Law
9.6: Units of Concentration
9.7: Dilution
9.8: Ions in Solution - Electrolytes
9.9: Properties of Solutions
9.10: Osmosis and Osmotic Pressure
9.11: Dialysis

10: Acids and Bases

10.1: Acids and Bases Definitions
10.2: Acid and Base Strength
10.3: Acid Dissociation Constants
10.4: Water as Both an Acid and a Base
10.5: Measuring Acidity in Aqueous Solutions- The pH Scale
10.6: Working with pH
10.7: Acid and Base Equivalents
10.8: Some Common Acid-Base Reactions
10.9: Acidity and Basicity of Salt Solutions
10.10: Buffer Solutions
10.11: Titration

11: Nuclear Chemistry

11.1: Nuclear Reactions
11.2: The Discovery and Nature of Radioactivity
11.3: Stable and Unstable Isotopes

11.4: Nuclear Decay
11.5: Radioactive Half-Life
11.6: Ionizing Radiation
11.7: Detecting and Measuring Radiation
11.8: Artificial Transmutation
11.9: Nuclear Fission and Nuclear Fusion

12: Introduction to Organic Chemistry - Alkanes

12.1: The Nature of Organic Molecules
12.2: Families of Organic Molecules - Functional Groups
12.3: The Structure of Organic Molecules - Alkanes and Their Isomers
12.4: Drawing Organic Structures
12.5: The Shapes of Organic Molecules
12.6: Naming Alkanes
12.7: Properties of Alkanes
12.8: Reactions of Alkanes
12.9: Cycloalkanes
12.10: Drawing and Naming Cycloalkanes

13: Alkenes, Alkynes, and Aromatic Compounds

13.1: Alkenes and Alkynes
13.2: Naming Alkenes and Alkynes
13.3: The Structure of Alkenes- Cis-Trans Isomerism
13.4: Properties of Alkenes and Alkynes
13.5: Types of Organic Reactions
13.6: Addition Reactions of Alkenes
13.7: Alkene Polymers
13.8: Aromatic Compounds and the Structure of Benzene
13.9: Naming Aromatic Compounds
13.10: Reactions of Aromatic Compounds

14: Some Compounds with Oxygen, Sulfur, or a Halogen

14.1: Alcohols, Phenols, and Ethers
14.2: Naming Alcohols
14.3: Properties of Alcohols
14.4: Reactions of Alcohols
14.5: Phenols
14.6: Acidity of Alcohols and Phenols
14.7: Ethers
14.8: Thiols and Disulfides
14.9: Halogen-Containing Compounds
14.10: Stereochemistry and Chirality

15: Aldehydes and Ketones

15.1: The Carbonyl Group

15.2: Naming Aldehydes and Ketones

15.3: Properties of Aldehydes and Ketones

15.4: Some Common Aldehydes and Ketones

15.5: Oxidation of Aldehydes

15.6: Reduction of Aldehydes and Ketones

15.7: Addition of Alcohols - Hemiacetals and Acetals

16: Amines

16.1: Classifying Amines

16.2: Naming and Drawing Amines

16.3: Properties of Amines

16.4: Heterocyclic Nitrogen Compounds

16.5: Basicity of Amines

16.6: Amine Salts

16.7: Amines in Plants- Alkaloids

17: Carboxylic Acids and their Derivatives

17.1: Carboxylic Acids and Their Derivatives- Properties and Names

17.2: Acidity of Carboxylic Acids

17.3: Reactions of Carboxylic Acids - Ester and Amide Formation

17.4: Hydrolysis of Esters and Amides

17.5: Polyamides and Polyesters

17.6: Phosphoric Acid Derivatives

18: Amino Acids and Proteins

18.1: An Introduction to Biochemistry

18.2: Proteins and Their Functions- An Overview

18.3: Amino Acids

18.4: Acid-Base Properties of Amino Acids

18.5: Peptides

18.6: Protein Structure- An Overview and Primary Protein Structure

18.7: Secondary Protein Structure

18.8: Tertiary Protein Structure

18.9: Quaternary Protein Structure

18.10: Chemical Properties of Proteins

19: Enzymes and Vitamins

19.1: Catalysis by Enzymes

19.2: Enzyme Cofactors

19.3: Enzyme Classification

19.4: How Enzymes Work

19.5: Factors Affecting Enzyme Activity
19.6: Enzyme Regulation - Inhibition
19.7: Enzyme Regulation- Allosteric Control and Feedback Inhibition
19.8: Enzyme Regulation - Covalent Modification and Genetic Control
19.9: Vitamins, Antioxidants, and Minerals

20: Carbohydrates

20.1: An Introduction to Carbohydrates
20.2: Handedness of Carbohydrates
20.3: Structure of Glucose and Other Monosaccharides
20.4: Some Important Monosaccharides
20.5: Reactions of Monosaccharides
20.6: Common Disaccharides
20.7: Some Important Polysaccharides Based on Glucose

21: The Generation of Biochemical Energy

21.1: Energy, Life, and Biochemical Reactions
21.2: Cells and Their Structure
21.3: An Overview of Metabolism and Energy Production
21.4: Strategies of Metabolism - ATP and Energy Transfer
21.5: Strategies of Metabolism - Metabolic Pathways and Coupled Reactions
21.6: Strategies of Metabolism- Oxidized and Reduced Coenzymes
21.7: The Citric Acid Cycle
21.8: The Electron-Transport Chain and ATP Production

22: Carbohydrate Metabolism

22.1: Digestion of Carbohydrates
22.2: Glucose Metabolism - An Overview
22.3: Glycolysis
22.4: Entry of Other Sugars into Glycolysis
22.5: The Fate of Pyruvate
22.6: Energy Output in Complete Glucose Catabolism
22.7: Regulation of Glucose Metabolism and Metabolism During Stress
22.8: Glycogen Metabolism- Glycogenesis and Glycogenolysis
22.9: Gluconeogenesis- Glucose Synthesis from Noncarbohydrates

23: Lipids

23.1: Structure and Classification of Lipids
23.2: Fatty Acids and Their Esters
23.3: Properties of Fats and Oils
23.4: Chemical Reactions of Triacylglycerols
23.5: Phospholipids and Glycolipids
23.6: Steroids

23.7: Cell Membranes- Structure and Transport

24: Lipid Metabolism

24.1: Digestion of Triacylglycerols

24.2: Lipoproteins for Lipid Transport

24.3: Triacylglycerol Metabolism - An Overview

24.4: Storage and Mobilization of Triacylglycerols

24.5: Oxidation of Fatty Acids

24.6: Ketone Bodies and Ketoacidosis

24.7: Biosynthesis of Fatty Acids

25: Protein and Amino Acid Metabolism

25.1: Digestion of Proteins

25.2: Amino Acid Metabolism - An Overview

25.3: Amino Acid Catabolism - The Amino Group

25.4: The Urea Cycle

25.5: Amino Acid Catabolism - The Carbon Atoms

25.6: Biosynthesis of Nonessential Amino Acids

26: Nucleic Acids and Protein Synthesis

26.1: DNA, Chromosomes, and Genes

26.2: Composition of Nucleic Acids

26.3: The Structure of Nucleic Acid Chains

26.4: Base Pairing in DNA- The Watson-Crick Model

26.5: Nucleic Acids and Heredity

26.6: Replication of DNA

26.7: Structure and Function of RNA

26.8: Transcription - RNA Synthesis

26.9: The Genetic Code

26.10: Translation- tRNA and Protein Synthesis

27: Genomics

27.1: Mapping the Human Genome

27.2: DNA and Chromosomes

27.3: Mutations and Polymorphisms

27.4: Recombinant DNA

27.5: Genomics- Using What We Know

28: Chemical Messengers- Hormones, Neurotransmitters, and Drugs

28.1: Messenger Molecules

28.2: Hormones and the Endocrine System

28.3: How Hormones Work - Epinephrine and Fight-or-Flight

28.4: Amino Acid Derivatives and Polypeptides as Hormones

28.5: Neurotransmitters

28.6: How Neurotransmitters Work- Acetylcholine, Its Agonists and Antagonists
28.7: Histamines, Antihistamines, and Important Neurotransmitters

29: Body Fluids

29.1: Body Water and Its Solutes
29.2: Fluid Balance
29.3: Blood
29.4: Plasma Proteins, White Blood Cells, and Immunity
29.5: Blood Clotting
29.6: Red Blood Cells and Blood Gases
29.7: The Kidney and Urine Formation
29.8: Urine Composition and Function

Index

Glossary

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1: MATTER AND MEASUREMENTS

What is chemistry? Simply put, chemistry is the study of the interactions of matter with other matter and with energy. This seems straightforward enough. However, the definition of chemistry includes a wide range of topics that must be understood to gain a mastery of the topic or even take additional courses in chemistry. In this book, we will lay the foundations of chemistry in a topic-by-topic fashion to provide you with the background you need to successfully understand chemistry.

1.1: Chemistry - The Central Science

1.2: States of Matter

1.3: Classification of Matter

1.4: Chemical Elements and Symbols

1.5: Chemical Reactions - Examples of Chemical Change

1.6: Physical Quantities - Units and Scientific Notation

1.7: Measuring Mass, Length, and Volume

1.8: Measurement and Significant Figures

1.9: Rounding Off Numbers

1.10: Problem Solving - Unit Conversions and Estimating Answers

1.11: Temperature, Heat, and Energy

1.12: Density and Specific Gravity

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1.1: Chemistry - The Central Science

Learning Objectives

- Define chemistry in relation to other sciences.
- Use physical and chemical properties, including phase, to describe matter.

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.

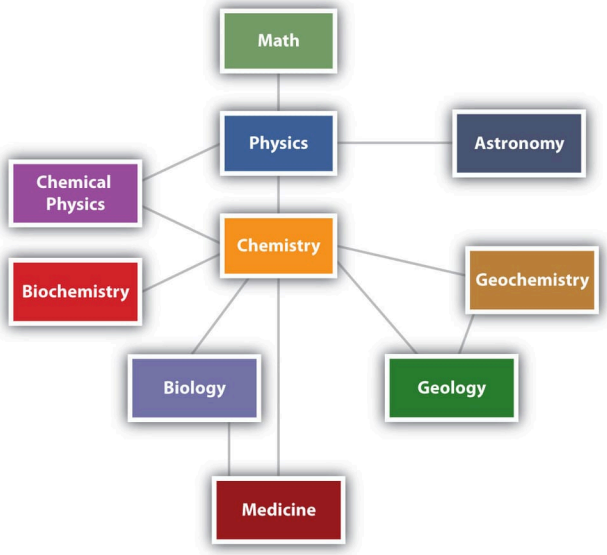


Figure 1.1.1: The Relationships between Some of the Major Branches of Science. Chemistry lies more or less in the middle, which emphasizes its importance to many branches of science. (CC BY-SA-NC; anonymous)

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.

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. The steps of the scientific method 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.

Physical and Chemical Properties and Changes

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. 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.



Figure 1.1.1: (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)

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 physical process in which a substance changes from one phase to another. Examples are summarized in Table 1.1.1.

Table 1.1.1: Physical Changes

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

Change	Name
gas to solid	deposition

The difference between a physical reaction and a chemical reaction is **composition**. In a chemical reaction, there is a change in the composition of the substances in question; in a **physical change** there is a difference in the appearance, smell, or simple display of a sample of matter without a change in composition. Although we call them physical "reactions," no reaction is actually occurring. In order for a reaction to take place, there must be a change in the elemental composition of the substance in question. Thus, we shall simply refer to "physical reactions" as physical changes from now on.

Example 1.1.1

Classify each of the following changes as physical or chemical:

a. condensation of steam
b. burning of gasoline
c. souring of milk
d. dissolving of sugar in water
e. melting of gold

Solution

The best way to determine whether a change is physical or chemical is to determine if the substance identity has changed or not.

a. Steam is water in the gas phase. When it condenses, changes from gas to liquid, it remains water. Therefore, this is a **physical** change.
b. When gasoline burns, it changes into different substances. This is a **chemical** change.
c. When milk becomes sour, several **chemical** changes have occured; proteins denature, sugars break down, and acid is produced. The milk is now made up of different substances.
d. Sugar dissolves easily into water but it still remains sugar. If the water is evaporated, the sugar will recrystalize as a solid again. Dissolving is a **physical** change, the substance does not change identity.
e. Melting solid gold into liquid gold is a **physical** change much like melting solid water (an ice cube) into liquid water is a physical change.

Exercise 1.1.1

Classify each of the following changes as physical or chemical:

a. coal burning
b. ice melting
c. mixing chocolate syrup with milk
d. explosion of a firecracker
e. magnetizing of a screwdriver

Answer a: available at the end of this section.

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.
- When a substance changes from one state to another, this is a physical change.
- If a substance undergoes a change into one or more different substances, this is a chemical change.

Answers

Exercise 1.1.1

chemical
physical
physical
chemical
physical

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1.2: States of Matter

Learning Objectives

- Describe the different physical states of matter; solid, liquid, and gas.
- Understand how external conditions can affect the states of matter.

Water can take many forms. At low temperatures (below $0^{\circ}\mathrm{C}$), it is a solid. When at "normal" temperatures (between $0^{\circ}\mathrm{C}$ and $100^{\circ}\mathrm{C}$), it is a liquid. While at temperatures above $100^{\circ}\mathrm{C}$, water is a gas (steam). The state the water is in depends upon the temperature. Each state (solid, liquid, and gas) has its own unique set of physical properties.

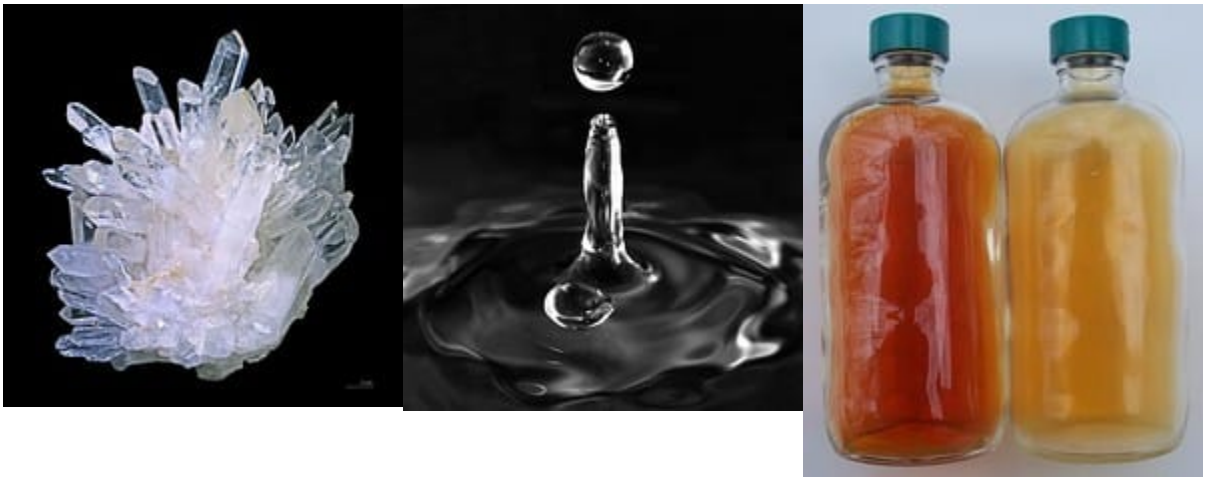


Figure $1.2.1$: Matter is usually classified into three classical states. From left to right: quartz (solid), water (liquid), nitrogen dioxide (gas).

Matter typically exists in one of three states: **solid**, **liquid**, or **gas** and these different states of matter have different properties (Table $1.2.1$):

- A **gas** is a state of matter in which atoms or molecules have enough energy to move freely. The molecules come into contact with one another only when they randomly collide. Forces between atoms or molecules are not strong enough to hold them together.
- A **liquid** is a state of matter in which atoms or molecules are constantly in contact but have enough energy to keep changing positions relative to one another. Forces between atoms or molecules are strong enough to keep the molecules relatively close together but not strong enough to prevent them from moving past one another.
- A **solid** is a state of matter in which atoms or molecules do not have enough energy to move. They are constantly in contact and in fixed positions relative to one another. Forces between atoms or molecules are strong enough to keep the molecules together and to prevent them from moving past one another.

The state a given substance exhibits is a physical property. Some substances exist as gases at room temperature (oxygen and carbon dioxide), while others, like water and mercury metal, exist as liquids. Most metals exist as solids at room temperature. All substances can exist in any of these three states. Figure $1.2.2$ shows the differences among solids, liquids, and gases at the molecular level. A solid has definite volume and shape, a liquid has a definite volume but no definite shape, and a gas has neither a definite volume nor shape (Table $1.2.1$).

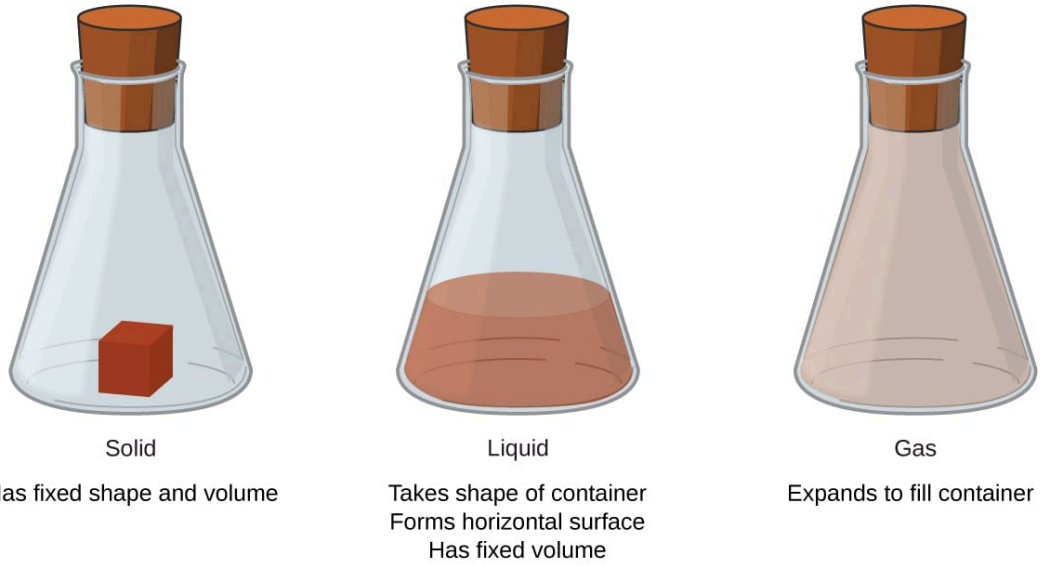


Figure 1.2.2: The three most common states or phases of matter are solid, liquid, and gas. (CC BY-4.0; OpenStax)

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.

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. 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).

Table 1.2.1: Characteristics of each Phase of Matter

	Gas	Liquid	Solid
Shape	no definite shape (takes the shape of its container)	no definite shape (takes the shape of its container)	definite shape (rigid)
Volume	particles move in random motion with little or no attraction to each other	has definite volume	definite volume
Mobility	particles move in random motion with little or no attraction to each other	particles are free to move over each other, but are still attracted to each other	particles vibrate around fixed axes
Compressibility	highly compressible	weakly compressible	weakly compressible

Adding energy to matter gives its atoms or molecules the ability to resist some of the forces holding them together. For example, heating ice to its **melting point** gives its molecules enough energy to move. The ice melts and becomes liquid water. Similarly, heating liquid water to its **boiling point** gives its molecules enough energy to pull apart from one another so they no longer have contact. The liquid water vaporizes and becomes water vapor.

State of Matter Depends on the External Conditions

The temperature of the melting and boiling points depend on the identity of the substance and the atmospheric pressure. Each substance has its own boiling and melting points that depend on the properties of the substance. As an example, the values for water are given in Table 1.2.2. Note how the boiling point of water varies greatly with pressure.

Table 1.2.1: Boiling point of water as a function of pressure

Altitude (ft)	Pressure (atm)	Boiling Point (°C)
-500	1.05	100.5
0	1.00	100
4000	0.892	96
7000	0.797	93

Example 1.2.1

Isopropyl alcohol is a colorless, flammable chemical compound with a strong odor. Its melting point is –89°C and it boiling point is 82.5°C. Is isopropyl alcohol a solid, liquid or gas at room temperature (25°C)?

Solution

Room temperature (25°C) is above the melting point of isopropyl alcohol (–89°C), but lower than its boiling point (82.5°C), therefore, it is a **liquid** at room temperature.

Exercise 1.2.1

Freon-12 is used as a refrigerant and aerosol spray propellant. Its melting point is –157.7°C and it boiling point is –29.8 °C. Is Freon-12 a solid, liquid or gas at room temperature (25°C).

Answer available at the end of this section.

Key Takeaways

- Matter exists in different physical states.
- Changes in conditions such as temperature and pressure can allow matter to change state.

Contributors and Attributions

-

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Answers

Exercise 1.2.1

Freon-12 is a **gas** at room temperature

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1.3: Classification of Matter

Learning Objectives

- Categorize different types of matter as a pure substances or mixtures.
- Explain the difference between an element and a compound.
- Explain the difference between a homogeneous mixture and a heterogeneous mixture.

One useful way of organizing our understanding of matter is to think of a hierarchy that extends down from the most general and complex substances to the simplest and most fundamental (Figure 1.3.1). At the top of this hierarchy is two broad categories into which all matter can be classified: pure substances and mixtures. A **pure substance** is a form of matter that has a constant composition (meaning that all samples of this substance have uniform composition) and properties that are constant throughout the sample (meaning that there is only one set of properties such as melting point, color, boiling point, etc. throughout the matter). If we take two or more pure substances and physically mix them together, we refer to this as a **mixture**. A mixture does not have constant composition or properties throughout.

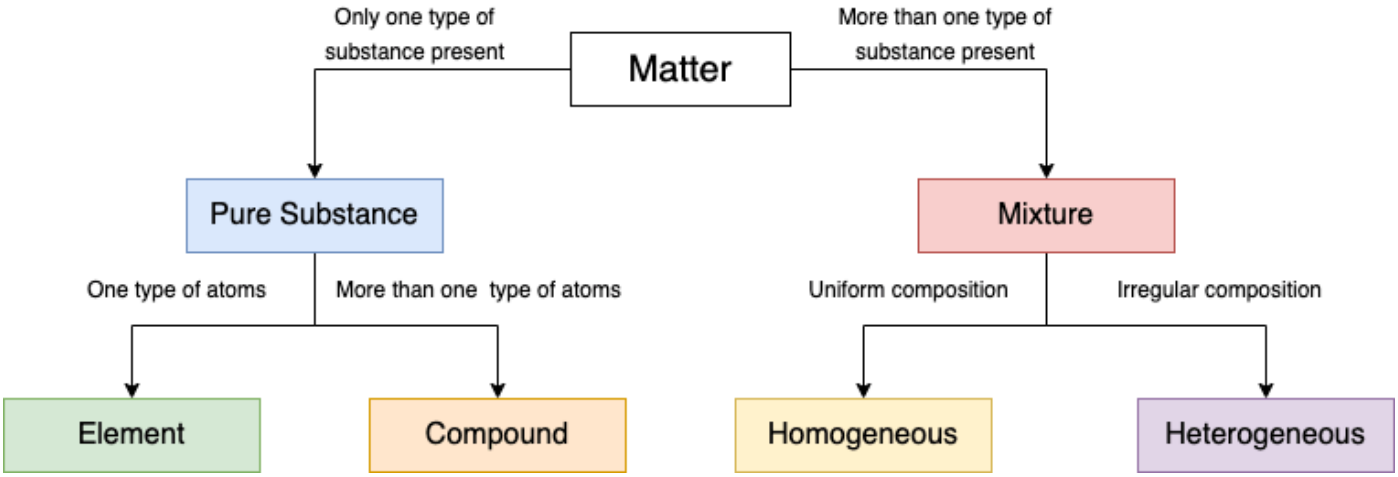


Figure 1.3.1: The Classification of Matter. Matter can be classified in a variety of ways, depending on its properties.

Elements and compounds are both examples of pure substances. A substance that cannot be broken down into chemically simpler components is an **element**. Oxygen, O, and hydrogen, H, are each examples of elements. A pure substance that can be broken down into chemically simpler components (because it made up of more than one element) is a **compound**. For example, the compound water, H_2O, is formed when hydrogen and oxygen chemically combine in a fixed ratio of 2 hydrogen atoms for every 1 oxygen atom.

Compounds may have different chemical and physical properties from the individual elements that they are composed of. Mixtures, on the other hand, are physical blends of two or more components, each of which retains its own identity and properties. Mixtures can always be separated again into the component pure substances, because bonding among the atoms of the constituent substances does not occur. For example sodium is a soft shiny metal and chlorine is a pungent green gas. These two elements chemically combine to form the *compound*, sodium chloride (table salt) which is a white, crystalline solid having *none* of the properties of either sodium or chlorine. If, however, you *mixed* table salt with ground pepper, you would still be able to see the individual grains of each of them and, if you were patient, you could take tweezers and carefully separate them back into pure salt and pure pepper.

Mixtures fall into two categories, based on the uniformity of their composition (Figure 1.3.1). The first, called a **heterogeneous mixture**, is distinguished by the fact that different samples of the mixture may have a different composition. For example, if you open a container of mixed nuts and pull out a series of small samples and examine them, the exact ratio of peanuts-to-almonds in the samples will always be slightly different, no matter how carefully you mix them. Common examples of heterogeneous mixtures include dirt, gravel, and vegetable soup.

In a **homogeneous mixture,** on the other hand, any sample that you examine will have exactly the *same* composition as any other sample. Within chemistry, the most common type of homogeneous mixture is a **solution** which is one substance dissolved completely within another. Think of a solution of pure sugar dissolved in pure water. Any sample of the solution that you examine will have *exactly* the same ratio of sugar-to-water, which means that it is a homogeneous mixture. Even in a homogeneous mixture, the properties of the components are generally recognizable. Thus, sugar-water tastes sweet (like sugar) and is wet (like water). Unlike a compound, which has a fixed, definite ratio, in a mixture the amounts of each component can vary. For example, when you add a little sugar to one cup of tea and a lot of sugar to another, each cup will contain a homogeneous mixture of tea and sugar but they will have a different ratio of sugar-to-tea and a different taste. If you add so much sugar that some does not dissolve and stays on the bottom, however, the mixture is no longer homogeneous, it is heterogeneous; you could easily separate the two components (Figure 1.3.1).

Example 1.3.1

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

a. filtered tea
b. freshly squeezed orange juice
c. a compact disc
d. aluminum oxide, a white powder that contains a 2:3 ratio of aluminum and oxygen atoms
e. selenium

Given: a chemical substance

Asked for: its classification

Strategy:

I. Decide whether a substance is chemically pure. If it is pure, the substance is either an element or a compound. If a substance can be separated into its elements, it is a compound.
II. If a substance is not chemically pure, it is either a heterogeneous mixture or a homogeneous mixture. If its composition is uniform throughout, it is a homogeneous mixture.

Solution

a. I. Tea is a solution of compounds in water, so it is not chemically pure. It is usually separated from tea leaves by filtration.
II. Because the composition of the solution is uniform throughout, it is ***a homogeneous mixture***.
b. I. Orange juice contains particles of solid (pulp) as well as liquid; it is not chemically pure.
II. Because its composition is not uniform throughout, orange juice is ***a heterogeneous mixture***.
c. I. A compact disc is a solid material that contains more than one element, with regions of different compositions visible along its edge. Hence a compact disc is not chemically pure.
II. The regions of different composition indicate that a compact disc is ***a heterogeneous mixture.***
d. I. Aluminum oxide is a single, chemically ***pure compound***.
e. I. Selenium is one of the known ***elements***.

Exercise 1.3.1

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

a. white wine
b. mercury
c. ranch-style salad dressing
d. table sugar (sucrose)

Answer a: available at the end of this section.

Example 1.3.2

How would a chemist categorize each example of matter?

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

Solution

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.
b. Soil is composed of small pieces of a variety of different materials, so it is a heterogeneous mixture.
c. Water is a substance; more specifically, because water is composed of a fixed ratio hydrogen and oxygen atoms, it is a compound.
d. Oxygen, a substance, is an element.

Exercise 1.3.2

How would a chemist categorize each example of matter?

a. coffee
b. hydrogen
c. an egg

Answer a: available at the end of this section.

Summary

Matter can be classified into two broad categories: pure substances and mixtures. A pure substance is a form of matter that has a constant composition and properties that are constant throughout the sample. Mixtures are physical combinations of two or more elements and/or compounds. Mixtures can be classified as homogeneous or heterogeneous. Elements and compounds are both examples of pure substances. Compounds are substances that are made up of more than one type of atom. Elements are the simplest substances made up of only one type of atom.

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Answers

Exercise 1.3.1

homogeneous mixture (solution)
element
heterogeneous mixture
compound

Exercise 1.3.2

Coffee, assuming it is filtered, is a variety of substances dissolved in water, therefore, it is a homogeneous mixture, or a solution.
Hydrogen is a known element.
An egg is composed of many different substances with different compositions between the yolk and white, it is a heterogeneous mixture.

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1.4: Chemical Elements and Symbols

Learning Objectives

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

As described in the previous section, an element is a pure substance that cannot be broken down into simpler chemical substances. There are about 90 naturally occurring elements known on Earth. Using technology, scientists have been able to create nearly 30 additional elements that do not occur in nature. Today, chemistry recognizes 118 elements—some of which were created an atom at a time. Figure 1.4.1 shows some of the chemical elements.



Figure 1.4.1: Samples of Elements. Gold is a yellowish solid, iron is a silvery solid, while mercury is a silvery liquid at room temperature. © Thinkstock

Elemental Names and Symbols

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

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

The names of the elements can be cumbersome to write in full, especially when combined to form the names of compounds. Therefore, each element name is abbreviated as a one- or two-letter chemical symbol. By convention, the first letter of a chemical symbol is a capital letter, while the second letter (if there is one) is a lowercase letter. The first letter of the symbol is usually the first letter of the element's name, while the second letter is some other letter from the name. Some elements have symbols that derive from earlier, mostly Latin names, so the symbols may not contain any letters from the English name. Table 1.4.1 lists the names and symbols of some of the most familiar elements.

Table 1.4.1: Element Names and Symbols

Element Name	Element Symbol	Element Name	Element Symbol
aluminum	Al	magnesium	Mg

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

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

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

Elements in Nature and the Human Body

The elements vary widely in abundance. In the universe as a whole, the most common element is hydrogen (about 90% of atoms), followed by helium (most of the remaining 10%). All other elements are present in relatively minuscule amounts, as far as we can detect. On the planet Earth, however, the situation is rather different (Table 1.4.2). Oxygen makes up 46.1% of the mass of Earth's crust (the relatively thin layer of rock forming Earth's surface), mostly in combination with other elements, while silicon makes up 28.2%. Hydrogen, the most abundant element in the universe, makes up only 0.14% of Earth's crust.

Table 1.4.2: Elemental Composition of Earth and the Human Body

Earth's Crust		Human Body	
Element	Percentage	Element	Percentage
oxygen	46.1	oxygen	61
silicon	28.2	carbon	23
aluminum	8.23	hydrogen	10

Earth's Crust		Human Body	
Element	Percentage	Element	Percentage
iron	5.53	nitrogen	2.6
calcium	4.15	calcium	1.4
sodium	2.36	phosphorus	1.1
magnesium	2.33	sulfur	0.20
potassium	2.09	potassium	0.20
titanium	0.565	sodium	0.14
hydrogen	0.14	chlorine	0.12
phosphorus	0.105	magnesium	0.027
all others	0.174	silicon	0.026
Source: D. R. Lide, ed. *CRC Handbook of Chemistry and Physics*, 89th ed. (Boca Raton, FL: CRC Press, 2008–9), 14–17.			

Table 1.4.2 also lists the relative abundances of elements in the human body. If you compare both compositions, you will find disparities between the percentage of each element in the human body and on Earth. Oxygen has the highest percentage in both cases, but carbon, the element with the second highest percentage in the body, is relatively rare on Earth and does not even appear as a separate entry; carbon is part of the 0.174% representing "other" elements.

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

Looking Closer: The Phosphorous Bottleneck

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

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



Figure 1.4.2: The eutrophication of the Potomac River is evident from the bright green water, caused by a dense bloom of cyanobacteria. (CC BY-SA 3.0; Alexandr Trubetskoy via Wikipedia)

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

Example 1.4.1

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

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

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

Solution

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

Exercise 1.4.1

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

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

e. silver

Answer a available at the end of this section.

Example 1.4.2

What element is represented by each chemical symbol?

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

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

Exercise 1.4.2

What element is represented by each chemical symbol?

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

Answer a available at the end of this section.

Chemical Formulas

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

$$\underbrace{\mathrm{H_2O}}_{\substack{2\text{ H atoms}\\1\text{ O atom}}} \quad \underbrace{\mathrm{H_2SO_4}}_{\substack{2\text{ H atoms}\\1\text{ S atom}\\4\text{ O atoms}}} \quad \underbrace{\mathrm{C_{12}H_{22}O_{11}}}_{\substack{12\text{ H atoms}\\22\text{ C atoms}\\11\text{ O atoms}}} \tag{1.4.1}$$

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

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

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

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

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

and decomposing this to elements gives

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

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

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

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

Exercise 1.4.3

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

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

Answer a available at the end of this section.

Key Takeaways

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

Contributors and Attributions

- Anonymous

Answers

Exercise 1.4.1

Mn
Mg
Ne
N
Ag

Exercise 1.4.2

lead
tin
uranium
oxygen
fluorine

Exercise 1.4.3

Sodium Na, oxygen O, and hydrogen H are present. This is sodium hydroxide and is also known as lye or caustic soda.
This is a 1:1:1 ratio of sodium, oxygen, and hydrogen, respectively.
Sodium Na and chlorine O are present. This is sodium chloride and is also known as table salt.
This is a 1:1 ratio of sodium and chlorine, respectively.
Calcium Ca and Chlorine Cl are present. This is calcium chloride and is a different type of salt than sodium chloride.
This is a 1:2 ratio of calcium and chlorine, respectively.
Carbon C, Oxygen O, and Hydrogen H are present. This is acetic acid and is also known as vinegar.
This is a 2:2:4 (or 1:1:2) ratio of carbon, oxygen, and hydrogen, respectively.

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1.5: Chemical Reactions - Examples of Chemical Change

Chemical reactions are the processes by which chemicals interact to form new chemicals with different compositions. Simply stated, a chemical reaction is the process where reactants are transformed into products. How chemicals react is dictated by the chemical properties of the element or compound- the ways in which a compound or element undergoes changes in composition.

Chemical reactions are constantly occurring in the world around us; everything from the rusting of an iron fence to the metabolic pathways of a human cell are all examples of chemical reactions. Chemistry is an attempt to classify and better understand these reactions. One key reaction in modern civilization is combustion



Figure 1.5.1: An ignited lighter showing the combustion of butane. (Public Domain; Kimmo Palosaari via Wikipedia)

A chemical reaction is typically represented by a **chemical equation**, which represents the change from reactants to products. The left hand side of the equation represents the **reactants**, while the right hand side represents the **products**. A typical chemical reaction is written with stoichiometric coefficients, which show the relative amounts of products and reactants involved in the reaction. Each compound is followed by a parenthetical note of the compound's physical state: (l) for liquid, (s) for solid, (g) for gas. The symbol (aq) is also commonly used in order to represent an aqueous solution, in which compounds are dissolved in water.

Butane is a gas at room temperature and atmospheric pressure and is highly flammable, colorless, easily liquefied gas (under light pressure). Butane can be used for gasoline blending, as a fuel gas, fragrance extraction solvent, either alone or in a mixture with propane, and as a feedstock for the manufacture of ethylene and butadiene, a key ingredient of synthetic rubber. The chemical formula of butane if $\mathrm{C_4H_{10}}$. When oxygen is plentiful, butane burns to form carbon dioxide and water vapor as observed in modern lighters (Figure 1.5.1).

This reaction in words is:

$$\text{butane} + \text{oxygen} \rightarrow \text{carbon dioxide} + \text{water} \tag{1.5.1}$$

and the corresponding chemical equation for this reaction is:

$$2\,\mathrm{C_4H_{10}\,(g)} + 13\,\mathrm{O_2\,(g)} \longrightarrow 8\,\mathrm{CO_2\,(g)} + 10\,\mathrm{H_2O\,(g)} \tag{1.5.2}$$

In the above chemical equation, C_4H_{10} and O_2 are the **reactants** that reacted to form the **products**: CO_2 and H_2O,

Writing Chemical Equations

To write an accurate chemical equation, two things must occur:

1. Each product and reactant must be written using its chemical formula
2. Coefficients are used in front of the chemical formulas to reflect the ratio species (discussed further in a later chapter)
3. Adding the phase of each chemical in parentheses (although this is often dropped for convenience)

Key Takeaways

- Chemical reactions are written to represent chemical changes.
- Chemical formulas are used to represent the reactants (starting substance) and the products (the new substances).

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1.6: Physical Quantities - Units and Scientific Notation

Learning Objectives

- Express quantities properly using a number and a unit.
- Recognize the different measurement systems used in chemistry.
- Describe how prefixes are used in the metric system and identify how the prefixes milli-, centi-, and kilo- compare to the base unit.
- Understand when and how to use scientific notation to represent measurements.

Measurements

A coffee maker's instructions tell you to fill the coffeepot with 4 cups of water and use 3 scoops of coffee. When you follow these instructions, you are measuring. When you visit a doctor's office, a nurse checks your temperature, height, weight, and perhaps blood pressure (Figure 1.6.1); the nurse is also measuring.



Figure 1.6.1: Measuring Blood Pressure. A nurse or a doctor measuring a patient's blood pressure is taking a measurement. (GNU Free Documentation License; Pia von Lützau via Wikipedia).

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

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

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

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

anticonvulsant, but a single dose of 100 g is more than 10 times the lethal amount.

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

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

Example 1.6.1

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

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

Answers

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

Answer available at the end of this section.

Exercise 1.6.2

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

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

Answer a available at the end of this section.

The International System of Units

How long is a yard? It depends on whom you ask and when you asked the question. Today we have a standard definition of the yard, which you can see marked on every football field. If you move the ball ten yards, you get a first down and it doesn't matter whether you are playing in Los Angeles, Dallas, or Green Bay. But at one time that yard was arbitrarily defined as the distance from the tip of the king's nose to the end of his outstretched hand. Of course, the problem there is simple: new king, new distance (and then you have to remark all those football fields).

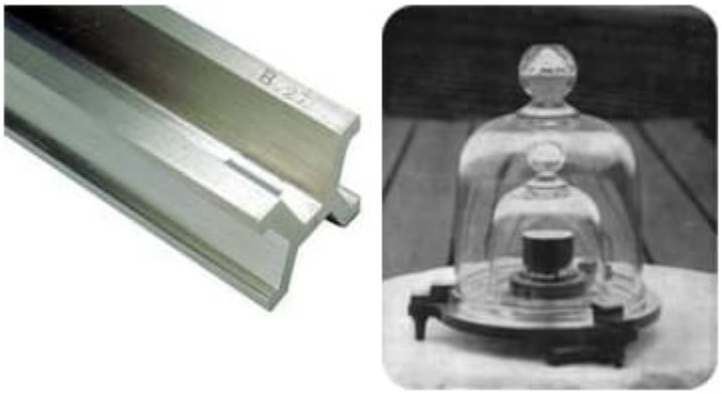


Figure 1.6.2: Meter standard (left) and Kilogram standard (right).

SI Base Units

All measurements depend on the use of units that are well known and understood. The **English system** of measurement units (inches, feet, ounces, etc.) are not used in science because of the difficulty in converting from one unit to another. The **metric system** is used because all metric units are based on multiples of 10, making conversions very simple. The metric system was originally established in France in 1795. **The International System of Units** is a system of measurement based on the metric system. The acronym **SI** is commonly used to refer to this system and stands for the French term, *Le Système International d'Unités*. The SI was adopted by international agreement in 1960 and is composed of seven base units in Table 1.6.1.

Table 1.6.1: SI Base Units of Measurement

Quantity	SI Base Unit	Symbol
Length	meter	m
Mass	kilogram	kg
Temperature	kelvin	K
Time	second	s
Amount of a Substance	mole	mol
Electric Current	ampere	A
Luminous Intensity	candela	cd

The first units are frequently encountered in chemistry. All other measurement quantities, such as volume, force, and energy, can be derived from these seven base units.

The Metric System is Not Ubiquitously Adopted

The map below shows the adoption of the SI units in countries around the world. The United States has legally adopted the metric system for measurements, but does not use it in everyday practice. Great Britain and much of Canada use a combination of metric and imperial units.

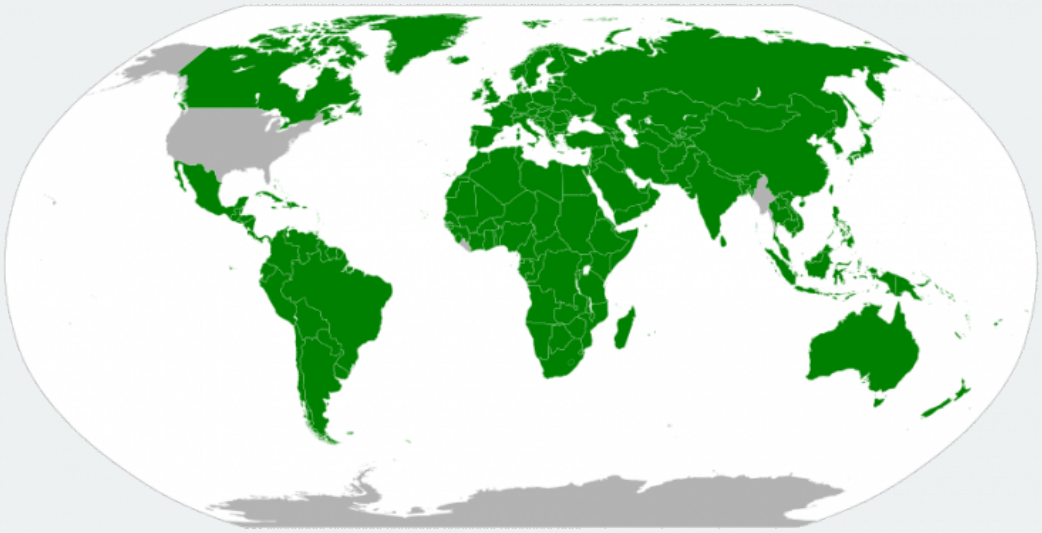


Figure 1.6.2: Areas of world using metric system (in green). Only a few countries are slow or resistant to adoption including the United States.

Metric Prefixes

Conversions between metric system units are straightforward because the system is based on powers of ten. For example, meters, centimeters, and millimeters are all metric units of length. There are 10 millimeters in 1 centimeter and 100 centimeters in 1 meter. **Metric prefixes** are used to distinguish between units of different size. These prefixes all derive from either Latin or Greek terms. For example, *mega* comes from the Greek word $\mu\varepsilon\gamma\alpha\varsigma$, meaning "great". Table 1.6.2 lists the most common metric prefixes and their relationship to the central unit that has no prefix. Length is used as an example to demonstrate the relative size of each prefixed unit.

Table 1.6.2: SI Prefixes. Commonly used prefixes are bolded.

Prefix	Unit Abbreviation	Meaning	Example
giga	G	1,000,000,000	1 gigameter $(\mathrm{Gm}) = 10^9\ \mathrm{m}$
mega	M	1,000,000	1 megameter $(\mathrm{Mm}) = 10^6\ \mathrm{m}$
kilo	k	**1,000**	**1 kilo**meter $(\mathrm{km}) = 1,000\ \mathrm{m}$
hecto	h	100	1 hectometer $(\mathrm{hm}) = 100\ \mathrm{m}$
deka	da	10	1 dekameter $(\mathrm{dam}) = 10\ \mathrm{m}$
		1	1 meter (m)
deci	d	**1/10**	**1 deci**meter $(\mathrm{dm}) = 0.1\ \mathrm{m}$
centi	c	**1/100**	**1 centi**meter $(\mathrm{cm}) = 0.01\ \mathrm{m}$
milli	m	**1/1,000**	**1 milli**meter $(\mathrm{mm}) = 0.001\ \mathrm{m}$
micro	μ	**1/1,000,000**	**1 micro**meter $(\mu\mathrm{m}) = 10^{-6}\ \mathrm{m}$
nano	n	1/1,000,000,000	1 nanometer $(\mathrm{nm}) = 10^{-9}\ \mathrm{m}$
pico	p	1/1,000,000,000,000	1 picometer $(\mathrm{pm}) = 10^{-12}\ \mathrm{m}$

Just as expressing a quantity without a unit is meaningless, so is using the incorrect format for units and prefixes. As you may have noticed, most metric abbreviations are lowercase. We use "m" for meter and not "M", which you will see later to represent solution concentration, something very different from length. However, when it comes to volume, the base unit "liter" is abbreviated as "L" and not "l". So we would write 3.5 milliliters as $3.5\ \mathrm{mL}$.

As a practical matter, whenever possible you should express the units in a small and manageable number. If you are measuring the weight of a material that weighs $6.5\ \text{kg}$, this is easier than saying it weighs $6500\ \text{g}$ or $0.65\ \text{dag}$. All three are correct, but the kg units in this case make for a small and easily managed number. However, if a specific problem needs grams instead of kilograms, go with the grams for consistency.

Example 1.6.2: Unit Abbreviations

Give the abbreviation for each unit and define the abbreviation in terms of the base unit.

a. kiloliter
b. microsecond
c. decimeter
d. nanogram

Solutions

Solutions to example explaining unit abbreviations.

	Explanation	Answer
a	The prefix kilo means "1,000 ×," so 1 kL equals 1,000 L	kL
b	The prefix micro implies 1/1,000,000th of a unit, so 1 µs equals 0.000001 s.	µs
c	The prefix deci means 1/10th, so 1 dm equals 0.1 m.	dm
d	The prefix nano means 1/1000000000, so a nanogram is equal to 0.000000001 g	ng

Exercise 1.6.2

Give the abbreviation for each unit and define the abbreviation in terms of the base unit.

a. kilometer
b. milligram
c. nanosecond
d. centiliter

Answer a available at the end of this section.

Answer b available at the end of this section.

Answer c available at the end of this section.

Answer d available at the end of this section.

Scientific Notation

Chemists often work with numbers that are exceedingly large or small. For example, entering the mass in grams of a hydrogen atom into a calculator would require a display with at least 24 decimal places. A system called **scientific notation** avoids much of the tedium and awkwardness of manipulating numbers with large or small magnitudes. In scientific notation, these numbers are expressed in the form

$$N \times 10^n \tag{1.6.1}$$

where N is a number greater than or equal to 1 and less than 10 ($1 \le N < 10$), and n is a positive or negative integer ($10^0 = 1$). The number 10 is called the base because it is this number that is raised to the power n. Although a base number may have values other than 10, the base number in scientific notation is always 10.

A simple way to convert numbers to scientific notation is to move the decimal point as many places to the left or right as needed to give a number from 1 to 10 (N). The magnitude of n is then determined as follows:

- If the decimal point is moved to the left n places, n is positive.
- If the decimal point is moved to the right n places, n is negative.

Another way to remember this is to recognize that as the number N decreases in magnitude, the exponent increases and vice versa. The application of this rule is illustrated in Example $1.6.1$.

Example $1.6.1$: Expressing Numbers in Scientific Notation

Convert each number to scientific notation.

a. 637.8
b. 0.0479
c. 7.86
d. 12,378
e. 0.00032
f. 61.06700
g. 2002.080
h. 0.01020

Solution

Solutions to example explaining how numbers look in scientific notation.

	Explanation	Answer
a	To convert 637.8 to a number from 1 to 10, we move the decimal point two places to the left: 637.8 Because the decimal point was moved two places to the left, n = 2.	6.378×10^{2}
b	To convert 0.0479 to a number from 1 to 10, we move the decimal point two places to the right: 0.0479 Because the decimal point was moved two places to the right, n = –2.	4.79×10^{-2}
c	This is usually expressed simply as 7.86. (Recall that $10^{0} = 1$.)	7.86×10^{0}
d	Because the decimal point was moved four places to the left, n = 4.	1.2378×10^{4}
e	Because the decimal point was moved four places to the right, n = –4.	3.2×10^{-4}
f	Because the decimal point was moved one place to the left, n = 1.	6.106700×10^{1}
g	Because the decimal point was moved three places to the left, n = 3.	2.002080×10^{3}
h	Because the decimal point was moved two places to the right, n = -2.	1.020×10^{-2}

Scientific Notation: Addition and Subtraction

Before numbers expressed in scientific notation can be added or subtracted, they must be converted to a form in which all the exponents have the same value. The appropriate operation is then carried out on the values of N. Example $1.6.2$ illustrates how to

do this.

Example 1.6.2: Expressing Sums and Differences in Scientific Notation

Carry out the appropriate operation and then express the answer in scientific notation.

a. $(1.36 \times 10^2) + (4.73 \times 10^3)$
b. $(6.923 \times 10^{-3}) - (8.756 \times 10^{-4})$

Solution

Solution to example explaining how sums and differences look in scientific notation.

	Explanation	Answer
a	Both exponents must have the same value, so these numbers are converted to either $$(1.36 \times 10^2) + (47.3 \times 10^2) = (1.36 + 47.3) \times 10^2 = 48.66 \times 10^2$$ or $$(0.136 \times 10^3) + (4.73 \times 10^3) = (0.136 + 4.73) \times 10^3) = 4.87 \times 10^3.$$ Choosing either alternative gives the same answer, reported to two decimal places: In converting 48.66 × 10^2 to scientific notation, n has become more positive by 1 because the value of N has decreased.	4.87×10^3
b	Converting the exponents to the same value gives either $$(6.923 \times 10^{-3}) - (0.8756 \times 10^{-3}) = (6.923 - 0.8756) \times 10^{-3}$$ or $$(69.23 \times 10^{-4}) - (8.756 \times 10^{-4}) = (69.23 - 8.756) \times 10^{-4} = 60.474 \times 10^{-4}.$$ In converting 60.474 × 10^{-4} to scientific notation, n has become more positive by 1 because the value of N has decreased.	6.047×10^{-3}

Scientific Notation: Multiplication and Division

When multiplying numbers expressed in scientific notation, we multiply the values of N and add together the values of n. Conversely, when dividing, we divide N in the dividend (the number being divided) by N in the divisor (the number by which we are dividing) and then subtract n in the divisor from n in the dividend. In contrast to addition and subtraction, the exponents do not have to be the same in multiplication and division. Examples of problems involving multiplication and division are shown in Example 1.6.3.

Example 1.6.3: Expressing Products and Quotients in Scientific Notation

Perform the appropriate operation and express your answer in scientific notation.

a. $[(6.022 \times 10^{23})(6.42 \times 10^{-2})$

b. $\dfrac{1.67 \times 10^{-24}}{9.12 \times 10^{-28}}$

c. $\dfrac{(6.63 \times 10^{-34})(6.0 \times 10)}{8.52 \times 10^{-2}}$

Solution

Solutions to example explaining how products and quotients look in scientific notation.

	Explanation
a	In multiplication, we add the exponents: $$(6.022 \times 10^{23})(6.42 \times 10^{-2}) = (6.022)(6.42) \times 10^{[23+(-2)]} = 38.7 \times 10^{21}$$ In converting 38.7×10^{21} to scientific notation, n has become more positive by 1 because the value of N has decreased.
b	In division, we subtract the exponents: $$\frac{1.67 \times 10^{-24}}{9.12 \times 10^{-28}} = \frac{1.67}{9.12} \times 10^{[-24-(-28)]} = 0.183 \times 10^{4}$$ In converting 0.183×10^{4} to scientific notation, n has become more negative by 1 because the value of N has increased.
c	This problem has both multiplication and division: $$\frac{(6.63 \times 10^{-34})(6.0 \times 10)}{(8.52 \times 10^{-2})} = \frac{39.78}{8.52} \times 10^{[-34+1-(-2)]}$$

Key Takeaways

- Identifying a quantity properly requires both a number and a unit.
- Metric prefixes derive from Latin or Greek terms. The prefixes are used to make the units manageable.
- The SI system is based on multiples of ten. There are seven basic units in the SI system. Five of these units are commonly used in chemistry.

Answers

Example 1.6.1

Exercise 1.6.2

The number is 99, and the unit is bottles of soda.
The number is 60, and the unit is miles per hour.
The number 32, and the unit is fluid ounces
The number is 98.6, and the unit is degrees Fahrenheit

Exercise 1.6.2

km

Exercise 1.6.2

mg

Exercise 1.6.2

ns

Exercise 1.6.2

cL

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1.7: Measuring Mass, Length, and Volume

Learning Objective

- Describe the units (and abbreviations) that go with various quantities.
- Derive new units by combining numerical prefixes with units.

Mass vs. Weight

One of the many interesting things about travel in outer space is the idea of weightlessness. If something is not fastened down, it will float in mid-air. Early astronauts learned that weightlessness had bad effects on bone structure. If there was no pressure on the legs, those bones would begin to lose mass. Weight provided by gravity is needed to maintain healthy bones. Specially designed equipment is now a part of every space mission so the astronauts can maintain good body fitness.

Mass is a measure of the amount of matter that an object contains. The mass of an object is made in comparison to the standard mass of 1 kilogram. The kilogram was originally defined as the mass of $1\ \mathrm{L}$ of liquid water at $4^{\circ}\mathrm{C}$ (volume of a liquid changes slightly with temperature). In the laboratory, mass is measured with a balance (see below), which must be calibrated with a standard mass so that its measurements are accurate.



Figure 1.7.1: An analytical balance makes very sensitive mass measurements in a laboratory, usually in grams.

Other common units of mass are the gram and the milligram. A gram is 1/1000th of a kilogram, meaning that there are $1000\ \mathrm{g}$ in $1\ \mathrm{kg}$. A milligram is 1/1000th of a gram, so there are $1000\ \mathrm{mg}$ in $1\ \mathrm{g}$.

The Difference Between Mass and Weight

The mass of a body is a measure of its inertial property or how much matter it contains. The weight of a body is a measure of the force exerted on it by gravity or the force needed to support it. Gravity on earth gives a body a downward acceleration of about 9.8 m/s^2. In common parlance, weight is often used as a synonym for mass in weights and measures. For instance, the verb “to weigh” means “to determine the mass of” or “to have a mass of.” The incorrect use of weight in place of mass should be phased out, and the term mass used when mass is meant. The SI unit of mass is the kilogram (kg). In science and technology, the weight of a body in a particular reference frame is defined as the force that gives the body an acceleration equal to the local acceleration of free fall in that reference frame. Thus, the SI unit of the quantity weight defined in this way (force) is the newton (N).

Length

Length is the measurement of the extent of something along its greatest dimension. The SI basic unit of length, or linear measure, is the **meter** (m). All measurements of length may be made in meters, though the prefixes listed in various tables will often be more convenient. The width of a room may be expressed as about 5 meters (m), whereas a large distance, such as the distance between New York City and Chicago, is better expressed as 1150 kilometers (km). Very small distances can be expressed in units such as the millimeter or the micrometer. The width of a typical human hair is about 10 micrometers $(\mu\mathrm{m})$.

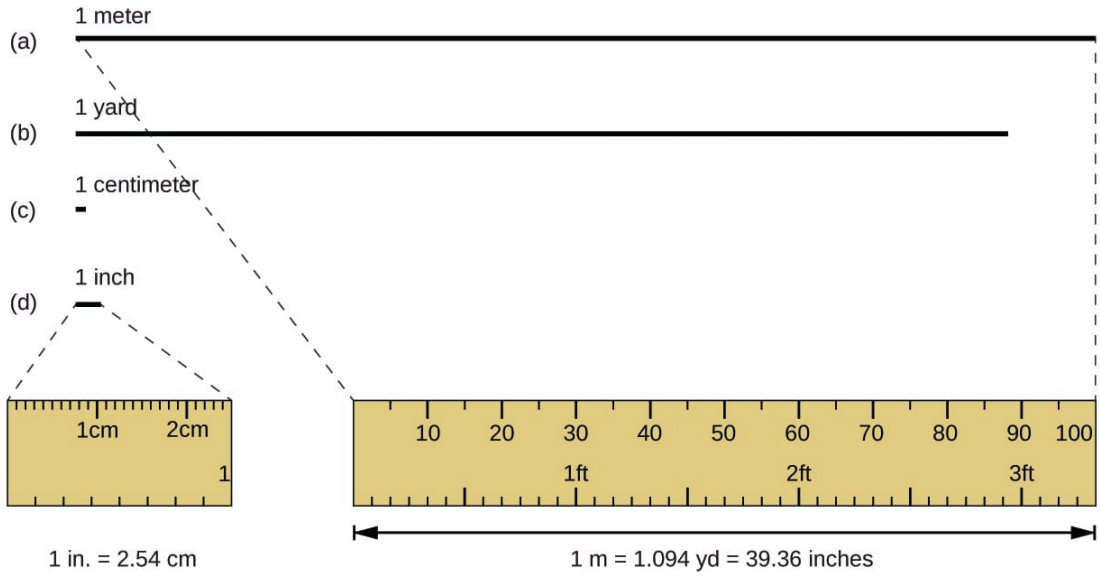


Figure 1.7.2: The relative lengths of 1 m, 1 yd, 1 cm, and 1 in. are shown (not actual size), as well as comparisons of 2.54 cm and 1 in., and of 1 m and 1.094 yd. (CC BY 4.0; OpenStax)

Volume

In addition to the fundamental units, SI also allows for **derived** units based on a fundamental unit or units. There are many derived units used in science. For example, the derived unit for *area* comes from the idea that area is defined as width times height. Because both width and height are lengths, they both have the fundamental unit of meter, so the unit of area is meter × meter, or meter^2 (m^2). This is sometimes spoken as "square meters." A unit with a prefix can also be used to derive a unit for area, so we can also have cm^2, mm^2, or km^2 as acceptable units for area.

Volume is the amount of space occupied by a sample of matter. The volume of a regular object can be calculated by multiplying its length by its width and its height. Since each of those is a linear measurement, we say that units of volume are derived from units of length. One unit of volume is the cubic meter (m^3), which is the volume occupied by a cube that measures $1\ \mathrm{m}$ on each side. This very large volume is not very convenient for typical use in a chemistry laboratory. A liter (L) is the volume of a cube that measures $10\ \mathrm{cm}\ (1\,\mathrm{dm})$ on each side. A liter is thus equal to both $1000\ \mathrm{cm}^3\ (10\,\mathrm{cm} \times 10\,\mathrm{cm} \times 10\,\mathrm{cm})$ and to $1\ \mathrm{dm}^3$. A smaller unit of volume that is commonly used is the milliliter (mL - note the capital L which is a standard practice). A milliliter is the volume of a cube that measures $1\ \mathrm{cm}$ on each side. Therefore, a milliliter is equal to a cubic centimeter (cm^3). There are $1000\ \mathrm{mL}$ in $1\ \mathrm{L}$, which is the same as saying that there are $1000\ \mathrm{cm}^3$ in $1\ \mathrm{dm}^3$.

Another definition of a liter is one-tenth of a meter cubed. Because one-tenth of a meter is 10 cm, then a liter is equal to 1,000 cm^3 (Figure 1.7.3). Because 1 L equals 1,000 mL, we conclude that 1 mL equals 1 cm^3; thus, these units are interchangeable.

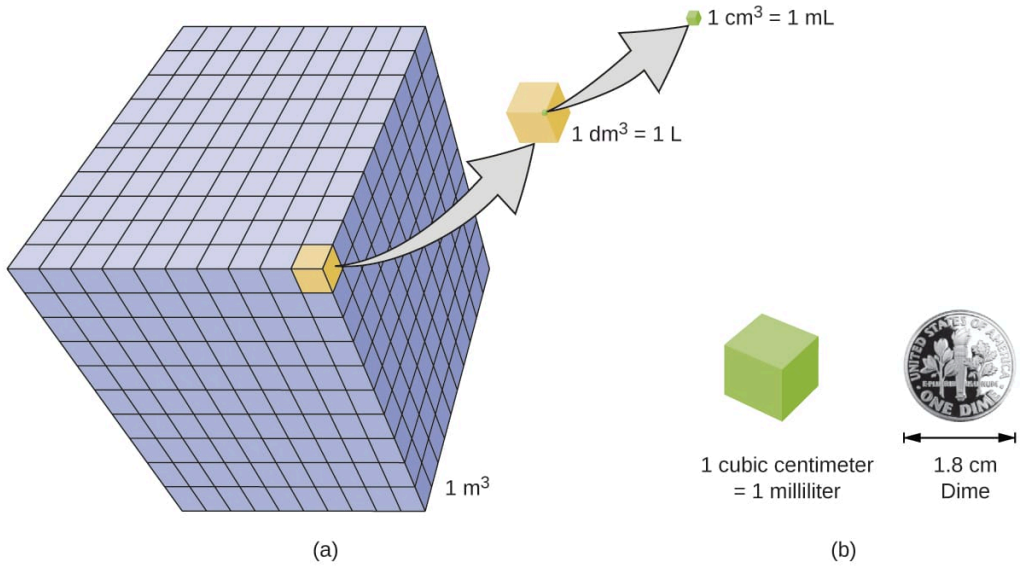


Figure 1.7.3: Units of Volume. (a) The relative volumes are shown for cubes of 1 m^3, 1 dm^3 (1 L), and 1 cm^3 (1 mL) (not to scale). A liter (L) is defined as a cube 1 dm (1/10th of a meter) on a side. A milliliter (mL), 1/1,000th of a liter, is equal to 1 cubic centimeter. (b) The diameter of a dime is compared relative to the edge length of a 1-cm^3 (1-mL) cube. (CC BY 4.0; OpenStax)

Units not only are multiplied together but also can be divided. For example, if you are traveling at one meter for every second of time elapsed, your velocity is 1 meter per second, or 1 m/s. The word *per* implies division, so velocity is determined by dividing a distance quantity by a time quantity. Other units for velocity include kilometers per hour (km/h) or even micrometers per nanosecond (μm/ns). Later, we will see other derived units that can be expressed as fractions.

Key Takeaways

- Mass is a measure of the amount of matter that an object contains. Mass is independent of location.
- Weight is a measure of force that is equal to the gravitational pull on an object. Weight depends on location.
- Units can be multiplied and divided to generate new units for quantities like the liter for volume.

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1.8: Measurement and Significant Figures

Learning Objectives

- Identify the number of significant figures in a reported value.
- Apply the concept of significant figures to report a measurement with the proper number of digits.

Scientists have established certain conventions for communicating the degree of **precision** of a measurement, which is dependent on the measuring device used (See Figure 1.8.1). Imagine, for example, that you are using a meterstick to measure the width of a table. The centimeters (cm) marked on the meterstick, tell you how many *centimeters* wide the table is. Many metersticks also have markings for millimeters (mm), so we can measure the table to the nearest *millimeter*. The measurement made using millimeters is more precise, it is closer to the actual length of the table. Most metersticks do not have any smaller (or more precise) markings indicated, so you cannot report the measured width of the table any more precise than to the nearest millimeter.

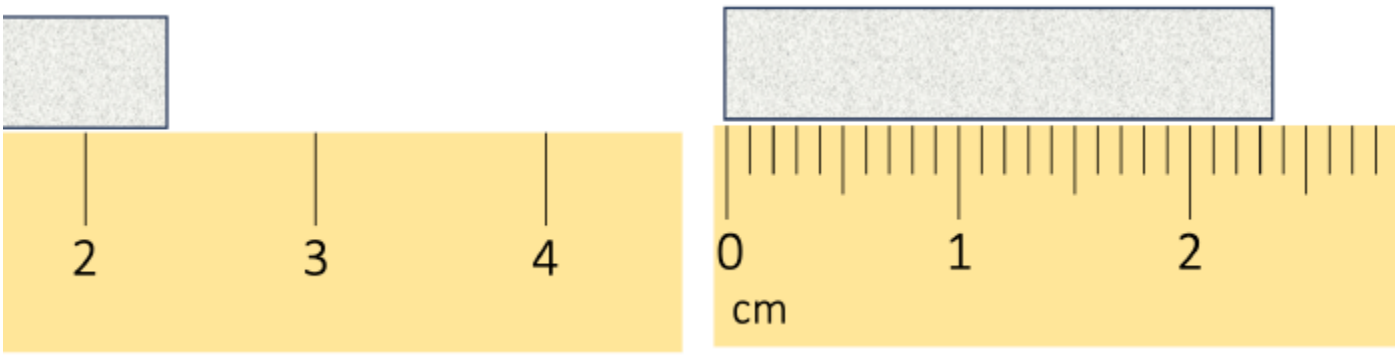


Figure 1.8.1: Different measuring devices have different degrees of **precision**. The ruler on the left has centimeter markings and the measurement of the box is 2.3 cm. Here, the first digit is *certain*, and the second digit is *estimated*, there are two digits reported for this measurement. The ruler on the right has millimeter markings (1/10 of a centimeter) and the measurement of the box is 2.36 cm. Here, the first two digits are *certain*, and the third digit is *estimated*, there are three digits reported for this measurement. The ruler on the right is more precise than the ruler on the left because more digits are reported. (Figure: Lisa Sharpe Elles)

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

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

Rules for Determination of Significant Figures

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

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

and the zero a value placeholder?

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

Rule 1: All nonzero digits in a measurement are significant.

- 237 has three significant figures.
- 1.897 has four significant figures.

Rule 2: Zeros that appear between other nonzero digits (i.e., "**middle zeros**") are always significant.

- 39,004 has five significant figures.
- 5.02 has three significant figures.

Rule 3: Zeros that appear in front of all of the nonzero digits are called **leading zeros**. Leading zeros are never significant.

- 0.008 has one significant figure.
- 0.000416 has three significant figures.

Rule 4: Zeros that appear after all nonzero digits are called **trailing zeros**. A number with trailing zeros that lacks a decimal point may or may not be significant.

- 1400 is ambiguous.
  - 1.4×10^3 has two significant figures.
  - 1.40×10^3 three significant figures.
  - 1.400×10^3 has four significant figures.

Rule 5: Trailing zeros in a number with a decimal point are significant. This is true whether the zeros occur before or after the decimal point.

- 620.0 has four significant figures.
- 19.000 has five significant figures.

It needs to be emphasized that just because a certain digit is not significant does not mean that it is not important or that it can be left out. Though the zero in a measurement of 140 may not be significant, the value cannot simply be reported as 14. An insignificant zero functions as a placeholder for the decimal point. When numbers are written in scientific notation, this becomes more apparent. The measurement 140 can be written as 1.4×10^2, with two significant figures in the coefficient or as 1.40×10^3, with three significant figures. A number less than one, such as 0.000416, can be written in scientific notation as 4.16×10^{-4}, which has 3 significant figures. In some cases, scientific notation is the only way to correctly indicate the correct number of significant figures. In order to report a value of 15,000,00 with four significant figures, it would need to be written as 1.500×10^7.

Exact Quantities

When numbers are known exactly, the significant figure rules do not apply. This occurs when objects are counted rather than measured. For example, a carton of eggs has 12 eggs. The actual value cannot be 11.8 eggs, since we count eggs in whole number quantities. So the 12 is an exact quantity. Exact quantities are considered to have an *infinite number* of significant figures; the importance of this concept will be seen later when we begin looking at how significant figures are dealt with during calculations. Numbers in many conversion factors, especially for simple unit conversions, are also exact quantities and have infinite significant figures. There are exactly 100 centimeters in 1 meter and exactly 60 seconds in 1 minute. Those values are definitions and are not the result of a measurement.

Example 1.8.2

Give the number of significant figures in each. Identify the rule for each.

a. 5.87
b. 0.031

c. 52.90
d. 00.2001
e. 500
f. 6 atoms

Solution

Solution to example explaining how many significant figures are in each number.

Explanation	Answer
a. All three numbers are significant (rule 1).	5.87 , three significant figures
b. The leading zeros are not significant (rule 3). The 3 and the 1 are significant (rule 1)	0.031, two significant figures
c. The 5, the 2 and the 9 are significant (rule 1). The trailing zero is also significant (rule 5).	52.90, four significant figures
d. The leading zeros are not significant (rule 3). The 2 and the 1 are significant (rule 1) and the middle zeros are also significant (rule 2).	00.2001, four significant figures
e. The number is ambiguous. It could have one, two or three significant figures.	500, ambiguous
f. The 6 is a counting number. A counting number is an exact number.	6, infinite

Exercise 1.8.2

Give the number of significant figures in each.

a. 36.7 m
b. 0.006606 s
c. 2,002 kg
d. 306,490,000 people
e. 3,800 g

Answer a: available at the end of this section.

Answer b: available at the end of this section.

Answer c: available at the end of this section.

Answer d: available at the end of this section.

Answer e: available at the end of this section.

Summary

Uncertainty exists in all measurements. The degree of uncertainty is affected in part by the quality of the measuring tool. Significant figures give an indication of the certainty of a measurement. Rules allow decisions to be made about how many digits to use in any given situation.

Answers

Exercise 1.8.2
three significant figures.

Exercise 1.8.2
four significant figures.

Exercise 1.8.2

four significant figures.

Exercise 1.8.2

Infinite (Exact number)

Exercise 1.8.2

Ambiguous, could be two, three or four significant figure.

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1.9: Rounding Off Numbers

Learning Objectives

- Use significant figures correctly in arithmetical operations.

Rounding

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

Consider the measurement $207.518\ \text{m}$. Right now, the measurement contains six significant figures. How would we successively round it to fewer and fewer significant figures? Follow the process as outlined in Table $1.9.1$.

Table $1.9.1$: Rounding examples

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

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

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

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

Rules for Calculations With Measured Numbers

How are significant figures handled in calculations? It depends on what type of calculation is being performed.

Multiplication and Division

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

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

38.65 times 105.93 equals 4094.1954, which should be rounded to 4 sig figs since the lowest count in the numbers being multiplied is 4 sig figs

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

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

Example 1.9.1

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

a. 23.096 × 90.300
b. 125 × 9.000

Solution

a

Solution to (a) in example question.

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

b

Solution to (b) in example question.

Explanation	Answer
The calculator gives 1,125 as the answer, but we limit it to three significant figures.	1.13×10^3

Addition and Subtraction

If the calculation is an addition or a subtraction, the rule is as follows: limit the reported answer to the rightmost column that all numbers have significant figures in common. For example, if you were to add 1.2 and 4.71, we note that the first number stops its significant figures in the tenths column, while the second number stops its significant figures in the hundredths column. We therefore limit our answer to the tenths column.

$$\begin{array}{r} 1.2 \\ \underline{4.41} \\ 5.61 \end{array}$$

↑ limit final answer to the tenths column: 5.6

We drop the last digit—the 1—because it is not significant to the final answer.

The dropping of positions in sums and differences brings up the topic of rounding. Although there are several conventions, in this text we will adopt the following rule: the final answer should be rounded up if the first dropped digit is 5 or greater and rounded down if the first dropped digit is less than 5.

$$\begin{array}{r} 77.2 \\ \underline{10.46} \\ 87.66 \end{array}$$

↑ limit final answer to the tenths column and round up: 87.7

Example 1.9.2

a. 13.77 + 908.226
b. 1,027 + 611 + 363.06

Solution

a

Solution to (a) in example question.

Explanation	Answer
The calculator answer is 921.996, but because 13.77 has its farthest-right significant figure in the hundredths place we need to round the final answer to the hundredths position. Because the first digit to be dropped (in the thousandths place) is greater than 5, we round up to 922.00	$922.00 = 9.2200 \times 10^2$

b

Solution to (b) in example question.

Explanation	Answer
The calculator gives 2,001.06 as the answer, but because 611 and 1027 has its farthest-right significant figure in the ones place, the final answer must be limited to the ones position.	$2,001.06 = 2.001 \times 10^3$

Exercise 1.9.2

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

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

Answer a: available at the end of this section.

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

Example 1.9.3

a. 2(1.008g) + 15.99 g
b. 137.3 s + 2(35.45 s)
c. $\frac{118.7g}{2} - 35.5g$

Solution

a

Solution to (a) in example question.

Explanation	Answer
2(1.008g) + 15.99 g = **Perform multiplication first.** 2 (1.008g *4 sig figs*) = **2.016 g** *4 sig figs* The number with the least number of significant figures is 1.008g; *the number 2 is an exact number and therefore has infinite number of significant figures*. **Then, perform the addition.** **2.016 g** *thousandths place* + 15.99 g *hundredths place (least precise)* = 18.006 g **Round the final answer.** Round the final answer to the hundredths place since 15.99 has its farthest right significant figure in the hundredths place (least precise).	18.01 g (rounding up)

b

Solution to (b) in example question.

Explanation	Answer
137.3 s + 2 (35.45 s) = **Perform multiplication first.** 2 (35.45 s *4 sig figs*) = **70.90 s** *4 sig figs* The number with the least number of significant figures is 35.45; *the number 2 is an exact number and therefore has infinite number of significant figures.* **Then, perform the addition.** 137.3 s *tenths place (least precise)* + **70.90 s** *hundredths place* = 208.20 s **Round the final answer.** Round the final answer to the tenths place based on 137.3 s.	208.2 s

c

Solution to (c) in example question.

Explanation	Answer
$\frac{118.7g}{2} - 35.5g$ = **Perform division first.** $\frac{118.7g}{2}$ *4 sig figs* = **59.35 g** *4 sig figs* The number with the least number of significant figures is 118.7g; the number 2 is an exact number and therefore has infinite number of significant figures. **Perform subtraction next.** **59.35 g** *hundredths place* – 35.5 g *tenths place (least precise)* = 23.85 g **Round the final answer.** Round the final answer to the tenths place based on 35.5 g.	23.9 g (rounding up)

Exercise 1.9.3

Complete the calculations and report your answers using the correct number of significant figures.

a. 5(1.008s) - 10.66 s
b. 99.0 cm+ 2(5.56 cm)

Answer a available at the end of this section.

Summary

- Rounding
  - If the number to be dropped is greater than or equal to 5, increase the number to its left by 1. e.g. 2.9699 rounded to three significant figures is 2.97
  - If the number to be dropped is less than 5, there is no change. e.g. 4.00443 rounded to four sig. figs. is 4.004
- The rule in multiplication and division is that the final answer should have the same number of significant figures as there are in the number with the fewest significant figures.
- The rule in addition and subtraction is that the answer is given the same number of decimal places as the term with the fewest decimal places.

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-
- Marisa Alviar-Agnew (Sacramento City College)
- Henry Agnew (UC Davis)

Answers

Exercise 1.9.2

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

$1,437 = 1.437 \times 10^{3}$

$156 = 1.56 \times 10^{2}$

$2.14 = 2.14 \times 10^{0}$

Exercise 1.9.3

-5.62 s

110.2 cm

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1.10: Problem Solving - Unit Conversions and Estimating Answers

Learning Objectives

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

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

Conversion Factors

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

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

or

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

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

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

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

$$\text{same quantity} \left\langle \frac{100 \text{ cm}}{1 \text{ m}} = 1 \right.$$

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

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

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

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

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

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

$$\frac{3.55}{1} \times \frac{100\text{ cm}}{1} = 355\text{ cm} \tag{1.10.1}$$

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

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

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

In the previous example (Equation 1.10.1), we used the fraction $\frac{100\text{ cm}}{1\text{ m}}$ as a conversion factor. Does the conversion factor $\frac{1\text{ m}}{100\text{ cm}}$ also equal 1? Yes, it does; it has the same quantity in the numerator as in the denominator (except that they are expressed in different units). Why did we not use *that* conversion factor? If we had used the second conversion factor, the original unit would not have canceled, and the result would have been meaningless. Here is what we would have gotten:

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

For the answer to be meaningful, we have to *construct the conversion factor in a form that causes the original unit to cancel out*. Figure 1.10.1 shows a **concept map** for constructing a proper conversion.

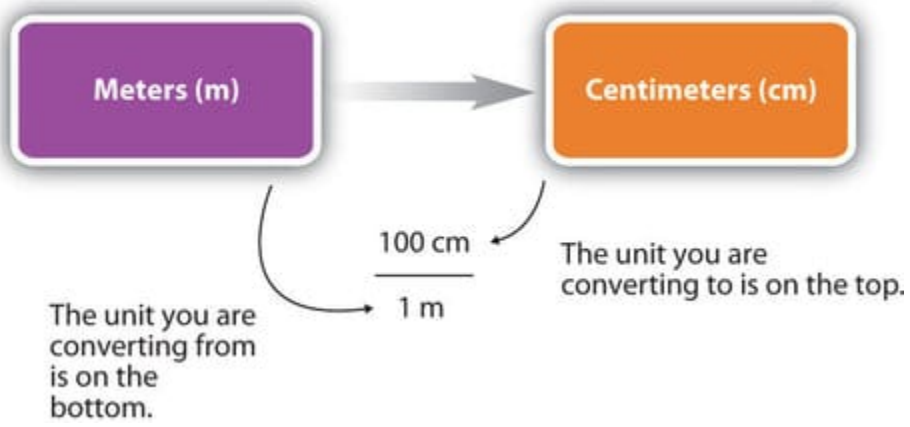


Figure 1.10.1: A Concept Map for Conversions. This is how you construct a conversion factor to convert from one unit to another.

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

Significant Figures in Conversions

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

Example 1.10.1

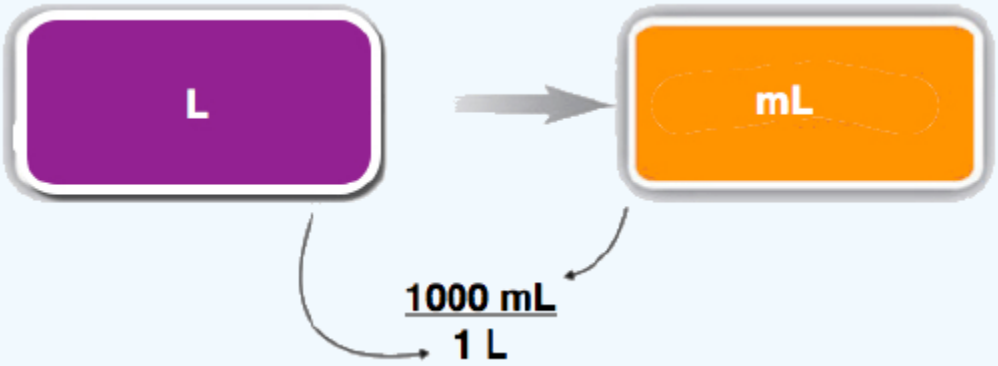
a. The average volume of blood in an adult male is 4.7 L. What is this volume in milliliters?
b. A hummingbird can flap its wings once in 18 ms. How many seconds are in 18 ms?

Solution

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

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

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



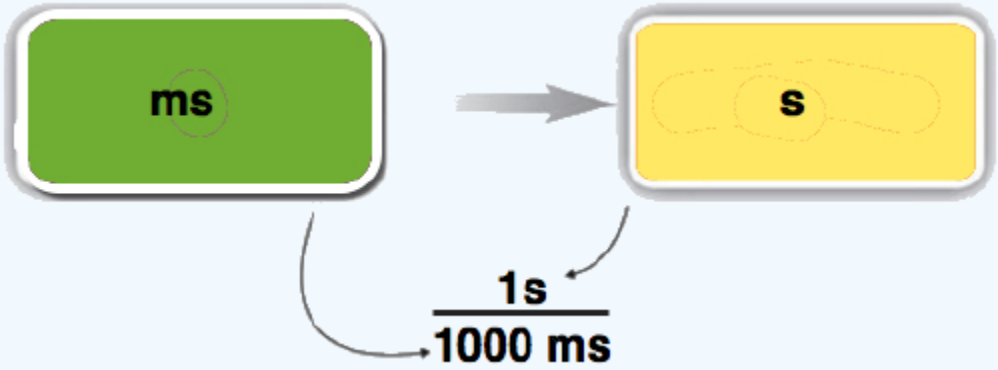
$$4.7\cancel{\text{L}} \times \frac{1,000\text{ mL}}{1\ \cancel{\text{L}}} = 4,700\text{ mL}$$

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

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

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

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



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

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

Exercise 1.10.1

Perform each conversion.

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

Answer a available at the end of this section.

Conversion Factors From Different Units

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

13.6 g mercury = 1 mL mercury

This relationship can be used to construct two conversion factors:

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

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

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

$$\approx 220\ \text{g}$$

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

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

Example 1.10.2: Mercury Thermometer

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

Solution

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

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

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

We have limited the final answer to three significant figures.

Exercise 1.10.2

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

Answer available at the end of this section.

Problem Solving With Multiple Conversions

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

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

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

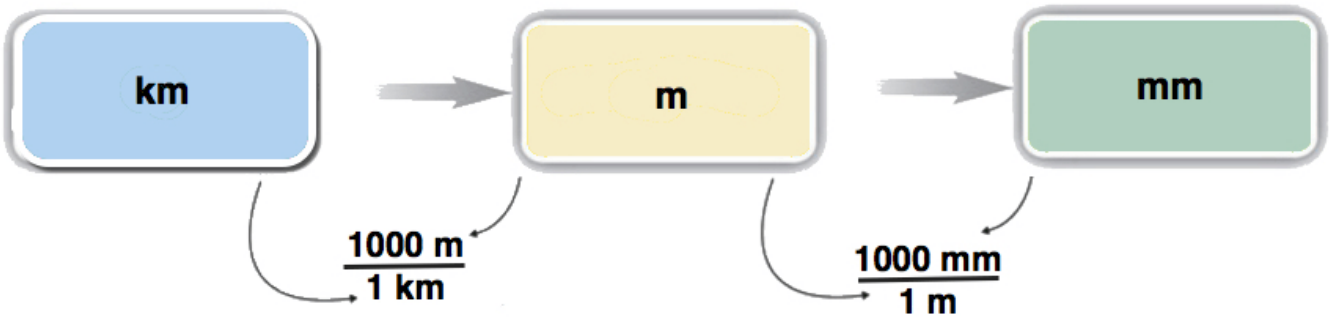
Then we take the result (54,700 m) and convert it to millimeters, remembering that there are $1,000 \text{ mm}$ for every 1 m:

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

We have expressed the final answer in scientific notation.

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

Concept Map



Calculation

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

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

Either method—one step at a time or all the steps together—is acceptable. If you do all the steps together, the restriction for the

proper number of significant figures should be done after the last step. As long as the math is performed correctly, you should get the same answer no matter which method you use.

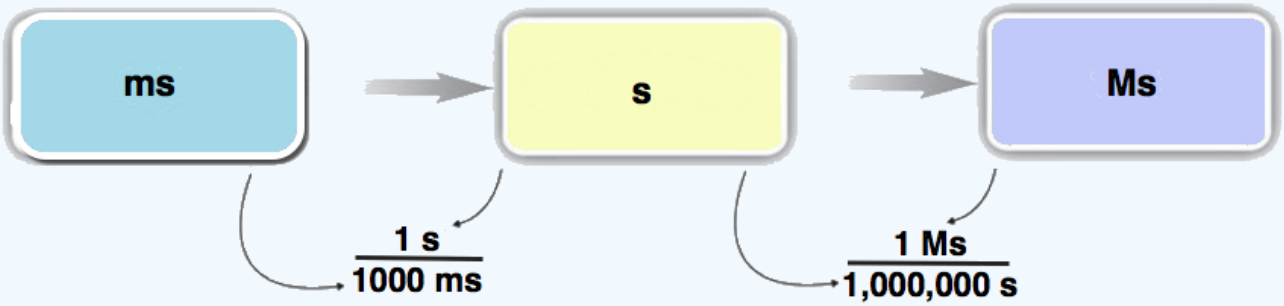
Example 1.10.3

Convert 58.2 ms to megaseconds in one multistep calculation.

Solution

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

Concept Map



To convert ms to s, put 1 s over 1000 ms in a fraction. To convert s to Ms, put 1 Ms over 1,000,000 s in a fraction.

Calculation

$$58.2 \ \cancel{\text{ms}} \times \frac{1 \cancel{\text{s}}}{1,000 \ \cancel{\text{ms}}} \times \frac{1 \text{ Ms}}{1,000,000 \ \cancel{\text{s}}} = 0.0000000582 \text{ Ms}$$

$$= 5.82 \times 10^{-8} \text{ Ms}$$

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

Exercise 1.10.3

Convert 43.007 mg to kilograms in one multistep calculation.

Answer available at the end of this section.

Career Focus: Pharmacist

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

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

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

Key Takeaway

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

Concept Review Exercises

1. How do you determine which quantity in a conversion factor goes in the denominator of the fraction?
2. State the guidelines for determining significant figures when using a conversion factor.
3. Write a concept map (a plan) for how you would convert 1.0×10^{12} *nano*liters (nL) to *kilo*liters (kL).

Answers

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



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

Answers

Exercise 1.10.1

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

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

Exercise 1.10.2

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

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

Exercise 1.10.3

$$43.007 \cancel{\text{mg}} \times \frac{1 \cancel{\text{g}}}{1,000 \cancel{\text{mg}}} \times \frac{1 \text{ kg}}{1,000 \cancel{\text{g}}} = 0.000043007 \text{ kg}$$

$$= 4.3007 \times 10^{-5} \text{ kg}$$

.

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

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1.11: Temperature, Heat, and Energy

Learning Objectives

- To identify the different between temperature and heat
- To recognize the different scales used to measuring temperature

Temperature

Temperature is a measure of the average kinetic energy of the particles in matter. In everyday usage, temperature indicates a measure of how hot or cold an object is. Temperature is an important parameter in chemistry. When a substance changes from solid to liquid, it is because there was in increase in the temperature of the material. Chemical reactions usually proceed faster if the temperature is increased. Many unstable materials (such as enzymes) will be viable longer at lower temperatures.



Figure 1.11.1: The glowing charcoal on the left represents high kinetic energy, while the snow and ice on the right are of much lower kinetic energy.

Three different scales are commonly used to measure temperature: Fahrenheit (expressed as °F), Celsius (°C), and Kelvin (K). Thermometers measure temperature by using materials that expand or contract when heated or cooled. Mercury or alcohol thermometers, for example, have a reservoir of liquid that expands when heated and contracts when cooled, so the liquid column lengthens or shortens as the temperature of the liquid changes.



Figure 1.11.2: Daniel Gabriel Fahrenheit (left), Anders Celsius (center), and Lord Kelvin (right)

The Fahrenheit Temperature Scale

The first thermometers were glass and contained alcohol, which expanded and contracted as the temperature changed. The German scientist, Daniel Gabriel Fahrenheit used mercury in the tube, an idea put forth by Ismael Boulliau. The Fahrenheit scale

was first developed in 1724 and tinkered with for some time after that. The main problem with this scale is the arbitrary definitions of temperature. The freezing point of water was defined as $32^{\circ}\mathrm{F}$ and the boiling point as $212^{\circ}\mathrm{F}$. The Fahrenheit scale is typically not used for scientific purposes.

The Celsius Temperature Scale

The Celsius scale of the metric system is named after Swedish astronomer Anders Celsius (1701 - 1744). The Celsius scale sets the freezing point and boiling point of water at $0^{\circ}\mathrm{C}$ and $100^{\circ}\mathrm{C}$ respectively. The distance between those two points is divided into 100 equal intervals, each of which is one degree. Another term sometimes used for the Celsius scale is "centigrade" because there are 100 degrees between the freezing and boiling points of water on this scale. However, the preferred term is "Celsius".

The Kelvin Temperature Scale

The Kelvin temperature scale is named after Scottish physicist and mathematician Lord Kelvin (1824 - 1907). It is based on molecular motion, with the temperature of $0\ \mathrm{K}$, also known as **absolute zero**, being the point where all molecular motion ceases. The freezing point of water on the Kelvin scale is $273.15\ \mathrm{K}$, while the boiling point is $373.15\ \mathrm{K}$. Notice that there is no "degree" used in the temperature designation. Unlike the Fahrenheit and Celsius scales where temperatures are referred to as "degrees F " or "degrees C", we simply designated temperatures in the Kelvin scale as kelvin.

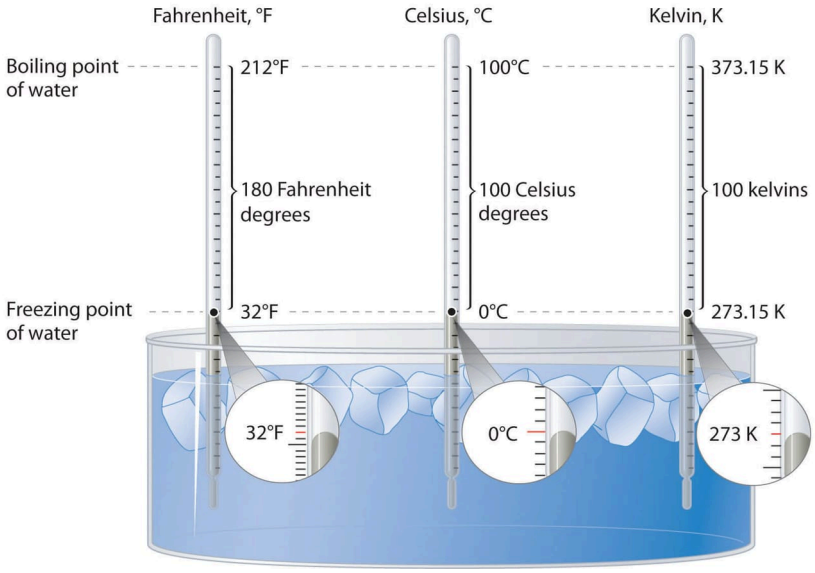


Figure 1.11.3: A Comparison of the Fahrenheit, Celsius, and Kelvin Temperature Scales. Because the difference between the freezing point of water and the boiling point of water is 100° on both the Celsius and Kelvin scales, the size of a degree Celsius (°C) and a kelvin (K) are precisely the same. In contrast, both a degree Celsius and a kelvin are 9/5 the size of a degree Fahrenheit (°F). (CC BY-SA-NC 3.0; anonymous)

The Kelvin is the same size as the Celsius degree, so measurements are easily converted from one to the other. The freezing point of water is 0°C = 273.15 K; the boiling point of water is 100°C = 373.15 K. The Kelvin and Celsius scales are related as follows:

$$T\,(\text{in °C}) + 273.15 = T\,(\text{in K}) \tag{3.10.1}$$

$$T\ \ (\text{in K}) - 273.15 = T\,(\text{in °C}) \tag{3.10.2}$$

Degrees on the Fahrenheit scale, however, are based on an English tradition of using 12 divisions, just as 1 ft = 12 in. The relationship between degrees Fahrenheit and degrees Celsius is as follows: where the coefficient for degrees Fahrenheit is exact. (Some calculators have a function that allows you to convert directly between °F and °C.) There is only one temperature for which the numerical value is the same on both the Fahrenheit and Celsius scales: –40°C = –40°F. The relationship between the scales are as follows:

$$^{\circ}C = \frac{5}{9} \times (^{\circ}F - 32) \tag{3.10.3}$$

$$°F = \frac{9}{5} \times (°C) + 32 \tag{3.10.4}$$

Example 1.11.1: Temperature Conversions

A student is ill with a temperature of 103.5°F. What is her temperature in °C and K?

Solution

Converting from Fahrenheit to Celsius requires the use of Equation 3.10.3:

$$\begin{aligned} °C &= \frac{5}{9} \times (103.5°F - 32) \\ &= 39.7\,°C \end{aligned}$$

Converting from Celsius to Kelvin requires the use of Equation 3.10.1:

$$\begin{aligned} K &= 39.7\,°C + 273.15 \\ &= 312.9\,K \end{aligned}$$

Exercise 1.11.1

Convert each temperature to °C and °F.

a. the temperature of the surface of the sun (5800 K)
b. the boiling point of gold (3080 K)
c. the boiling point of liquid nitrogen (77.36 K)

Answer (a) available at the end of this section.

Answer (b) available at the end of this section.

Answer (c) available at the end of this section.

Heat

While the concept of temperature may seem familiar to you, many people confuse temperature with heat. as discussed above, **Temperature** is a measure of how hot or cold an object is relative to another object (its thermal energy content), whereas **heat** is the flow of thermal energy between objects with different temperatures.

When scientists speak of ***heat***, they are referring to energy that is transferred from an object with a higher temperature to an object with a lower temperature as a result of the temperature difference. Heat will "flow" from the hot object to the cold object until both end up at the same temperature. When you cook with a metal pot, you witness energy being transferred in the form of heat. Initially, only the stove element is hot – the pot and the food inside the pot are cold. As a result, heat moves from the hot stove element to the cold pot. After a while, enough heat is transferred from the stove to the pot, raising the temperature of the pot and all of its contents.

Energy

Just like matter, energy is a term that we are all familiar with and use on a daily basis. Before you go on a long hike, you eat an *energy* bar; every month, the *energy* bill is paid; on TV, politicians argue about the *energy* crisis. But what is energy? If you stop to think about it, energy is very complicated. When you plug a lamp into an electric socket, you see energy in the form of light, but when you plug a heating pad into that same socket, you only feel warmth. Without energy, we couldn't turn on lights, we couldn't brush our teeth, we couldn't make our lunch, and we couldn't travel to school. In fact, without energy, we couldn't even wake up because our bodies require energy to function. We use energy for every single thing that we do, whether we're awake or asleep.

Energy is measured in one of two common units: the calorie and the joule. The joule (J) is the SI unit of energy. The calorie is familiar because it is commonly used when referring to the amount of energy contained within food. A **calorie** (cal) is the quantity of heat required to raise the temperature of 1 gram of water by $1^{\circ}\mathrm{C}$. For example, raising the temperature of $100\ \mathrm{g}$ of water from $20^{\circ}\mathrm{C}$ to $22^{\circ}\mathrm{C}$ would require $100 \times 2 = 200\ \mathrm{cal}$.

Calories contained within food are actually kilocalories (kcal). In other words, if a certain snack contains 85 food calories, it actually contains $85\ \mathrm{kcal}$ or $85,000\ \mathrm{cal}$. In order to make the distinction, the dietary calorie is written with a capital C.

$$1\ \text{kilocalorie} = 1\ \text{Calorie} = 1000\ \text{calories} \tag{1.11.1}$$

To say that the snack "contains" 85 Calories means that $85\ \mathrm{kcal}$ of energy are released when that snack is processed by your body.

Heat changes in chemical reactions are typically measured in joules rather than calories. The conversion between a joule and a calorie is shown below.

$$1\ \mathrm{J} = 0.2390\ \mathrm{cal}\ \text{or}\ 1\ \mathrm{cal} = 4.184\ \mathrm{J} \tag{1.11.2}$$

We can calculate the amount of heat released in kilojoules when a 400. Calorie hamburger is digested.

$$400\ \mathrm{Cal} = 400\ \mathrm{kcal} \times \frac{4.184\ \mathrm{kJ}}{1\ \mathrm{kcal}} = 1.67 \times 10^{3}\ \mathrm{kJ} \tag{1.11.3}$$

Heat Capacity and Specific Heat

If a swimming pool and wading pool, both full of water at the same temperature, were subjected to the same input of heat energy, the wading pool would certainly rise in temperature more quickly than the swimming pool. Because of its much larger mass, the swimming pool of water has a larger "heat capacity" than the wading pool. Similarly, different substances respond to heat in different ways. If a metal chair sits in the bright sun on a hot day, it may become quite hot to the touch. An equal mass of water in the same sun will not become nearly as hot.

We would say that water has a high **heat capacity** (the amount of heat required to raise the temperature of an object by $1^{\circ}\mathrm{C}$). Water is very resistant to changes in temperature, while metals in general are not. The **specific heat** of a substance is the amount of energy required to raise the temperature of 1 gram of the substance by $1^{\circ}\mathrm{C}$. The symbol for specific heat is c_p, with the p subscript referring to the fact that specific heats are measured at constant pressure. The units for specific heat can either be joules per gram per degree $(\mathrm{J/g^{\circ}C})$ or calories per gram per degree $(\mathrm{cal/g^{\circ}C})$ (Table 1.11.1). This text will use $\mathrm{J/g^{\circ}C}$ for specific heat.

$$\text{specific heat} = \frac{\text{heat}}{\text{mass} \times \mathrm{cal/g^{\circ}C}} \tag{1.11.4}$$

Notice that water has a very high specific heat compared to most other substances.

Table 1.11.1: Specific Heat Capacities

Substance	Specific Heat Capacity at 25°C in J/g °C	Substance	Specific Heat Capacity at 25°C in J/g °C
$\mathrm{H_2}$ gas	14.267	steam @ 100°C	2.010
He gas	5.300	vegetable oil	2.000
$\mathrm{H_2O\,(l)}$	4.184	sodium	1.23
lithium	3.56	air	1.020
ethyl alcohol	2.460	magnesium	1.020
ethylene glycol	2.200	aluminum	0.900
ice @ 0oC	2.010	Concrete	0.880
steam @ 100oC	2.010	glass	0.840

Water is commonly used as a coolant for machinery because it is able to absorb large quantities of heat (see table above). Coastal climates are much more moderate than inland climates because of the presence of the ocean. Water in lakes or oceans absorbs heat from the air on hot days and releases it back into the air on cool days.



Figure 1.11.4: This power plant in West Virginia, like many others, is located next to a large lake so that the water from the lake can be used as a coolant. Cool water from the lake is pumped into the plant, while warmer water is pumped out of the plant and back into the lake.

Example 1.11.1: Measuring Heat

A flask containing 8.0×10^2 g of water is heated, and the temperature of the water increases from 21 °C to 85 °C. How much heat did the water absorb?

Solution

To answer this question, consider these factors:

- the specific heat of the substance being heated (in this case, water)
- the amount of substance being heated (in this case, 800 g)
- the magnitude of the temperature change (in this case, from 21 °C to 85 °C).

The specific heat of water is 4.184 J/g °C, so to heat 1 g of water by 1 °C requires 4.184 J. We note that since 4.184 J is required to heat 1 g of water by 1 °C, we will need 800 times as much to heat 800 g of water by 1 °C. Finally, we observe that since 4.184 J are required to heat 1 g of water by 1 °C, we will need 64 times as much to heat it by 64 °C (that is, from 21 °C to 85 °C).

This can be summarized using the equation:

$$\begin{aligned} q &= c \times m \times \Delta T \\ &= c \times m \times (T_{\text{final}} - T_{\text{initial}}) \\ &= (4.184\ \text{J}/\cancel{\text{g}}^\circ\text{C}) \times (800\ \cancel{\text{g}}) \times (85 - 21)^\circ\text{C} \\ &= (4.184\ \text{J}/\cancel{\text{g}}^\circ\cancel{\text{C}}) \times (800\ \cancel{\text{g}}) \times (64)^\circ\cancel{\text{C}} \\ &= 210,000\ \text{J} (= 210\ \text{kJ}) \end{aligned}$$

Because the temperature increased, the water absorbed heat and q is positive

Exercise 1.11.1

How much heat, in joules, must be added to a 5.00×10^2 g iron skillet to increase its temperature from 25 °C to 250 °C? The specific heat of iron is 0.451 J/g °C.

Answer

Answer available at the end of this section.

Summary

- Three different scales are commonly used to measure temperature: Fahrenheit (expressed as °F), Celsius (°C), and Kelvin (K).
- Heat capacity is the amount of heat required to raise the temperature of an object by 1°C).
- The specific heat of a substance is the amount of energy required to raise the temperature of 1 gram of the substance by 1°C.

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-
- Template:OpenStax
- Marisa Alviar-Agnew (Sacramento City College)
- Henry Agnew (UC Davis)

Answers

Exercise 1.11.1
5527 K, 9980 °F

Exercise 1.11.1
2807 K, 5084 °F

Exercise 1.11.1
-195.79 K, -320.42 °F

Exercise 1.11.1
5.05×10^4 J

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1.12: Density and Specific Gravity

Learning Objectives

- Define density and specific gravity.
- Perform calculations involving both density and specific gravity.

After trees are cut, logging companies often move these materials down a river to a sawmill where they can be shaped into building materials or other products. The logs float on the water because they are less dense than the water they are in. Knowledge of density is important in the characterization and separation of materials. Information about density allows us to make predictions about the behavior of matter.

Density

A golf ball and a table tennis ball are about the same size. However, the golf ball is much heavier than the table tennis ball. Now imagine a similar size ball made out of lead. That would be very heavy indeed! What are we comparing? By comparing the mass of an object relative to its size, we are studying a property called **density**. Density is the ratio of the mass of an object to its volume.

$$\text{density} = \frac{\text{mass}}{\text{volume}} \tag{1.12.1}$$

$$D = \frac{m}{V} \tag{1.12.2}$$

Density is usually a measured property of a substance, so its numerical value affects the significant figures in a calculation. Notice that density is defined in terms of two dissimilar units, mass and volume. That means that density overall has *derived units*, just like velocity. Common units for density include g/mL, g/cm^3, g/L, kg/L, and even kg/m^3. Densities for some common substances are listed in Table $1.12.1$.

Table $1.12.1$*: Densities of Some Common Substances*

Liquids and Solids	Density at 20°C (g/mL)	Gases	Density at 20°C (g/L)
Ethanol	0.79	Hydrogen	0.084
Ice (0°C)	0.917	Helium	0.166
Corn oil	0.922	Air	1.20
Water	0.998	Oxygen	1.33
Water (4°C)	1.000	Carbon dioxide	1.83
Corn syrup	1.36	Radon	9.23
Aluminum	2.70		
Copper	8.92		
Lead	11.35		
Mercury	13.6		
Gold	19.3		

The SI units of density are kilograms per cubic meter $\left(\text{kg/m}^3\right)$, since the kg and the m are the SI units for mass and length respectively. In everyday usage in a laboratory, this unit is awkwardly large. Most solids and liquids have densities that are conveniently expressed in grams per cubic centimeter $\left(\text{g/cm}^3\right)$. Since a cubic centimeter is equal to a milliliter, density units can also be expressed as g/mL. Gases are much less dense than solids and liquids, so their densities are often reported in g/L. Water

has a density of $1.0\ \mathrm{g/mL}$.

File:Separatory_funnel_with_oil_and_colored_water.jpgfile
File:Separatory_funnel_with_oil_and_colored_water.jpg



Figure 1.12.1: Separatory Funnel containing oil and colored water to display density differences. (CC BY-SA 3.0; PRHaney vai Wikipedia).

Because of how it is defined, density can act as a conversion factor for switching between units of mass and volume. For example, suppose you have a sample of aluminum that has a volume of 7.88 cm^3. How can you determine what mass of aluminum you have without measuring it? You can use the volume to calculate it. If you multiply the given volume by the known density (from Table 1.12.1), the volume units will cancel and leave you with mass units, telling you the mass of the sample:

Start with Equation 1.12.1

$$\text{density} = \frac{m}{V}$$

and insert the relavant numbers

$$\frac{2.7g}{cm^3} = \frac{m}{7.88\,cm^3}$$

Cross multiplying both sides (right numerator x left denominator = left numerator x right denominator), we get the following expression with answer and appropriate unit.

$$7.88\,\cancel{cm^3} \times \frac{2.7\,g}{\cancel{cm^3}} = 21g \text{ of aluminum}$$

Since most materials expand as temperature increases, the density of a substance is temperature dependent and usually decreases as temperature increases. You known that ice floats in water and it can be seen from the table that ice is less dense. Alternatively, corn syrup, being denser, would sink if placed in water.

Example 1.12.1

An $18.2\ \mathrm{g}$ sample of zinc metal has a volume of $2.55\ \mathrm{cm^3}$. Calculate the density of zinc.

Solution

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

Known

- Mass $= 18.2\ \text{g}$
- Volume $= 2.55\ \text{cm}^3$

Unknown

- Density $=?\ \text{g/cm}^3$

Use Equation 1.12.1 to solve the problem.

Step 2: Calculate

$$D = \frac{m}{V} = \frac{18.2\ \text{g}}{2.55\ \text{cm}^3} = 7.14\ \text{g/cm}^3 \tag{1.12.3}$$

Step 3: Think about your result.

If $1\ \text{cm}^3$ of zinc has a mass of about 7 grams, then 2 and a half cm^3 will have a mass about 2 and a half times as great. Metals are expected to have a density greater than that of water and zinc's density falls within the range of the other metals listed above.

Since density values are known for many substances, density can be used to determine an unknown mass or an unknown volume. Dimensional analysis will be used to ensure that units cancel appropriately.

Example 1.12.2

1. What is he mass of $2.49\ \text{cm}^3$ of aluminum?
2. What is the volume of $50.0\ \text{g}$ of aluminum?

Solution

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

Known

- Density $= 2.70\ \text{g/cm}^3$
- 1. Volume $= 2.49\ \text{cm}^3$
- 2. Mass $= 50.0\ \text{g}$

Unknown

- 1. Mass $=?\ \text{g}$
- 2. Volume $=?\ \text{cm}^3$

Use the equation for density, $D = \frac{m}{V}$, and dimensional analysis to solve each problem.

Step 2: Calculate

$$1.\ 2.49\ \text{cm}^3 \times \frac{2.70\ \text{g}}{1\ \text{cm}^3} = 6.72\ \text{g} \tag{1.12.4}$$

$$2.\ 50.0\ \text{g} \times \frac{1\ \text{cm}^3}{2.70\ \text{g}} = 18.5\ \text{cm}^3 \tag{1.12.5}$$

In problem 1, the mass is equal to the density multiplied by the volume. In problem 2, the volume is equal to the mass divided by the density.

Step 3: Think about your results.

Because a mass of $1\ \text{cm}^3$ of aluminum is $2.70\ \text{g}$, the mass of about $2.5\ \text{cm}^3$ should be about 2.5 times larger. The $50\ \text{g}$ of aluminum is substantially more than its density, so that amount should occupy a relatively large volume.

Specific Gravity

Specific gravity is the ratio of the density (mass of a unit volume) of a substance to the density of a given reference material, often a liquid.

$$\text{specific gravity} = \frac{\text{Density of a substance}(\ \cancel{g/mL}\ )}{\text{Density of the water at the same temperature}(\ \cancel{g/mL}\ )} \tag{1.12.6}$$

If a substance's relative density is less than one then it is less dense than water and similarly, if greater than 1 then it is denser than water. If the relative density is exactly 1 then the densities are equal. For example, an ice cube, with a relative density of about 0.91, will float on water and a substance with a relative density greater than 1 will sink.

A *hydrometer* is an instrument used for measuring the specific density of liquids based on the concept of buoyancy (Figure 1.12.2). A hydrometer usually consists of a sealed hollow glass tube with a wider bottom portion for buoyancy, a ballast such as lead or mercury for stability, and a narrow stem with graduations for measuring. The liquid to test is poured into a tall container, often a graduated cylinder, and the hydrometer is gently lowered into the liquid until it floats freely. The point at which the surface of the liquid touches the stem of the hydrometer correlates to relative density. Hydrometers can contain any number of scales along the stem corresponding to properties correlating to the density.



Figure 1.12.2: A US Navy Aviation Boatswain's Mate tests the specific gravity of JP-5 fuel. (Public Domain; U.S. Navy via Wikipedia)

Summary

- Density is the ratio of the mass of an object to its volume.
- Gases are less dense than either solids or liquids.
- Both liquid and solid materials can have a variety of densities.
- For liquids and gases, the temperature will affect the density to some extent.

Contributors and Attributions

-

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2: ATOMS AND THE PERIODIC TABLE

2.1: Atomic Theory and the Structure of Atoms

2.2: Elements and Atomic Number

2.3: Isotopes and Atomic Weight

2.4: The Periodic Table

2.5: Some Characteristics of Different Groups

2.6: Electronic Structure of Atoms

2.7: Electron Configurations

2.8: Electron Configurations and the Periodic Table

2.9: Electron-Dot Symbols

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2.1: Atomic Theory and the Structure of Atoms

Learning Objectives

- State the modern atomic theory.
- Describe how atoms are constructed.

The smallest piece of an element that maintains the identity of that element is called an atom. Individual atoms are extremely small. It would take about fifty million atoms in a row to make a line that is 1 cm long. The period at the end of a printed sentence has several million atoms in it. Atoms are so small that it is difficult to believe that all matter is made from atoms-but it is.

The modern atomic theory, proposed about 1803 by the English chemist John Dalton, 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).

Dalton studied the weights of various elements and compounds. He noticed that matter always combined in fixed ratios based on weight, or volume in the case of gases. Chemical compounds always contain the same proportion of elements by mass, regardless of amount, which provided further support for Proust's law of definite proportions. Dalton also observed that there could be more than one combination of two elements.

From his experiments and observations, as well as the work from peers of his time, Dalton proposed a new theory of the **atom**. This later became known as Dalton's **atomic theory**. The general tenets of this theory were as follows:

- All matter is composed of extremely small particles called atoms.
- Atoms of a given element are identical in size, mass, and other properties. Atoms of different elements differ in size, mass, and other properties.
- Atoms cannot be subdivided, created, or destroyed.
- Atoms of different elements can combine in simple whole number ratios to form chemical compounds.
- In chemical reactions, atoms are combined, separated, or rearranged.

> Dalton's atomic theory has been largely accepted by the scientific community, with the exception of three changes. We know now that (1) an atom can be further subdivided, (2) all atoms of an element are not identical in mass, and (3) using nuclear fission and fusion techniques, we can create or destroy atoms by changing them into other atoms.

These concepts form the basis of chemistry. Although the word *atom* comes from a Greek word that means "indivisible," we understand now that atoms themselves are composed of smaller parts called **subatomic particles**. The first part to be discovered was the **electron**, a tiny subatomic particle with a negative charge. It is often represented as e^-, with the right superscript showing the negative charge. Later, two larger particles were discovered. The **proton**, a subatomic particle with a positive charge. is a more massive (but still tiny) subatomic particle with a positive charge, represented as p^+. The **neutron** is a subatomic particle with about the same mass as a proton but no charge. It is represented as either n or n^0. We now know that all atoms of all elements are composed of electrons, protons, and (with one exception) neutrons. Table 2.1.1 summarizes the properties of these three subatomic particles.

Table 2.1.1: Properties of the Three Subatomic Particles

Name	Symbol	Mass (approx.; g)	Mass (approx.; amu)	Charge
Proton	p^+	1.673×10^{-24}	1.0073	+1
Neutron	n, n^0	1.675×10^{-24}	1.0087	none
Electron	e^-	9.109×10^{-28}	5.486×10^{-4}	−1

Atoms and subatomic particles are so small that it doesn't quite make sense to measure their masses in grams. A more useful unit to measure atomic mass is the **atomic mass unit (**amu**)**, where 1 amu = 1.660539×10^{-24} g or one-twelfth of the mass of a carbon-12 atom. As you can see in the table above, the mass of 1 proton and 1 neutron are each 1 amu in this system. Carbon-12 contains six protons and six neutrons and is assigned a mass of exactly 12 amu.



Figure 2.1.1: Electrons are *much smaller* than protons or neutrons. If an electron was the mass of a penny (right), a proton or a neutron would have the mass of a large bowling ball (left)!

How are these subatomic particles arranged in atoms? They are not arranged at random. Experiments by Ernest Rutherford in England in the 1910's pointed to a nuclear model with atoms that has the protons and neutrons in a central nucleus with the electrons in orbit about the nucleus. The relatively massive protons and neutrons are collected in the center of an atom, in a region called the **nucleus** of the atom (plural *nuclei*). The electrons are outside the nucleus and spend their time orbiting in space about the nucleus. (Figure 2.1.2). Because protons and neutrons are so massive compared to electrons, Table 2.1.1, nearly all of the mass of an atom is contained in the nucleus.

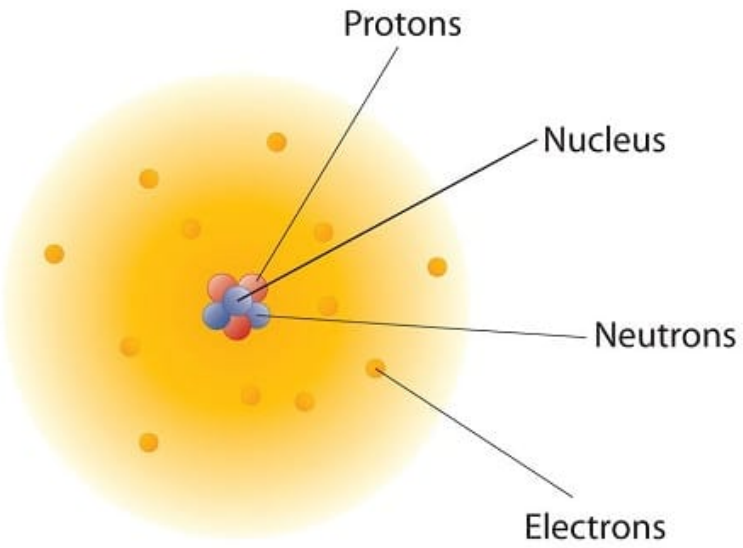


Figure 2.1.2: The Structure of the Atom. Atoms have protons and neutrons in the center, making the nucleus, while the electrons orbit the nucleus.

Note Atoms In Action

The evidence for atoms is so great that few doubt their existence. In fact, individual atoms are now routinely observed with state-of-the art technologies. Moreover, they can even be used for making pretty images or as IBM research demonstrate in Video 2.1.1, control of individual atoms can be use used create animations.

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Video 2.1.1: A Boy And His Atom - The World's Smallest Movie. A Boy and His Atom is a 2012 stop-motion animated short film released by IBM Research. The movie tells the story of a boy and a wayward atom who meet and become friends. It depicts a boy playing with an atom that takes various forms. It was made by moving carbon monoxide molecules viewed with a scanning tunneling microscope, a device that magnifies them 100 million times. These molecules were moved to create images, which were then saved as individual frames to make the film.

Key Takeaways

- Chemistry is based on the modern atomic theory, which states that all matter is composed of atoms.
- Atoms themselves are composed of protons, neutrons, and electrons.
- Each element has its own atomic number, which is equal to the number of protons in its nucleus.

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2.2: Elements and Atomic Number

Learning Objectives

- Use the atomic number and mass number to describe an atom.

The modern atomic theory states that atoms of one element are the same, while atoms of different elements are different. What makes atoms of different elements different? The fundamental characteristic that all atoms of the same element share is the *number of protons*. All atoms of hydrogen have one and only one proton in the nucleus; all atoms of iron have 26 protons in the nucleus. This number of protons is so important to the identity of an atom that it is called the **atomic number (*Z*).** The number of protons in an atom is the atomic number of the element. Thus, hydrogen has an atomic number of 1, while iron has an atomic number of 26. Each element has its own characteristic atomic number.

Atoms are electrically *neutral*, meaning that the overall electric charge is zero. This is because the number of protons (positive charge) equals the number of electrons (negative charge). Therefore, the atomic number also provides the number of electrons. For example, helium has Z = 2, which tells us that there are 2 protons in the nucleus and 2 electrons outside of the nucleus. Sometimes atoms will gain or lose electrons resulting in a difference in the number of protons and electrons, which means the charge is no longer zero. Atoms that have a charge are called *ions* and will be discussed further in later chapters.

$$atomic\ number = Z = p^{+} = e^{-1} \tag{2.2.1}$$

As we learned previously, protons and neutrons, which are found in the nucleus of an atom, each have a mass of ~1 amu. Because an electron has negligible mass relative to that of a proton or a neutron, the majority of an atom's mass is in the nucleus. The **mass number (*A*)** is defined as the total number of protons (p^{+}) and neutrons (n) in an atom:

$$mass\ number = A = p^{+} + n \tag{2.2.2}$$

Atoms of the same element always have the same number of protons, same Z, but often have different numbers of neutrons, therefore, different mass numbers. These atoms are called **isotopes** and will be discussed in more detail in the next chapter.

Example 2.2.1

a. The most common carbon atoms have six protons and six neutrons in their nuclei. What are the atomic number and the mass number of these carbon atoms?
b. An isotope of uranium has an atomic number of 92 and a mass number of 235. What are the number of protons and neutrons in the nucleus of this atom?

Solution

a. If a carbon atom has six protons in its nucleus, its atomic number is 6. If it also has six neutrons in the nucleus, then the mass number is 6 + 6, or 12.
b. If the atomic number of uranium is 92, then that is the number of protons in the nucleus. Because the mass number is 235, then the number of neutrons in the nucleus is 235 – 92, or 143.

Exercise 2.2.1

The number of protons in the nucleus of a tin atom is 50, while the number of neutrons in the nucleus is 68. What are the atomic number and the mass number of this isotope?

Answer available at the end of this section.

Example 2.2.2:

a. What is the symbol for an isotope of uranium that has an atomic number of 92 and a mass number of 235?
b. How many protons and neutrons are in $^{56}_{26}\mathrm{Fe}$

Solution

a. The symbol for this isotope is $^{235}_{92}\mathrm{U}$
b. This iron atom has 26 protons and 56 – 26 = 30 neutrons.

Exercise 2.2.2

How many protons are in $^{23}_{11}\mathrm{Na}$

Answer available at the end of this section.

Key Takeaways

- Atoms themselves are composed of protons, neutrons, and electrons.
- Each element has its own atomic number, which is equal to the number of protons in its nucleus.
- Isotopes of an element contain different numbers of neutrons.
- Elements are represented by an atomic symbol.

Contributors

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Answers

Exercise 2.2.1
Atomic number = 50, mass number = 118

Exercise 2.2.2
11 protons

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2.3: Isotopes and Atomic Weight

Learning Objectives

- Explain how isotopes differ from one another.
- Calculate the atomic mass of an element from the masses and relative percentages of the isotopes of the element.

Isotopes

As introduced previously, atoms of a specific element are distinguished from other elements by their atomic number, (the number of protons). Atoms of the same element always have the same number of protons, however, the number of neutrons can vary. **Isotopes** are atoms of the same element that contain *different* numbers of *neutrons*. This difference in neutron amount affects the mass number (*A*) but not the atomic number (*Z*). In a chemical laboratory, isotopes of an element appear and react the same. For this reason, it is difficult to distinguish between different isotopes. In contrast, nuclear scientists can identify and separate different types of atomic nuclei. The technology required for this process is more sophisticated that what could be found in a typical chemical laboratory.

Figure $2.3.1$ shows an easy way to represent isotopes with a **nuclear symbol**, which includes the atomic or element symbol (represented by X), the mass number, A, and the atomic number, Z. Thus, for the isotope of carbon that has 6 protons and 6 neutrons, the symbol is:

$$^{12}_{6}\mathrm{C}$$

where C is the symbol for carbon, 6 represents the atomic number, and 12 represents the mass number.

It is also common to state the mass number after the name of an element to indicate a particular isotope. *Carbon-12* represents an isotope of carbon with 6 protons and 6 neutrons, while *uranium-238* is an isotope of uranium that has 92 protons and 146 neutrons.

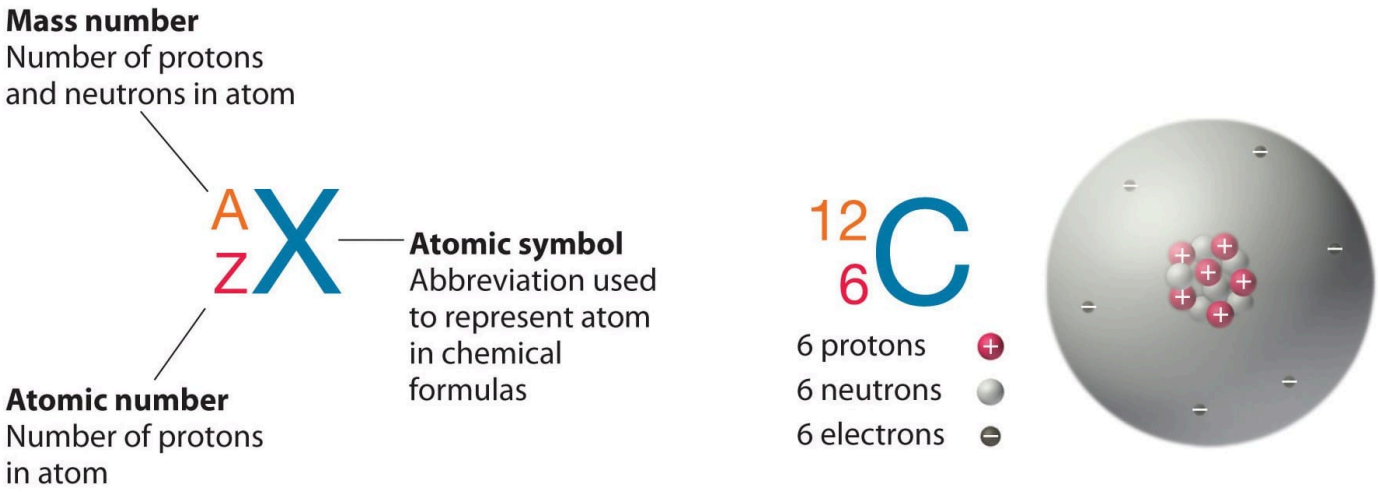


Figure $2.3.1$: Nuclear Symbol. Unlike protons, the number of neutrons is not absolutely fixed for most elements. Atoms that have the same number of protons, and hence the same atomic number, but different numbers of neutrons are called isotopes. All isotopes of an element have the same number of protons and electrons, which means they exhibit the same chemistry. The isotopes of an element differ only in their atomic mass, which is given by the mass number (A), the sum of the numbers of protons and neutrons. (CC BY-NC-SA 4.0; anonymous by request)

Most elements on the periodic table have at least two stable isotopes. For example, in addition to $^{12}\mathrm{C}$, a typical sample of carbon contains 1.11% $^{13}_{6}\mathrm{C}$, with 7 neutrons and 6 protons, and a trace of $^{14}_{6}\mathrm{C}$, with 8 neutrons and 6 protons. The nucleus of $^{14}_{6}\mathrm{C}$ is not stable, however, but undergoes a slow radioactive decay that is the basis of the carbon-14 dating technique used in archeology.

Many elements other than carbon have more than one stable isotope; tin, for example, has 10 isotopes. There are about twenty elements that exist in only one isotopic form (sodium and fluorine are examples of these).

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 2.3.2 compares the three isotopes of hydrogen.

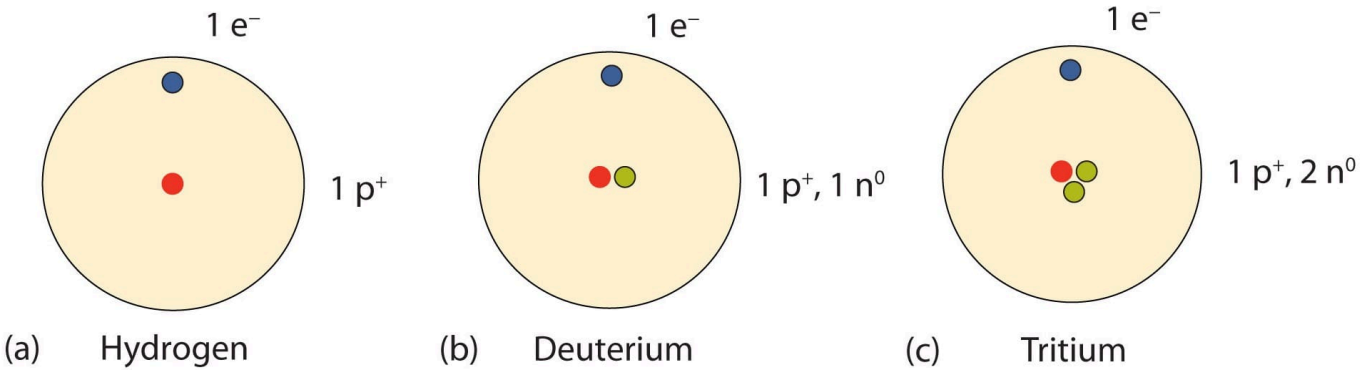


Figure 2.3.2: Isotopes of Hydrogen. Most hydrogen atoms have only a proton in the nucleus (a). A small amount of hydrogen exists as the isotope deuterium, which has one proton and one neutron in its nucleus (b). A tiny amount of the hydrogen isotope tritium, with one proton and two neutrons in its nucleus, also exists on Earth (c). The nuclei and electrons are proportionately much smaller than depicted here.

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. A/Z and symbol-mass formats can be used to display periodic table information. When viewing either of these two notations, isotopic differences can be obtained.

> 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.

Look at the **A/Z formats** for the three isotopes of hydrogen in Table 2.3.1. Note how the atomic number (bottom value) remains the same while the atomic masses (top number) are varied. All isotopes of a particular element will vary in neutrons and mass. This variance in mass will be visible in the **symbol-mass format** of same isotopes as well.

Table 2.3.1

Common Name	A/Z formats	symbol-mass format	Expanded Name
Hydrogen	${}^{1}_{1}\mathrm{H}$	H-1	hydrogen-1
Deuterium	${}^{2}_{1}\mathrm{H}$	H-2	hydrogen-2
Tritium	${}^{3}_{1}\mathrm{H}$	H-3	hydrogen-3

Both A/Z or symbol-mass formats can be utilized to determine the amount of subatomic particles (protons, neutrons, and electrons) contained inside an isotope. When given either format, these mass values should be used to calculate the number of neutrons in the nucleus.

Atomic Weight

Since most naturally occurring elements samples are mixtures of isotopes, it is useful to use an average weight of an element. The **atomic mass** of an element is the weighted mass of all the naturally presented isotopes (on earth). To determine the most abundant isotopic form of an element, compare given isotopes to the weighted average on the periodic table. For example, the three hydrogen isotopes in Figure 2.3.2 are H-1, H-2, and H-3. The atomic mass or weighted average of hydrogen is around 1.008 amu (look again to the periodic table). Of the three hydrogen isotopes, H-1 is closest in mass to the weighted average; therefore, it is the most abundant. The other two isotopes of hydrogen are quite rare, but are very exciting in the world of nuclear science.

You can calculate the atomic mass (or average mass) of an element provided you know the **relative abundances** (the fraction of an element that is a given isotope), the element's naturally occurring isotopes, and the masses of those different isotopes. We can calculate this by the following equation:

$$\text{Atomic mass} = (\%_1)\,(\text{mass}_1) + (\%_2)\,(\text{mass}_2) + \cdots \tag{2.3.1}$$

Averages like Equation 1 are known as *weighted averages*. An element's atomic mass can be calculated provided the relative abundances of the element's naturally occurring isotopes and the masses of those isotopes are known. If all the abundances are not provided, it is safe to assume that all numbers should add up to 100%.

For example, Boron has two naturally occurring isotopes. In a sample of boron, 20% of the atoms are B-10, which is an isotope of boron with 5 neutrons and mass of $10\ \text{amu}$. The other 80% of the atoms are B-11, which is an isotope of boron with 6 neutrons and a mass of $11\ \text{amu}$. How do we calculate the atomic mass of boron?

Boron has two isotopes so we will use the Equation 2.3.1 and substitute the relative abundances and atomic masses of Boron into Equation 2.3.1:

$$\begin{aligned}\text{Atomic mass} &= (0.20)\,(10) + (0.80)\,(11)\\ &= 10.8\,\text{amu}\end{aligned}$$

The mass of an average boron atom, and thus boron's atomic mass, is $10.8\ \text{amu}$.

Example 2.3.1: Atomic Weight of Neon

Neon has three naturally occurring isotopes. In a sample of neon, 90.92% of the atoms are Ne-20, which is an isotope of neon with 10 neutrons and a mass of $19.99\ \text{amu}$. Another 0.3% of the atoms are Ne-21, which is an isotope of neon with 11 neutrons and a mass of $20.99\ \text{amu}$. The final 8.85% of the atoms are Ne-22, which is an isotope of neon with 12 neutrons and a mass of $21.99\ \text{amu}$. What is the atomic mass of neon?

Solution

Neon has three isotopes. We will use the equation:

$$\text{Atomic mass} = (\%_1)\,(\text{mass}_1) + (\%_2)\,(\text{mass}_2) + \cdots$$

Substitute these into the equation, and we get:

$$\begin{aligned}\text{Atomic mass} &= (0.9092)\,(19.99) + (0.003)\,(20.99) + (0.0885)\,(21.99)\\ &= 20.17\,\text{amu}\end{aligned}$$

The mass of an average neon atom is $20.17\ \text{amu}$

Exercise 2.3.1

Magnesium has the three isotopes listed in the following table:

Table showing the 3 isotopes of magnesium, the exact mass of each, and the percent abundance of each.

Isotope	Exact Mass (amu)	Percent Abundance (%)
^{24}Mg	23.98504	78.70
^{25}Mg	24.98584	10.13
^{26}Mg	25.98259	11.17

Use these data to calculate the atomic mass of magnesium.

Answer available at the end of this section.

Applications of Isotopes

During the Manhattan project, the majority of federal funding was dedicated the separation of uranium isotopes. The two most common isotopes of uranium are U-238 and U-235. About 99.3% of uranium is of the U-238 variety, this form is not fissionable and will not work in a nuclear weapon or reaction. The remaining 0.7% is U-235 which is fissionable, but first had to be separated from U-238. This separation process is called *enrichment*. During World War II, a nuclear facility was built in Oak Ridge, Tennessee to accomplish this project. At the time, the enrichment process only produced enough U-235 for one nuclear weapon. This fuel was placed inside the smaller of the two atomic bombs (Little Boy) dropped over Japan.



Figure 2.3.3: A billet of highly enriched uranium that was recovered from scrap processed at the Y-12 National Security Complex Plant. Original and unrotated.

A billet of highly enriched uranium that was recovered from scrap processed at the Y-12 National Security Complex Plant.

Uranium is a natural element that can be found in several different countries. Countries that do not have natural uranium supplies would need to obtain it from one of the countries below. Most nuclear reactors that provide energy rely on U-235 as a source of fuel. Fortunately, reactors only need 2-5% U-235 for the production of megawatts or even gigawatts of power. If the purification process exceeds this level, than it is likely a country is focusing on making nuclear weapons. For example, Manhattan Project scientists enriched U-235 up to 90% in order to produce the Little Boy weapon.

Abbreviations like HEU (highly enriched uranium) and LEU (low-enriched uranium) are used frequently by nuclear scientists and groups. HEU is defined as being over 20% pure U-235 and would not be used in most commercial nuclear reactors. This type of material is used to fuel larger submarines and aircraft carriers. If the purification of U-235 reaches 90%, then the HEU is further classified as being weapons grade material. This type of U-235 could be used to make a nuclear weapon (fission or even fusion based). As for LEU, its U-235 level would be below this 20% mark. LEU would be used for commercial nuclear reactors and smaller, nuclear powered submarines. LEU is not pure enough to be used in a conventional nuclear weapon, but could be used in a dirty bomb. This type of weapon uses conventional explosives like dynamite to spread nuclear material. Unlike a nuclear weapon, dirty bombs are not powerful enough to affect large groups of buildings or people. Unfortunately, the spread of nuclear material would cause massive chaos for a community and would result in casualties.

Summary

- The isotopes of an element have different masses and are identified by their mass numbers.
- An element's atomic mass is the weighted average of the masses of the isotopes of an element
- An element's atomic mass can be calculated provided the relative abundances of the element's naturally occurring isotopes

and the masses of those isotopes are known. If all the abundances are not provided, it is safe to assume that all numbers should add up to 100%.

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.

Contributors and Attributions

-

- Elizabeth R. Gordon (Furman University)

Answers

Exercise 2.3.1

24.31 amu

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2.4: 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 2.4.1. Most periodic tables provide additional data (such as atomic mass) in a box that contains each element's symbol. The elements are listed in order of atomic number.

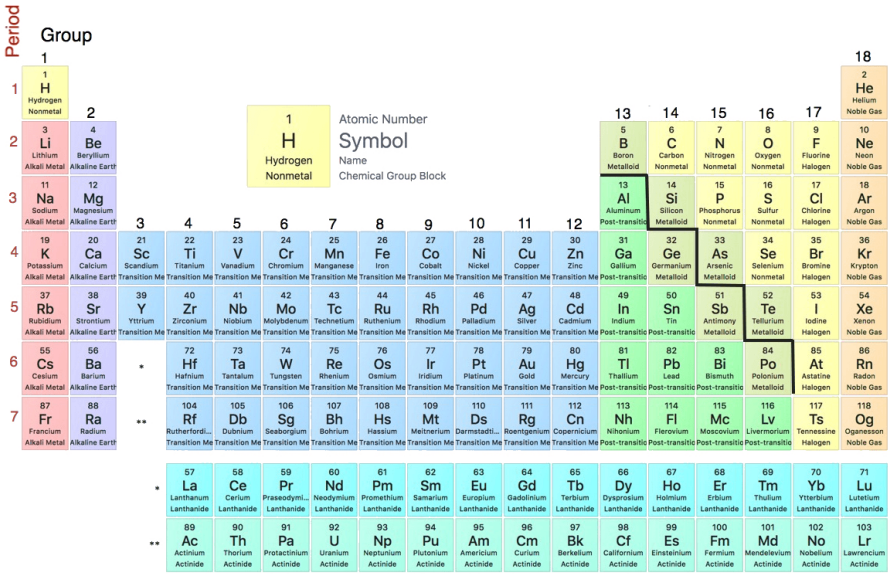


Figure 2.4.1: Modern Periodic Table. (Public Domain; PubChem modified Leticia Colmenares). An interactive Periodic table can be found here.

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

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

Metals, Nonmetals, and Metalloids

Certain elemental properties become apparent in a survey of the periodic table as a whole. Every element can be classified as either a metal, a nonmetal, or a semimetal, as shown in Figure 2.4.2. 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 2.4.2, **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.

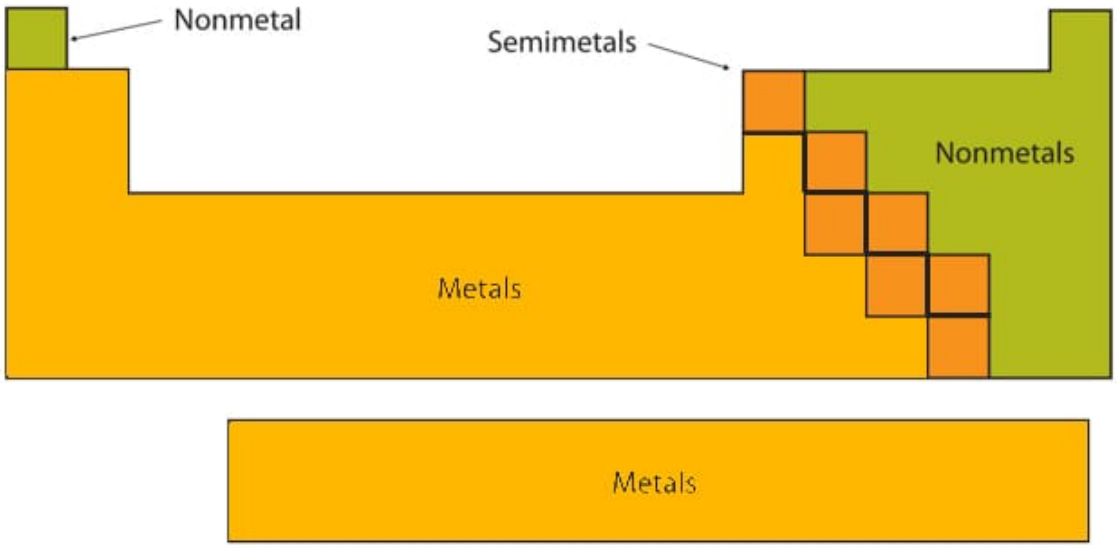


Figure 2.4.2: Types of Elements. Elements are either metals, nonmetals, or semimetals. Each group is located in a different part of the periodic table.

Example 2.4.1

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

a. Se
b. Mg
c. Ge

Solution

a. The atomic number of selenium is 34, which places it in period 4 and group 16. In Figure 2.4.2, selenium lies above and to the right of the diagonal line marking the boundary between metals and nonmetals, so it should be a nonmetal. Note, however, that because selenium is close to the metal-nonmetal dividing line, it would not be surprising if selenium were similar to a semimetal in some of its properties.
b. Magnesium lies to the left of the diagonal line marking the boundary between metals and nonmetals, so it should be a metal.
c. Germanium lies within the diagonal line marking the boundary between metals and nonmetals, so it should be a metalloid.

Exercise 2.4.1

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

Answer available at the end of this section.

Representative, Transition, and Inner-transition

Another way to categorize the elements of the periodic table is shown in Figure 2.4.3. The first two columns on the left (groups 1 and 2) and the last six columns on the right (groups 13-19) are called the **main group** or **representative** elements. The ten-column block between these columns (groups 3-12) contains the **transition metals**. The two rows beneath the main body of the periodic table contain the **inner transition metals**. The elements in these two rows are also referred to as, respectively, the lanthanide metals and the actinide metals.

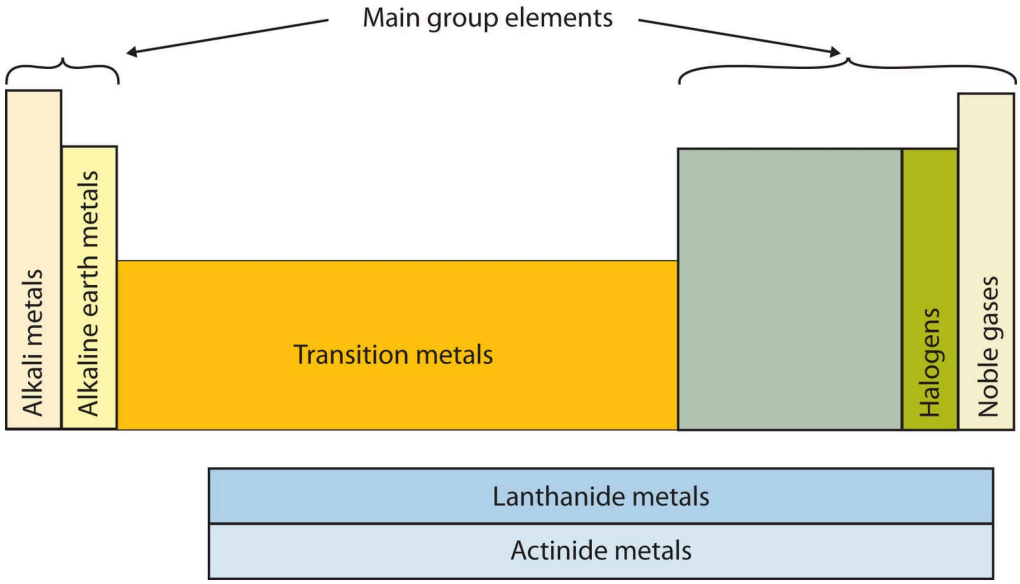


Figure 2.4.3: Special Names for Sections of the Periodic Table. Some sections of the periodic table have special names. The elements lithium, sodium, potassium, rubidium, cesium, and francium are collectively known as alkali metals.

To Your Health: Transition Metals in the Body

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

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

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

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

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

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Answers

Exercise 2.4.1

metal

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2.5: Some Characteristics of Different Groups

Learning Objectives

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

The periodic table is useful for understanding atomic properties that show **periodic trends**. Periodic trends are specific patterns that are present in the periodic table that illustrate different aspects of a certain element, including its size and its electronic properties. Major periodic trends include atomic radius, melting point, among many other properties as we will discuss. Periodic trends, arising from the arrangement of the periodic table, provide chemists with an invaluable tool to quickly predict an element's properties. These trends exist because of the similar atomic structure of the elements within their respective group families or periods, and because of the periodic nature of the elements.

One important atomic property is the **atomic radius**, which is a measure of the atomic size, usually the distance from the nucleus to the out electron shell. However, since this boundary is not well-defined, there are multiple definitions of atomic radius. Irrespective of the definition used, a clear periodic trend can be observed when atomic radius is plotted vs. atomic number (Figure 2.5.1). The radii generally decrease along each row of the table and increase down each group. The radius increases sharply between the noble gas at the end of each period and the alkali metal at the beginning of the next period. The largest atoms are found in the lower left corner of the periodic table and the smallest are found in the upper right corner

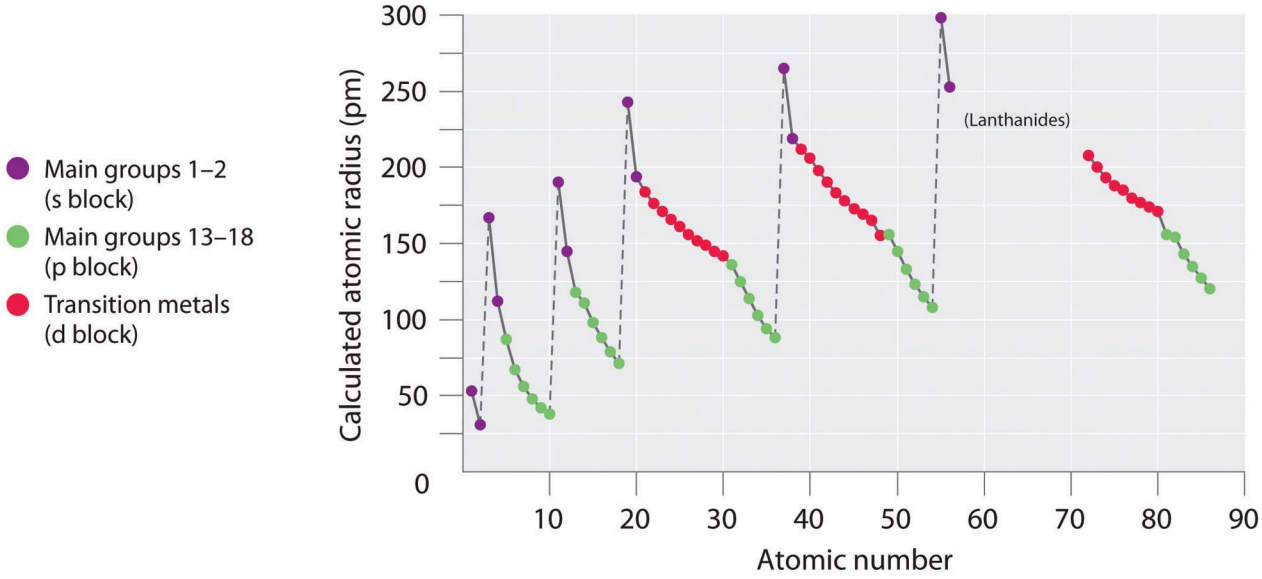


Figure 2.5.1: A Plot of Periodic Variation of Atomic Radius with Atomic Number for the First Six Rows of the Periodic Table.

The melting point is a metric of the energy required to transform the solid phase of a substance into a liquid. Generally, the stronger the bond between the atoms of an element, the more energy required to break that bond. The melting points exhibit comparable, albeit more complex, periodic trends as observed in the atomic radii (Figure 2.5.2). Key feature of these trends are:

- Metals generally possess a *high melting point*.
- Most non-metals possess *low melting points*.
- The non-metal carbon possesses *the highest melting point of all the elements*. The semi-metal boron also possesses a high melting point.

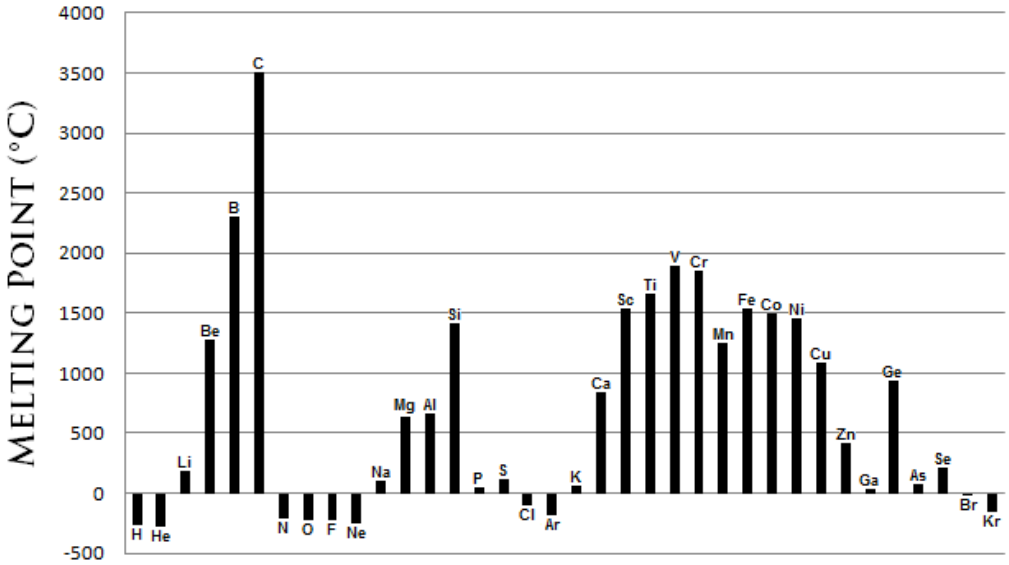


Figure 2.5.2: A plot of melting point vs. atomic number show a periodic trend.

The trends of the atomic radii and melting points (and other chemical and physical properties of the elements) can be explained by the electron shell theory of the atom discussed in the following sections.

Element Characteristics By Group

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 –** lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), and francium (Fr) are soft, shiny, and highly reactive metals. 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. *Hydrogen is unique in that it is generally placed in Group 1, but it is not a metal.*
- **Group 2: The Alkaline Earth Metals –** beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra) are shiny, slivery-white, somewhat reactive metals. 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 –** fluorine (F), chlorine (Cl), bromine (Br), iodine (I), and astatine (At) are nonmetals. 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).
- **Group 18: The Noble Gases –** helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), and radon (Rn) are gases at room temperature and pressure. Because the noble gases are composed of only single atoms, they are called monatomic. Because of their lack of reactivity, for many years they were called **inert gases** or rare gases. However, the first chemical compounds containing the noble gases were prepared in 1962. Although the noble gases are relatively minor constituents of the atmosphere, natural gas contains substantial amounts of helium. Because of its low reactivity, argon is often used as an unreactive (inert) atmosphere for welding and in light bulbs. The red light emitted by neon in a gas discharge tube is used in

neon lights.

To Your Health: Radon

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

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

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

Example 2.5.1: Groups

Provide the family/group names and period numbers (horizontal values) of each element.

a. Li
b. Ar
c. Ra

Solution:

a. Lithium is an alkali metal. It is located in period two.
b. Argon is a noble gas. It is located in period three.
c. Radium is an alkaline metal. It is located in period seven.

Example 2.5.2: Classification of Elements

Provide elemental names for the following combinations:

a. The alkali metal in period three.
b. The halogen in period two
c. A metalloid in period four
d. A transition metal in period three

Solution:

a. Sodium
b. Fluorine
c. Germanium or Arsenic
d. There are no transition metals in period three (gotcha!)

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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2.6: Electronic Structure of Atoms

Learning Objectives

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

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

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

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

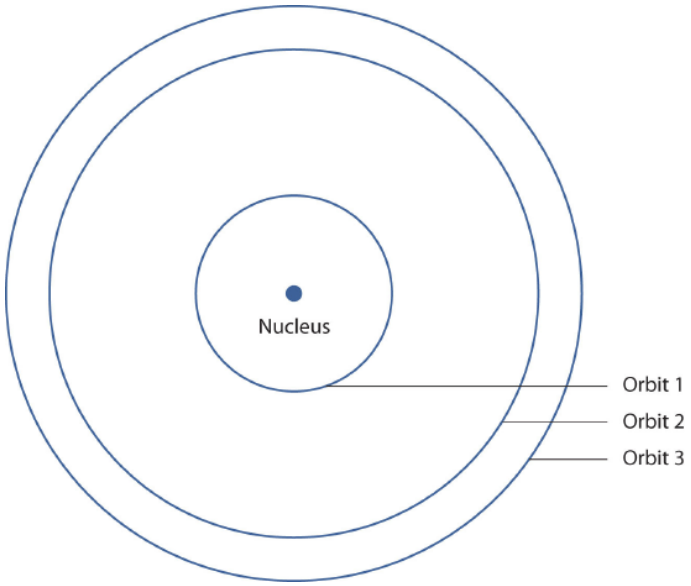


Figure 2.6.1: Bohr's Model of the Hydrogen Atom. Bohr's description of the hydrogen atom had specific orbits for the electron, which had quantized energies.

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

In the quantum-mechanical model of an atom, which is the modern and currently accepted model, the location of electrons in the atom are described by four **quantum numbers**, not just the one predicted by Bohr. Much like your home address can be used to locate you in a specific state, city, street, and house number, the first three quantum numbers identify approximately where electrons are in an atom. The fourth quantum number describes the electron and whether it is spin up or down (clockwise or

counterclockwise). The theory and mathematics behind these four quantum numbers are well beyond the scope of this textbook, however, it is useful to learn some of the basics in order to understand how atoms behave and interact with (react) with other atoms.

Electron Arrangements: Shells, Subshells, and Orbitals

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

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

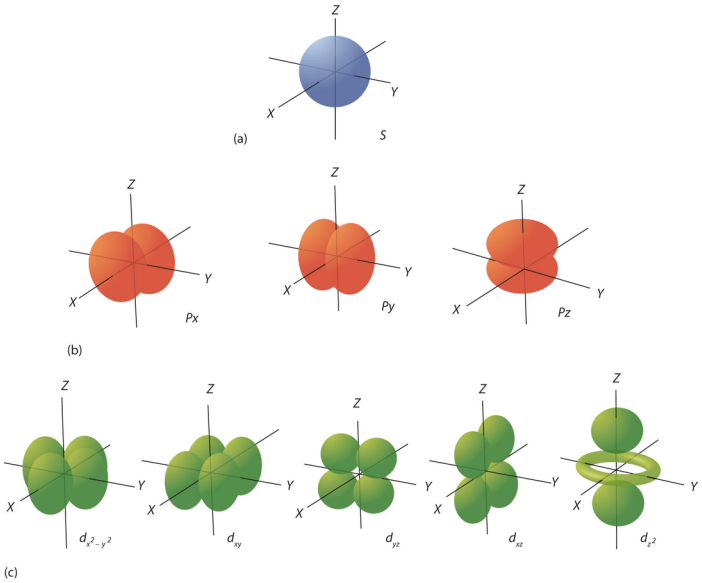


Figure 2.6.1: Electron Orbitals. (a) The lone *s* orbital in an *s* subshell is spherical in distribution. (b) The three *p* orbitals have two lobes, shaped kind of like dumbbells, each is oriented around the nucleus along a different axis. (c) The five *d* orbitals have four lobes, except for the d_{z^2}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

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

Table 2.6.1: Shells and Subshells

Shell (*n*)	Number of Subshells	Names of Subshells	Number of Orbitals (*per Subshell*)	Number of Electrons (*per Subshell*)	Total Electrons (*per Shell*)
1	1	*1s*	1	2	2

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

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

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2.7: Electron Configurations

Learning Objectives

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

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

We use numbers to indicate which shell an electron is in. The first shell, closest to the nucleus and with the lowest-energy electrons, is shell 1. This first shell has only one subshell, which is labeled 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 $\mathbf{1s^1}$ (spoken as "one-ess-one") to describe the electron arrangement or distribution of electrons in hydrogen. This structure is called an **electron configuration** and is unique to hydrogen.

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

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

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

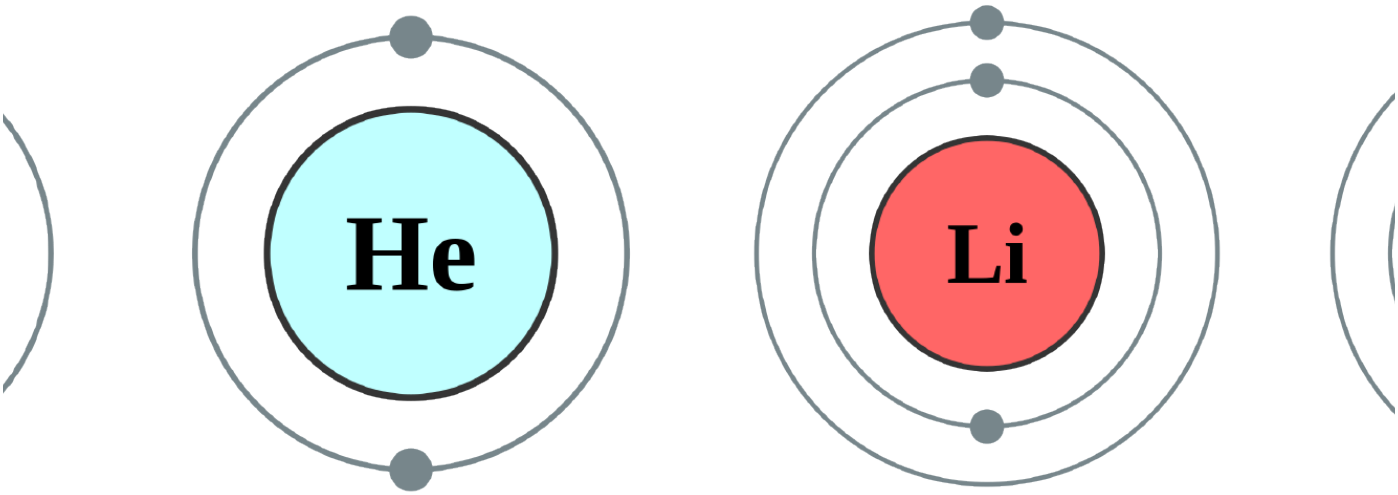


Figure 2.7.1: Shell diagrams of hydrogen (H), helium (He), lithium (Li), and Berryellium (Be) atoms. (CC BY-SA 2.0 UK; Greg Robson modified by Pumbaa via Wikipedia)

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

- **Rule 1 (Aufbau Principle):** Electrons occupy the lowest-energy orbitals (closest to the nucleus) possible, starting with 1s, then 2*s*, 2*p*, and continuing on to higher energy (further away from the nucleus). Shells increase in energy in order from 1 to

2 to 3, and so on. Within these shells, an s subshell is the lowest energy followed by *p*, then *d*, then *f*.

- **Rule 2 (Hund's Rule):** When electrons occupy degenerate orbitals (i.e. same shell and subshell), they must first singly occupy (half-fill) each empty orbital in a subshell before double occupying (completely filling) them. Furthermore, the most stable configuration results when the spins are parallel (i.e. all spin up or all spin down). For example, all three *p* orbitals in a *p* subshell will have one electron before a single *p* orbital contains two electrons.
- **Rule 3 (Pauli-Exclusion Principle):** Each electron is described with a unique set of four quantum numbers (a unique address). Therefore, if two electrons occupy the same orbital, they must have different spins. This is the reason all orbitals can hold a maximum of two electrons.

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

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

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

Table 2.7.1: Electron Configurations of the First 20 Elements

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

Atomic Number	Element Symbol	Outermost Shell	Electron Configuration	Noble Gas Configuration
16	S	3	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$	[Ne] $3s^2\ 3p^4$
17	Cl	3	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$	[Ne] $3s^2\ 3p^5$
18	Ar	3	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$	[Ne] $3s^2\ 3p^6$
19	K	4	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$	[Ar] $4s^1$
20	Ca	4	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$	[Ar] $4s^2$

Noble Gas Configuration

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

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

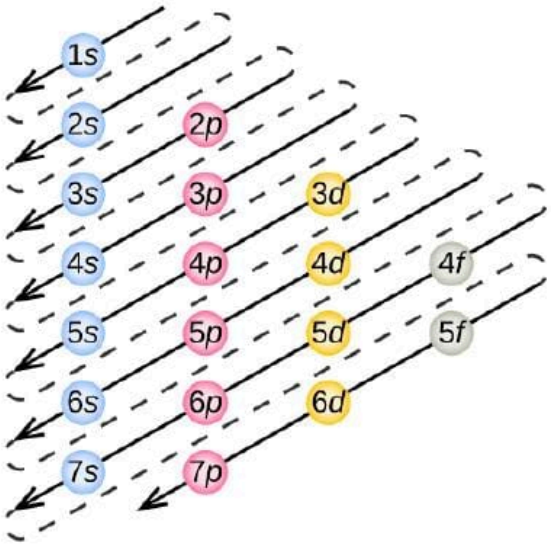


Figure $2.7.2$: The order of electron filling in an atom. Follow each arrow in order **from top to bottom**. The subshells you reach along each arrow give the ordering of filling of subshells in larger atoms.

Example $2.7.1$: Electronic Configuration of Phosphorus Atoms

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

Solution

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

Exercise 2.7.1: Electronic Configuration of Chlorine Atoms

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

Answer available at the end of this section.

Orbital Diagrams

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

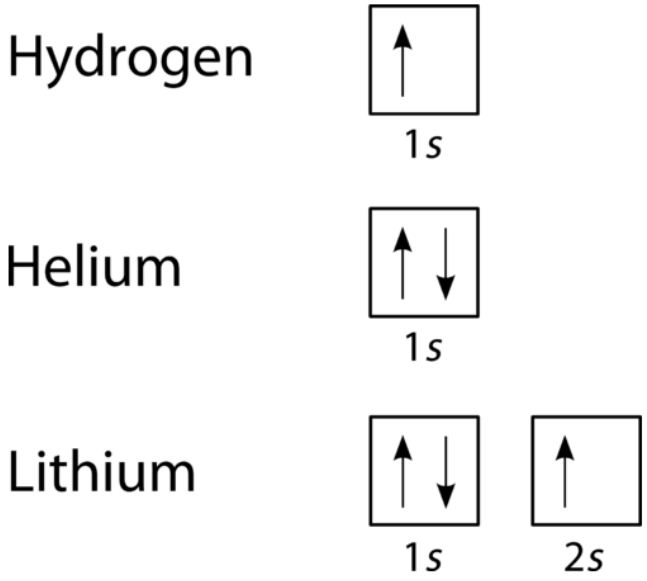


Figure 2.7.3: Orbital diagrams for hydrogen, helium, and lithium.

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

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

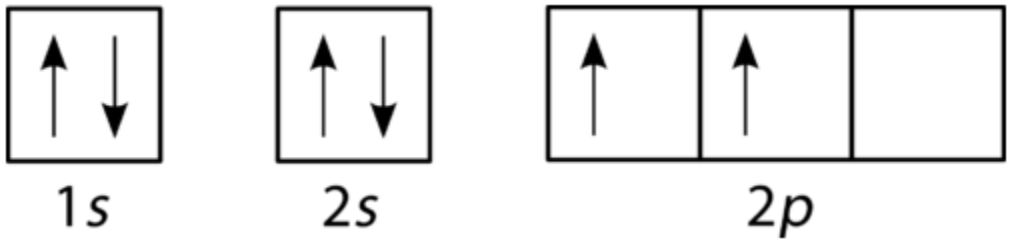


Figure 2.7.4: Orbital diagram for carbon.

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

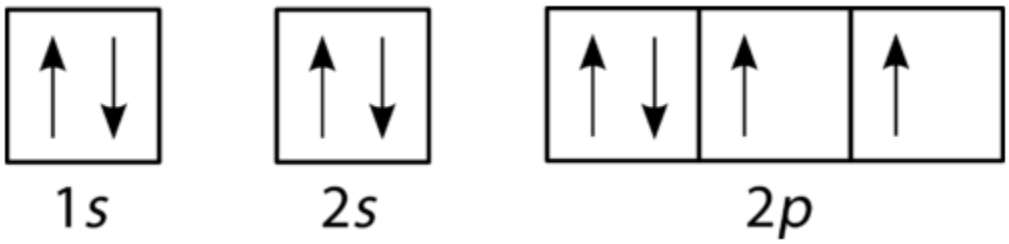


Figure 2.7.5: Orbital diagram for oxygen.

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

Example 2.7.3: Carbon Atoms

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

Solution

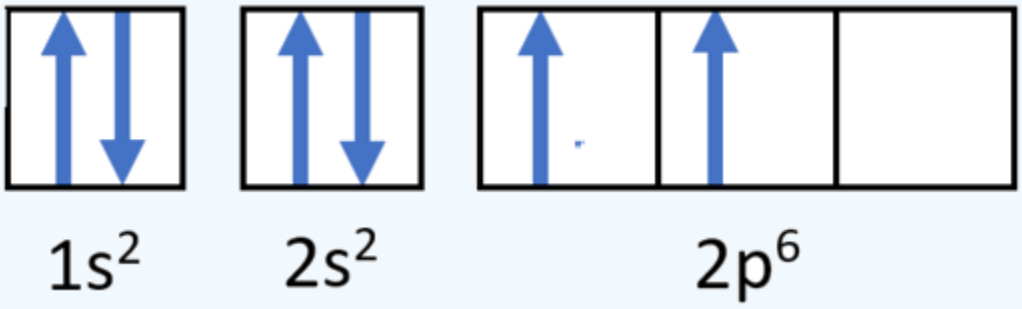
Step 1: List the known quantities and plan the problem.

Known

- Atomic number of carbon, Z=6

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

Step 2: Construct the diagram.



Orbital filling diagram for carbon.

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

Step 3: Think about your result.

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

Answers

Exercise 2.7.1**: Electronic Configuration of Chlorine Atoms**

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

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2.8: Electron Configurations and the Periodic Table

Learning Objectives

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

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

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

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

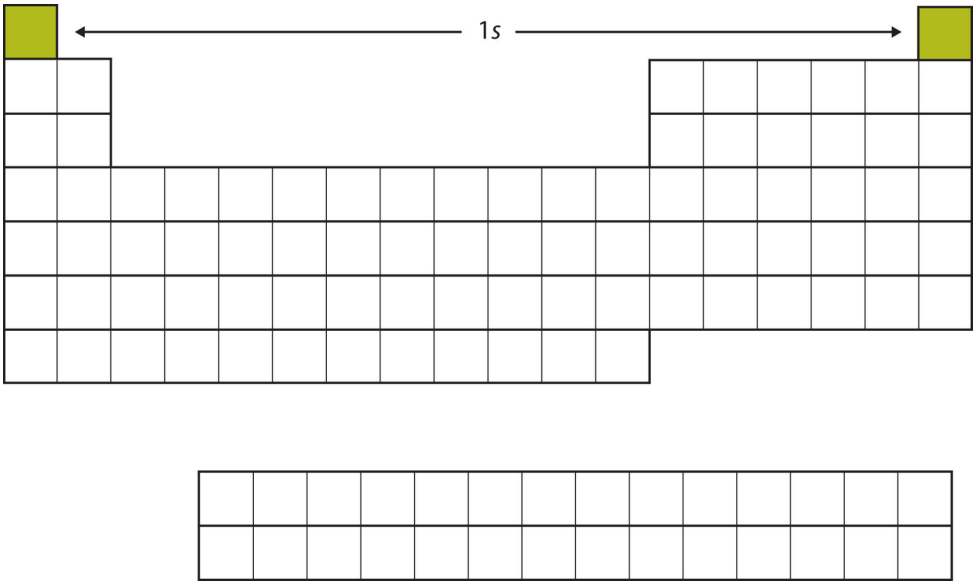


Figure 2.8.1: The 1s Subshell. H and He represent the filling of the 1s subshell.

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

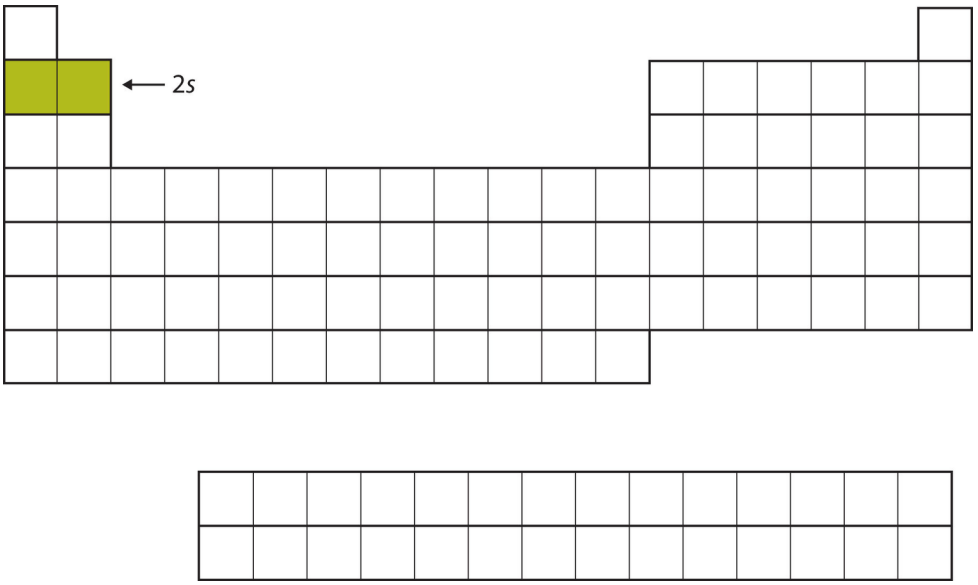


Figure 2.8.2: The 2s Subshell. In Li and Be, the 2s subshell is being filled.

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

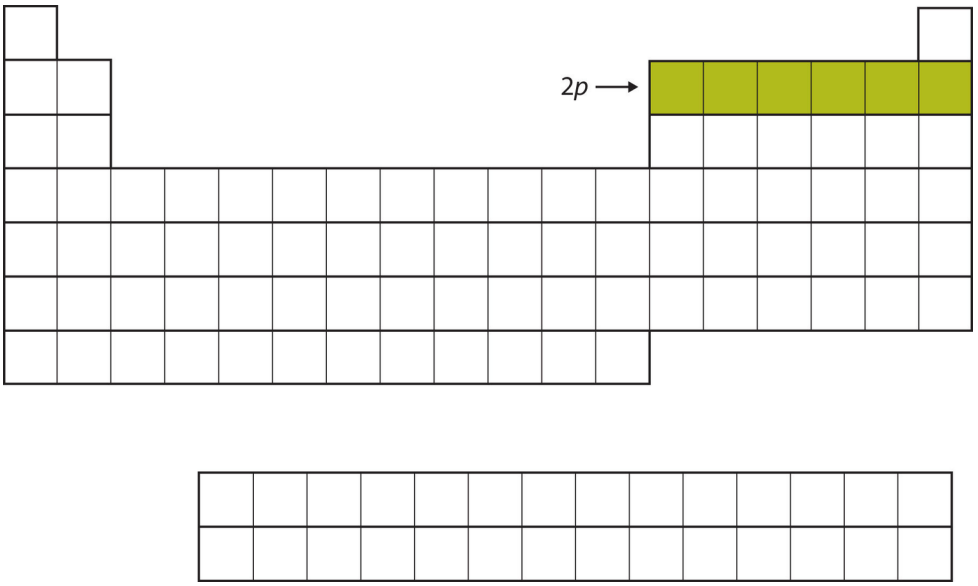


Figure 2.8.3: The 2*p* Subshell. For B through Ne, the 2*p* subshell is being occupied.

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

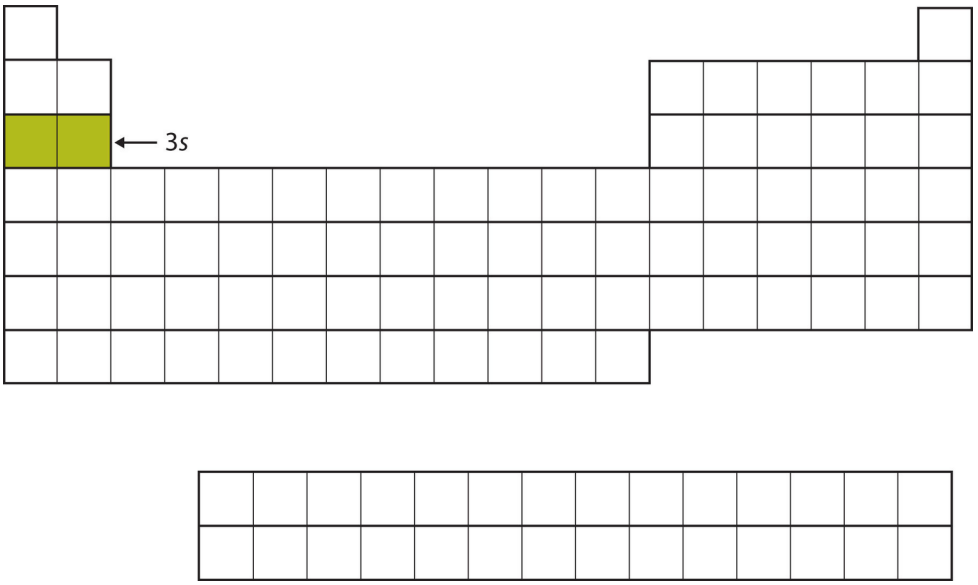


Figure 2.8.4: The 3s Subshell. Now the 3s subshell is being occupied.

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

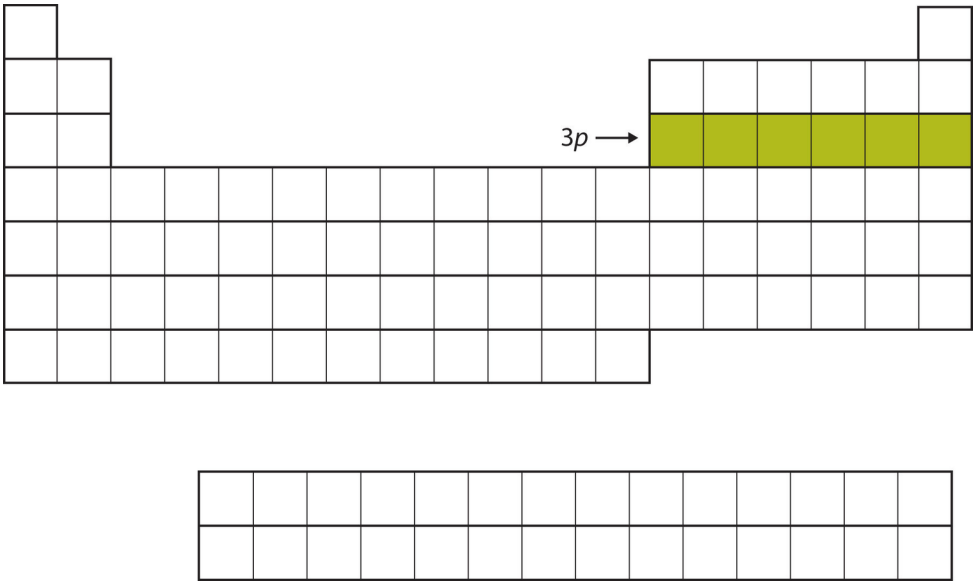


Figure 2.8.5: The 3*p* Subshell. Next, the 3*p* subshell is filled with electrons.

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

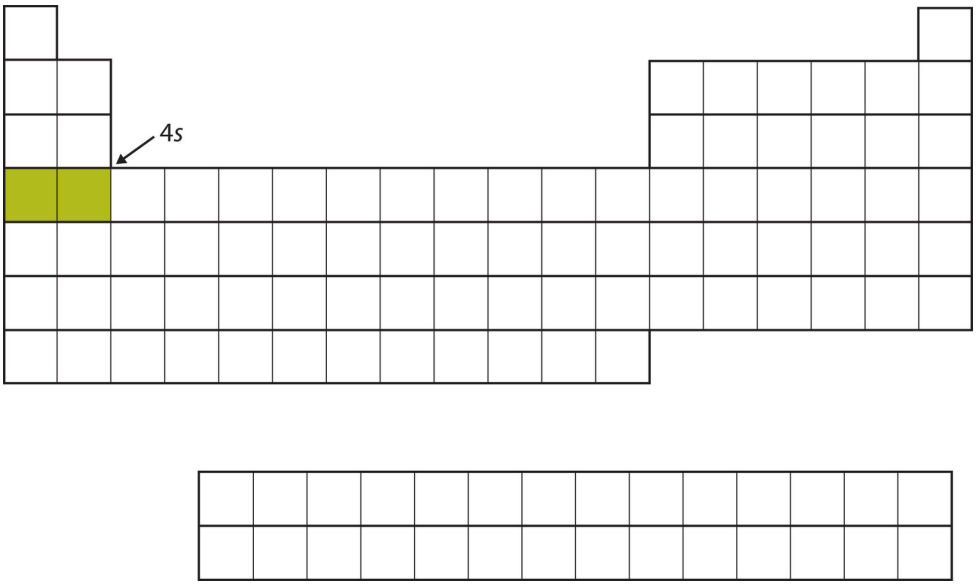


Figure 2.8.6: The 4s Subshell. The 4s subshell is filled before the 3*d* subshell. This is reflected in the structure of the periodic table.

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

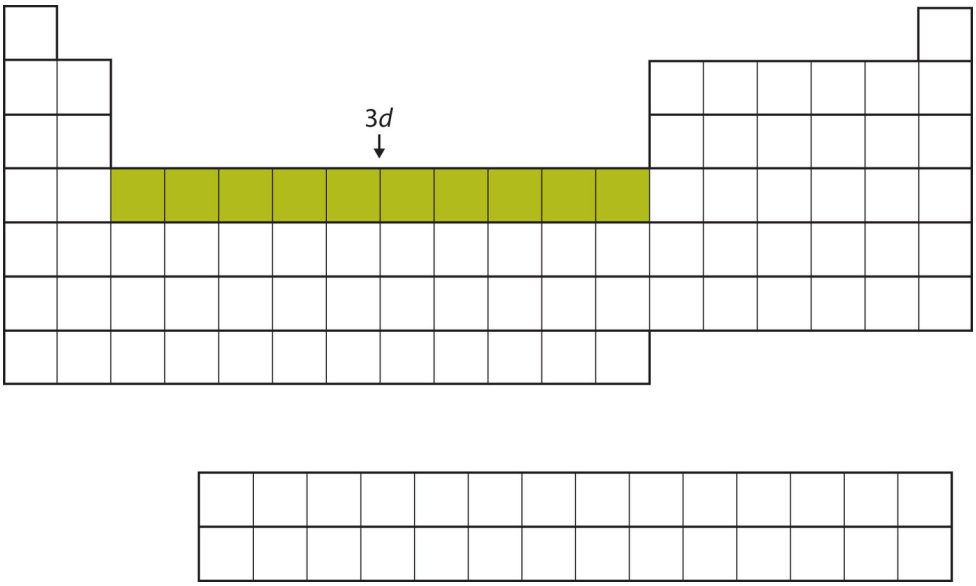


Figure 2.8.7: The 3*d* Subshell. The 3*d* subshell is filled in the middle section of the periodic table.

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

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

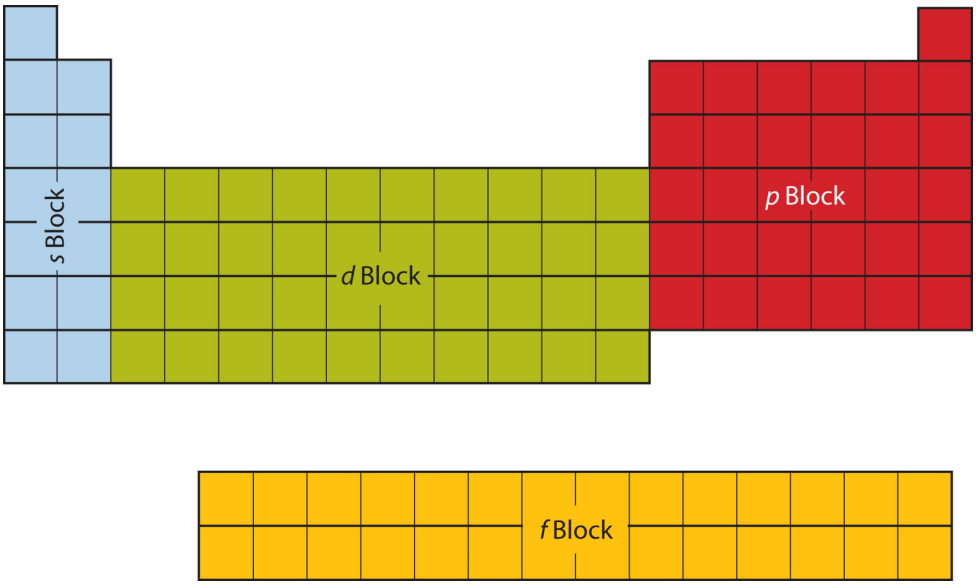


Figure 2.8.8: Blocks on the Periodic Table. The periodic table is separated into blocks depending on which subshell is being filled for the atoms that belong in that section.

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

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

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

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

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

Similarity of valence shell electron configuration implies that we can determine the electron configuration of an atom solely by its position on the periodic table. Consider Se, as shown in Figure 2.8.9. It is in the fourth column of the *p* block. This means that its electron configuration should end in a p^4 electron configuration. Indeed, the electron configuration of Se is $[Ar]4s^{2}3d^{10}4p^{4}$, as expected.

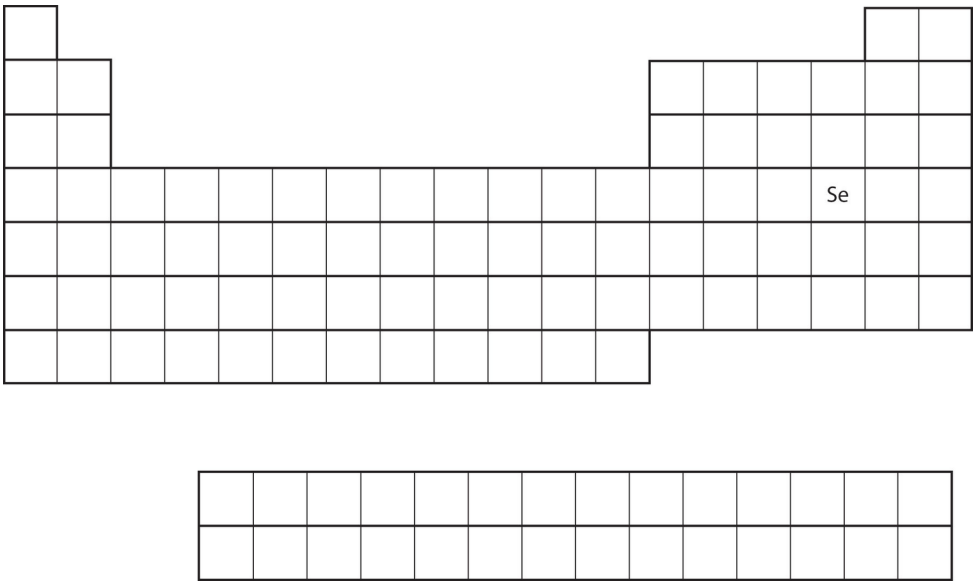


Figure 2.8.9: Selenium on the Periodic Table

Example 2.8.1

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

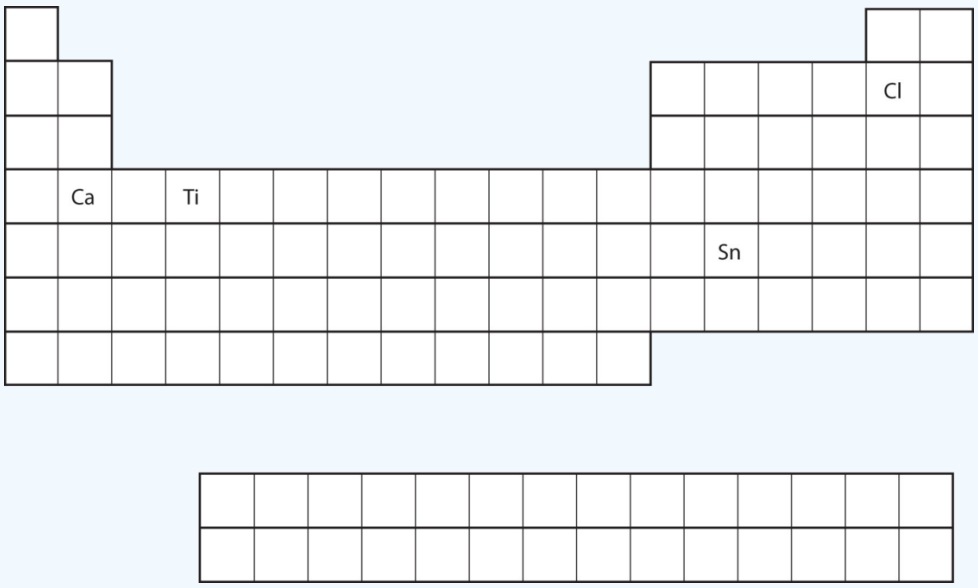


Figure 2.8.10: Various Elements on the Periodic Table

1. Ca
2. Sn

Solution

1. Ca is located in the second column of the s block. We would expect that its electron configuration should end with s^2. Calcium's electron configuration is $[Ar]4s^2$.

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

Exercise 2.8.1

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

a. Ti
b. Cl

Answer a available at the end of this section.

Example 2.8.2: Aluminum

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

Solution

Aluminum has 13 electrons.

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

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 **$1s^2 2s^2 2p^6 3s^2 3p^1$**

Exercise 2.8.2

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

Answer available at the end of this section.

Summary

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

Answers

Exercise 2.8.1

[Ar]$4s^2 3d^2$

[Ne]$3s^2 3p^5$

Exercise 2.8.2

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

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

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

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

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

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2.9: Electron-Dot Symbols

Learning Objective

- Draw a Lewis electron dot symbol for a given atom.

In almost all cases, chemical bonds are formed by interactions of valence electrons in atoms. To facilitate our understanding of how valence electrons interact, a simple way of representing those valence electrons would be useful.

A **Lewis electron-dot symbol** (or electron-dot symbol or a Lewis symbol) is a representation of the valence electrons of an atom that uses dots around the symbol of the element. The number of dots equals the number of valence electrons in the atom. These dots are arranged to the right and left and above and below the symbol, with no more than two dots on a side. (It does not matter what order the positions are used.) For example, the electron-dot symbol for hydrogen is simply

$$\mathbf{H}\cdot \tag{2.9.1}$$

Because the side is not important, the electron-dot symbol could also be drawn as follows:

$$\dot{\mathbf{H}} \;\; or \;\; \cdot\mathbf{H} \;\; or \;\; \underset{\cdot}{\mathbf{H}} \tag{2.9.2}$$

The electron-dot symbol for helium, with two valence electrons, is as follows:

$$\mathbf{He}\text{:} \tag{2.9.3}$$

By putting the two electrons together on the same side, we emphasize the fact that these two electrons are both in the 1s subshell; this is the common convention we will adopt, although there will be exceptions later. The next atom, lithium, has an electron configuration of $1s^2 2s^1$, so it has only one electron in its valence shell. Its electron dot diagram resembles that of hydrogen, except the symbol for lithium is used:

$$\mathbf{Li}\cdot \tag{2.9.4}$$

Beryllium has two valence electrons in its 2*s* shell, so its eelectron-dot symbol is like that of helium:

$$\mathbf{Be}\text{:} \tag{2.9.5}$$

The next atom is boron. Its valence electron shell is $2s^2 2p^1$, so it has three valence electrons. The third electron will go on another side of the symbol:

$$\dot{\mathbf{B}}\mathbf{e}\text{:} \tag{2.9.6}$$

Again, it does not matter on which sides of the symbol the electron dots are positioned.

For carbon, there are four valence electrons, two in the 2*s* subshell and two in the 2*p* subshell. As usual, we will draw two dots together on one side, to represent the 2*s* electrons. However, conventionally, we draw the dots for the two *p* electrons on different sides. As such, the electron-dot symbol for carbon is as follows:

$$\cdot\dot{\mathbf{C}}\text{:} \tag{2.9.7}$$

With N, which has three *p* electrons, we put a single dot on each of the three remaining sides:

$$\cdot\underset{\cdot}{\dot{\mathbf{N}}}\text{:} \tag{2.9.8}$$

For oxygen, which has four *p* electrons, we now have to start doubling up on the dots on one other side of the symbol. When doubling up electrons, make sure that a side has no more than two electrons.

$$\cdot\ddot{\underset{\cdot}{\mathrm{O}}}: \tag{2.9.9}$$

Fluorine and neon have seven and eight dots, respectively:

$$:\ddot{\underset{\cdot}{\mathrm{F}}}: \tag{2.9.10}$$

$$:\ddot{\underset{\cdot\,\cdot}{\mathrm{N}}}\mathrm{e}: \tag{2.9.11}$$

With the next element, sodium, the process starts over with a single electron because sodium has a single electron in its highest-numbered shell, the n = 3 shell. By going through the periodic table, we see that the electron-dot symbol of atoms will never have more than eight dots around the atomic symbol.

Example 2.9.1:

What is the electron-dot symbol for each element?

a. aluminum
b. selenium

Solution

a. The valence electron configuration for aluminum is $3s^2 3p^1$. So it would have three dots around the symbol for aluminum, two of them paired to represent the 3s electrons:

$$\dot{Al}:$$

2. The valence electron configuration for selenium is $4s^2 4p^4$. In the highest-numbered shell, the n = 4 shell, there are six electrons. Its electron dot diagram is as follows:

$$\cdot\ddot{\underset{\cdot\,\cdot}{\mathrm{S}}}\mathrm{e}:$$

Exercise 2.9.1

What is the electron-dot symbol for each element?

a. phosphorus
b. argon

Answer

$$\cdot\ddot{\underset{\cdot}{\mathrm{P}}}:$$

$$:\ddot{\underset{\cdot\,\cdot}{\mathrm{A}}}\mathrm{r}:$$

Summary

- Lewis electron-dot symbols use dots to represent valence electrons around an atomic symbol.

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3: IONIC COMPOUNDS

When you think of bonding, you may not think of ions or molecules. Like most of us, you probably think of bonding between people. Like people, molecules bond — and some bonds are stronger than others. It's hard to break up a mother and baby, or a molecule made up of one oxygen and two hydrogen atoms! A chemical bond is a force of attraction between atoms or ions. Bonds form when atoms share or transfer valence electrons. Valence electrons are the electrons in the outer energy level of an atom that may be involved in chemical interactions. Valence electrons are the basis of all chemical bonds.

3.1: Ions

3.2: Ions and the Octet Rule

3.3: Ions of Some Common Elements

3.4: Periodic Properties and Ion Formation

3.5: Naming Monoatomic Ions

3.6: Polyatomic Ions

3.7: Ionic Bonds

3.8: Formulas of Ionic Compounds

3.9: Naming Ionic Compounds

3.10: Some Properties of Ionic Compounds

3.11: H^+ and OH^- Ions - An Introduction to Acids and Bases

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3.1: Ions

Learning Objectives

- Describe how an ion is formed.
- Distinguish the difference between the two types of ions.

Ions

As introduced previously, atoms contain a nucleus with neutrons and positively charged protons, surrounded by negatively charged electrons. In an atom, the total number of electrons, negative charge, *equals* the total number of protons, positive charge, and therefore, atoms are electrically neutral or uncharged. If an atom loses or gains electrons, it will become a positively or negatively charged particle, called an **ion**. The *los*s of one or more electrons results in more protons than electrons and an overall positively charged ion, called a **cation**. For example, a sodium atom with one less electron is a cation, Na^+, with a +1 charge (Figure 3.1.1).

Figure 3.1.1: A sodium atom (Na) has equal numbers of protons and electrons (11) and is uncharged. When it loses an electron, the resulting sodium cation has one more proton (11) than electrons (10), giving it an overall positive one charge, Na+.

When an atom *gains* one or more electrons, it becomes a negatively charged **anion**, because there are more electrons than protons. When chlorine gains one electron it forms a chloride ion, Cl^-, with a –1 charge (Figures 3.1.2)

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

Figure 3.1.2: A chlorine atom (Cl) has equal numbers of protons and electrons (17) and is uncharged. When it gains an electron, the resulting chlorine anion has one more electron (18) than protons (17), giving it an overall negative one charge, Cl–.

Note Naming Ions

Cations are named using the element name plus "*ion*" to indicate it is charged. Anions are named by changing the element name ending to "*ide*". For example, a magnesium ion is formed when neutral magnesium loses electrons and a fluor*ide* ion is formed when neutral fluorine gains electrons.

Example 3.1.1

A calcium (Ca) atom loses two electrons and a sulfur (S) atom gains two electrons. Determine if the resulting ions are cations or anions? Write the ion symbols for each.

Solution

When calcium (Z = 20) gains two electrons the resulting ion will have 18 electrons and 20 protons and therefore a charge of +2 (there are two more positive protons than negative electrons), it is a cation. The symbol for a calcium ion is Ca^{2+}.

When sulfur (Z = 16) gains two electrons the resulting ion will have 18 electrons and 16 protons and therefore a charge of –2 (there are two more negative electrons than positive protons), it is an anion. The symbol for a sulf*ide* ion is S^{2-}.

Key Takeaways

- Ions are formed when atoms gain or lose electrons.
- Ions can be positively charged (cations) or negatively charged (anions).

Contributors

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3.2: Ions and the Octet Rule

Learning Objectives

- Use the octet rule and electron configurations to determine if an atom will gain or lose electrons forming anions or cations.

Ions are formed when an atom, usually on the left side of the periodic table, *reacts with* and *transfers* one or more electrons to another atom, usually on the right side of the periodic table. These electrons are usually *lost from* or *gained into* the **valence shell**, or outermost energy level (shell). Why do some atoms lose electrons and others gain electrons? How can we predict the number of electrons lost or gained? Which ions are stable and which ions do not form at all? These questions are best answered by looking at electron configurations and considering what is called the **octet rule**, which states that atoms gain or lose electrons to form a stable, noble gas configuration, i.e., a filled subshell containing *eight* electrons. Therefore, it is useful to take a closer look at electron configurations to further illustrate ion formation and electron transfer between atoms.

The electron configuration for sodium shows that there are ten core electrons and one valence electron in the third energy level. When sodium loses the single valence electron, forming the cation Na^+, the electron configuration is now identical to that of neon, a stable noble gas with eight valence electrons.

$$\begin{array}{ccc} \mathrm{Na} & \rightarrow & \mathrm{Na^+ + e^-} \\ 1s^2\ 2s^2\ 2p^6\ 3s^1 & & 1s^2\ 2s^2\ 2p^6 \end{array} \tag{3.2.1}$$

Chlorine also has ten core electrons and valence electrons in the third energy level. However, chlorine has seven valence electrons, one less than the noble gas argon, which has eight valence electrons. Thus, chlorine will gain one electron, forming the anion, Cl^-, and achieving a stable noble gas configuration.

$$\begin{array}{ccc} \mathrm{Cl + e^-} & \rightarrow & \mathrm{Cl^-} \\ 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5 & & 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 \end{array} \tag{3.2.2}$$

The octet rule and the periodic table can be used to predict what ions will form; main group elements on the left side of the periodic table (metals in groups 1, 2, and 13) tend to lose electrons (form cations) to achieve the same electron configuration as the noble gas just *before* them in the table. The number of electrons the atom will lose depends on what group the atom is in, i.e., how many valence electrons it has. Main group elements on the right side of the periodic table (nonmetals in groups 15-17) will gain electrons to achieve the same electron configuration as the noble gas just *after* them in the table. Again, the number of electrons the atom will gain depends on the number of valence electrons it has and how many are needed to reach the filled subshell, eight electrons.

Note Violation of the Octet Rule

It is *not impossible* to violate the octet rule. Consider sodium: in its elemental form, it has one valence electron and is stable. It is rather reactive, however, and does not require a lot of energy to remove that electron to make the Na^+ ion. We *could* remove another electron by adding even *more* energy to the ion, to make the Na^{2+} ion. However, that requires much more energy than is normally available in chemical reactions, so sodium stops at a 1+ charge after losing a single electron. It turns out that the Na^+ ion has a complete octet in its new valence shell, the n = 2 shell, which satisfies the octet rule. The octet rule is a result of trends in energies and is useful in explaining why atoms form the ions that they do.

Example 3.2.1

Write the electron configuration of aluminum atom (Z = 13) and underline the *valence electrons*. How many electrons are gained/lost to form an aluminum ion? Write the symbol and the electron configuration for an aluminum ion.

Solution

The electron configuration of Al atom is $1s^2 2s^2 2p^6 3s^2 3p^1$. Aluminum has three valence electrons in the third energy level, ($3s^2 3p^1$). The cation, Al^{3+}, is formed when these three valence electrons are **lost**, leaving the configuration for the noble gas neon, $1s^2 2s^2 2p^6$.

Exercise 3.2.1

Write the electron configuration of oxygen atom (Z = 8) and underline the valence electrons. How many electrons are gained/lost to form an oxide ion? Write the symbol and electron configuration for oxide ion.

Answer available at the end of this section.

Answers

Exercise 3.2.1

The electron configuration of O atom is $1s^2 2s^2 2p^4$. Oxygen has six valence electrons in the second energy level, ($2s^2 2p^4$). The anion O^{2-} is formed when two electrons are **gained** in the valence shell. The resulting electron configuration, $1s^2 2s^2 2p^6$, which is also identical to the configuration for the noble gas neon.

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3.3: Ions of Some Common Elements

Learning Objectives

- Become familiar with the charge of some common ions.
- Use the periodic table to predict ion charge.

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, as introduced previously, the periodic table becomes a tool for remembering the charges on many ions. For example, all ions made from alkali metals, the first column on the periodic table, have a +1 charge. Ions made from alkaline earth metals, the second group on the periodic table, have a +2 charge. On the other side of the periodic table, the next-to-last column, the halogens, form ions having a –1 charge. Figure 3.3.1 shows how the charge on many ions can be predicted by the location of an element on the periodic table.

Some elements, especially transition metals, can form ions with variable charges. Figure 3.3.1 shows the characteristic charges for some of these ions. Notice that there is no simple pattern for transition metal ions (or for the larger main group elements) as there is with the main group ions. This is because the transition metals have electrons in *d* subshell and do not follow the octet rule. In order for an element such as iron (Fe) to achieve the same noble gas configuration of argon (Ar), it would need to lose 6 electrons in the *3d* subshell and 2 electrons in the *4s* subshell. An iron ion with a charge of +8 is not very likely, therefore, the octet rule is not applicable to transition elements.

Note

For a multiply-charged ion, the correct convention is to write the charge number first followed by the sign. For example, the barium cation is written Ba^{2+}, not Ba^{+2}.

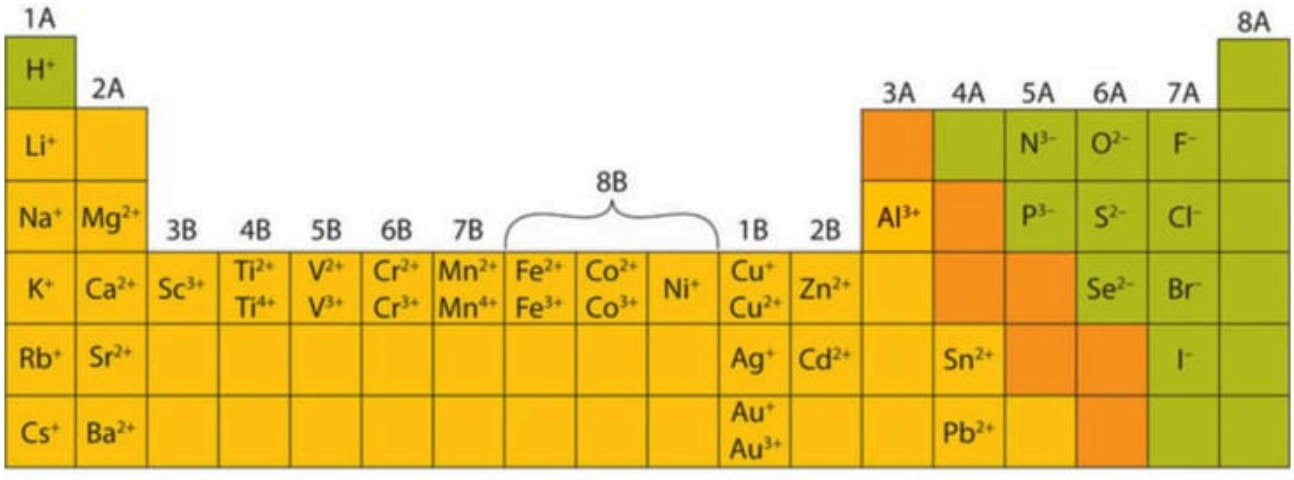


Figure 3.3.1: Common ions formed by specific elements on the periodic table. The charge that a representative (main group element) acquires when it becomes an ion is related to the location on the periodic table. Note that some metal atoms, specifically the transition elements, commonly form ions with variable charges.

3.3.1 Exam

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

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

Solution

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

3.3.2 Exerc

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

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

Answer available at the end of this section.

Answers

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

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3.4: Periodic Properties and Ion Formation

Learning Objectives

- Describe ionization energy and electron affinity and how this relates to ion formation trends.

We have seen that elements often gain or lose enough electrons to achieve the valence electron configuration of the nearest noble gas. Why is this so? In this section, we develop a more quantitative approach to predicting such reactions by examining periodic trends in the energy changes that accompany ion formation.

Ionization Energy

Because atoms do not spontaneously lose electrons, energy is *required* to remove an electron from an atom to form a cation. Chemists define the ionization energy (IE) of an element as the amount of energy needed to remove an electron from the gaseous atom A in its ground state. IE is therefore the energy required for the reaction:

$$A(g) \rightarrow A^{+}(g) + e^{-} \qquad \text{energy required=IE} \tag{3.4.1}$$

Because an input of energy is required, the ionization energy is always positive ($IE > 0$) for the reaction as written in Equation 3.4.1. Larger values of (IE) mean that the electron is more tightly bound to the atom and thus, harder to remove. Typical units for ionization energies are kilojoules/mole (kJ/mol) or electron volts (eV):

$$1\ eV/atom = 96.49\ kJ/mol \tag{3.4.2}$$

As you move *across* a row on the periodic table, the ionization energies generally tend to increase. This means that elements on the left side of the periodic table lose electrons more easily (requires less energy to remove an electron) than those on the right side of the periodic table. The trend in ionization energy can be explained by considering the trend in atomic radius (explained in an earlier chapter). As you move from left to right on the periodic table, the atomic size decreases and the electrostatic interactions between the nucleus and valence electrons increases, which increases the energy required to remove electrons, thus the (IE) increases.

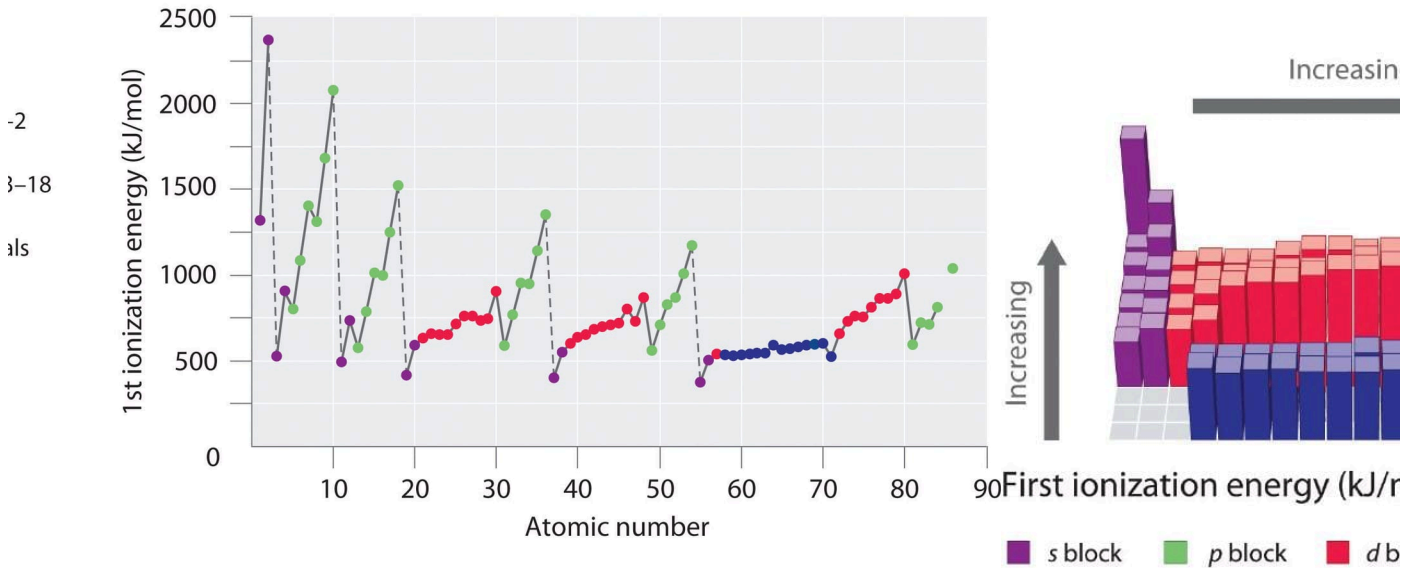


Figure 3.4.1: Ionization Energy Trends on the Periodic Table. (Left Figure) A Plot of Periodic Variation of First Ionization Energy with Atomic Number for the First Six Rows of the Periodic Table. There is a decrease in ionization energy within a group (most easily seen here for groups 1 and 18). (Right Figure) First Ionization Energies of the *s*-, *p*-, *d*-, and *f*-Block Elements

If you look closely at the trends in ionization energy, you will notice that there are some "exceptions" where you see a decrease in energy rather than an increase. In periods 1 and 2, you can see this decrease in (IE) between groups 2 and 3 and again between groups 5 and 6. These variations in the trend can be further explained by looking closely at the electron configurations of the atoms in question. As you move from magnesium to aluminum, one electron is added to the 3*p* subshell. This 3*p* electron is slightly further from the nucleus (higher in energy) and is therefore, more easy to remove compared to the 3s electrons. The decrease between phosphorous and sulfur occurs because the added electron in sulfur is the first to be paired in the *p* subshell. These two electrons in the same *p* orbital repel each other, making the sulfur atom slightly less stable than would otherwise be expected, as is true of all the group 16 elements. This electron is easier to remove because it will lead to more stability.

Example 3.4.1: Lowest First Ionization Energy

Use their locations in the periodic table to predict which element has the lowest first ionization energy: Ca, K, Mg, Na, Rb, or Sr.

Given: six elements

Asked for: element with lowest first ionization energy

Strategy:

Locate the elements in the periodic table. Based on trends in ionization energies across a row and down a column, identify the element with the lowest first ionization energy.

Solution:

These six elements form a rectangle in the two far-left columns of the periodic table. Because we know that ionization energies increase from left to right in a row and from bottom to top of a column, we can predict that the element at the bottom left of the rectangle will have the lowest first ionization energy: Rb.

Exercise 3.4.1: Highest First Ionization Energy

Use their locations in the periodic table to predict which element has the highest first ionization energy: As, Bi, Ge, Pb, Sb, or Sn.

Answer available at the end of this section.

Electron Affinity

The electron affinity (EA) of an element A is defined as the energy change that occurs when an electron is added to a gaseous atom or ion:

$$A(g) + e^- \rightarrow A^-(g) \qquad \text{energy change} = EA \tag{3.4.3}$$

Unlike ionization energies, which are always positive for a neutral atom because energy is required to remove an electron, electron affinities can be negative (energy is released when an electron is added), positive (energy must be added to the system to produce an anion), or zero (the process is energetically neutral). This sign convention is consistent with a negative value corresponded to the energy change for an exothermic process, which is one in which heat is released (Figure 3.4.2).

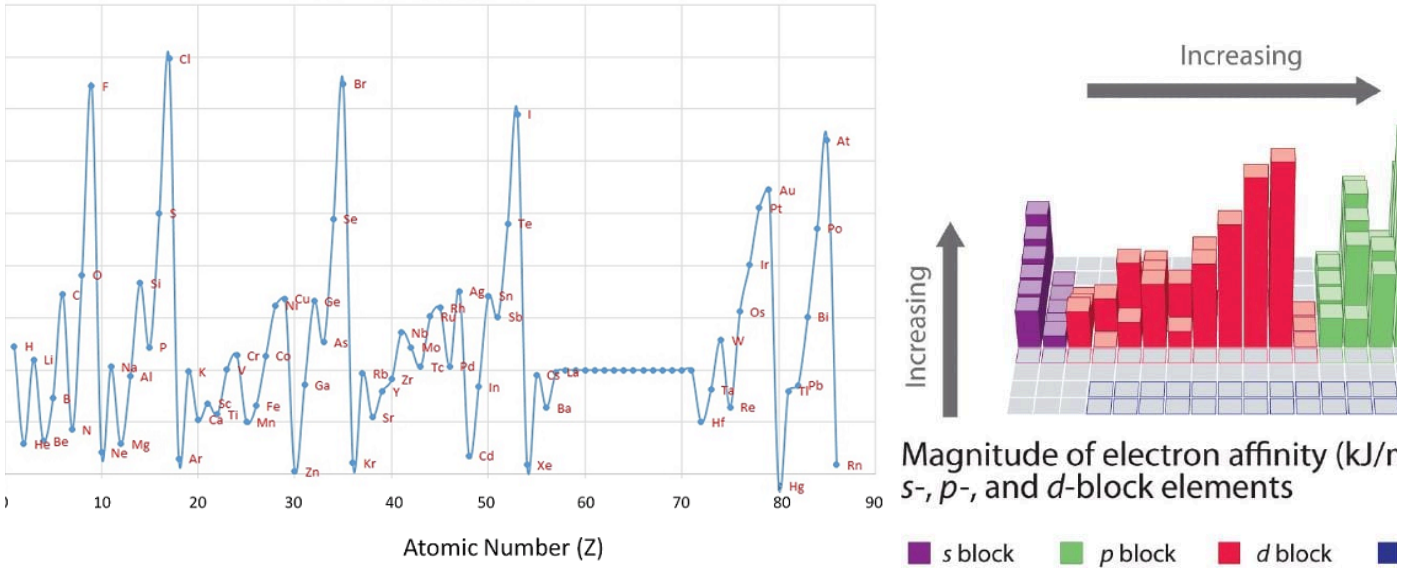


Figure 3.4.2: Electron Affinity Trends. (Left) A Plot of Periodic Variation of Electron Affinity with Atomic Number for the First Six Rows of the Periodic Table. Notice that electron affinities can be both negative and positive. from Robert J. Lancashire (University of the West Indies). (Right) Electron Affinities (in kJ/mol) of the *s*-, *p*-, and *d*-Block Elements.

The chlorine atom has the most negative electron affinity of any element, which means that more energy is released when an electron is added to a gaseous chlorine atom than to an atom of any other element:

$$\mathrm{Cl\,(g) + e^- \rightarrow Cl^-\,(g)} \qquad EA = -346\ kJ/mol \tag{3.4.4}$$

In contrast, beryllium does not form a stable anion, so its effective electron affinity is

$$\mathrm{Be\,(g) + e^- \rightarrow Be^-\,(g)} \qquad EA \geq 0 \tag{3.4.5}$$

In general, electron affinities of the main-group elements become less negative as we proceed down a column. This is because as the energy level increases, the extra electrons enter orbitals that are increasingly far from the nucleus, and it is less easy to gain extra electrons forming anions.

Example 3.4.2: Contrasting Electron Affinities of Sb, Se, and Te

Based on their positions in the periodic table, which of Sb, Se, or Te would you predict to have the most negative electron affinity?

Given: three elements

Asked for: element with most negative electron affinity

Strategy:

A. Locate the elements in the periodic table. Use the trends in electron affinities going down a column for elements in the same group. Similarly, use the trends in electron affinities from left to right for elements in the same row.
B. Place the elements in order, listing the element with the most negative electron affinity first.

Solution:

We know that electron affinities become less negative going down a column (except for the anomalously low electron affinities of the elements of the second row), so we can predict that the electron affinity of Se is more negative than that of Te. We also know that electron affinities become more negative from left to right across a row, and that the group 15 elements

tend to have values that are less negative than expected. Because Sb is located to the left of Te and belongs to group 15, we predict that the electron affinity of Te is more negative than that of Sb. The overall order is Se < Te < Sb, so Se has the most negative electron affinity among the three elements.

Exercise 3.4.2: Contrasting Electron Affinities of Rb, Sr, and Xe

Based on their positions in the periodic table, which of Rb, Sr, or Xe would you predict to most likely form a gaseous anion?

Answer available at the end of this section.

Answers

Exercise 3.4.1: Highest First Ionization Energy

As

Exercise 3.4.2: Contrasting Electron Affinities of Rb, Sr, and Xe

Rb

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3.5: Naming Monoatomic Ions

Learning Objectives

- Name monoatomic ions using the defined nomenclature rules.

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 Cations

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 ionic compound with unique physical and chemical properties. Thus, we need a different name for each iron ion to distinguish Fe^{2+} from Fe^{3+}. The same issue arises for other ions with more than one possible charge.

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

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

Table 3.5.1: Names of Some Cations

Element	Charge	Symbol	Common System Name	Stock System Name
chromium	2+	Cr^{2+}	chrom*ous* ion	chromium(II) ion
	3+	Cr^{3+}	chrom*ic* ion	chromium(III) ion
copper	1+	Cu^+	cupr*ous* ion	copper(I) ion
	2+	Cu^{2+}	cupr*ic* ion	copper(II) ion
iron	2+	Fe^{2+}	ferr*ous* ion	iron(II) ion
	3+	Fe^{3+}	ferr*ic* ion	iron(III) ion
lead	2+	Pb^{2+}	plumb*ous* ion	lead(II) ion
	4+	Pb^{3+}	plumb*ic* ion	lead(IV) ion
tin	2+	Sn^{2+}	stann*ous* ion	tin(II) ion
	4+	Sn^{4+}	stann*ic* ion	tin(IV) ion

Naming Anions

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

Table 3.5.2: Some Monatomic Anions

Element	Charge	Symbol	Name
fluorine	1–	F^-	fluoride ion
chlorine	1–	Cl^-	chloride ion
bromine	1–	Br^-	bromide ion
iodine	1–	I^-	iodide ion
oxygen	2–	O^{2-}	oxide ion
sulfur	2–	S^{2-}	sulfide ion
phosphorous	3–	P^{3-}	phosphide ion
nitrogen	3–	N^{3-}	nitride ion

Example 3.5.1

Name each ion.

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

Answer a available at the end of this section.

Exercise 3.5.1

Name each ion.

a. Fe^{2+}
b. Fe^{3+}
c. SO_4^{2-}
d. Ba^{2+}
e. HCO_3^-

Answer a available at the end of this section.

Example 3.5.2

Write the formula for each ion.

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

Answer a available at the end of this section.

Exercise 3.5.2

Write the formula for each ion.

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

Answer a available at the end of this section.

Note Chemistry Is Everywhere: Salt

The element sodium (part [a] in the accompanying figure) is a very reactive metal; given the opportunity, it will react with the sweat on your hands and form sodium hydroxide, which is a very corrosive substance. The element chlorine (part [b] in the accompanying figure) is a pale yellow, corrosive gas that should not be inhaled due to its poisonous nature. Bring these two hazardous substances together, however, and they react to make the ionic compound sodium chloride (part [c] in the accompanying figure), known simply as salt.

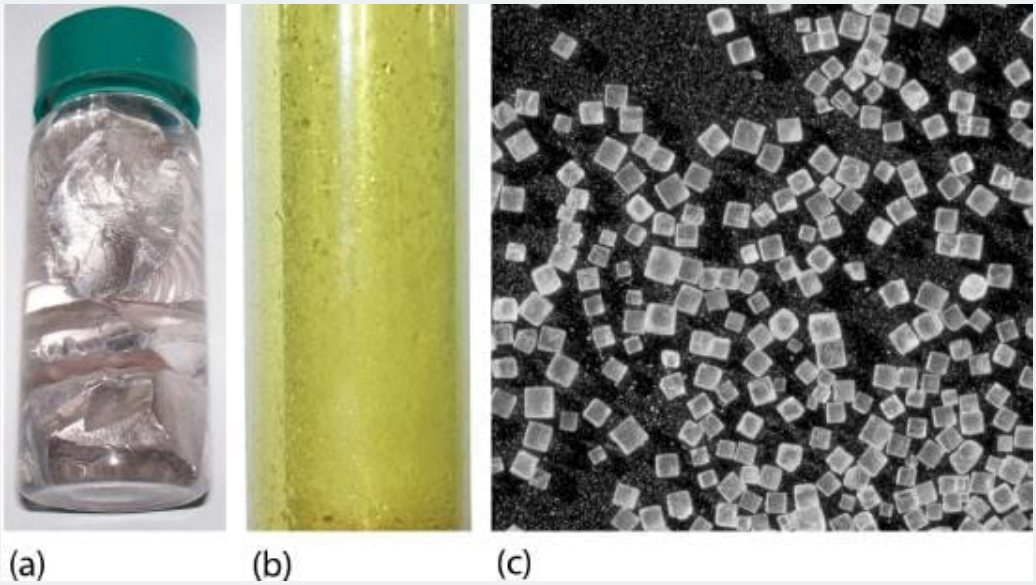


Figure 3.5.1: Sodium + Chlorine = Sodium Chloride (a) Sodium is a very reactive metal. (b) Chlorine is a pale yellow, noxious gas. (c) Together, sodium and chlorine make sodium chloride-salt-which is necessary for our survival. Source: Photo(opens in new window) on the left courtesy of Greenhorn1. Photo(opens in new window) in the center courtesy of Benjah-bmm27, . Photo on the right © Thinkstock.

Salt is necessary for life. Na^+ ions are one of the main ions in the human body and are necessary to regulate the fluid balance in the body. Cl^- ions are necessary for proper nerve function and respiration. Both of these ions are supplied by salt. The taste of salt is one of the fundamental tastes; salt is probably the most ancient flavoring known, and one of the few rocks we eat.

> The health effects of too much salt are still under debate, although a 2010 report by the US Department of Agriculture concluded that "excessive sodium intake...raises blood pressure, a well-accepted and extraordinarily common risk factor for stroke, coronary heart disease, and kidney disease."US Department of Agriculture Committee for Nutrition Policy and Promotion, Report of the Dietary Guidelines Advisory Committee on the Dietary Guidelines for Americans, accessed January 5, 2010. It is clear that most people ingest more salt than their bodies need, and most nutritionists recommend curbing salt intake. Curiously, people who suffer from low salt (called *hyponatria*) do so not because they ingest too little salt but because they drink too much water. Endurance athletes and others involved in extended strenuous exercise need to watch their water intake so their body's salt content is not diluted to dangerous levels.

Answers

Example 3.5.1

the calcium ion

the sulfide ion (from Table 3.5.2)

the sulfite ion

the ammonium ion

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

Exercise 3.5.1

the iron (II) or ferrous ion

the iron (III) or ferric ion

the sulfate ion

the barium ion

the bicarbonate ion or hydrogen carbonate ion

Example 3.5.2

Br^-

PO_4^{3-}

Cu^{2+}

Mg^{2+}

Exercise 3.5.2

F^-

CO_3^{2-}

Fe^{2+}

K^+

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3.6: Polyatomic Ions

Learning Objectives

- To identify and name 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 structures, names, and formulas of some polyatomic ions are found in the below figure and table.

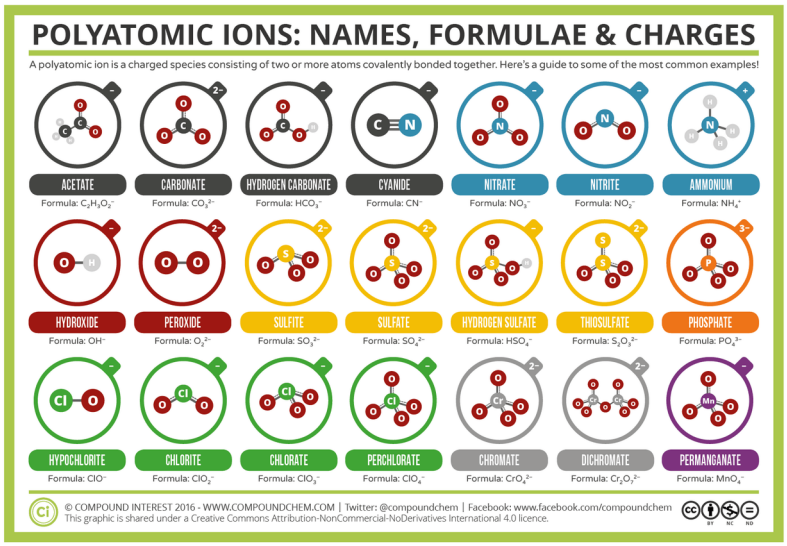


Figure 3.6.1: Polyatomic Ions Infographic

Polyatomic ions have defined formulas, names, and charges that cannot be modified in any way. Table 3.6.1 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.

Table 3.6.1: Common Polyatomic Ion Names and Formulas

Ion Name	Ion Formula
hyddronium ion	H_3O^+
ammonium ion	NH_4^+
hydroxide ion	OH^-
cyanide ion	CN^-
carbonate ion	CO_3^{2-}
bicarbonate or hydrogen carbonate	HCO_3^-
acetate ion	$C_2H_3O_2^-$ **or** $CH_3CO_2^-$
nitr**ate** ion	NO_3^-
nitr**ite** ion	NO_2^-

Ion Name	Ion Formula
sulf**ate** ion	SO_4^{2-}
sulf**ite** ion	SO_3^{2-}
phosph**ate** ion	PO_4^{3-}
phosph**ite** ion	PO_3^{3-}

Note that only two polyatomic ions in this table are cations, hydronium ion (H_3O^+) and ammonium ion (NH_4^+), 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 ions. 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. 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, both the nitrate ion, symbolized as NO_3^-, and the sulfate ion, symbolized as SO_4^{2-}, share an "-ate" suffix, however, the former contains three oxygens, and 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.

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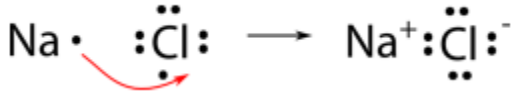
3.7: Ionic Bonds

Learning Objectives

- Define an ionic bond, ionic compound, and electrostatic force
- Recognize the complexity of three-dimensional ionic bond interactions involved in ionic compounds

Oppositely charged particles attract each other. This attractive force is often referred to as an **electrostatic attraction**. An **ionic bond** is the electrostatic electrostatic attraction that holds ions together in an **ionic compound**. The strength of the ionic bond is directly dependent upon the quantity of the charges and inversely dependent on the distance between the charged particles. A cation with a 2+ charge will make a stronger ionic bond than a cation with a 1+ charge. A larger ion makes a weaker ionic bond because of the greater distance between its electrons and the nucleus of the oppositely charged ion.

We will use sodium chloride as an example to demonstrate the nature of the ionic bond and how it forms. As you know, sodium is a metal and loses its one valence electron to become a cation. Chlorine is a nonmetal and gains one electron in becoming an anion. However, electrons cannot be simply "lost" to nowhere in particular. A more accurate way to describe what is happening is that a single electron is transferred from the sodium atom to the chlorine atom as shown below.



The ionic bond is the attraction of the $\mathrm{Na^+}$ ion for the $\mathrm{Cl^-}$ ion. It is conventional to show show the cation without dots around the symbol to emphasize that the original energy level that contained the valence electron is now empty. The anion is now shown with a complete octet of electrons.

Ionic compounds are held together by attractive electrostatic interactions between cations and anions. In contrast to the simplified electron transfer depicted above for sodium and chlorine, the cations and anions in ionic compounds are arranged in space to form an extended three-dimensional array that maximizes the number of attractive electrostatic interactions and minimizes the number of repulsive electrostatic interactions (Figure 3.7.1). In other words, each ion is attracted to many of its neighboring ions forming a sodium chloride crystal or **ionic solid**.

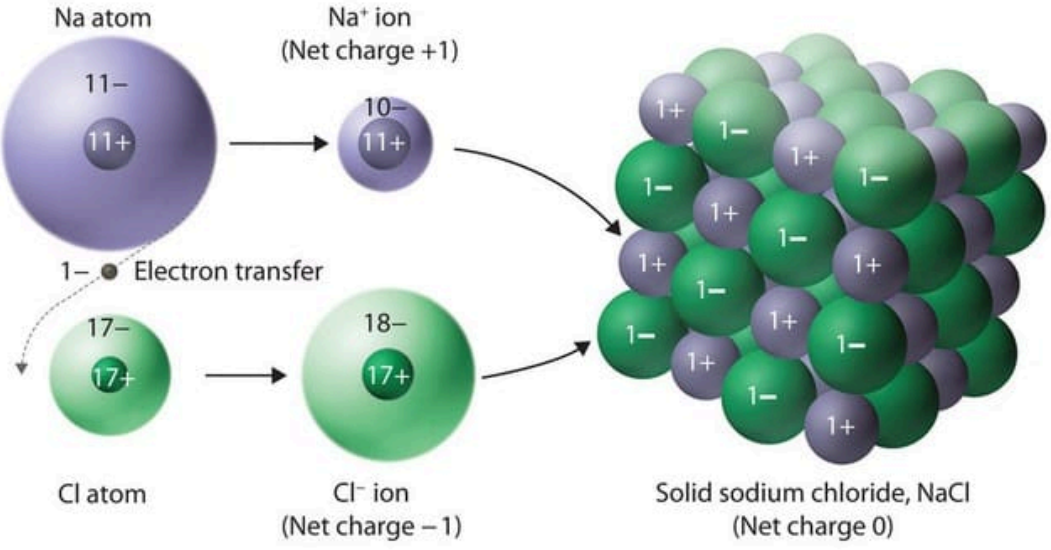


Figure 3.7.1: Ionic Bonding. The ionic compound NaCl forms when electrons from sodium atoms are transferred to chlorine atoms. The resulting $\mathrm{Na^+}$ and $\mathrm{Cl^-}$ ions form a three-dimensional solid that is held together by attractive electrostatic interactions.

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3.8: Formulas of Ionic Compounds

Learning Objectives

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

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

Ionic Compounds Formed From Monoatomic Ions

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

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

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

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

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

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

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

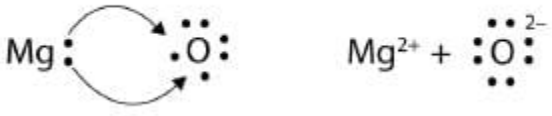
$$[Ne] \qquad [Ne]\,3s^2 3p^6$$

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

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

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

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



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

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

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

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

$$\mathrm{Na}\cdot \rightharpoonup \cdot\ddot{\mathrm{O}}:$$

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



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

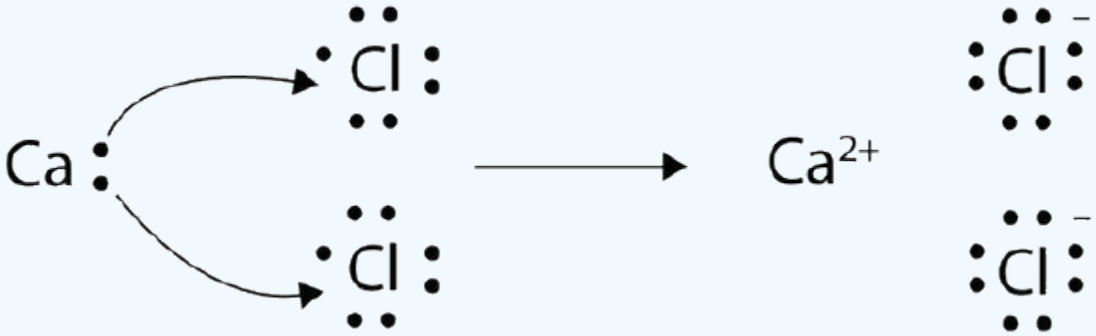
These three ions attract each other to form an overall neutrally charged ionic compound, which we write as Na_2O. The need for the number of electrons lost to be equal to the number of electrons gained explains why ionic compounds have the ratio of cations to anions that they do. This is also required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

Example 3.8.1

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

Solution

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



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

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

Exercise 3.8.1

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

Answer available at the end of this section.

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

3.3.2.

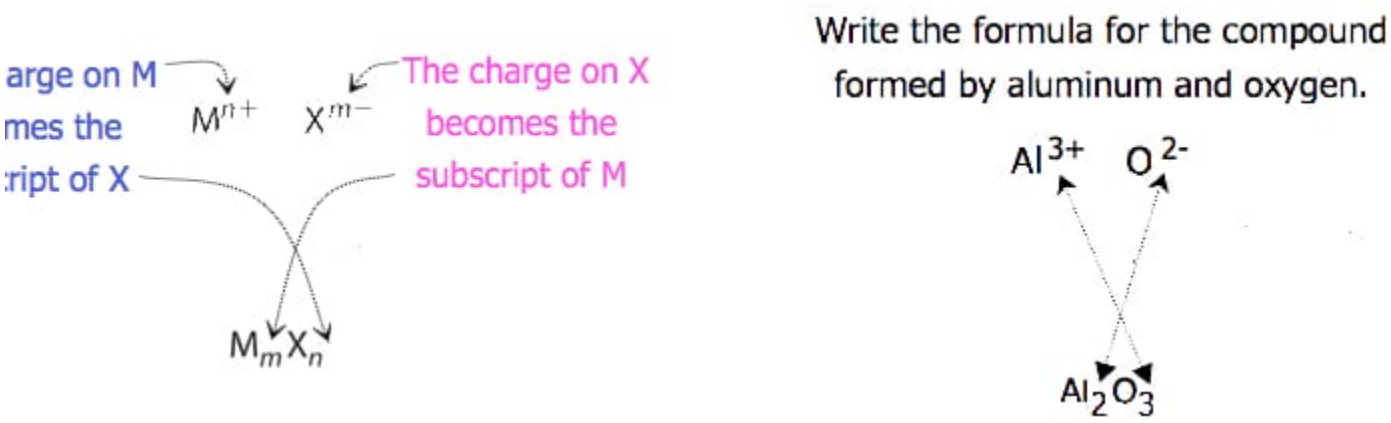


Figure 3.8.1: Crossing charges. One method for obtaining subscripts in the empirical formula is by crossing charges.

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

Example 3.8.2: Predicting the Formula of an Ionic Compound

The gemstone sapphire (Figure 3.8.2) is mostly a compound of aluminum and oxygen that contains aluminum cations, Al^{3+}, and oxygen anions, O^{2-}. What is the formula of this compound?



Figure 3.8.2: Although pure aluminum oxide is colorless, trace amounts of iron and titanium give blue sapphire its characteristic color. (credit: modification of work by Stanislav Doronenko)

Solution

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

Exercise 3.8.2

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

Answer available at the end of this section.

Ionic Compounds Formed From Polyatomic Ions

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

Example 3.8.3: Predicting the Formula of a Compound with a Polyatomic Anion

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

Solution

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

Exercise 3.8.3

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

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

Answer a: available at the end of this section.

Formula Unit

Ionic compounds exist as alternating positive and negative ions in regular, three-dimensional arrays called crystals (Figure 3.8.3). As you can see, there are no individual $NaCl$ "particles" in the array; instead, there is a continuous lattice of alternating sodium and chloride ions. However, we can use the ratio of sodium ions to chloride ions, expressed in the lowest possible whole numbers or *simplest formula*, as a way of describing the compound. In the case of sodium chloride, the ratio of sodium ions to chloride ions, expressed in lowest whole numbers, is 1:1, so we use $NaCl$ (one Na symbol and one Cl symbol) to represent the compound. Thus, $NaCl$ is the chemical formula for sodium chloride, which is a concise way of describing the relative number of different ions in the compound. A macroscopic sample is composed of myriads of NaCl pairs; each individual pair called a **formula unit**. Although it is convenient to think that $NaCl$ crystals are composed of individual $NaCl$ units, Figure 3.8.3 shows that no single ion

is exclusively associated with any other single ion. Each ion is surrounded by ions of opposite charge.

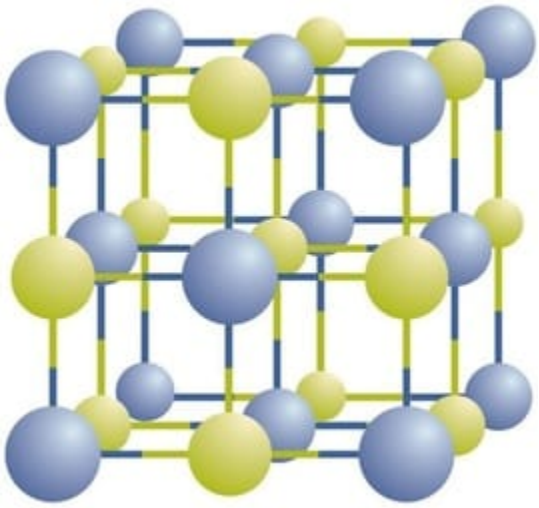
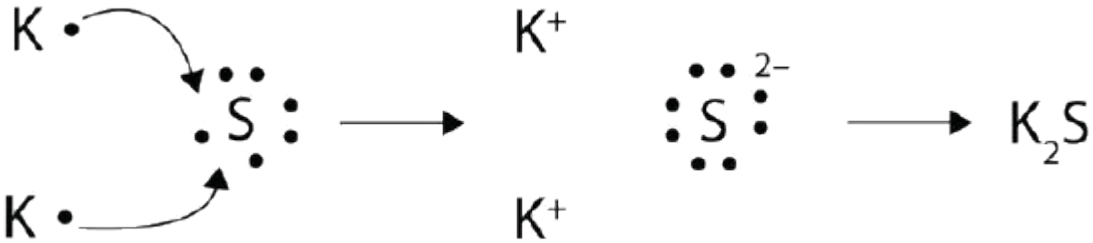


Figure 3.8.3: A Sodium Chloride Crystal. A crystal contains a three-dimensional array of alternating positive and negative ions. The precise pattern depends on the compound. A crystal of sodium chloride, shown here, is a collection of alternating sodium and chlorine ions.

Answers

Exercise 3.8.1



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

Exercise 3.8.2

Na_2S

Exercise 3.8.3

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

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

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3.9: Naming Ionic Compounds

Learning Objectives

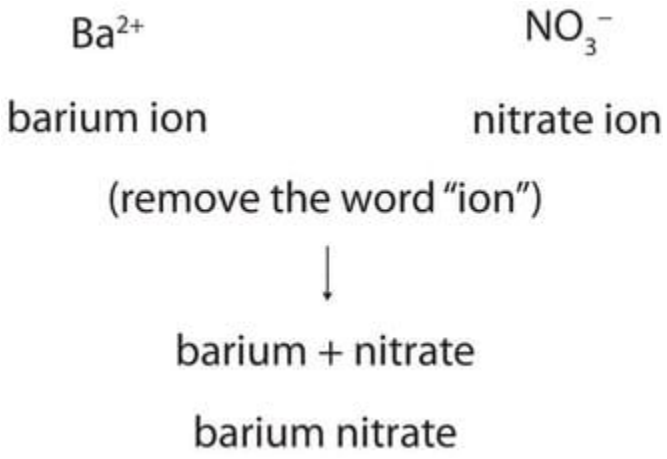
- Write the names for ionic compounds by recognizing and naming the ions in the formula unit.

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

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

Type I Ionic Compounds

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



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

Type II Ionic Compounds

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

ferric chloride, respectively.

Ionic Compounds in Your Cabinets

Every day you encounter and use a large number of ionic compounds. Some of these compounds, where they are found, and what they are used for are listed in Table 3.9.1. Look at the label or ingredients list on the various products that you use during the next few days, and see if you run into any of those in this table, or find other ionic compounds that you could now name or write as a formula.

Table 3.9.1: Everyday Ionic Compounds

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

As you practice naming compounds, use Figure 3.9.1 as a guide.

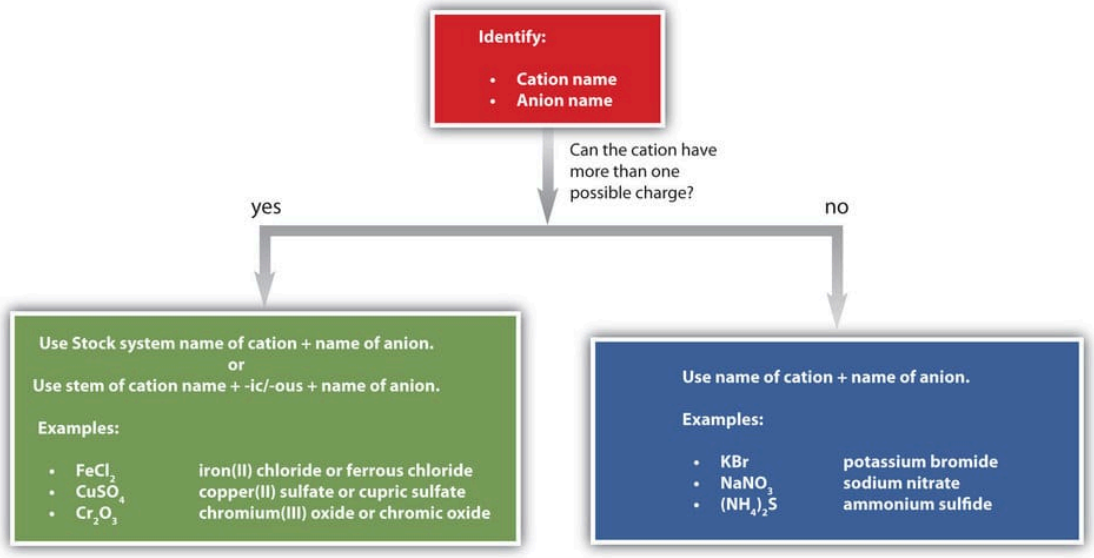


Figure 3.9.1: A Guide to Naming Simple Ionic Compounds. Follow these steps to name a simple ionic compound.

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

Example 3.9.3

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

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

Answer a available at the end of this section.

Exercise 3.9.3

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

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

Answer a available at the end of this section.

Answers

Example 3.9.3

calcium phosphate

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

potassium chloride

copper(I) chloride or cuprous chloride
tin(II) fluoride or stannous fluoride

Exercise 3.9.3

zinc bromide
iron (III) nitrate or ferric nitrate
aluminum oxide
copper (II) fluoride or cupric fluoride
silver fluoride

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3.10: Some Properties of Ionic Compounds

Learning Objectives

- Describe the basic physical properties of ionic compounds.

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

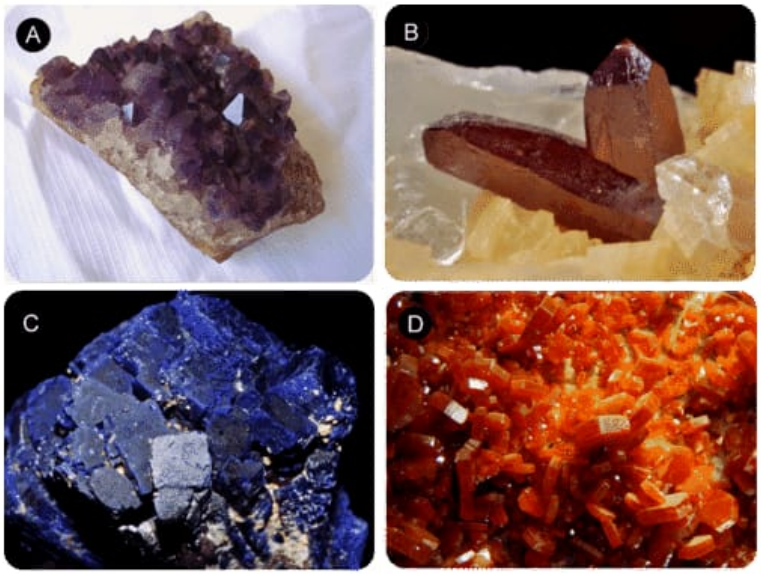


Figure 3.10.1: *In nature, the ordered arrangement of ionic solids gives rise to beautiful crystals. (A) Amethyst - a form of quartz, SiO_2, whose purple color comes from iron ions. (B) Cinnabar - the primary ore of mercury is mercury (II) sulfide, HgS (C) Azurite - a copper mineral, $Cu_3(CO_3)_2(OH)_2$. (D) Vanadinite - the primary ore of vanadium, $Pb_3(VO_4)_3Cl$.*

Melting Points

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

Shattering

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

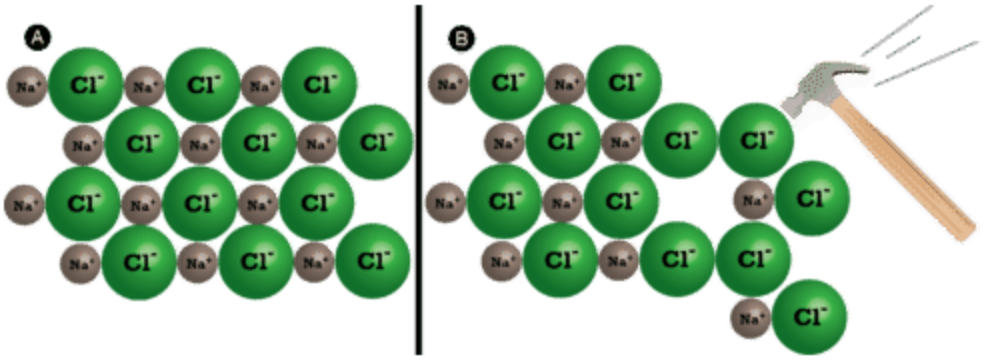


Figure 3.10.2: *(A) The sodium chloride crystal is shown in two dimensions. (B) When struck by a hammer, the negatively-charged chloride ions are forced near each other and the repulsive force causes the crystal to shatter.*

Conductivity

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

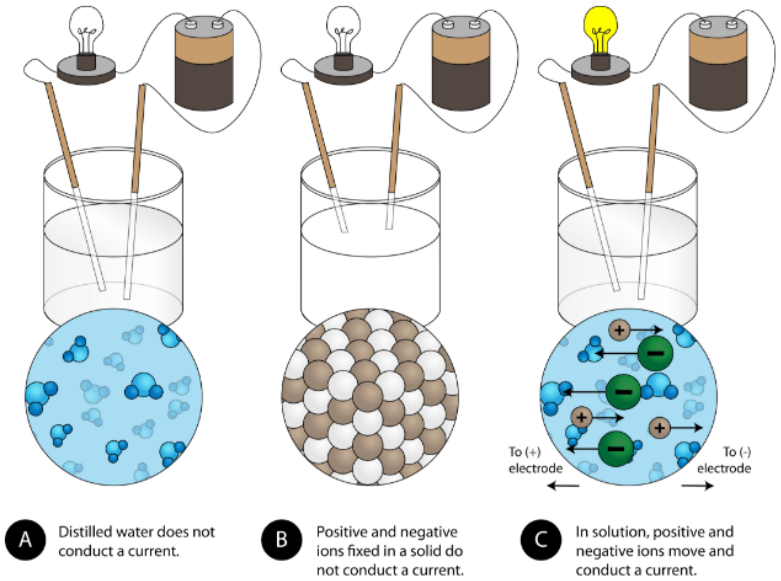


Figure 3.10.3: *(A) Distilled water does not conduct electricity. (B) A solid ionic compound also does not conduct. (C) A water solution of an ionic compound conducts electricity well.*

In the first beaker, distilled water does not conduct a current because water is a molecular compound. In the second beaker, solid sodium chloride also does not conduct a current. Despite being ionic and thus composed of charged particles, the solid crystal lattice does not allow the ions to move between the electrodes. Mobile charged particles are required for the circuit to be complete and the light bulb to light up. In the third beaker, the NaCl has been dissolved into the distilled water. Now the crystal lattice has been broken apart and the individual positive and negative ions can move.

Example 3.10.1

Write the dissociation equation of solid NaCl in water.

Solution

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

Exercise 3.10.1

Write the dissociation equation of solid NH_4NO_3 in water.

Answer available at the end of this section.

Key Takeaways

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

Contributors and Attributions

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Answers

Exercise 3.10.1

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

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3.11: H⍰ and OH⍰ Ions - An Introduction to Acids and Bases

Learning Objectives

- To identify H^+ as an acid and OH^- as a base.

You may have some idea, from your day-to-day experiences, of some chemical substances that are considered acids or bases. Generally, a compound that is sour is recognized as being an acid. Some familiar acids may include citric acid, which is a molecule found in citrus fruits such as lemons and limes, and acetic acid, the molecule that makes up vinegar. Bases, on the other hand, include chemicals such as sodium bicarbonate (baking soda), which is bitter-tasting, and sodium hydroxide, which is found in cleaning substances and is not recommended for ingestion.

More details about acids, bases, and the reactions they undergo will be discussed later in this text. However, because you have just learned about ions and ionic compounds, it is worth pointing out two important ions that are used to identify and distinguish if a substance is acidic or basic; hydrogen ions, H^+, and hydroxide ions, OH^-. In fact, one definition of acids and bases states that an **acid** will produce H^+ when dissolved in water and a **base** will produce a OH^- when dissolved in water.

Ionic compounds that are basic are easily recognized because the hydroxide ion is part of the formula and name. Some common examples are sodium *hydroxide*, $NaOH$, and calcium *hydroxide*, $Ca(OH)_2$. When dissolved in water, sodium hydroxide will split into its constituent ions, sodium ions (Na^+) and hydroxide ions (OH^-) in a 1:1 ratio. However, according to it's chemical formula, calcium hydroxide will produce two hydroxide ions for every one calcium ion, a 1:2 ratio.

Compounds that produce hydrogen ions in water contain one or more hydrogen ions in the chemical formula and usually have special names to help recognize them as acids. Hydrochloric acid (HCl), nitric acid (HNO_3), and carbonic acid (H_2CO_3) are all acids. HCl and HNO_3 each dissolve in water producing a H^+ and an anion (chloride and nitrate respectively). As indicated by the formula for carbonic acid there are two H^+ for every one carbonate ion. The below table lists some common acids. See if you can determine the ratio of H^+ to anions produced when these compounds are dissolved in water.

Table 3.11.1 *Common Acids and Their Anions*

Acid Name	Acid Formula	Anion Name	Anion Formula
acetic acid	CH_3COOH	acetate ion	CH_3COO^-
carbonic acid	H_2CO_3	bicarbonate ion	HCO_3^-
		carbonate ion	CO_3^{2-}
hydrobromic acid	HBr	bromide ion	Br^-
nitric acid	HNO_3	nitrate ion	NO_3^-
nitrous acid	HNO_2	nitrous ion	NO_2^-
phosphoric acid	H_3PO_4	dihydrogen phosphate ion	$H_2PO_4^-$
		hydrogen phosphate ion	HPO_4^{2-}
		phosphate ion	PO_4^{3-}
sulfuric acid	H_2SO_4	hydrogen sulfate ion	HSO_4^-
		sulfate ion	SO_4^{2-}
sulfurous acid	H_2SO_3	hydrogen sulfite ion	HSO_3^-
		sulfite ion	SO_3^{2-}

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4: MOLECULAR COMPOUNDS

4.1: Covalent Bonds

4.2: Covalent Bonds and the Periodic Table

4.3: Multiple Covalent Bonds

4.4: Coordinate Covalent Bonds

4.5: Characteristics of Molecular Compounds

4.6: Molecular Formulas and Lewis Structures

4.7: Drawing Lewis Structures

4.8: The Shapes of Molecules

4.9: Polar Covalent Bonds and Electronegativity

4.10: Polar Molecules

4.11: Naming Binary Molecular Compounds

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4.1: Covalent Bonds

Learning Objectives

- Describe how covalent bonds form using the octet rule.

Formation of Covalent Bonds

Nonmetal atoms frequently form covalent bonds with other nonmetal atoms. Covalent bonds are formed between two atoms when both have similar tendencies to attract electrons to themselves (i.e., when both atoms have identical or fairly similar ionization energies and electron affinities). For example, two hydrogen atoms bond covalently to form an H_2 molecule; each hydrogen atom in the H_2 molecule has two electrons stabilizing it, giving each atom the same number of valence electrons as the noble gas He.

The bond in a hydrogen molecule, measured as the distance between the two nuclei, is about 7.4×10^{-11} m, or 74 picometers (pm; 1 pm = 1×10^{-12} m). This particular bond length represents the lowest potential energy state of two hydrogen atoms and is 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.

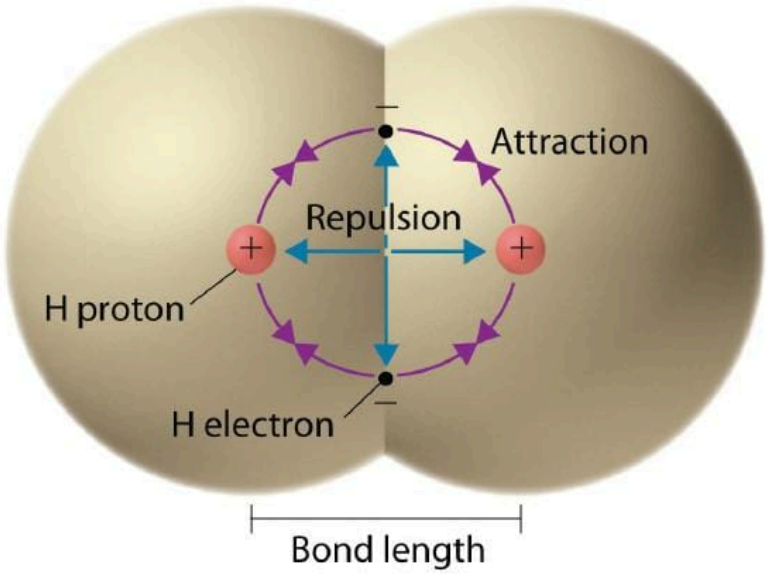


Figure 4.1.1: Attractive and Repulsive Interactions between Electrons and Nuclei in the Hydrogen Molecule. Electron–electron and proton–proton interactions are repulsive; electron–proton interactions are attractive. At the observed bond distance, the repulsive and attractive interactions are balanced.

A plot of the potential energy of the system as a function of the internuclear distance (Figure 4.1.2) shows that energy decreases as two hydrogen atoms move toward each other. Starting on the far right, we have two separate hydrogen atoms with a particular potential energy, indicated by the red line. Along the *x*-axis is the distance between the two atoms. As the two atoms approach each other (moving left along the *x*-axis), their valence orbitals (1s) begin to overlap. The single electrons on each hydrogen atom then interact with both atomic nuclei, occupying the space around both atoms. The strong attraction of each shared electron to both nuclei stabilizes the system, and the potential energy decreases as the bond distance decreases. If the atoms continue to approach each other, the positive charges in the two nuclei begin to repel each other, and the potential energy increases.

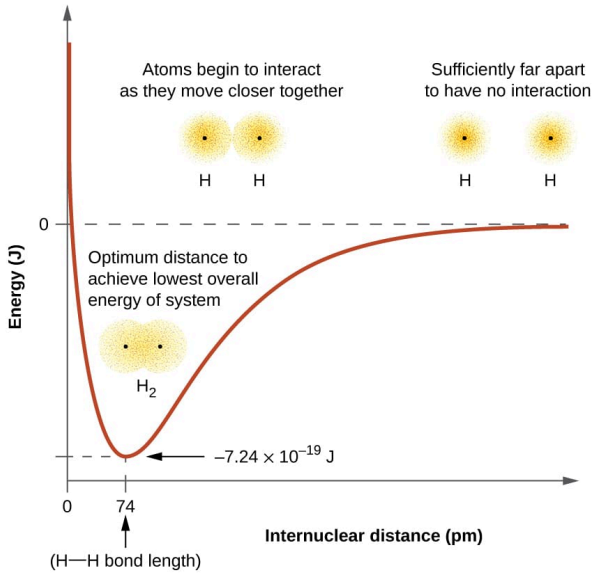


Figure 4.1.2: The interaction of two hydrogen atoms changes as a function of distance. The energy of the system changes as the atoms interact. The lowest (most stable) energy occurs at a distance of 74 pm, which is the bond length observed for the H_2 molecule.

Lewis Structures

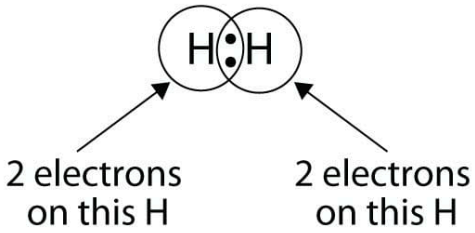
Chemists frequently use Lewis structures to represent covalent bonding in molecular substances. For example, the Lewis symbols of two separate hydrogen atoms are as follows:



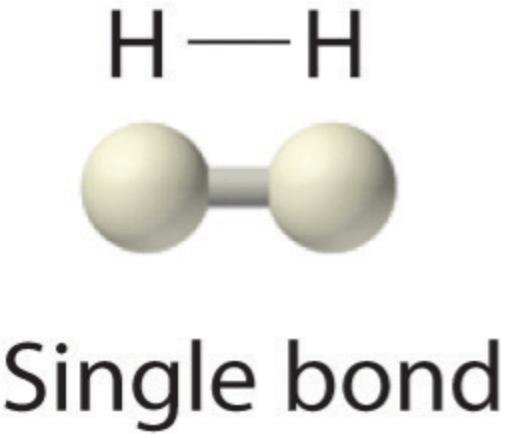
The Lewis structures of two hydrogen atoms sharing electrons looks like this:



We can use circles to show that each H atom has two electrons around the nucleus, completely filling each atom's valence shell:



Because each H atom has a filled valence shell, this bond is stable, and we have made a diatomic hydrogen molecule. For simplicity's sake, it is common to represent the covalent bond with a dash, instead of with two dots:



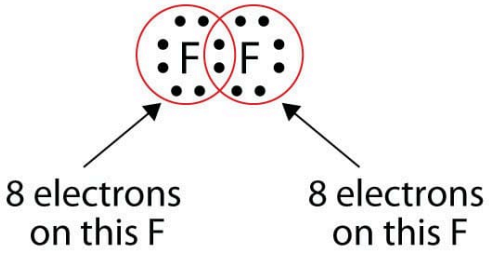
Because two atoms are sharing one pair of electrons, this covalent bond is called a **single bond**. As another example, consider fluorine. F atoms have seven electrons in their valence shell:



These two atoms can do the same thing that the H atoms did; they share their unpaired electrons to make a covalent bond.



Note that each F atom has a *complete octet* around it now:



We can also write this using a dash to represent the shared electron pair:



You will notice that there are two different types of electrons in the fluorine diatomic molecule. The **bonding electron pair** makes the covalent bond. Each F atom has three other pairs of electrons that do not participate in the bonding; they are called **lone pair electrons**. Each F atom has one bonding pair and three lone pairs of electrons.

Diatomic Molecules

Hydrogen (H_2) and fluorine (F_2) are both described as *diatomic molecules*. These elements and others (see Table $4.1.1$) exist naturally as molecules rather than as individual atoms. It is important to note that the names of these elements represent molecules and not individual atoms. When describing a single atom rather than a molecule, the word atom is used.

Table $4.1.1$: Elements That Exist as Diatomic Molecules

Hydrogen (H_2)	Oxygen (O_2)	Nitrogen (N_2)	Fluorine (F_2)
Chlorine (Cl_2)	Bromine (Br_2)	Iodine (I_2)	

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4.2: Covalent Bonds and the Periodic Table

Learning Objectives

- Predict the number of covalent bonds formed based on the elements involved and their position on the periodic table.
- Describe the important exceptions to the octet rule.

Diatomic molecules such as hydrogen (H_2), chlorine (Cl_2), fluorine (F_2), etc. containing covalent bonds between two of the same type of atom are only a few examples of the vast number of molecules that can form. Two different atoms can also share electrons and form covalent bonds. For example, water, (H_2O), has two covalent bonds between a single oxygen atom and two hydrogen atoms. Ammonia, (NH_3, is a central nitrogen atom bonded to three hydrogen atoms. Methane, (CH_4, is a single carbon atom covalently bonded to four hydrogen atoms. In these examples the central atoms form different numbers of bonds to hydrogen atoms in order to complete their valence subshell and form octets.

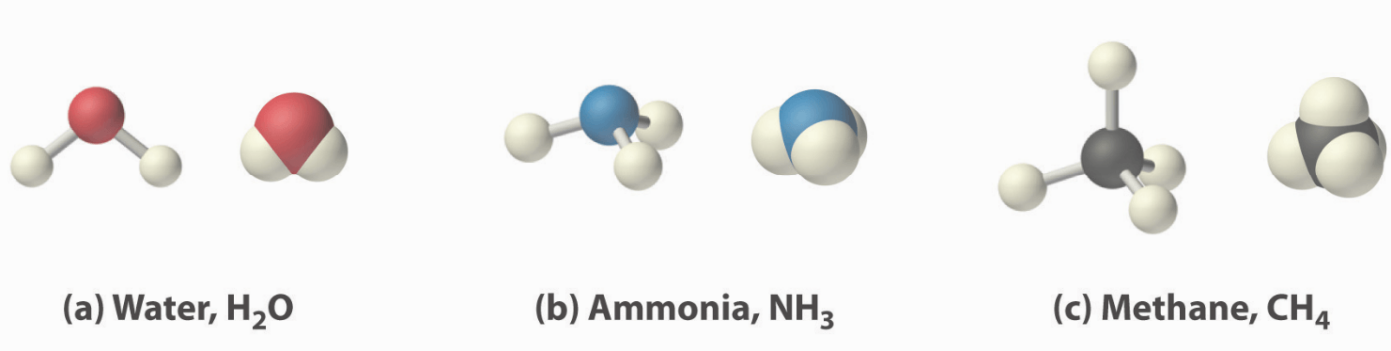
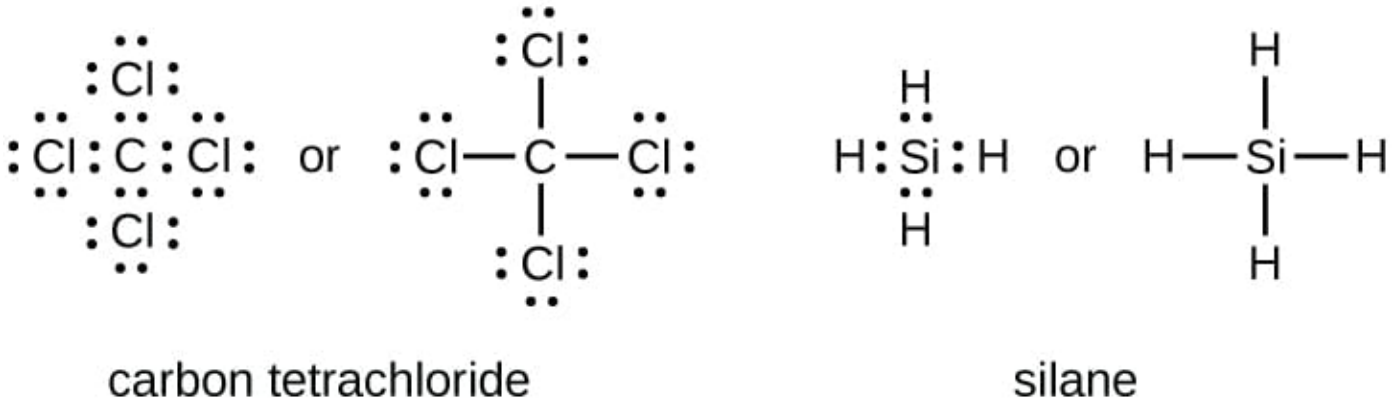


Figure 4.2.4: 3D molecule examples. From left to right: water molecule, ammonia molecule, and methane molecule

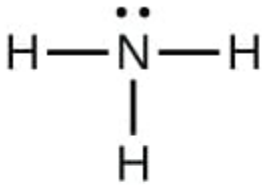
How Many Covalent Bonds Are Formed?

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); this is especially true of the nonmetals of the second period of the periodic table (C, N, O, and F). For example, each atom of a group 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 CCl_4 (carbon tetrachloride) and silicon in SiH_4 (silane). Because hydrogen only needs two electrons to fill its valence shell, it is an exception to the octet rule and only needs to form one bond. 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.

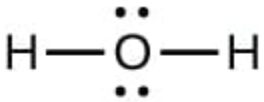


Group 15 elements such as nitrogen have five valence electrons in the atomic Lewis symbol: one lone pair and three unpaired

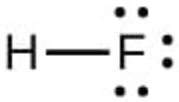
electrons. To obtain an octet, these atoms form three covalent bonds, as in NH_3 (ammonia). Oxygen and other atoms in group 16 obtain an octet by forming two covalent bonds:



ammonia



Water



hydrogen fluoride

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.

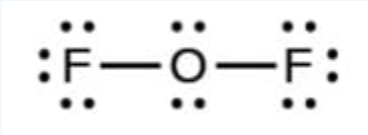
Table showing 4 different atoms, each of their number of bonds, and each of their number of lone pairs.

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

Because hydrogen only needs two electrons to fill its valence shell, it follows the *duet rule*. Hydrogen only needs to form one bond to complete a duet of electrons. This is the reason why H is always a terminal atom and never a central atom.

Example 4.2.1

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?

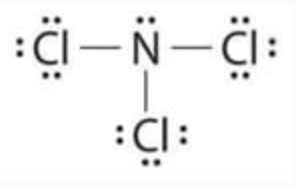


Solution

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

Exercise 4.2.1

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



Answer available at the end of this section.

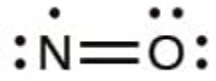
Octet Rule Exceptions

As important and useful as the octet rule is in chemical bonding, there are many covalent molecules with central atoms that do not have eight electrons in their Lewis structures. This does not mean that the octet rule is useless—quite the contrary. As with many rules, there are exceptions, or violations. These molecules fall into three categories:

- Odd-electron molecules have an odd number of valence electrons, and therefore have an unpaired electron.
- Electron-deficient (diminished octet) molecules have a central atom that has fewer electrons than needed for a noble gas configuration.
- Expanded octet (hypervalent) molecules have a central atom that has more electrons than needed for a noble gas configuration.

Odd-electron molecules

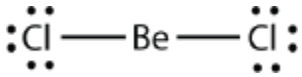
Although they are few, some stable compounds, often called *free radicals*, have an odd number of electrons in their valence shells. With an odd number of electrons, at least one atom in the molecule will have to violate the octet rule. Examples of stable, odd-electron molecules are NO, $\mathrm{NO_2}$, and $\mathrm{ClO_2}$. The Lewis electron dot diagram for NO, a compound produced in internal combustion engines when oxygen and nitrogen react at high temperatures, is as follows:



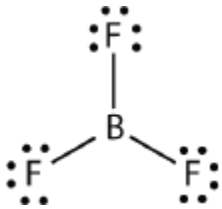
As you can see, the nitrogen and oxygen share four electrons between them. The oxygen atom has an octet of electrons but the nitrogen atom has only seven valence electrons, two electrons in the double bond, one lone pair, and one additional lone electron. Although NO is a stable compound, it is very chemically reactive, as are most other odd-electron compounds.

Electron-deficient molecules

These stable compounds have less than eight electrons around an atom in the molecule, i.e. they have less than an octet. The most common examples are the covalent compounds of beryllium and boron. For example, beryllium can form two covalent bonds, resulting in only four electrons in its valence shell:

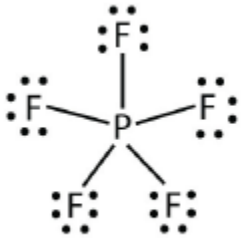


Boron commonly makes only three covalent bonds, resulting in only six valence electrons around the B atom. A well-known example is $\mathrm{BF_3}$:

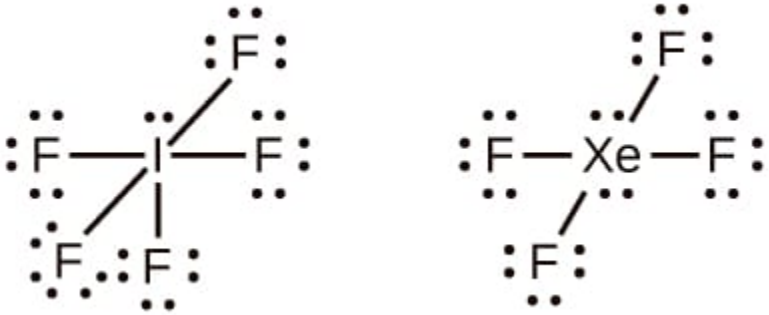


Expanded Octet Molecules

Elements in the second period of the periodic table ($n = 2$) can accommodate only eight electrons in their valence shell orbitals because they have only four valence orbitals (one 2*s* and three 2*p* orbitals). Elements in the third and higher periods ($n \geq 3$) have more than four valence orbitals and can share more than four pairs of electrons with other atoms because they have empty *d* orbitals in the same shell. Molecules formed from these elements have expanded octets and are sometimes called hypervalent molecules. Phosphorous pentachloride shares five pairs of electrons for a total of ten electrons in the valence shell.



In some expanded octet molecules, such as IF_5 and XeF_4, some of the electrons in the outer shell of the central atom are lone pairs:



Example 4.2.2

Identify each violation to the octet rule by drawing a Lewis electron dot diagram.

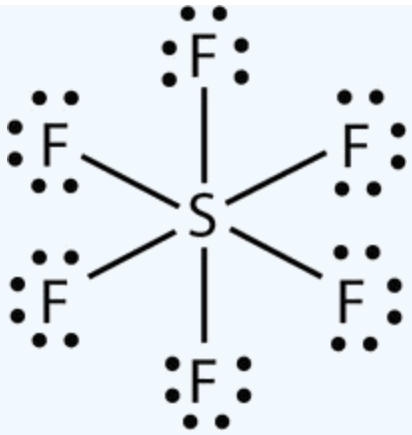
a. ClO
b. $\mathrm{SF_6}$

Solution

1. With one Cl atom and one O atom, this molecule has 6 + 7 = 13 valence electrons, so it is an odd-electron molecule. A Lewis electron dot diagram for this molecule is as follows:



2. In $\mathrm{SF_6}$, the central S atom makes six covalent bonds to the six surrounding F atoms, so it is an expanded valence shell molecule. Its Lewis electron dot diagram is as follows:



Exercise 4.2.2: Xenon Difluoride

Identify the violation to the octet rule in $\mathrm{XeF_2}$ by drawing a Lewis electron dot diagram.

Answer available at the end of this section.

Concept Review Exercises

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

Answers

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

Answers

Exercise 4.2.1

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.

Exercise 4.2.2**: Xenon Difluoride**

The Xe atom has an expanded valence shell with more than eight electrons around it.



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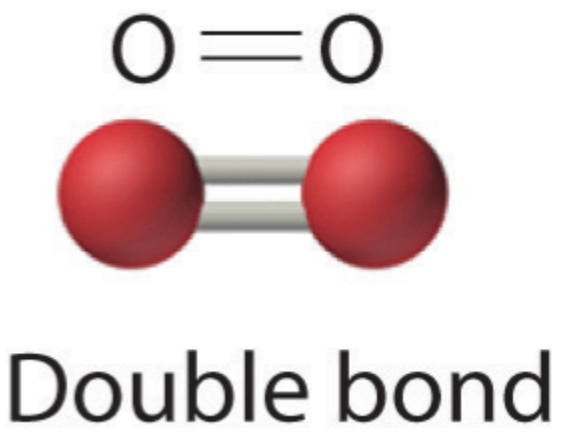
4.3: Multiple Covalent Bonds

Learning Objectives

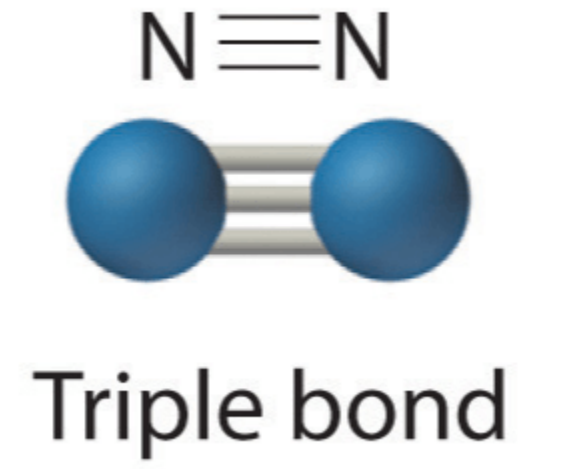
- Identify when a multiple bond (double or triple) is needed to complete an octet.

The sharing of a pair of electrons represents a single covalent bond, usually just referred to as a ***single bond***. However, in many molecules atoms attain complete octets by sharing more than one pair of electrons between them:

- Two electron pairs shared a ***double bond***



- Three electron pairs shared a ***triple bond***

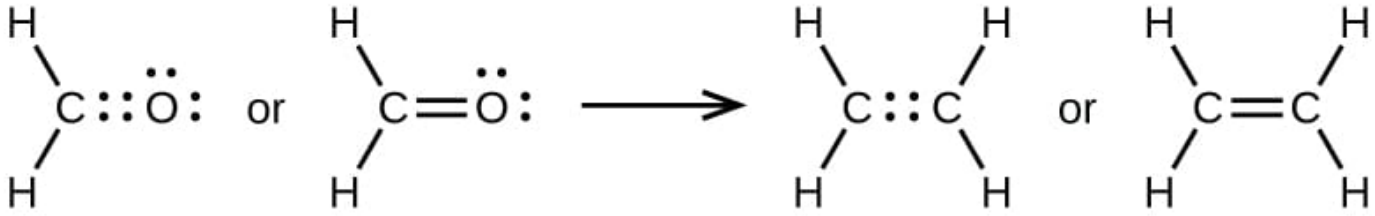


Because each nitrogen contains 5 valence electrons, they need to share 3 pairs to each achieve a valence octet. N_2 is fairly inert, due to the strong triple bond between the two nitrogen atoms.

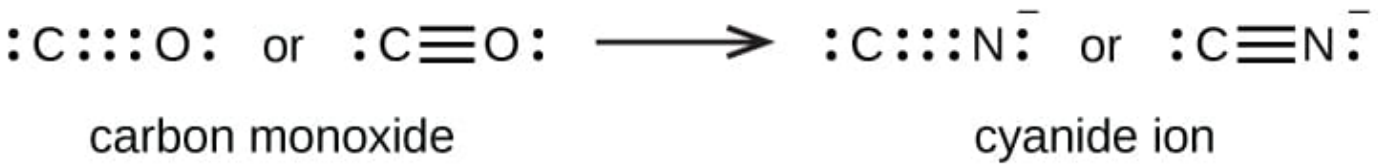


In addition to nitrogen and oxygen, carbon will also commonly form multiple bonds to complete valence octets. Additional examples involving these three atoms are shown below.

A double bond is formed between the carbon and oxygen atoms in CH_2O (formaldehyde) and between the two carbon atoms in C_2H_4 (ethylene):



A triple bond is formed between carbon and oxygen in carbon monoxide (CO) and between carbon and nitrogen in the cyanide ion (CN^-):



Example 4.3.1: Writing Lewis Structures

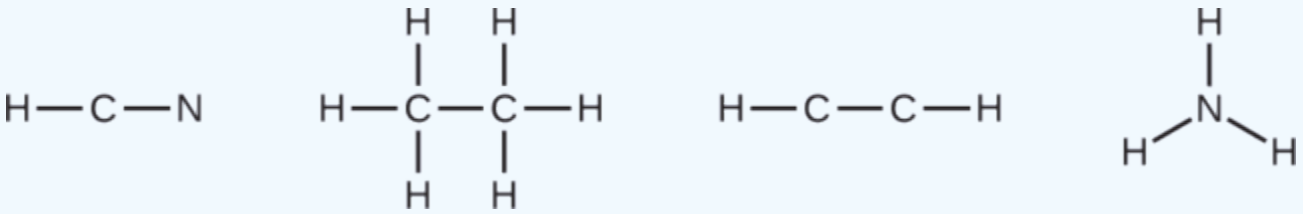
NASA's Cassini-Huygens mission detected a large cloud of toxic hydrogen cyanide (HCN) on Titan, one of Saturn's moons. Titan also contains ethane (H_3CCH_3), acetylene (HCCH), and ammonia (NH_3). What are the Lewis structures of these molecules?

Solution

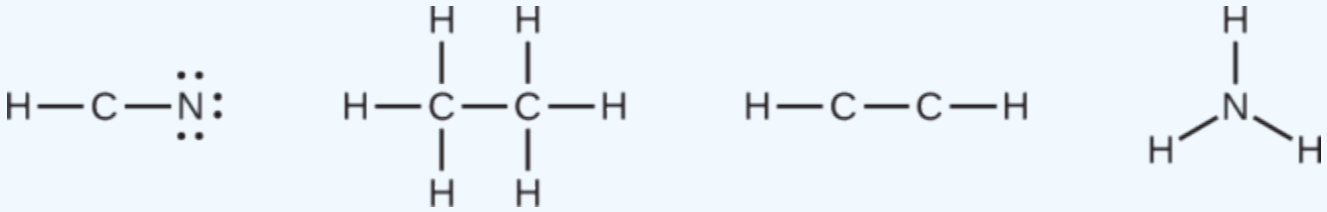
Calculate the number of valence electrons.

- HCN: (1 × 1) + (4 × 1) + (5 × 1) = 10
- H_3CCH_3: (1 × 3) + (2 × 4) + (1 × 3) = 14
- HCCH: (1 × 1) + (2 × 4) + (1 × 1) = 10
- NH_3: (5 × 1) + (3 × 1) = 8

Draw a skeleton and connect the atoms with single bonds. Remember that H is never a central atom:

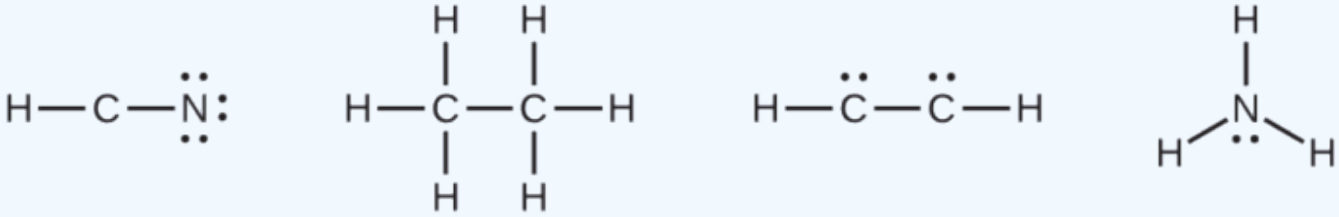


Where needed, distribute electrons to the terminal atoms:



- HCN: six electrons placed on N
- H_3CCH_3: no electrons remain
- HCCH: no terminal atoms capable of accepting electrons
- NH_3: no terminal atoms capable of accepting electrons

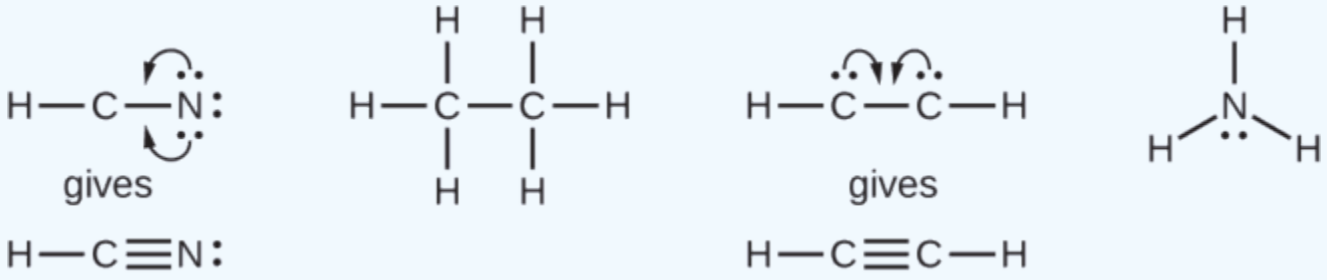
Where needed, place remaining electrons on the central atom:



- HCN: no electrons remain
- H_3CCH_3: no electrons remain
- HCCH: four electrons placed on carbon
- NH_3: two electrons placed on nitrogen

Where needed, rearrange electrons to form multiple bonds in order to obtain an octet on each atom:

- HCN: form two more C–N bonds
- H_3CCH_3: all atoms have the correct number of electrons
- HCCH: form a triple bond between the two carbon atoms
- NH_3: all atoms have the correct number of electrons



Exercise 4.3.1

Both carbon monoxide, CO, and carbon dioxide, CO_2, are products of the combustion of fossil fuels. Both of these gases also cause problems: CO is toxic and CO_2 has been implicated in global climate change. What are the Lewis structures of these two molecules?

Answer available at the end of this section.

Answers

Exercise 4.3.1



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4.4: Coordinate Covalent Bonds

Learning Objectives

- Describe the difference between a covalent bond and a coordinate covalent bond.
- Identify molecules that form coordinate covalent bonds.

Remember when you were younger, and were told to share your favorite toy with your brother, sister, or friend? You probably didn't want to share, but did anyway. It likely turned out that you had more fun playing with the toy together than if you had kept it to yourself. Atoms often share electrons with other atoms that have nothing to contribute to the situation forming a **coordinate covalent bond**; the end result is a new structure.

Coordinate Covalent Bonds

Each of the covalent bonds that we have looked at so far has involved each of the atoms that are bonding contributing one of the electrons to the shared pair. There is an alternate type of covalent bond in which one of the atoms provides *both* of the electrons in a shared pair. Carbon monoxide, CO, is a toxic gas that is released as a byproduct during the burning of fossil fuels. The bonding between the C atom and the O atom can be thought of in the following procession:

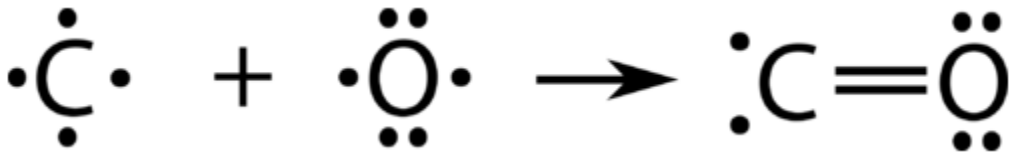


Figure $4.4.2$: Formation of a CO double bond (incorrect structure). (Credit: Joy Sheng; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

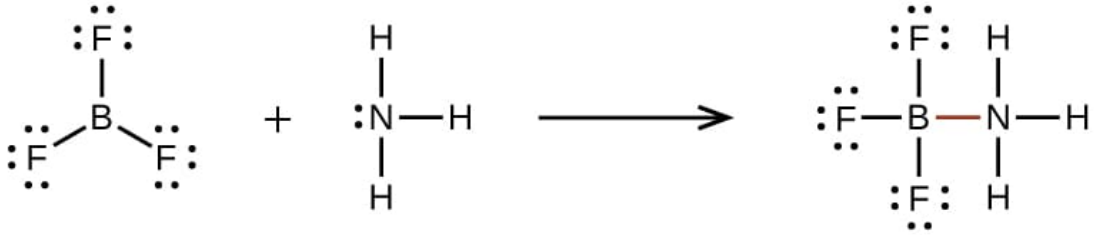
At this point, a double bond has formed between the two atoms, with each atom providing one of the electrons to each bond. The oxygen atom now has a stable octet of electrons, but the carbon atom only has six electrons and is unstable. This situation is resolved if the oxygen atom contributes one of its lone pairs in order to make a third bond with the carbon atom.



Figure $4.4.3$: Correct CO structure. (Credit: Joy Sheng; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

The carbon monoxide molecule is correctly represented by a triple covalent bond between the carbon and oxygen atoms. One of the bonds formed is a coordinate covalent bond, a covalent bond in which one of the atoms contributes both of the electrons in the shared pair. Once formed, a coordinate covalent bond is the same as any other covalent bond. It is not as if the two conventional bonds in the CO molecule are stronger or different in any other way than the coordinate covalent bond.

Electron-deficient molecules, like $\mathrm{BF_3}$, are very reactive and will often combine with other molecules forming coordinate covalent bonds. The central boron atom in $\mathrm{BF_3}$ does not have eight electrons, and is therefore very reactive. It can readily combine with a molecule containing a central atom with a lone pair of electrons. For example, $\mathrm{NH_3}$ reacts with $\mathrm{BF_3}$ because the lone pair on nitrogen can be shared with the boron atom:



Summary

- Coordinate covalent bonds can form when one atom provides a lone pair of electrons to the bond.
- Coordinate covalent bonds are as strong as other covalent bonds.

Review

1. Where does the third covalent bond in the CO molecule come from?
2. Why is the incorrect structure for CO above wrong?
3. Are coordinate covalent bonds stronger or weaker than regular covalent bonds?

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4.5: Characteristics of Molecular Compounds

Learning Objectives

- Compare the properties of ionic and 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 further in a later chapter) 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 4.5.1: 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.

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4.6: Molecular Formulas and Lewis Structures

Learning Objectives

- Understand the different ways to represent molecules.

There are many "universal languages" in the world. Musicians of every culture recognize music embodied in a series of notes on a staff. This passage from a Bach cello suite could be played by any trained musician from any country, because there is an agreement as to what the symbols on the page mean. In the same way, molecules are represented using symbols and a language that all chemists agree upon.
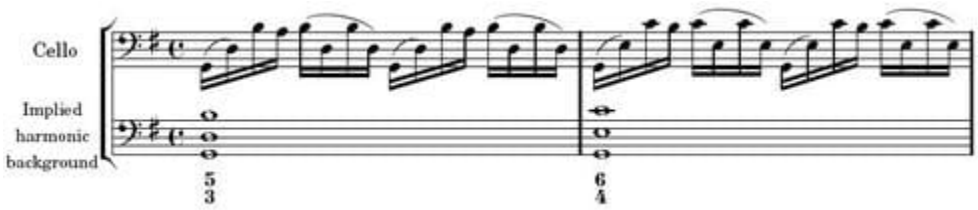


Figure 4.6.1 (Credit: J. S. Bach; Source: http://commons.wikimedia.org/wiki/File:Bach_cello_harmony.JPG(opens in new window); License: Public Domain)

Molecular Formulas

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

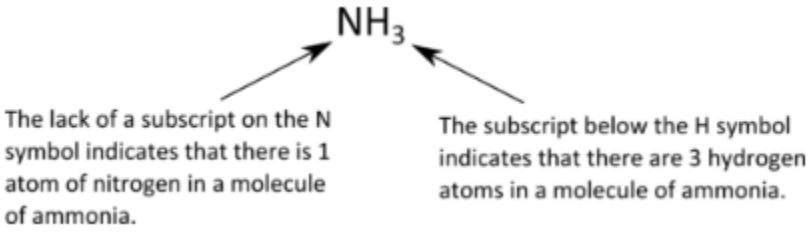


Figure 4.6.2: The molecular formula for ammonia. (Credit: Joy Sheng; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

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

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

Figure 4.6.3 shows some of the different ways to portray the structure of a slightly more complex molecule: methanol. These representations differ greatly in their information content. For example, the molecular formula for methanol (Figure 4.6.3*a*) gives only the number of each kind of atom; writing methanol as CH_4O tells nothing about its structure. In contrast, the structural formula (Figure 4.6.3*b*) indicates how the atoms are connected, but it makes methanol look as if it is planar (which it is not). Both the ball-and-stick model (part (c) in Figure 4.6.3) and the perspective drawing (Figure 4.6.3*d*) show the three-dimensional structure of the molecule. The latter (also called a wedge-and-dash representation) is the easiest way to sketch the structure of a molecule

in three dimensions. It shows which atoms are above and below the plane of the paper by using wedges and dashes, respectively; the central atom is always assumed to be in the plane of the paper. The space-filling model (part (e) in Figure 4.6.3) illustrates the approximate relative sizes of the atoms in the molecule, but it does not show the bonds between the atoms. In addition, in a space-filling model, atoms at the "front" of the molecule may obscure atoms at the "back."

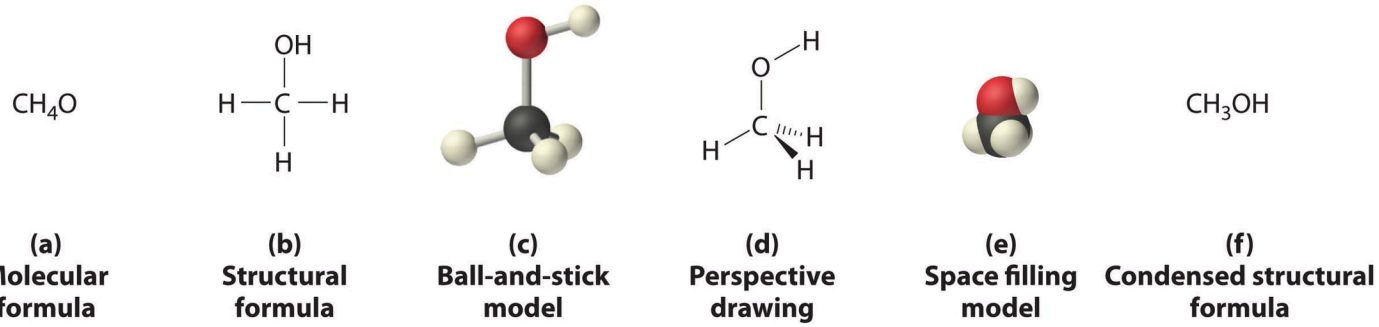


Figure 4.6.3: Different Ways of Representing the Structure of a Molecule. (a) The molecular formula for methanol gives only the number of each kind of atom present. (b) The structural formula shows which atoms are connected. (c) The ball-and-stick model shows the atoms as spheres and the bonds as sticks. (d) A perspective drawing (also called a wedge-and-dash representation) attempts to show the three-dimensional structure of the molecule. (e) The space-filling model shows the atoms in the molecule but not the bonds. (f) The condensed structural formula is by far the easiest and most common way to represent a molecule.

Although a structural formula, a ball-and-stick model, a perspective drawing, and a space-filling model provide a significant amount of information about the structure of a molecule, each requires time and effort. Consequently, chemists often use a condensed structural formula (part (f) in Figure 4.6.3), which omits the lines representing bonds between atoms and simply lists the atoms bonded to a given atom next to it. Multiple groups attached to the same atom are shown in parentheses, followed by a subscript that indicates the number of such groups. For example, the condensed structural formula for methanol is CH_3OH, which indicates that the molecule contains a CH_3 unit that looks like a fragment of methane (CH_4). Methanol can therefore be viewed either as a methane molecule in which one hydrogen atom has been replaced by an –OH group or as a water molecule in which one hydrogen atom has been replaced by a $–CH_3$ fragment. Because of their ease of use and information content, we use condensed structural formulas for molecules throughout this text. Ball-and-stick models are used when needed to illustrate the three-dimensional structure of molecules, and space-filling models are used only when it is necessary to visualize the relative sizes of atoms or molecules to understand an important point.

Example 4.6.1: Molecular Formulas

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

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

Given: condensed structural formula

Asked for: molecular formula

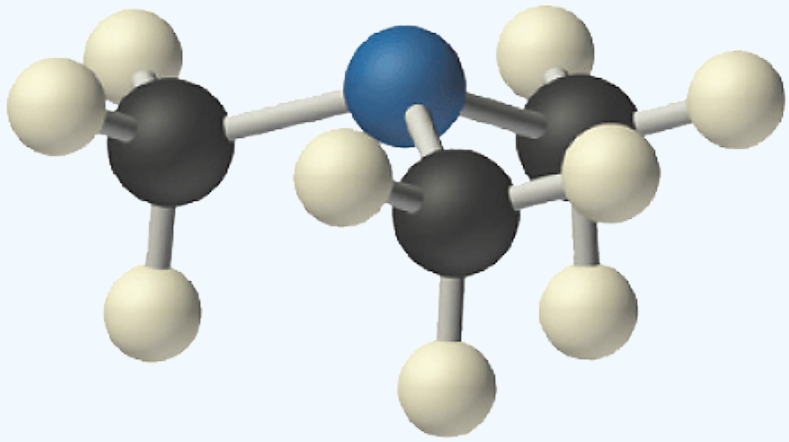
Strategy:

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

Solution:

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

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

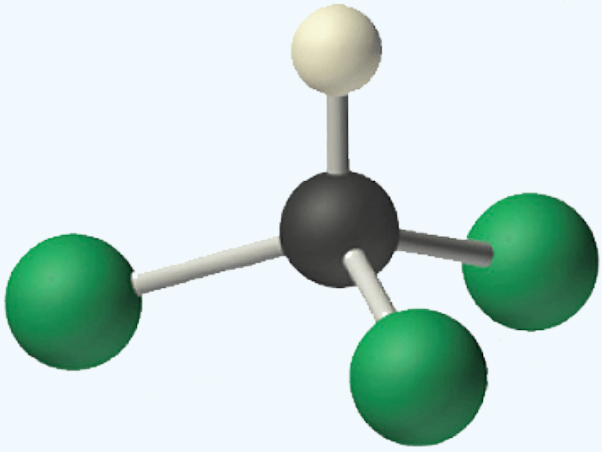


Trimethylamine

Exercise 4.6.1: Molecular Formulas

Write the molecular formula for each molecule.

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



Chloroform

Answer a available at the end of this section.

Answers

Exercise 4.6.1**: Molecular Formulas**

$CHCl_3$

N_2H_4

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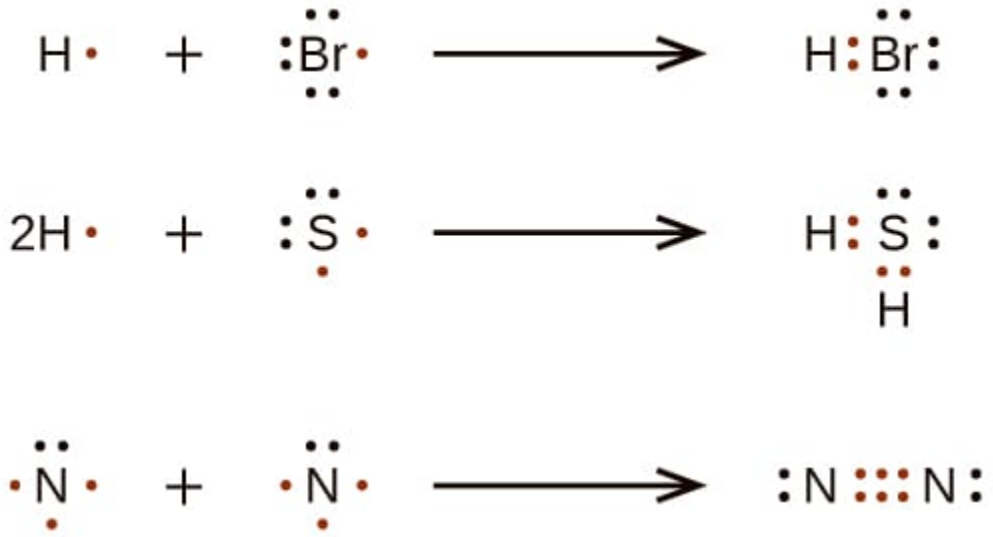
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4.7: Drawing Lewis Structures

Learning Objectives

- Draw Lewis structures for molecules.

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



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

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

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

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

The H_2O Molecule

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



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

The OCl^- Ion

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



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

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

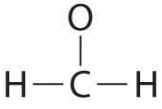
The CH_2O Molecule

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



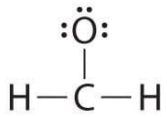
2. Each hydrogen atom (group 1) has one valence electron, carbon (group 14) has 4 valence electrons, and oxygen (group 16) has 6 valence electrons, for a total of [(2)(1) + 4 + 6] = 12 valence electrons.

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



Six electrons are used, and 6 are left over.

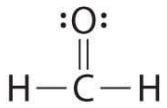
4. Adding all 6 remaining electrons to oxygen (as three lone pairs) gives the following:



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

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

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



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

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

Example 4.7.1

Write the Lewis electron structure for each species.

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

Given: chemical species

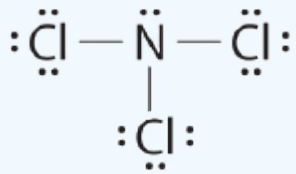
Asked for: Lewis electron structures

Strategy:

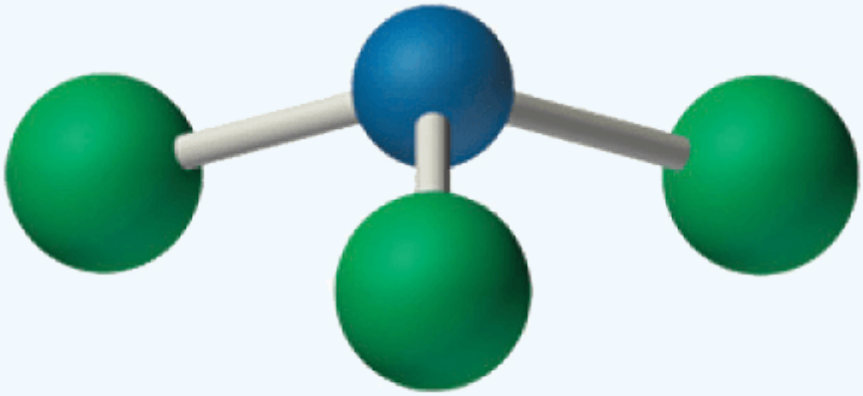
Use the six-step procedure to write the Lewis electron structure for each species.

Solution:

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

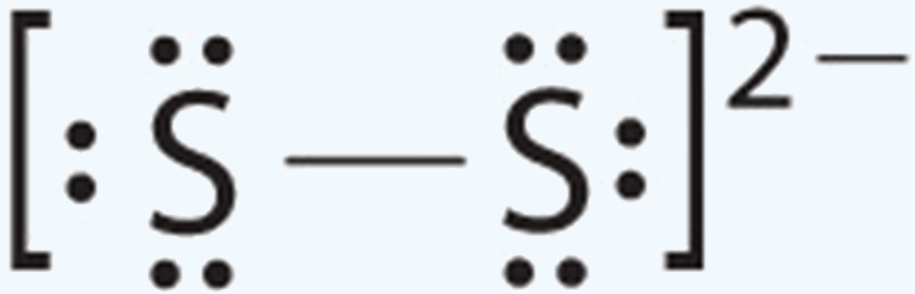


Nitrogen trichloride is an unstable oily liquid once used to bleach flour; this use is now prohibited in the United States.



Nitrogen trichloride

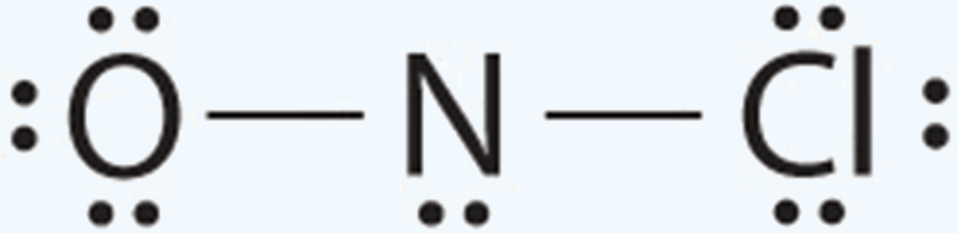
b. In a diatomic molecule or ion, we do not need to worry about a central atom. Each sulfur atom (group 16) contains 6 valence electrons, and we need to add 2 electrons for the –2 charge, giving a total of 14 valence electrons. Using 2 electrons for the S–S bond, we arrange the remaining 12 electrons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



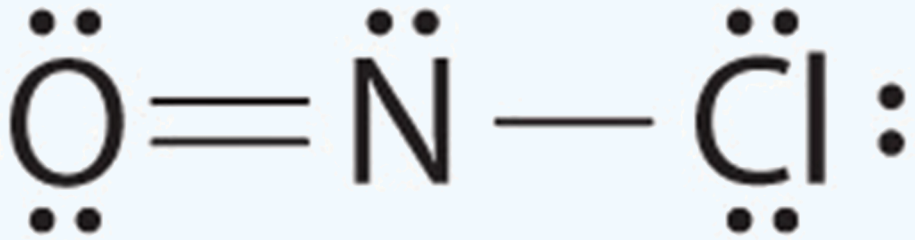
c. Because nitrogen is less electronegative than oxygen or chlorine, it is the central atom. The N atom (group 15) has 5 valence electrons, the O atom (group 16) has 6 valence electrons, and the Cl atom (group 17) has 7 valence electrons, giving a total of 18 valence electrons. Placing one bonding pair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



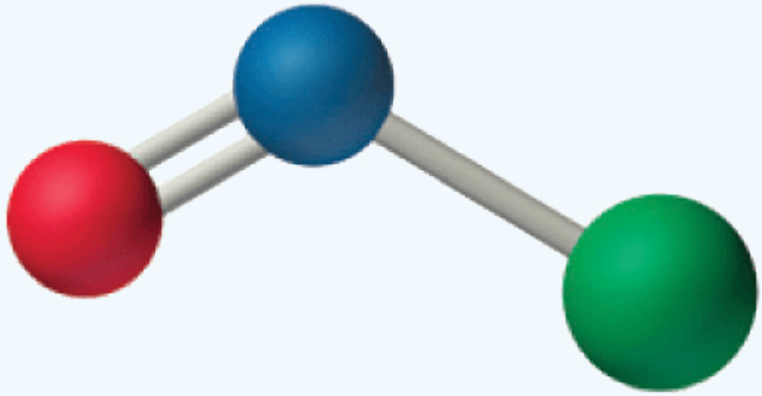
Adding three lone pairs each to oxygen and to chlorine uses 12 more electrons, leaving 2 electrons to place as a lone pair on nitrogen:



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



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



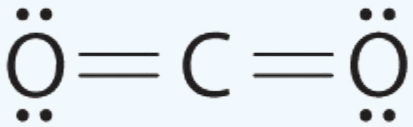
Nitrosyl chloride

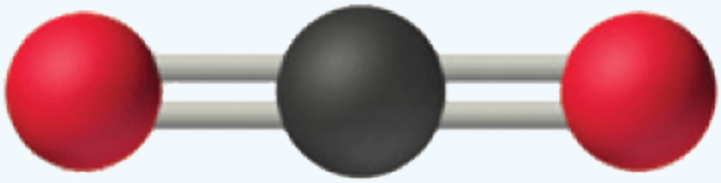
Exercise 4.7.1

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

Answer

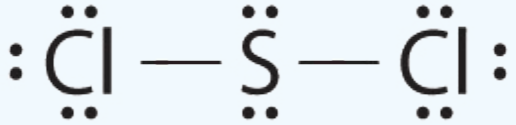
1.



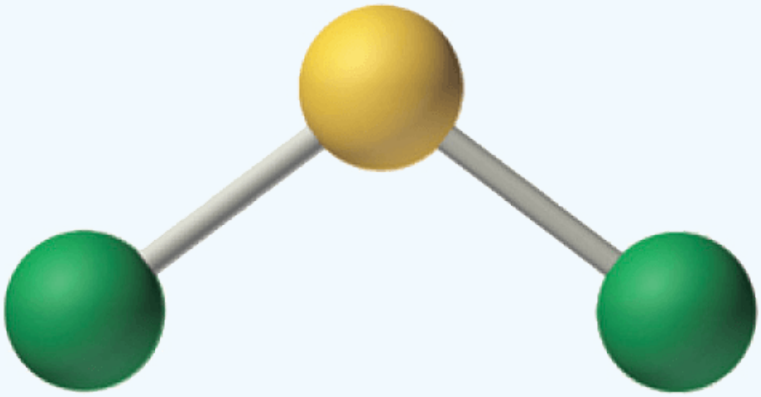


Carbon dioxide

2.



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



Sulfur dichloride

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4.8: The Shapes of Molecules

Learning Objectives

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

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

The VSEPR Model

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

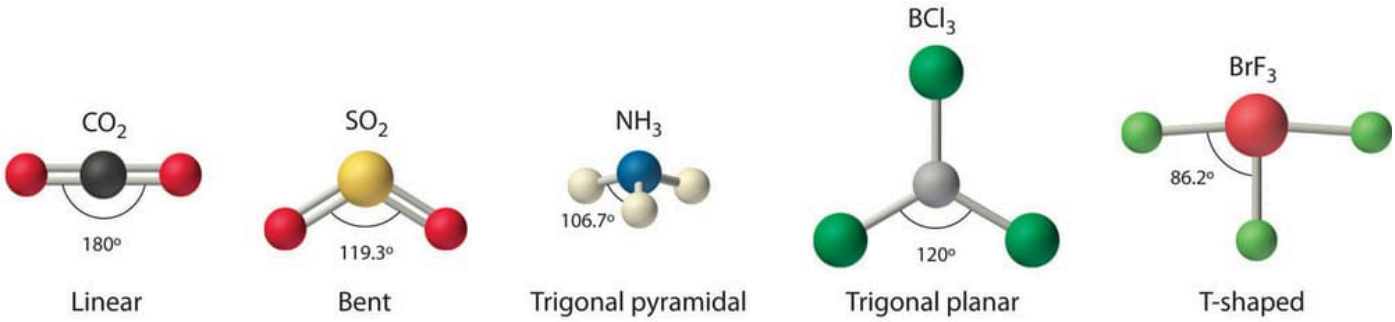


Figure 4.8.1: Common Structures for Molecules and Polyatomic Ions That Consist of a Central Atom Bonded to Two or Three Other Atoms. (CC BY-NC-SA; anonymous)

We can use the VSEPR model to predict the geometry of most polyatomic molecules and ions by focusing only on the number of electron pairs around the *central atom*, ignoring all other valence electrons present. According to this model, valence electrons in the Lewis structure form **electron groups** (regions of electron density), which may consist of a single bond, a double bond, a triple bond, a lone pair of electrons, or even a single unpaired electron, which in the VSEPR model is counted as a lone pair. Because electrons repel each other electrostatically, the most stable arrangement of electron groups (i.e., the one with the lowest energy) is the one that minimizes repulsions. Groups are positioned around the central atom in a way that produces the molecular structure with the lowest energy, as illustrated in Figure 4.8.1.

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

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

pairs around the central atom, but they will be *different* when there are lone pairs present on the central atom.

Predicting Electron Group Geometry and Molecular Structure

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

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

Table 4.8.1 summarizes the shapes of molecules based on the number of electron groups and surrounding atoms.

Table 4.8.1: Summary of Electron Group Geometries and Molecular Structures

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

Two Electron Groups

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



Figure 4.8.2: Beryllium hydride and carbon dioxide bonding.

Three Electron Groups

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

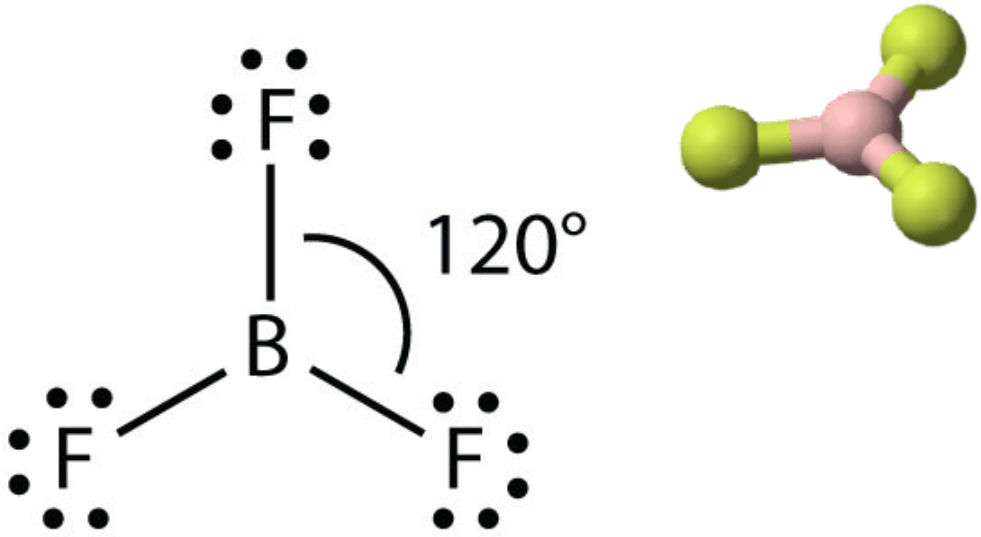


Figure 4.8.3: Boron trifluoride bonding. (CK12 Licence)

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

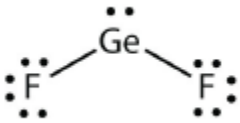


Figure 4.8.4: Germanium difluoride bonding.

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

Four Electron Groups

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

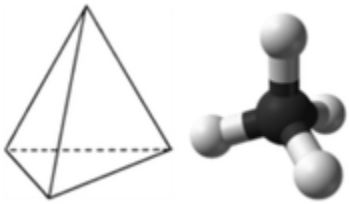


Figure 4.8.5: Tetrahedral structure of methane. (CK12 Licence)

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

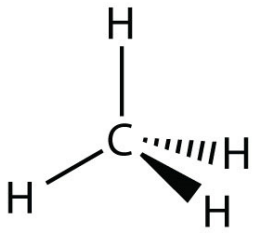


Figure 4.8.6: Methane bonding. (CK12 Licence)

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

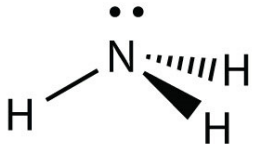


Figure 4.8.7: Ammonia bonding. (CK12 Licence)

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

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

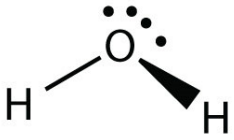


Figure 4.8.8: Water bonding.

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

Shapes of Molecules with Double or Triple Bonds

Double or triple bonds count as a single electron group. The Lewis electron dot diagram of formaldehyde (CH_2O) is shown in Figure 4.8.9.

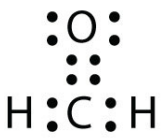


Figure 4.8.9: Lewis Electron Dot Diagram of Formaldehyde.

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

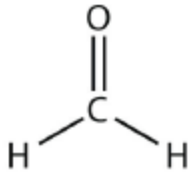


Figure 4.8.10: Formaldehyde bonding.

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

Example 4.8.1

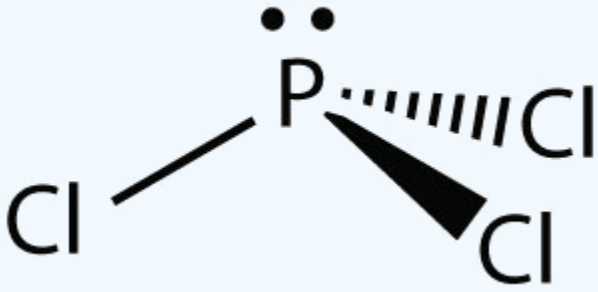
What is the approximate shape of each molecule?

a. PCl_3
b. NOF

Solution

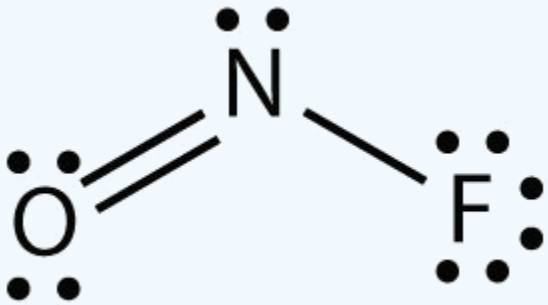
The first step is to draw the Lewis structure of the molecule.

For PCl_3, the electron dot diagram is as follows:



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

The electron dot diagram for NOF is as follows:



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

Exercise 4.8.1

What is the approximate molecular shape of $\mathrm{CH_2Cl_2}$?

Answer available at the end of this section.

Exercise 4.8.2

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

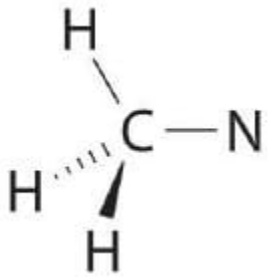
Answer available at the end of this section.

Answer available at the end of this section.

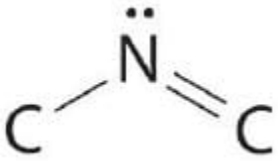
Molecules With Multiple Central Atoms

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

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



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



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

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

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

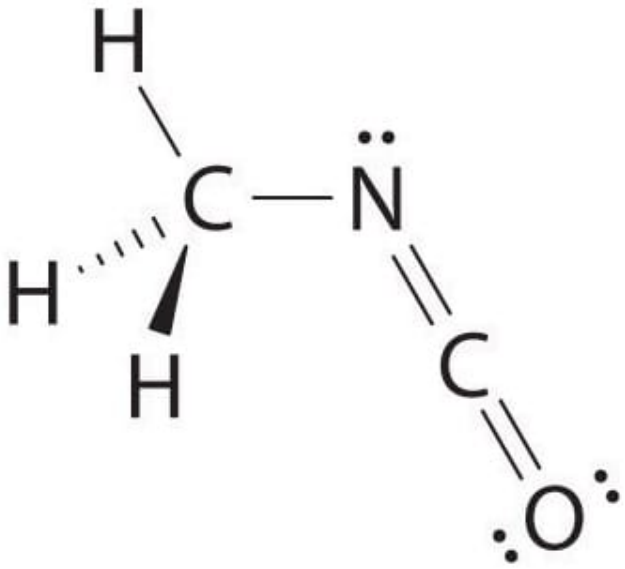


Figure 4.8.11). The Lewis Structure of Methyl Isocyanate

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

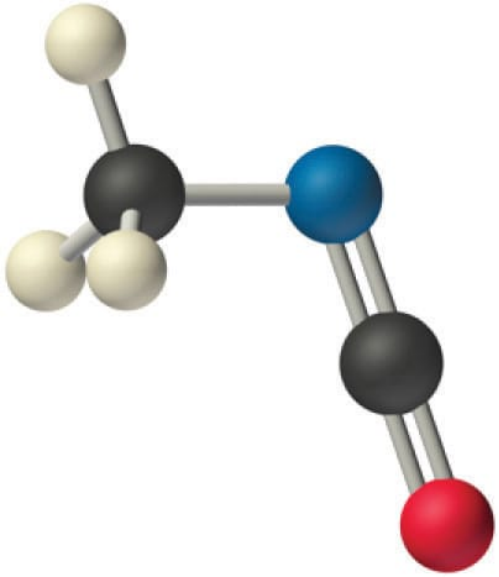


Figure 4.8.12: The Experimentally Determined Structure of Methyl Isocyanate

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

Example 4.8.3

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

Given: chemical compound

Asked for: molecular geometry

Strategy:

Count the number of electron groups around each carbon, recognizing that in the VSEPR model, a multiple bond counts as a single group. Use Figure 4.8.3 to determine the molecular geometry around each carbon atom and then deduce the structure of the molecule as a whole.

Solution:

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

Exercise 4.8.3

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

Answer available at the end of this section.

Answers

Exercise 4.8.1

Tetrahedral

Exercise 4.8.2

Exercise 4.8.2

Trigonal planar about both central C atoms.

Exercise 4.8.3

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

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4.9: Polar Covalent Bonds and Electronegativity

Learning Objectives

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

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

Bond Polarity

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

- A **nonpolar covalent bond** (Figure $4.9.1a$)is one in which the electrons are shared *equally* between two atoms.
- A **polar covalent bond** (Figure $4.9.1b$) 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 $4.9.1c$).

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 $4.9.1b$ 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).

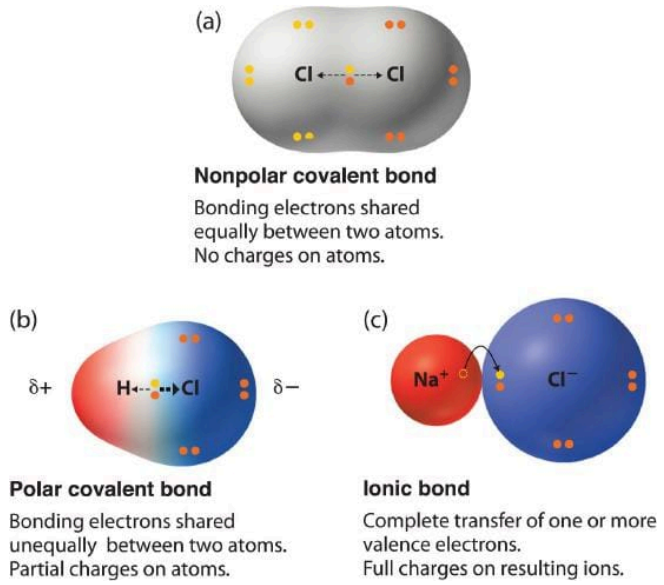


Figure 4.9.1: The Electron Distribution in a Nonpolar Covalent Bond, a Polar Covalent Bond, and an Ionic Bond Using Lewis Electron Structures. In a purely covalent bond (a), the bonding electrons are shared equally between the atoms. In a purely ionic bond (c), an electron has been transferred completely from one atom to the other. A polar covalent bond (b) is intermediate between the two extremes: the bonding electrons are shared unequally between the two atoms, and the electron distribution is asymmetrical with the electron density being greater around the more electronegative atom. Electron-rich (negatively charged) regions are shown in blue; electron-poor (positively charged) regions are shown in red.

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

Electronegativity

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

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

Electronegativity is a function of:

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

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

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

The Pauling Electronegativity Scale

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

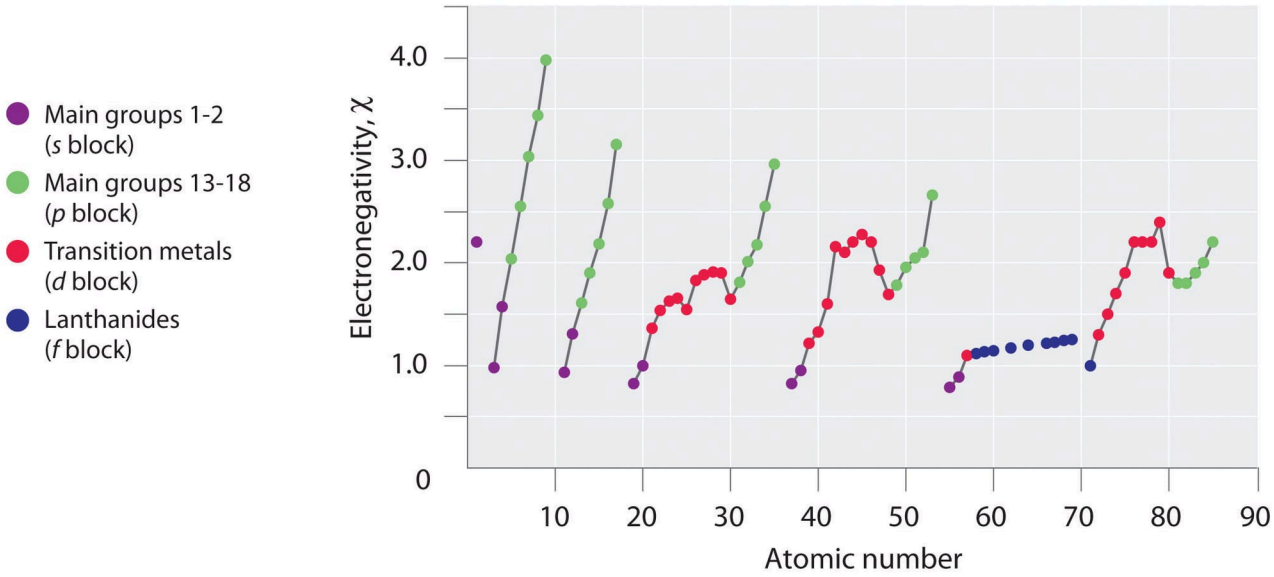


Figure 4.9.2: A Plot of Periodic Variation of Electronegativity with Atomic Number for the First Six Rows of the Periodic Table

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 4.9.2 and 4.9.3. If we ignore the inert gases and elements for which no stable isotopes are known, we see that fluorine is the most electronegative element and cesium is the least electronegative nonradioactive element. Because electronegativities generally increase diagonally from the lower left to the upper right of the periodic table, elements lying on diagonal lines running from upper left to lower right tend to have comparable values (e.g., O and Cl, and N, S, and Br).

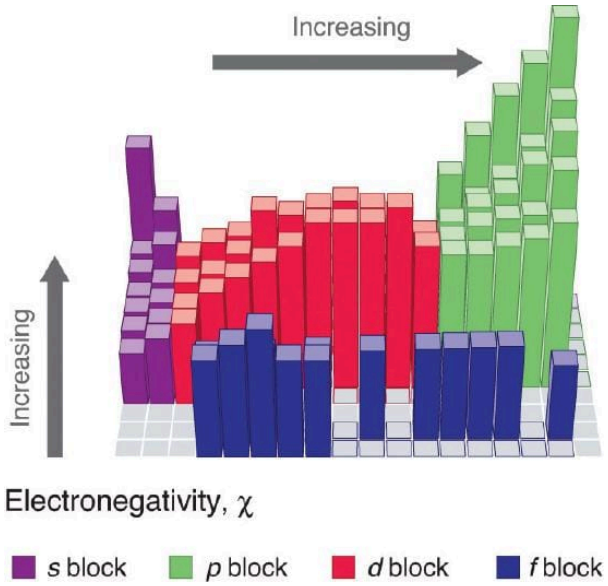


Figure 4.9.3: Pauling Electronegativity Values of the *s*-, *p*-, *d*-, and *f*-Block Elements. Values for most of the actinides are approximate. Elements for which no data are available are shown in gray. Source: Data from L. Pauling, *The Nature of the Chemical Bond*, 3rd ed. (1960).

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 4.9.5), 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.

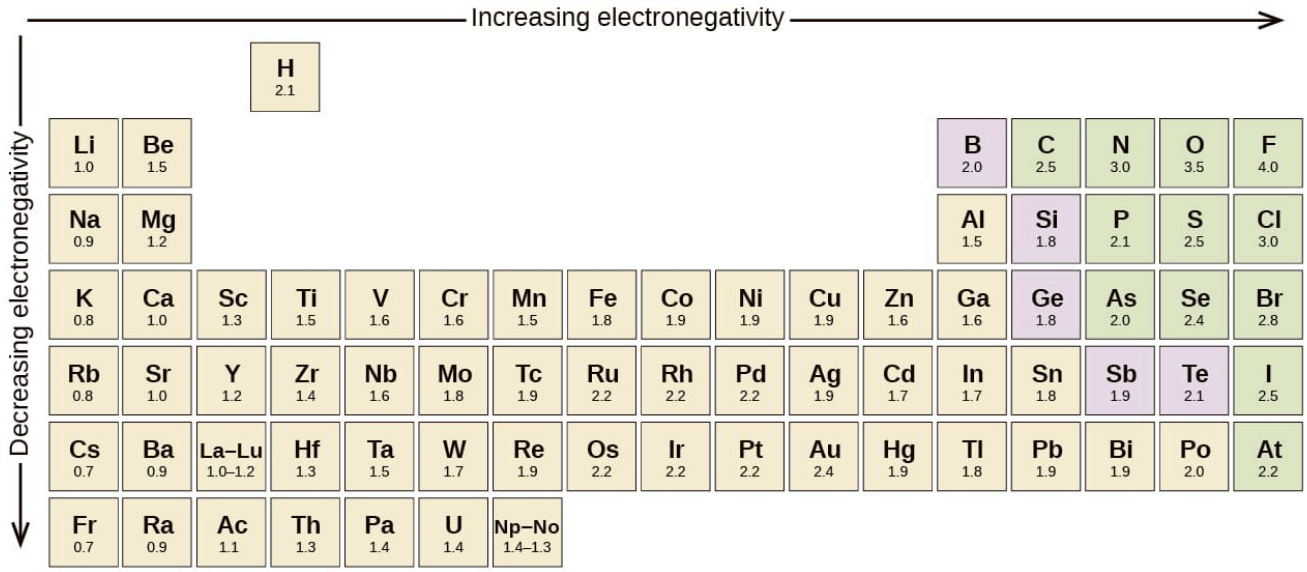
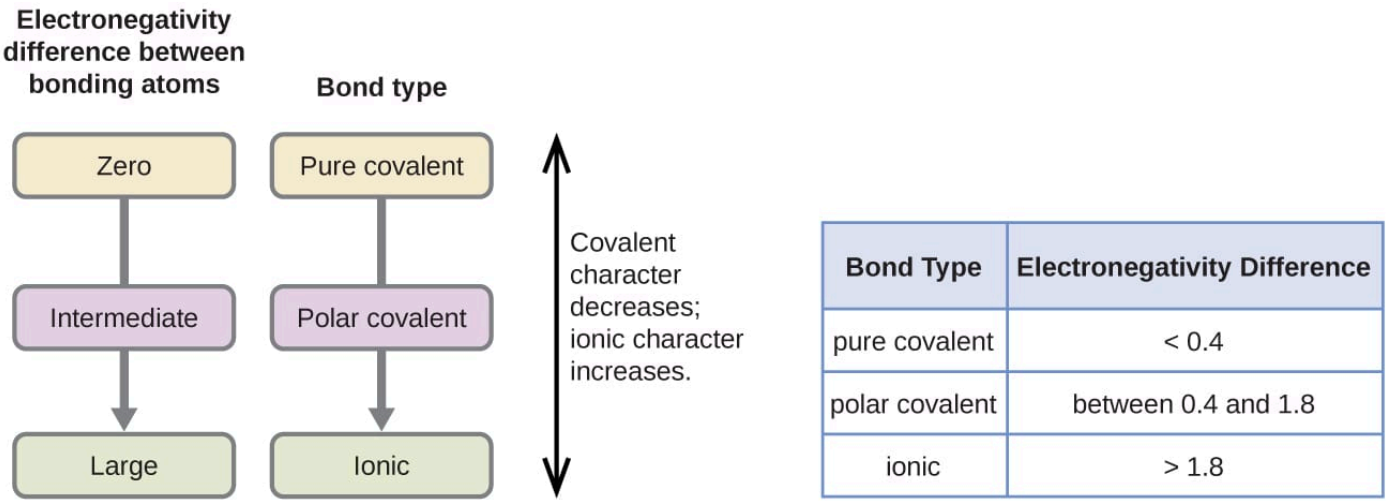


Figure 4.9.4 The electronegativity values derived by Pauling follow predictable periodic trends with the higher electronegativities toward the upper right of the periodic table. Fluorine has the highest value (4.0).



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

Figure 4.9.5: As the electronegativity difference increases between two atoms, the bond becomes more ionic.

Example 4.9.1

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 4.9.1

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

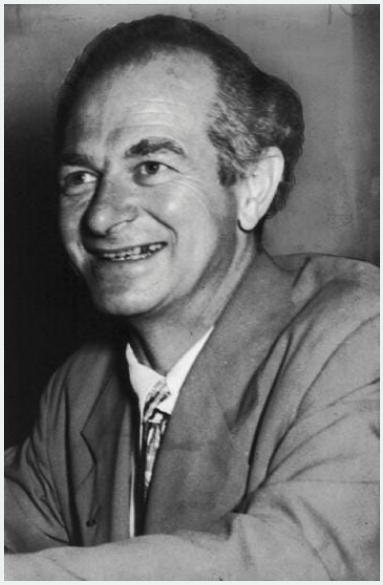
a. C and O
b. K and Br
c. N and N
d. Cs and F

Answer a: available at the end of this section.

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.

Answers

Exercise 4.9.1

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.

The EN difference is greater than 1.8, hence ionic.

Identical atoms have zero EN difference, hence nonpolar.

The EN difference is greater than 1.8, hence ionic.

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4.10: Polar Molecules

Learning Objectives

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

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

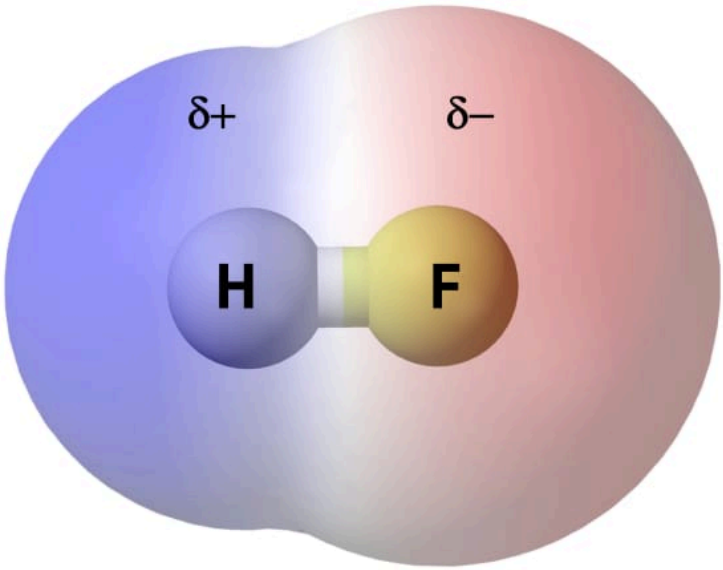


Figure $4.10.1$: A molecular dipole results from the unequal distribution of electron density throughout a molecule. The H, with less electron density is partially positive and the F, with more electron density is partially negative. (Figure modified from: Wikipedia [en.Wikipedia.org])

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

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

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

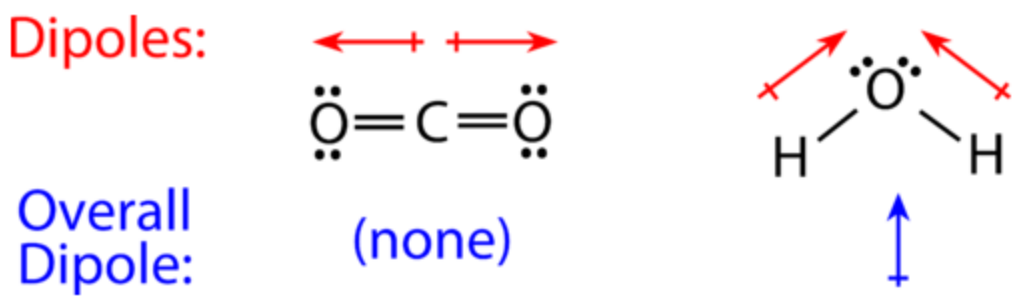


Figure 4.10.2: The molecular geometry of a molecule affects its polarity. Each CO bond has a dipole moment, but they point in opposite directions so that the net CO_2 molecule is nonpolar. In contrast, water is polar because the OH bond dipole moments do not cancel out. There is a net separation of charge or overall dipole moment.

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

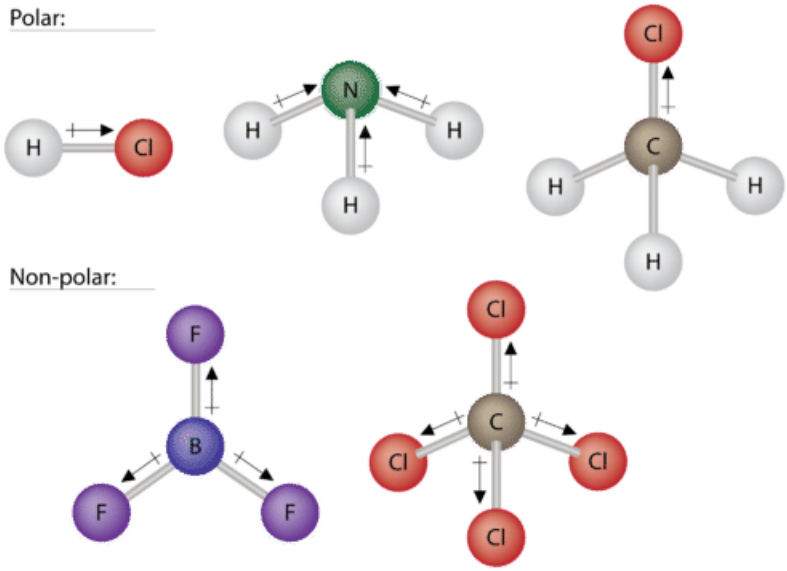


Figure 4.10.3: Some examples of polar and nonpolar molecules based on molecular geometry.

To summarize, to be polar, a molecule must:

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

Steps to Identify Polar Molecules

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

Properties of Polar Molecules

Polar molecules tend to align when placed in an electric field with the positive end of the molecule oriented toward the negative

plate and the negative end toward the positive plate (Figure 4.10.4). We can use an electrically charged object to attract polar molecules, but nonpolar molecules are not attracted. Also, polar solvents are better at dissolving polar substances, and nonpolar solvents are better at dissolving nonpolar substances.

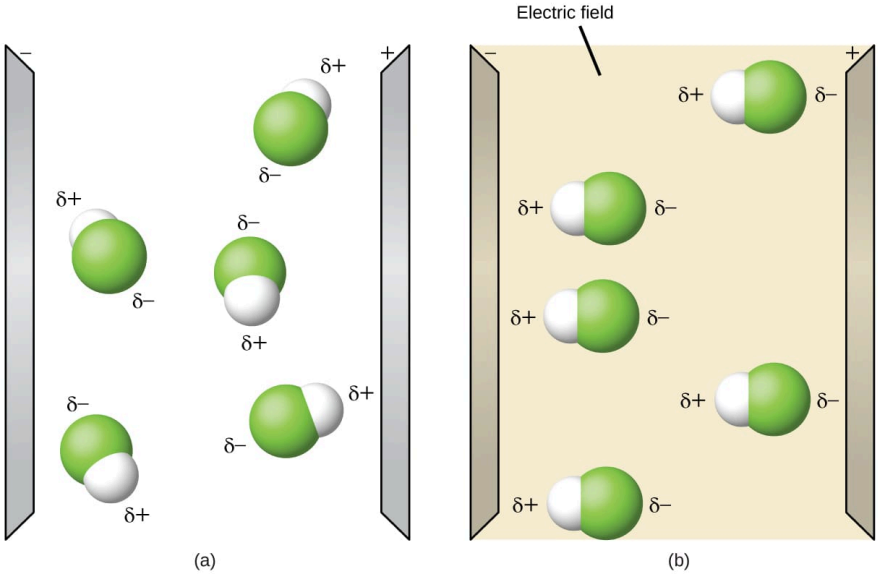


Figure 4.10.4: (a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction. (OpenStax CC-BY-SA);

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

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

Interactive Element: Molecular Polarity

The following simulation is very useful in exploring more about bond and molecular polarity. Explore on your own or use the exercise and examples below.

Example 4.10.1: Polarity Simulations

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

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

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

Solution

a. Molecular dipole moment points immediately between A and C.

b. Molecular dipole moment points along the A–B bond, toward A.

Exercise 4.10.1

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

Answer available at the end of this section.

Answers

Exercise 4.10.1

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

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4.11: 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 4.11.1. 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 4.11.1: Numerical Prefixes for Naming Binary Covalent Compounds

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

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

Example 4.11.1

Write the molecular formula for each compound.

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

Solution

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

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

Exercise 4.11.1

Write the molecular formula for each compound.

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

Answer a: available at the end of this section.

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

Example 4.11.2

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 4.11.2

Write the name for each compound.

a. CF_4
b. $SeCl_2$
c. SO_3

Answer a: available at the end of this section.

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.

Answers

Exercise 4.11.1

a. NO_2

O_2F_2

SF_6

SeO

Exercise 4.11.2

carbon tetrafluoride

selenium dichloride

sulfur trioxide

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5: CLASSIFICATION AND BALANCING OF CHEMICAL REACTIONS

5.1: Chemical Equations

5.2: Balancing Chemical Equations

5.3: Precipitation Reactions and Solubility Guidelines

5.4: Acids, Bases, and Neutralization Reactions

5.5: Redox Reactions

5.6: Recognizing Redox Reactions

5.7: Net Ionic Equations

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5.1: Chemical Equations

Learning Objectives

- Define *chemical reaction*.
- Understand the Law of Conservation of Matter

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

"*hydrogen and oxygen react to make water*"

is one way to represent that process, which is called a chemical reaction. Figure 5.1.1 shows a rather dramatic example of this very reaction.

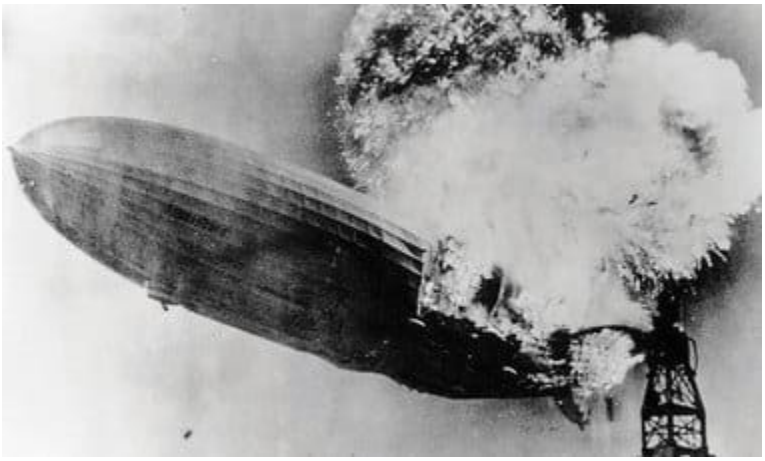


Figure 5.1.1: The Formation of Water. Hydrogen and oxygen combine to form water. Here, the hydrogen gas in the zeppelin SS *Hindenburg* reacts with oxygen in the air to make water. Source: Photo courtesy of the US Navy. For a video of this see www.youtube.com/watch?v=CgWHbpMVQ1U.

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 ($\rightarrow$) represents the chemical change:

$$\mathrm{H_2 + O_2 \ \rightarrow H_2O} \tag{5.1.1}$$

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

$$\mathrm{H_2\,(g) + O_2\,(g) \ \rightarrow H_2O\ (\ell)} \tag{5.1.2}$$

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).

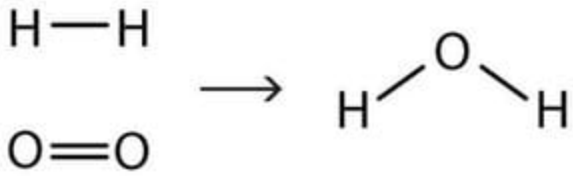


Figure 5.1.2: Balanced—Yes or No? By counting the atoms of each element, we can see that the reaction is not balanced as written.

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:

$$\mathrm{H_2\,(g) + O_2\,(g)\ \rightarrow 2\,H_2O\ (\ell)} \tag{5.1.3}$$

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

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

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

$$\mathrm{2\,H_2\,(g) + O_2\,(g)\ \rightarrow 2\,H_2O\ (\ell)} \tag{5.1.4}$$

Now we have four hydrogen atoms and two oxygen atoms on each side of the equation. The law of conservation of matter is satisfied because we now have the *same number* of atoms of each element in the reactants and in the products. We say that the reaction is 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.

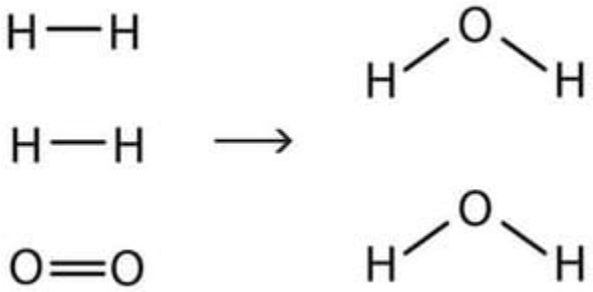


Figure 5.1.3: Balanced—Yes or No? By counting the atoms of each element, we can see that the reaction is now balanced.

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

5.1.1 Exam

Is each chemical equation balanced?

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

Solution

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

5.1.1 Exerc

Is each chemical equation balanced?

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

Answer a: available at the end of this section.

Answers

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

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

For example, to balance the equation

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

$$\mathrm{CH_4 + Cl_2 \rightarrow CCl_4 + HCl} \tag{5.2.1}$$

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:

$$\mathrm{CH_4 + Cl_2 \rightarrow CCl_4 + 4\,HCl} \tag{5.2.3}$$

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:

$$\mathrm{CH_4 + 4\,Cl_2 \rightarrow CCl_4 + 4\,HCl} \tag{5.2.5}$$

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.

$$\mathrm{Pb(NO_3)_2}\,(aq) + \mathrm{NaCl}\,(aq) \rightarrow \mathrm{NaNO_3}\,(aq) + \mathrm{PbCl_2}\,(s) \tag{5.2.7}$$

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 $\mathrm{NO_3}^-$ ions	1 $\mathrm{NO_3}^-$ ions
1 Na atom	1 Na atom
1 Cl atom	2 Cl atoms

(5.2.8)

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 $\mathrm{NaNO_3}$. The result is:

$$\mathrm{Pb(NO_3)_2}\,(aq) + 2\mathrm{NaCl}\,(aq) \rightarrow 2\mathrm{NaNO_3}\,(aq) + \mathrm{PbCl_2}\,(s) \tag{5.2.9}$$

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

Reactants	Products
1 Pb atom	1 Pb atom
2 $\mathrm{NO_3}^-$ ions	2 $\mathrm{NO_3}^-$ ions
2 Na atom	2 Na atom
2 Cl atom	2 Cl atoms

(5.2.10)

Step 5: Think about the result.

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

Exercise 5.2.2

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



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

Answer available at the end of this section.

Answers

Exercise 5.2.2

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

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5.3: Precipitation Reactions and Solubility Guidelines

Learning Objectives

- Use solubility rules to predict whether a precipitate will form.
- Write and balance chemical equations for precipitation reactions.

There are many types of chemical reactions that you will learn about in chemistry. In this chapter, we will focus on some reactions of ionic compounds: *precipitation reactions* (a type of *double-replacement reaction*), *acid-base neutralization reaction*s, and *oxidation-reduction reaction*s.

The practice of barter (trading one thing for another) has been in existence since the beginning of time. In the past, for example, items like chickens were bartered for newspapers. Person A had something that person B wanted, and vice versa. So, when person A and person B traded items, they each had something new. Some chemical reactions are like that—compounds swap parts, and the products are new materials.

A **double-replacement reaction** is a reaction in which the positive and negative ions of two ionic compounds exchange places to form two new compounds. The general form of a double-replacement (also called double-displacement) reaction is:

$$\mathrm{AB} + \mathrm{CD} \rightarrow \mathrm{AD} + \mathrm{CB} \tag{5.3.1}$$

In this reaction, A and C are positively-charged cations, while B and D are negatively-charged anions. Double-replacement reactions generally occur between substances in aqueous solution. In order for a reaction to occur, one of the products is usually a solid precipitate, a gas, or a molecular compound such as water.

Formation of a Precipitate

A **precipitate** forms in a double-replacement reaction when the cations from one of the reactants combine with the anions from the other reactant to form an insoluble ionic compound. When aqueous solutions of potassium iodide and lead (II) nitrate are mixed, the following reaction occurs:

$$2\mathrm{KI}\,(aq) + \mathrm{Pb(NO_3)_2}\,(aq) \rightarrow 2\mathrm{KNO_3}\,(aq) + \mathrm{PbI_2}\,(s) \tag{5.3.2}$$

There are very strong attractive forces that occur between $\mathrm{Pb^{2+}}$ and $\mathrm{I^-}$ ions and the result is a brilliant yellow precipitate (see Figure $5.3.1$ below). The other product of the reaction, potassium nitrate, remains soluble.



Figure $5.3.1$: Formation of lead iodide precipitate. (CC BY-NC; CK-12)

To judge whether double-replacement reactions will occur, we need to know what kinds of ionic compounds form precipitates. For this, we use **solubility rules**, which are general statements that predict which ionic compounds dissolve (are soluble) and which do not (are not soluble, or insoluble). Table $5.3.1$ lists some general solubility rules. We need to consider each ionic compound

(both the reactants and the possible products) in light of the solubility rules. If a compound is soluble, we use the (*aq*) label with it, indicating that it dissolves. If a compound is not soluble, we use the (s) label with it and assume that it will precipitate out of solution. If everything is soluble, then no reaction will be expected.

Table 5.3.1: Solubility Rules: Soluble Compounds and Their Exceptions

These compounds generally dissolve in water (are soluble):	**Exceptions:**
All compounds of Li^+, Na^+, K^+, Rb^+, Cs^+, and NH_4^+	None
All compounds of NO_3^- and $C_2H_3O_2^-$	None
Compounds of Cl^-, Br^-, I^-	Ag^+, Hg_2^{2+}, Pb^{2+}
Compounds of SO_4^{2}	Hg_2^{2+}, Pb^{2+}, Sr^{2+}, Ba^{2+}

Table 5.3.2: Solubility Rules: Insoluble Compounds and Their Exceptions

These compounds generally do not dissolve in water (are insoluble):	**Exceptions:**
Compounds of CO_3^{2-} and PO_4^{3-}	Compounds of Li^+, Na^+, K^+, Rb^+, Cs^+, and NH_4^+
Compounds of OH^-	Compounds of Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, Sr^{2+}, and Ba^{2+}

For example, consider the possible double-replacement reaction between Na_2SO_4 and $SrCl_2$. The solubility rules say that all ionic sodium compounds are soluble and all ionic chloride compounds are soluble, except for Ag^+, Hg_2^{2+}, and Pb^{2+}, which are not being considered here. Therefore, Na_2SO_4 and $SrCl_2$ are both soluble. The possible double-replacement reaction products are NaCl and $SrSO_4$. Are these soluble? NaCl is (by the same rule we just quoted), but what about $SrSO_4$? Compounds of the sulfate ion are generally soluble, but Sr^{2+} is an exception: we expect it to be insoluble—a precipitate. Therefore, we expect a reaction to occur, and the balanced chemical equation would be:

$$\mathrm{Na_2SO_4\,(aq) + SrCl_2\,(aq) \longrightarrow 2\,NaCl\,(aq) + SrSO_4\,(s)}$$

You would expect to see a visual change corresponding to $SrSO_4$ precipitating out of solution (Figure 5.3.2).



Figure 5.3.2: Double-Replacement Reactions. Some double-replacement reactions are obvious because you can see a solid precipitate coming out of solution. Source: Photo courtesy of Choij, Wikimedia(opens in new window) [commons.wikimedia.org].

A blue solution is shown in a glass beaker. White precipitate can be seen forming at the bottom of the beaker.

Example 5.3.4:

Will a precipitation reaction occur? If so, identify the products.

1. $Ca(NO3)2 + KBr \rightarrow ?$
2. $NaOH + FeCl2 \rightarrow ?$

Solution

1. According to the solubility rules, both $Ca(NO3)2$ and KBr are soluble. Now we consider what the double-replacement products would be by switching the cations (or the anions)—namely, $CaBr2$ and $KNO3$. However, the solubility rules predict that these two substances would also be soluble, so no precipitate would form. Thus, we predict no reaction in this case.
2. According to the solubility rules, both NaOH and $FeCl2$ are expected to be soluble. If we assume that a double-replacement reaction may occur, we need to consider the possible products, which would be NaCl and $Fe(OH)2$. NaCl is soluble, but, according to the solubility rules, $Fe(OH)2$ is not. Therefore, a reaction would occur, and $Fe(OH)2$(s) would precipitate out of solution. The balanced chemical equation is

$$2\,\mathrm{NaOH\,(aq)} + \mathrm{FeCl_2\,(aq)} \longrightarrow 2\,\mathrm{NaCl\,(aq)} + \mathrm{Fe(OH)_2\,(s)}$$

Exercise 5.3.4

$$\mathrm{Sr(NO_3)_2} + \mathrm{KCl} \longrightarrow$$

Answer available at the end of this section.

Key Takeaways

- A single-replacement reaction replaces one element for another in a compound.
- The periodic table or an activity series can help predict whether single-replacement reactions occur.
- A double-replacement reaction exchanges the cations (or the anions) of two ionic compounds.
- A precipitation reaction is a double-replacement reaction in which one product is a solid precipitate.

- Solubility rules are used to predict whether some double-replacement reactions will occur.

Answers

Exercise 5.3.4

No reaction; all possible products are soluble.

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5.4: Acids, Bases, and Neutralization Reactions

Learning Objectives

- Identify an acid-base neutralization reaction and predict its products.

Previously, you learned that 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:

$$\text{acid} + \text{base} \longrightarrow \text{water} + \text{salt}$$

where the term **salt** is generally used to define any ionic compound (soluble or insoluble) that is formed from a reaction between an acid and a base. (In chemistry, the word *salt* refers to more than just table salt.) For example, the balanced chemical equation for the reaction between HCl(aq) and KOH(aq) is

$$\mathrm{HCl\,(aq)} + \mathrm{KOH\,(aq)} \longrightarrow \mathrm{H_2O(\ell)} + \mathrm{KCl\,(aq)}$$

where the salt is KCl. By counting the number of atoms of each element, we find that only one water molecule is formed as a product. However, in the reaction between HCl(aq) and $Mg(OH)_2$(aq), additional molecules of HCl and H_2O are required to balance the chemical equation:

$$2\,\mathrm{HCl\,(aq)} + \mathrm{Mg(OH)_2\,(aq)} \longrightarrow 2\,\mathrm{H_2O(\ell)} + \mathrm{MgCl_2\,(aq)}$$

Here, the salt is $MgCl_2$. (This is one of several reactions that take place when a type of antacid, a base, is used to treat stomach acid.)

Example 5.4.1:

Write the neutralization reactions between each acid and base.

a. HNO_3(aq) and $Ba(OH)_2$(aq)
b. H_3PO_4(aq) and $Ca(OH)_2$(aq)

Solution

First, we will write the chemical equation with the formulas of the reactants and the expected products; then we will balance the equation.

a. The expected products are water and barium nitrate, so the initial chemical reaction is

$$\mathrm{HNO_3\,(aq) + Ba(OH)_2\,(aq) \longrightarrow H_2O(\ell) + Ba(NO_3)_2\,(aq)}$$

To balance the equation, we need to realize that there will be two H2O molecules, so two HNO3 molecules are required:

$$\mathrm{2\,HNO_3\,(aq) + Ba(OH)_2\,(aq) \longrightarrow 2\,H_2O(\ell) + Ba(NO_3)_2\,(aq)}$$

This chemical equation is now balanced.

b. The expected products are water and calcium phosphate, so the initial chemical equation is

$$\mathrm{H_3PO_4\,(aq) + Ca(OH)_2\,(aq) \longrightarrow H_2O(\ell) + Ca_3(PO_4)_2\,(s)}$$

According to the solubility rules, Ca3(PO4)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:

$$\mathrm{2\,H_3PO_4\,(aq) + 3\,Ca(OH)_2\,(aq) \longrightarrow 6\,H_2O(\ell) + Ca_3(PO_4)_2\,(s)}$$

This chemical equation is now balanced.

Exercise 5.4.1

Write the neutralization reaction between H2SO4(aq) and Sr(OH)2(aq).

Answer

$$\mathrm{H_2SO_4\,(aq) + Sr(OH)_2\,(aq) \longrightarrow 2\,H_2O(\ell) + SrSO_4\,(aq)}$$

Neutralization reactions are one type of chemical reaction that proceeds even if one reactant is not in the aqueous phase. For example, the chemical reaction between HCl(aq) and Fe(OH)3(s) still proceeds according to the equation:

$$\mathrm{3\,HCl\,(aq) + Fe(OH)_3\,(s) \longrightarrow 3\,H_2O(\ell) + FeCl_3\,(aq)}$$

even though Fe(OH)3 is not soluble. When one realizes that Fe(OH)3(s) is a component of rust, this explains why some cleaning solutions for rust stains contain acids; the neutralization reaction produces products that are soluble and wash away. (Washing with acids like HCl is one way to remove rust and rust stains, but HCl must be used with caution!)

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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5.5: Redox Reactions

Learning Objectives

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

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

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

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

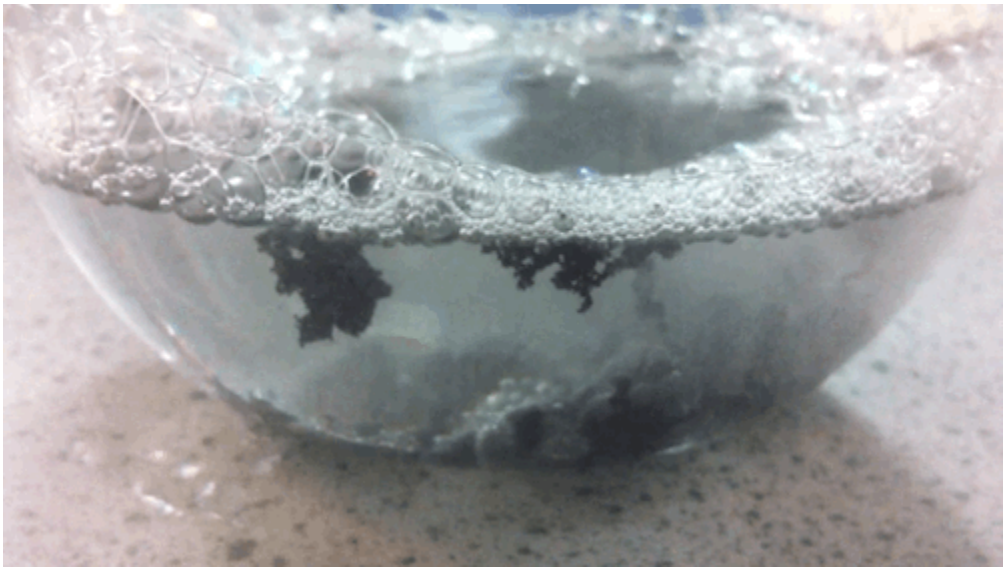


Figure $5.5.1$: Zinc Metal plus Hydrochloric Acid. It is fairly obvious that zinc metal reacts with aqueous hydrochloric acid! The bubbles are hydrogen gas (right side of Equation $5.5.1$).

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Example 5.5.1: Reducing Silver Ions

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

Solution

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

$$\mathrm{Ag^+ + Al \longrightarrow Ag + Al^{3+}}$$

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

Reduction half-reaction:

$$\mathrm{Ag^+ + e^- \longrightarrow Ag}$$

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

Oxidation half-reaction:

$$\mathrm{Al} \longrightarrow \mathrm{Al}^{3+} + 3\,\mathrm{e}^-$$

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

$$3\left(\mathrm{Ag}^+ + \mathrm{e}^- \rightarrow \mathrm{Ag}\right)$$

$$\underline{\qquad\qquad \mathrm{Al} \rightarrow \mathrm{Al}^{3+} + 3\mathrm{e}^- \qquad\qquad}$$

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

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 5.5.1

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

Answer available at the end of this section.

To Your Health: Redox Reactions and Pacemaker Batteries

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

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

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

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

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

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



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

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

$$2\,CH_3CHO + O_2 \longrightarrow 2\,CH_3COOH$$

Thus, acetaldehyde is being oxidized.

Similarly, reduction and oxidation can be defined in terms of the gain or loss of hydrogen atoms. If a molecule adds hydrogen atoms, it is being reduced. If a molecule loses hydrogen atoms, the molecule is being oxidized. For example, in the conversion of acetaldehyde into ethanol (CH_3CH_2OH), hydrogen atoms are added to acetaldehyde, so the acetaldehyde is being reduced:

$$CH_3CHO + H_2 \longrightarrow CH_3CH_2OH$$

Table 5.5.1: 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 5.5.2

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

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

Solution

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

Exercise 5.5.2

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

a. $CH_4 \rightarrow CO_2 + H_2O$
b. $NO_2 \rightarrow N_2$
c. $CH_2{=}CH_2 \rightarrow CH_3CH_3$

Answer a: available at the end of this section.

Answer b: available at the end of this section.

Answer a: available at the end of this section.

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.

Answers

Exercise 5.5.1

Reduction: $Ca^{2+} + 2e^- \rightarrow Ca$

Oxidation: $2\ (K \rightarrow K^+ + e^-)$

Combined: $Ca^{2+} + 2K \rightarrow Ca + 2K^+$

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

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

Exercise 5.5.2

Oxygen is being added. Oxidation is occurring.

Exercise 5.5.2

Oxygen is being removed. Reduction is occurring.

Exercise 5.5.2

Hydrogen is being added. Reduction is occurring.

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5.6: 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 5.6.1

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,

   $x + (-6) = -1x = +5$

   Thus the oxidation number on the N atom in the NO_3^- ion is +5.

Exercise 5.6.1: Phosphoric Acid

Assign oxidation numbers to the atoms in H_3PO_4.

Answer available at the end of this section.

All redox reactions occur with a simultaneous change in the oxidation numbers of some atoms. At least two elements must change their oxidation numbers. When an oxidation number of an atom is increased in the course of a redox reaction, that atom is being *oxidized*. When an oxidation number of an atom is decreased in the course of a redox reaction, that atom is being *reduced*. Oxidation and reduction can also be defined in terms of increasing or decreasing oxidation numbers, respectively.

Example 5.6.2:

Identify what is being oxidized and reduced in this redox reaction.

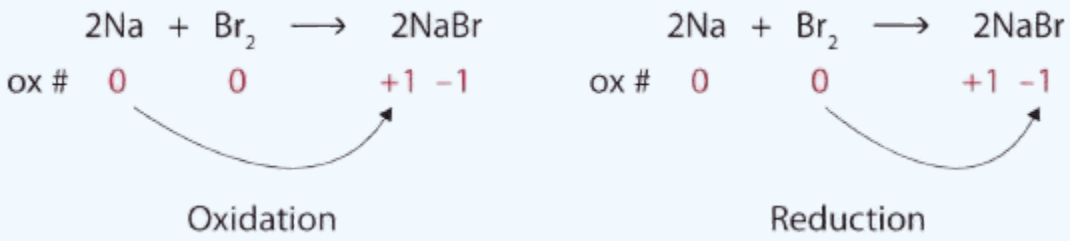
$$2\,\mathrm{Na} + \mathrm{Br_2} \longrightarrow 2\,\mathrm{NaBr}$$

Solution

Both reactants are the elemental forms of their atoms, so the Na and Br atoms have oxidation numbers of 0. In the ionic product, the Na^+ ions have an oxidation number of +1, while the Br^- ions have an oxidation number of –1.

$$\overset{0}{2Na} + \overset{0}{Br_2} \rightarrow \overset{+1-1}{2NaBr}$$

Sodium is increasing its oxidation number from 0 to +1, so it is being oxidized; bromine is decreasing its oxidation number from 0 to –1, so it is being reduced:



Because oxidation numbers are changing, this is a redox reaction. The total number of electrons being lost by sodium (two, one lost from each Na atom) is gained by bromine (two, one gained for each Br atom).

Exercise 5.6.2

Identify what is being oxidized and reduced in this redox reaction.

$$\mathrm{C} + \mathrm{O_2} \longrightarrow \mathrm{CO_2}$$

Answer available at the end of this section.

Oxidation reactions can become quite complex, as attested by the following redox reaction:

$$6H^+(aq) + 2\underset{+7}{MnO_4^-}(aq) + 5\underset{-1}{H_2O_2}(l) \rightarrow 2\underset{+2}{Mn^{2+}}(aq) + 5\underset{0}{O_2}(g) + 8H_2O(l)$$

To demonstrate that this is a redox reaction, the oxidation numbers of the species being oxidized and reduced are listed; can you determine what is being oxidized and what is being reduced?

Food and Drink Application: Fortifying Food with Iron

Iron is an essential mineral in our diet; iron-containing compounds like the heme protein in hemoglobin could not function without it. Most biological iron has the form of the Fe^{2+} ion; iron with other oxidation numbers is almost inconsequential in human biology (although the body does contain an enzyme to reduce Fe^{3+} to Fe^{2+}, so Fe^{3+} must have some biological significance, albeit minor). To ensure that we ingest enough iron, many foods are enriched with iron. Although Fe^{2+} compounds are the most logical substances to use, some foods use "reduced iron" as an ingredient (bread and breakfast cereals are the most well-known examples). Reduced iron is simply iron metal; iron is added as a fine metallic powder. The metallic iron is oxidized to Fe^{2+} in the digestive system and then absorbed by the body, but the question remains: Why are we ingesting metallic iron? Why not just use Fe^{2+} salts as an additive?

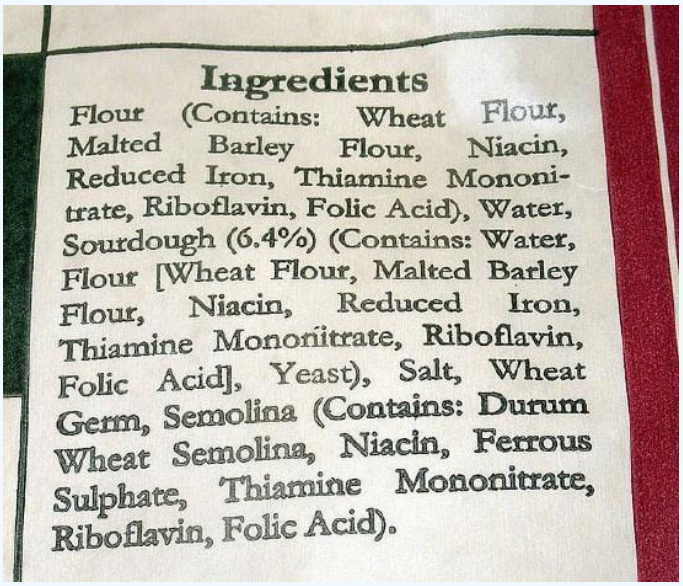


Figure 5.6.1 Ingredients. Many prepared foods list reduced iron in their ingredients list.

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.

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).

Answers

Exercise 5.6.1**: Phosphoric Acid**

H: +1; O: −2; P: +5

Exercise 5.6.2

C is being oxidized from 0 to +4; O is being reduced from 0 to −2.

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5.7: 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.

Net Ionic Equations

We can write a molecular equation for the formation of silver chloride precipitate:

$$\mathrm{NaCl}+\mathrm{AgNO_3} \rightarrow \mathrm{NaNO_3} + \mathrm{AgCl}$$

The corresponding **ionic equation** is written to show the *ions* that are dissolved in solution:

$$\mathrm{Na^+}\,(aq) + \mathrm{Cl^-}\,(aq) + \mathrm{Ag^+}\,(aq) + \mathrm{NO_3{}^-}\,(aq) \rightarrow \mathrm{Na^+}\,(aq) + \mathrm{NO_3{}^-}\,(aq) + \mathrm{AgCl}\,(s)$$

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 $\mathrm{Na^+}$ nor the $\mathrm{NO_3{}^-}$ ions participate in the reaction. They can be eliminated from the reaction.

$$\cancel{\mathrm{Na^+}\,(aq)} + \mathrm{Cl^-}\,(aq) + \mathrm{Ag^+}\,(aq) + \cancel{\mathrm{NO_3{}^-}\,(aq)} \rightarrow \cancel{\mathrm{Na^+}\,(aq)} + \cancel{\mathrm{NO_3{}^-}\,(aq)} + \mathrm{AgCl}\,(s)$$

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:

$$\mathrm{Ag^+}\,(aq) + \mathrm{Cl^-}\,(aq) \rightarrow \mathrm{AgCl}\,(s)$$

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 5.7.1

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:

$$3\mathrm{CuCl_2}\,(aq) + 2\mathrm{K_3PO_4}\,(aq) \rightarrow 6\mathrm{KCl}\,(aq) + \mathrm{Cu_3(PO_4)_2}\,(s)$$

Ionic equation:

$$3[\blacksquare]\,(aq) + 6\mathrm{Cl^-}\,(aq) + 6\mathrm{K^+}\,(aq) + 2{\mathrm{PO_4}}^{3-}\,(aq) \rightarrow 6\mathrm{K^+}\,(aq) + 6\mathrm{Cl^-}\,(aq) + \mathrm{Cu_3(PO_4)_2}\,(s)$$

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, $\mathrm{K^+}$ and $\mathrm{Cl^-}$, can be eliminated.

Net ionic equation:

$$3[\blacksquare]\,(aq) + 2{\mathrm{PO_4}}^{3-}\,(aq) \rightarrow \mathrm{Cu_3(PO_4)_2}\,(s)$$

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.

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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6: CHEMICAL REACTIONS - MOLE AND MASS RELATIONSHIPS

6.1: The Mole and Avogadro's Number
6.2: Gram-Mole Conversions
6.3: Mole Relationships and Chemical Equations
6.4: Mass Relationships and Chemical Equations
6.5: Limiting Reagent and Percent Yield

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6.1: The Mole and Avogadro's Number

Learning Objectives

- Calculate formula masses for covalent and ionic compounds.
- Define the amount unit mole and the related quantity Avogadro's number.
- Calculate molar mass of a compound from the molecular formula.

We can argue that modern chemical science began when scientists started exploring the quantitative as well as the qualitative aspects of chemistry. For example, Dalton's atomic theory was an attempt to explain the results of measurements that allowed him to calculate the relative masses of elements combined in various compounds. Understanding the relationship between the masses of atoms and the chemical formulas of compounds allows us to quantitatively describe the composition of substances.

Formula Mass

In an earlier chapter, we described the development of the atomic mass unit, the concept of average atomic masses, and the use of chemical formulas to represent the elemental makeup of substances. These ideas can be extended to calculate the **formula mass** of a substance, which is equal to the sum of the atomic masses for all the atoms represented in the substance's formula.

Formula Mass for Covalent Substances

For covalent substances, the formula represents the numbers and types of atoms composing a single molecule of the substance; therefore, the formula mass may be correctly referred to as a molecular mass. Consider chloroform ($CHCl_3$), a covalent compound once used as a surgical anesthetic and now primarily used in the production of tetrafluoroethylene, the building block for the "anti-stick" polymer, Teflon. The molecular formula of chloroform indicates that a single molecule contains one carbon atom, one hydrogen atom, and three chlorine atoms. The average molecular mass of a chloroform molecule is therefore equal to the sum of the average atomic masses of these atoms. Figure 6.1.1 outlines the calculations used to derive the molecular mass of chloroform, which is 119.37 amu.

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	1	×	12.01	=	12.01
H	1	×	1.008	=	1.008
Cl	3	×	35.45	=	106.35
				Molecular mass	119.37

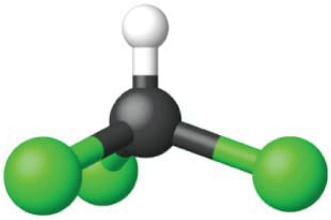


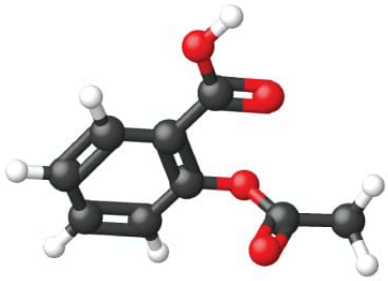
Figure 6.1.1: The average mass of a chloroform molecule, $CHCl_3$, is 119.37 amu, which is the sum of the average atomic masses of each of its constituent atoms. The model shows the molecular structure of chloroform.

A table and diagram are shown. The table is made up of six columns and five rows. The header row reads: "Element," "Quantity," a blank space, "Average atomic mass (a m u)," a blank space, and "Subtotal (a m u)." The first column contains the symbols "C," "H," "C l" and a blank, merged cell that runs the width of the first five columns. The second column contains the numbers "1," "1," and "3" as well as the merged cell. The third column contains the multiplication symbol in each cell except for the last, merged cell. The fourth column contains the numbers "12.01," "1.008," and "35.45" as well as the merged cell. The fifth column contains the symbol "=" in each cell except for the last, merged cell. The sixth column contains the values "12.01," "1.008," "106.35," and "119.37." There is a thick black line below the number 106.35. The merged cell under the first five columns reads "Molecular mass." To the left of the table is a diagram of a molecule. Three green spheres are attached to a slightly smaller black sphere, which is also attached to a smaller white sphere. The green spheres lie beneath and to the sides of the black sphere while the white sphere is located straight up from the black sphere.

Likewise, the molecular mass of an aspirin molecule, $C_9H_8O_4$, is the sum of the atomic masses of nine carbon atoms, eight

hydrogen atoms, and four oxygen atoms, which amounts to 180.15 amu (Figure 6.1.2).

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	9	×	12.01	=	108.09
H	8	×	1.008	=	8.064
O	4	×	16.00	=	64.00
				Molecular mass	180.15



Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	9	×	12.01	=	108.09
H	8	×	1.008	=	8.064
O	4	×	16.00	=	64.00
				Molecular mass	180.15

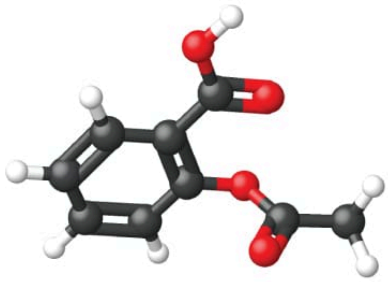


Figure 6.1.2: The average mass of an aspirin molecule is 180.15 amu. The model shows the molecular structure of aspirin, $C_9H_8O_4$.

A table and diagram are shown. The table is made up of six columns and five rows. The header row reads: “Element,” “Quantity,” a blank space, “Average atomic mass (a m u),” a blank space, and “Subtotal (a m u).” The first column contains the symbols “C,” “H,” “O,” and a merged cell. The merged cell runs the length of the first five columns. The second column contains the numbers “9,” “8,” and “4” as well as the merged, cell. The third column contains the multiplication symbol in each cell except for the last, merged cell. The fourth column contains the numbers “12.01,” “1.008,” and “16.00” as well as the merged cell. The fifth column contains the symbol “=” in each cell except for the last, merged cell. The sixth column contains the values: “108.09,” “8.064,” “64.00,” and “180.15.” There is a thick black line below the number 64.00. The merged cell under the first five columns reads “Molecular mass.” To the left of the table is a diagram of a molecule. Six black spheres are located in a six-sided ring and connected by alternating double and single black bonds. Attached to each of the four black spheres is one smaller white sphere. Attached to the farthest right black sphere is a red sphere, connected to two more black spheres, all in a row. Attached to the last black sphere of that row are two more white spheres. Attached to the first black sphere of that row is another red sphere. A black sphere, attached to two red spheres and a white sphere is attached to the black sphere on the top right of the six-sided ring.

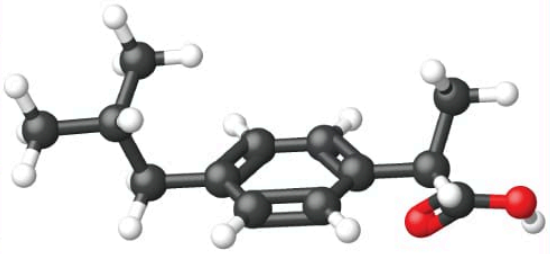
Example 6.1.1: Computing Molecular Mass for a Covalent Compound

Ibuprofen, $C_{13}H_{18}O_2$, is a covalent compound and the active ingredient in several popular nonprescription pain medications, such as Advil and Motrin. What is the molecular mass (amu) for this compound?

Solution

Molecules of this compound are comprised of 13 carbon atoms, 18 hydrogen atoms, and 2 oxygen atoms. Following the approach described above, the average molecular mass for this compound is therefore:

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	13	×	12.01	=	156.13
H	18	×	1.008	=	18.114
O	2	×	16.00	=	32.00
				Molecular mass	206.27



Exercise 6.1.1

Acetaminophen, $C_8H_9NO_2$, is a covalent compound and the active ingredient in several popular nonprescription pain medications, such as Tylenol. What is the molecular mass (amu) for this compound?

Answer available at the end of this section.

Formula Mass for Ionic Compounds

Ionic compounds are composed of discrete cations and anions combined in ratios to yield electrically neutral bulk matter. The formula mass for an ionic compound is calculated in the same way as the formula mass for covalent compounds: by summing the average atomic masses of all the atoms in the compound's formula. Keep in mind, however, that the formula for an ionic compound does not represent the composition of a discrete molecule, so it may not correctly be referred to as the "molecular mass."

As an example, consider sodium chloride, NaCl, the chemical name for common table salt. Sodium chloride is an ionic compound composed of sodium cations, Na^+, and chloride anions, Cl^-, combined in a 1:1 ratio. The formula mass for this compound is computed as 58.44 amu (Figure 6.1.3).

Element	Quantity		Average atomic mass (amu)		Subtotal
Na	1	×	22.99	=	22.99
Cl	1	×	35.45	=	35.45
				Formula mass	58.44

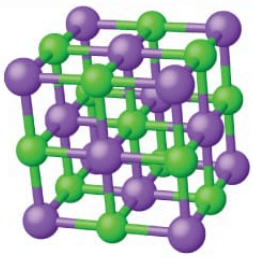


Figure 6.1.3: Table salt, NaCl, contains an array of sodium and chloride ions combined in a 1:1 ratio. Its formula mass is 58.44 amu.

A table and diagram are shown. The table is made up of six columns and four rows. The header row reads: "Element," "Quantity," a blank space, "Average atomic mass (a m u)," a blank space and "Subtotal (a m u)." The first column contains the symbols "N a", "C l," and a merged cell. The merged cell runs the length of the first five columns. The second column contains the numbers "1" and "1" as well as the merged cell. The third column contains the multiplication symbol in each cell except for the last, merged cell. The fourth column contains the numbers "22.99" and "35.45" as well as the merged cell. The fifth column contains the symbol "=" in each cell except for the last, merged cell. The sixth column contains the values "22.99," "35.45," and "58.44." There is a thick black line below the number "35.45." The merged cell under the first five columns reads "Formula mass." To the left of the table is a diagram of a chemical structure. The diagram shows green and purple spheres placed in an alternating pattern, making up the corners of eight stacked cubes to form one larger cube. The green spheres are slightly smaller than the purple spheres.

Note that the average masses of neutral sodium and chlorine atoms were used in this computation, rather than the masses for sodium cations and chlorine anions. This approach is perfectly acceptable when computing the formula mass of an ionic compound. Even though a sodium cation has a slightly smaller mass than a sodium atom (since it is missing an electron), this difference will be offset by the fact that a chloride anion is slightly more massive than a chloride atom (due to the extra electron).

Moreover, the mass of an electron is negligibly small with respect to the mass of a typical atom. Even when calculating the mass of an isolated ion, the missing or additional electrons can generally be ignored, since their contribution to the overall mass is negligible, reflected only in the nonsignificant digits that will be lost when the computed mass is properly rounded. The few exceptions to this guideline are very light ions derived from elements with precisely known atomic masses.

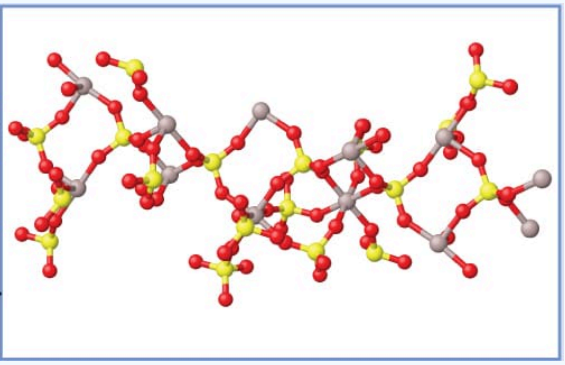
Example 6.1.2: Computing Formula Mass for an Ionic Compound

Aluminum sulfate, $Al_2(SO_4)_3$, is an ionic compound that is used in the manufacture of paper and in various water purification processes. What is the formula mass (amu) of this compound?

Solution

The formula for this compound indicates it contains Al^{3+} and SO_4^{2-} ions combined in a 2:3 ratio. For purposes of computing a formula mass, it is helpful to rewrite the formula in the simpler format, $Al_2S_3O_{12}$. Following the approach outlined above, the formula mass for this compound is calculated as follows:

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
Al	2	×	26.98	=	53.96
S	3	×	32.06	=	96.18
O	12	×	16.00	=	192.00
				Molecular mass	342.14



Exercise 6.1.2

Calcium phosphate, $Ca_3(PO_4)_2$, is an ionic compound and a common anti-caking agent added to food products. What is the formula mass (amu) of calcium phosphate?

Answer available at the end of this section.

The Mole

So far, we have been talking about chemical substances in terms of individual atoms and molecules. Yet we do not typically deal with substances one atom or molecule at a time; we work with millions, billions, and trillions of atoms and molecules at a time. We need a way to deal with macroscopic, rather than microscopic, amounts of matter. We need a unit of amount that relates quantities of substances on a scale that we can interact with.

Chemistry uses a unit called **mole**. The mole (mol) is an counting term similar to familiar units like pair, dozen, gross, etc. It provides a specific measure of *the number* of atoms or molecules in a bulk sample of matter. A mole is defined as the amount of substance containing the same number of discrete entities (such as atoms, molecules, and ions) as the number of atoms in a sample of pure ^{12}C weighing exactly 12 g. One Latin connotation for the word “mole” is “large mass” or “bulk,” which is consistent with its use as the name for this unit. The mole provides a link between an easily measured macroscopic property, bulk mass, and an extremely important fundamental property, number of atoms, molecules, and so forth.

The number of entities composing a mole has been experimentally determined to be $6.02214179 \times 10^{23}$, a fundamental constant named **Avogadro’s number** (N_A) or the Avogadro constant in honor of Italian scientist Amedeo Avogadro. This constant is properly reported with an explicit unit of “per mole,” a conveniently rounded version being $6.022 \times 10^{23}/\text{mol}$.

How big is a mole? It is very large. Suppose you had a mole of dollar bills that need to be counted. If everyone on earth (about 6

billion people) counted one bill per second, it would take about 3.2 million years to count all the bills. A mole of sand would fill a cube about 32 km on a side. A mole of pennies stacked on top of each other would have about the same diameter as our galaxy, the Milky Way. Atoms and molecules are very tiny, so one mole of carbon atoms would make a cube that is 1.74 cm on a side, small enough to carry in your pocket. One mole of water molecules is approximately 18 mL or just under 4 teaspoons of water.

Example 6.1.3

How many molecules are present in 2.76 mol of H_2O? How many atoms is this?

Solution

The definition of a mole is an equality that can be used to construct a conversion factor. Also, because we know that there are three atoms in each molecule of H_2O, we can also determine the number of atoms in the sample.

$$2.76\ \cancel{mol\ H_2O} \times \frac{6.022 \times 10^{23} molecules\ H_2O}{\cancel{mol\ H_2O}} = 1.66 \times 10^{24} molecules\ H_2O$$

To determine the total number of atoms, we have

$$1.66 \times 10^{24}\ \cancel{molecules\ H_2O} \times \frac{3\ atoms}{1\ molecule} = 4.99 \times 10^{24}\ atoms$$

Exercise 6.1.3

How many molecules are present in 4.61×10^{-2} mol of O_2?

Answer available at the end of this section.

Molar Mass

Why is the mole unit so important? It represents the link between the microscopic and the macroscopic, especially in terms of mass. *A mole of a substance has the same mass in grams as one unit (atom or molecules) has in atomic mass units*. The mole unit allows us to express amounts of atoms and molecules in visible amounts that we can understand.

For example, we already know that, by definition, a mole of carbon has a mass of exactly 12 g. This means that exactly 12 g of C has 6.022×10^{23} atoms:

$$12\ g\ C = 6.022 \times 10^{23}\ atoms\ C$$

We can use this equality as a conversion factor between the number of atoms of carbon and the number of grams of carbon. How many grams are there, say, in 1.50×10^{25} atoms of carbon? This is a one-step conversion:

$$1.50 \times 10^{25}\ \cancel{atoms\ C} \times \frac{12.0000\ g\ C}{6.022 \times 10^{23}\ \cancel{atoms\ C}} = 299\ g\ C$$

But it also goes beyond carbon. Previously we defined atomic and molecular masses as the number of atomic mass units per atom or molecule. Now we can do so in terms of grams. The atomic mass of an element is the number of grams in 1 mol of atoms of that element, while the molecular mass of a compound is the number of grams in 1 mol of molecules of that compound. Sometimes these masses are called **molar masses** to emphasize the fact that they are the mass for 1 mol of things. (The term *molar* is the adjective form of mole and has nothing to do with teeth.)

Consistent with its definition as an amount unit, 1 mole of any element contains the same number of atoms as 1 mole of any other element. The masses of 1 mole of different elements, however, are different, since the masses of the individual atoms are drastically different. The molar mass of an element (or compound) is the mass in grams of 1 mole of that substance, a property

expressed in units of grams per mole (g/mol) (Figure 6.1.1).

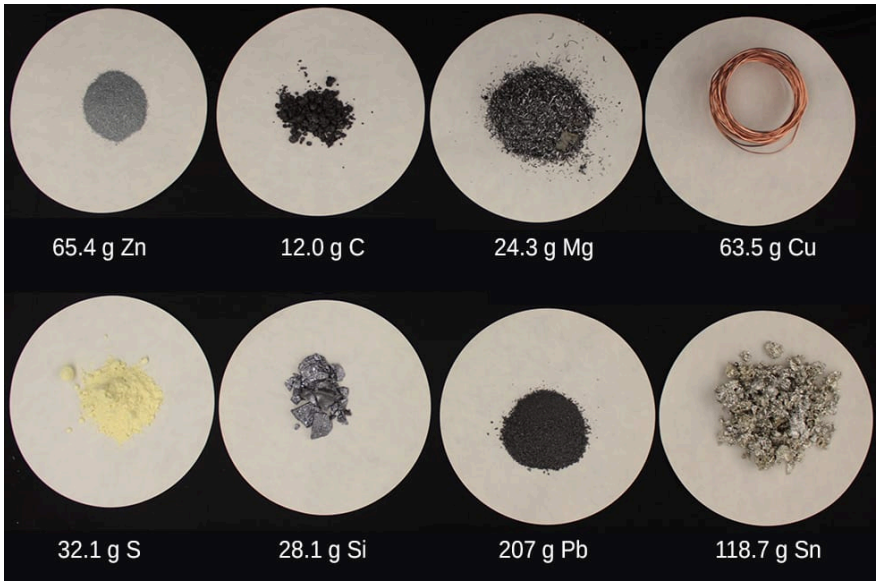


Figure 6.1.1: Each sample contains 6.022×10^{23} atoms —1.00 mol of atoms. From left to right (top row): 65.4 g zinc, 12.0 g carbon, 24.3 g magnesium, and 63.5 g copper. From left to right (bottom row): 32.1 g sulfur, 28.1 g silicon, 207 g lead, and 118.7 g tin. (credit: modification of work by Mark Ott).

This figure contains eight different substances displayed on white circles. The amount of each substance is visibly different.

Because the definitions of both the mole and the atomic mass unit are based on the same reference substance, ^{12}C, the molar mass of any substance is numerically equivalent to its atomic or formula weight in amu. Per the amu definition, a single ^{12}C atom weighs 12 amu (its atomic mass is 12 amu). According to the definition of the mole, 12 g of ^{12}C contains 1 mole of ^{12}C atoms (its molar mass is 12 g/mol). This relationship holds for all elements, since their atomic masses are measured relative to that of the amu-reference substance, ^{12}C.

Table 6.1.1: Mass of one mole of elements

Element	Average Atomic Mass (amu)	Molar Mass (g/mol)	Atoms/Mole
C	12.01	12.01	6.022×10^{23}
H	1.008	1.008	6.022×10^{23}
O	16.00	16.00	6.022×10^{23}
Na	22.99	22.99	6.022×10^{23}
Cl	33.45	35.45	6.022×10^{23}

While atomic mass and molar mass are numerically equivalent, keep in mind that they are vastly different in terms of scale, as represented by the vast difference in the magnitudes of their respective units (amu versus g). To appreciate the enormity of the mole, consider a small drop of water after a rainfall. Although this represents just a tiny fraction of 1 mole of water (~18 g), it contains more water molecules than can be clearly imagined. If the molecules were distributed equally among the roughly seven billion people on earth, each person would receive more than 100 billion molecules.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Video 6.1.1: The mole is used in chemistry to represent 6.022×10^{23} of something, but it can be difficult to conceptualize such a large number. Watch this video and then complete the "Think" questions that follow. Explore more about the mole by reviewing the information under "Dig Deeper."

The relationships between formula mass, the mole, and Avogadro's number can be applied to compute various quantities that describe the composition of substances and compounds. For example, if we know the mass and chemical composition of a substance, we can determine the number of moles and calculate number of atoms or molecules in the sample. Likewise, if we know the number of moles of a substance, we can derive the number of atoms or molecules and calculate the substance's mass.

Here are some examples. The mass of 1 hydrogen atom is 1.0079 u; the mass of 1 mol of hydrogen atoms is 1.0079 g. Elemental hydrogen exists as a diatomic molecule, H_2. One molecule has a mass of 1.0079 u + 1.0079 u = 2.0158 u, while 1 mol of H_2 has a mass of 1.0079 g + 1.0079 g = 2.0158 g. One molecule of H_2O has a mass of about 18.01 u; 1 mol H_2O has a mass of 18.01 g. A single unit of NaCl has a mass of 58.45 u; NaCl has a molar mass of 58.45 g. In each of these moles of substances, there are 6.022×10^{23} units: 6.022×10^{23} atoms of H, 6.022×10^{23} molecules of H_2 and H_2O, 6.022×10^{23} units of NaCl ions. These relationships give us plenty of opportunities to construct conversion factors for simple calculations.

Example 6.1.4: Sugar

What is the molar mass of sugar ($C_6H_{12}O_6$)?

Solution

To determine the molar mass, we simply add the atomic masses of the atoms in the molecular formula; but express the total in grams per mole, not atomic mass units. The masses of the atoms can be taken from the periodic table.

6 C = 6 × 12.011	= 72.066
12 H = 12 × 1.0079	= 12.0948
6 O = 6 × 15.999	= 95.994
TOTAL	= 180.155 g/mol

Per convention, the unit *grams per mole* is written as a fraction.

Exercise 6.1.4

What is the molar mass of $AgNO_3$?

Answer available at the end of this section.

Summary

The mole is a key unit in chemistry. The molar mass of a substance, in grams, is numerically equal to one atom's or molecule's mass in atomic mass units.

Answers

Exercise 6.1.1

151.16 amu

Exercise 6.1.2

310.18 amu

Exercise 6.1.3

2.78×10^{22} molecules

Exercise 6.1.4

169.87 g/mol

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6.2: Gram-Mole Conversions

Learning Objectives

- To convert between mass units and mole units.

As we just discussed, **molar mass** is defined as the mass (in grams) of 1 mole of substance (or Avogadro's number of molecules or formula units).

The simplest type of manipulation using molar mass as a *conversion factor* is a mole-gram conversion (or its reverse, a gram-mole conversion).

We also established that 1 mol of Al has a mass of 26.98 g (Example 6.2.1). Stated mathematically,

$$1 \text{ mol Al} = 26.98 \text{ g Al}$$

We can divide both sides of this expression by either side to get one of two possible conversion factors:

$$\frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \quad \text{and} \quad \frac{26.98 \text{ g Al}}{1 \text{ mol Al}}$$

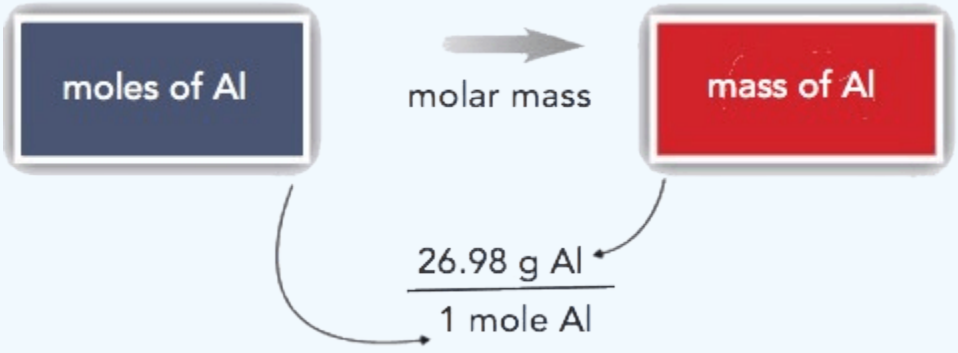
The first conversion factor can be used to convert from mass to moles, and the second converts from moles to mass. Both can be used to solve problems that would be hard to do “by eye.”

Example 6.2.1

What is the mass of 3.987 mol of Al?

Solution

The first step in a conversion problem is to decide what conversion factor to use. Because we are starting with mole units, we want a conversion factor that will cancel the mole unit and introduce the unit for mass in the numerator. Therefore, we should use the $\frac{26.98 \text{ g Al}}{1 \text{ mol Al}}$ conversion factor. We start with the given quantity and multiply by the conversion factor:



$$3.987 \text{ mol Al} \times \frac{26.98 \text{ g Al}}{1 \text{ mol Al}}$$

Note that the mol units cancel algebraically. (The quantity 3.987 mol is understood to be in the numerator of a fraction that has 1 in the unwritten denominator.) Canceling and solving gives

$$3.987 \text{ mol Al} \times \frac{26.98 \text{ g Al}}{1 \text{ mol Al}} = 107.6 \text{ g Al}$$

Our final answer is expressed to four significant figures.

Exercise 6.2.1

How many moles are present in 100.0 g of Al? (Hint: you will have to use the other conversion factor we obtained for aluminum.)

Answer available at the end of this section.

Conversions like this are possible for any substance, as long as the proper atomic mass, formula mass, or molar mass is known (or can be determined) and expressed in grams per mole. Figure 6.2.1 is a chart for determining what conversion factor is needed, and Figure 6.2.2 is a flow diagram for the steps needed to perform a conversion.

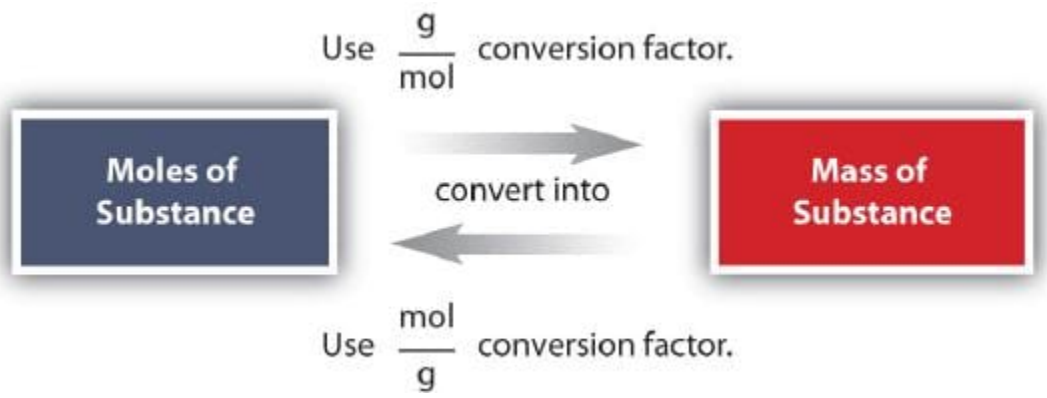


Figure 6.2.1 A Simple Flowchart for Converting between Mass and Moles of a Substance. It takes one mathematical step to convert from moles to mass or from mass to moles.

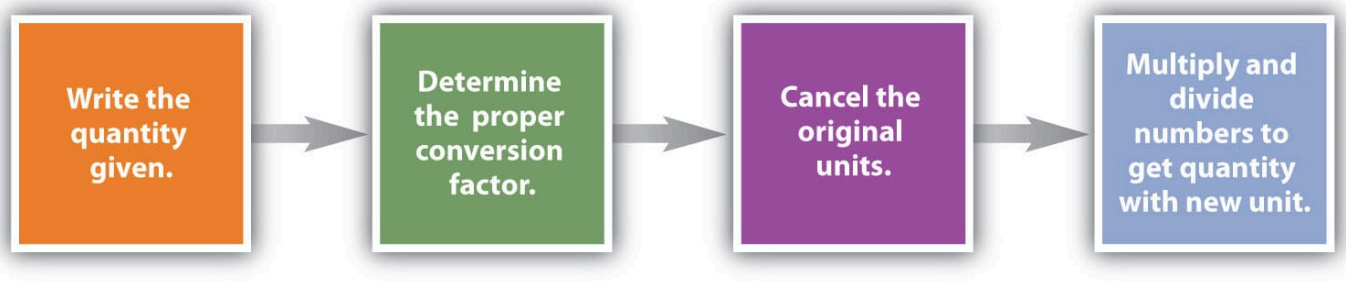


Figure 6.2.2 A Flowchart Illustrating the Steps in Performing a Unit Conversion. When performing many unit conversions, the same logical steps can be taken.

Example 6.2.2

A biochemist needs 0.00655 mol of bilirubin ($C_{33}H_{36}N_4O_6$) for an experiment. How many grams of bilirubin will that be?

Solution

To convert from moles to mass, we need the molar mass of bilirubin, which we can determine from its chemical formula:

33 C molar mass:	33 × 12.01 g =	396.33 g
36 H molar mass:	36 × 1.01 g =	36.36 g

4 N molar mass:	4 × 14.01 g =	56.04 g
6 O molar mass:	6 × 16.00 g =	96.00 g
Total:		584.73 g

The molar mass of bilirubin is 584.73 g. Using the relationship

$$1 \text{ mol bilirubin} = 584.73 \text{ g bilirubin}$$

we can construct the appropriate conversion factor for determining how many grams there are in 0.00655 mol. Following the steps from Figure 6.2.2:

$$0.00655 \text{ mol bilirubin} \times \frac{584.73 \text{ g bilirubin}}{\text{mol bilirubin}} = 3.83 \text{ g bilirubin}$$

The mol bilirubin unit cancels. The biochemist needs 3.83 g of bilirubin.

Exercise 6.2.2

A chemist needs 457.8 g of $KMnO_4$ to make a solution. How many moles of $KMnO_4$ is that?

Answer available at the end of this section.

To Your Health: Minerals

For our bodies to function properly, we need to ingest certain substances from our diets. Among our dietary needs are minerals, the noncarbon elements our body uses for a variety of functions, such developing bone or ensuring proper nerve transmission. The US Department of Agriculture has established some recommendations for the RDIs of various minerals. The accompanying table lists the RDIs for minerals, both in mass and moles, assuming a 2,000-calorie daily diet.

Table 6.2.1: Essential Minerals and their Composition in Humans

Mineral	Male (age 19–30 y)		Female (age 19–30 y)	
Ca	1,000 mg	0.025 mol	1,000 mg	0.025 mol
Cr	35 µg	6.7×10^{-7} mol	25 µg	4.8×10^{-7} mol
Cu	900 µg	1.4×10^{-5} mol	900 µg	1.4×10^{-5} mol
F	4 mg	2.1×10^{-4} mol	3 mg	1.5×10^{-4} mol
I	150 µg	1.2×10^{-6} mol	150 µg	1.2×10^{-6} mol
Fe	8 mg	1.4×10^{-4} mol	18 mg	3.2×10^{-4} mol
K	3,500 mg	9.0×10^{-2} mol	3,500 mg	9.0×10^{-2} mol
Mg	400 mg	1.6×10^{-2} mol	310 mg	1.3×10^{-2} mol
Mn	2.3 mg	4.2×10^{-5} mol	1.8 mg	3.3×10^{-5} mol
Mo	45 mg	4.7×10^{-7} mol	45 mg	4.7×10^{-7} mol
Na	2,400 mg	1.0×10^{-1} mol	2,400 mg	1.0×10^{-1} mol
P	700 mg	2.3×10^{-2} mol	700 mg	2.3×10^{-2} mol

Mineral	Male (age 19–30 y)		Female (age 19–30 y)	
Se	55 µg	7.0×10^{-7} mol	55 µg	7.0×10^{-7} mol
Zn	11 mg	1.7×10^{-4} mol	8 mg	1.2×10^{-4} mol

Table 6.2.1 illustrates several things. First, the needs of men and women for some minerals are different. The extreme case is for iron; women need over twice as much as men do. In all other cases where there is a different RDI, men need more than women.

Second, the amounts of the various minerals needed on a daily basis vary widely—both on a mass scale and a molar scale. The average person needs 0.1 mol of Na a day, which is about 2.5 g. On the other hand, a person needs only about 25–35 µg of Cr per day, which is under one millionth of a mole. As small as this amount is, a deficiency of chromium in the diet can lead to diabetes-like symptoms or neurological problems, especially in the extremities (hands and feet). For some minerals, the body does not require much to keep itself operating properly.

Although a properly balanced diet will provide all the necessary minerals, some people take dietary supplements. However, too much of a good thing, even minerals, is not good. Exposure to too much chromium, for example, causes a skin irritation, and certain forms of chromium are known to cause cancer (as presented in the movie *Erin Brockovich*).

Answers

Exercise 6.2.1

$$100.0 \text{ g Al} \times \frac{1 \text{ mol Al}}{26.98 \text{ g Al}} = 3.706 \text{ mol Al}$$

Exercise 6.2.2

$$457.8 \text{ g } \mathrm{KMnO_4} \times \frac{1 \text{ mol } \mathrm{KMnO_4}}{158.04 \text{ g } \mathrm{KMnO_4}} = 2.897 \text{ mol } \mathrm{KMnO_4}$$

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6.3: Mole Relationships and Chemical Equations

Learning Objectives

- To use a balanced chemical reaction to determine molar relationships between the substances.

Previously, you learned to balance chemical equations by comparing the numbers of each type of atom in the reactants and products. The coefficients in front of the chemical formulas represent the numbers of molecules or formula units (depending on the type of substance). Here, we will extend the meaning of the coefficients in a chemical equation.

Consider the simple chemical equation

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

The convention for writing balanced chemical equations is to use the lowest whole-number ratio for the coefficients. However, the equation is balanced as long as the coefficients are in a 2:1:2 ratio. For example, this equation is also balanced if we write it as

$$4\,H_2 + 2\,O_2 \longrightarrow 4\,H_2O$$

The ratio of the coefficients is 4:2:4, which reduces to 2:1:2. The equation is also balanced if we were to write it as

$$22\,H_2 + 11\,O_2 \longrightarrow 22\,H_2O$$

because 22:11:22 also reduces to 2:1:2.

Suppose we want to use larger numbers. Consider the following coefficients:

$$12.044 \times 10^{23}\ H_2 + 6.022 \times 10^{23}\ O_2 \rightarrow 12.044 \times 10^{23}\ H_2O$$

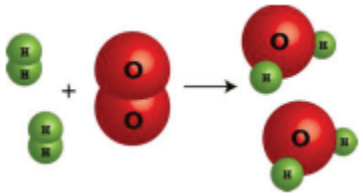
These coefficients also have the ratio 2:1:2 (check it and see), so this equation is balanced. But 6.022×10^{23} is 1 mol, while 12.044×10^{23} is 2 mol (and the number is written that way to make this more obvious), so we can simplify this version of the equation by writing it as

$$2\ \text{mol}\ \ H_2 + 1\ \ \text{mol}\ \ O_2 \longrightarrow 2\ \text{mol}\ \ H_2O$$

We can leave out the word *mol* and not write the 1 coefficient (as is our habit), so the final form of the equation, still balanced, is

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

Now we interpret the coefficients as referring to molar amounts, not individual molecules. The lesson? *Balanced chemical equations are balanced not only at the molecular level but also in terms of molar amounts of reactants and products*. Thus, we can read this reaction as “two moles of hydrogen react with one mole of oxygen to produce two moles of water.”



2 molecules H_2 1 molecule O_2 2 molecules H_2O

2 moles H_2 1 mole O_2 2 moles H_2O

2 x 2.02 g=4.04 g H_2 32.0 g O_2 2 x 18.02 g=36.04 g H_2O

Figure 6.3.1: This representation of the production of water from oxygen and hydrogen show several ways to interpret the quantitative information of a chemical reaction.

By the same token, the ratios we constructed to describe molecules reaction can also be constructed in terms of moles rather than molecules. For the reaction in which hydrogen and oxygen combine to make water, for example, we can construct the following ratios:

$$\frac{2\ \text{mol}\ \text{H}_2}{1\ \text{mol}\ \text{O}_2}\ \text{or}\ \frac{1\ \text{mol}\ \text{O}_2}{2\ \text{mol}\ \text{H}_2}$$

$$\frac{2\ \text{mol}\ \text{H}_2\text{O}}{1\ \text{mol}\ \text{O}_2}\ \text{or}\ \frac{1\ \text{mol}\ \text{O}_2}{2\ \text{mol}\ \text{H}_2\text{O}}$$

$$\frac{2\ \text{mol}\ \text{H}_2}{2\ \text{mol}\ \text{H}_2\text{O}}\ \text{or}\ \frac{2\ \text{mol}\ \text{H}_2\text{O}}{2\ \text{mol}\ \text{H}_2}$$

We can use these ratios to determine what amount of a substance, in moles, will react with or produce a given number of moles of a different substance. The study of the numerical relationships between the reactants and the products in balanced chemical reactions is called ***stoichiometry*.** The ratio of coefficients in a balanced chemical equation, used in computations relating amounts of reactants and products is called the **stoichiometric factor.**

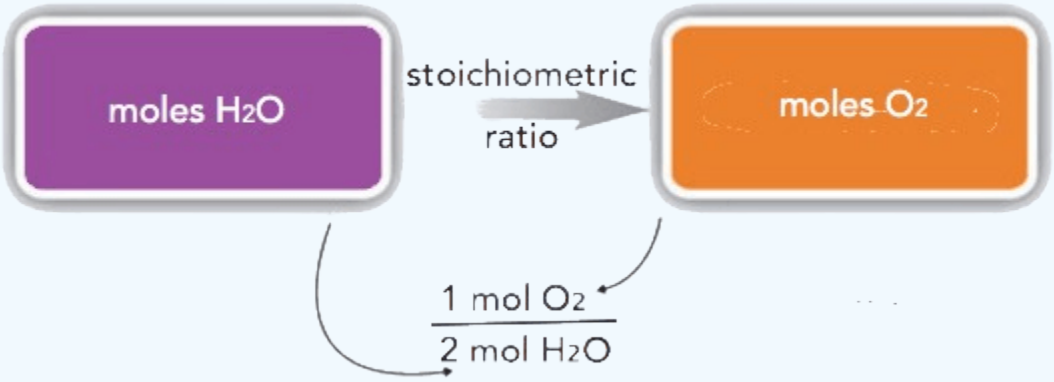
Example 6.3.1

How many moles of oxygen react with hydrogen to produce 27.6 mol of H_2O? The balanced equation is as follows:

$$2\,\text{H}_2 + \text{O}_2 \longrightarrow 2\,\text{H}_2\text{O}$$

Solution

Because we are dealing with quantities of H_2O and O_2, we will use the **stoichiometric ratio** that relates those two substances. Because we are given an amount of H_2O and want to determine an amount of O_2, we will use the ratio that has H_2O in the denominator (so it cancels) and O_2 in the numerator (so it is introduced in the answer). Thus,



$$27.6\ \text{mol}\ \text{H}_2\text{O} \times \frac{1\ \text{mol}\ \text{O}_2}{2\ \text{mol}\ \text{H}_2\text{O}} = 13.8\ \text{mol}\ \text{O}_2$$

To produce 27.6 mol of H_2O, 13.8 mol of O_2 react.

Exercise 6.3.1

Using $2H_2 + O_2 \rightarrow 2H_2O$, how many moles of hydrogen react with 3.07 mol of oxygen to produce H_2O?

Answer available at the end of this section.

Key Takeaway

- The balanced chemical reaction can be used to determine molar relationships between substances.

Answers

Exercise 6.3.1

$$3.07 \text{ mol } O_2 \times \frac{2 \text{ mol } H_2}{1 \text{ mol } O_2} = 6.14 \text{ mol } H_2$$

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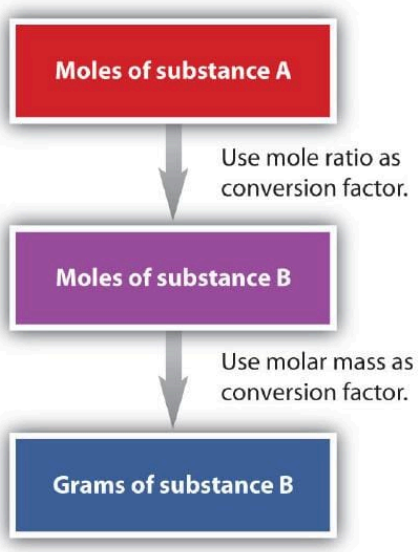
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6.4: Mass Relationships and Chemical Equations

Learning Objectives

- To convert from mass or moles of one substance to mass or moles of another substance in a chemical reaction.

We have established that a balanced chemical equation is balanced in terms of moles as well as atoms or molecules. We have used balanced equations to set up ratios, now in terms of moles of materials, that we can use as conversion factors to answer stoichiometric questions, such as how many moles of substance A react with so many moles of reactant B. We can extend this technique even further. Recall that we can relate a molar amount to a mass amount using molar mass. We can use that ability to answer stoichiometry questions in terms of the masses of a particular substance, in addition to moles. We do this using the following sequence:



Collectively, these conversions are called mole-mass calculations.

As an example, consider the balanced chemical equation

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

If we have 3.59 mol of Fe_2O_3, how many grams of SO_3 can react with it? Using the mole-mass calculation sequence, we can determine the required mass of SO_3 in two steps. First, we construct the appropriate molar ratio, determined from the balanced chemical equation, to calculate the number of moles of SO_3 needed. Then using the molar mass of SO_3 as a conversion factor, we determine the mass that this number of moles of SO_3 has.

The first step resembles the exercises we did in Section 6.4. As usual, we start with the quantity we were given:

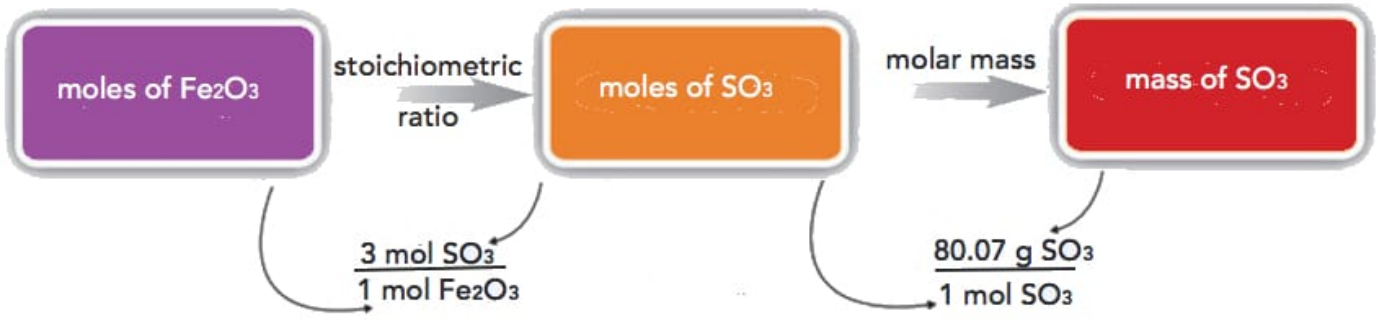
$$3.59\ \text{mol}\ Fe_2O_3 \times \frac{3\ \text{mol}\ SO_3}{1\ \text{mol}\ Fe_2O_3} = 10.77\ \text{mol}\ SO_3$$

The mol Fe_2O_3 units cancel, leaving mol SO_3 unit. Now, we take this answer and convert it to grams of SO_3, using the molar mass of SO_3 as the conversion factor:

$$10.77\ \text{mol}\ SO_3 \times \frac{80.07\ \text{g}\ SO_3}{1\ \text{mol}\ SO_3} = 862.4\ \text{g}\ SO_3$$

Our final answer is expressed to three significant figures. Thus, in a two-step process, we find that 862 g of SO_3 will react with 3.59 mol of Fe_2O_3. Many problems of this type can be answered in this manner.

The same two-step problem can also be worked out in a single line, rather than as two separate steps, as follows:



$$3.59\ \text{mol}\ Fe_2O_3 \times \underbrace{\frac{3\ \text{mol}\ SO_3}{1\ \text{mol}\ Fe_2O_3}}_{\text{converts to moles of } SO_3} \times \underbrace{\frac{80.07\ \text{g}\ SO_3}{1\ \text{mol}\ SO_3}}_{\text{converts to grams of } SO_3} = 862.4\ \text{g}\ SO_3$$

We get exactly the same answer when combining all the math steps together as we do when we calculate one step at a time.

Example 6.4.1

How many grams of CO_2 are produced if 2.09 mol of HCl are reacted according to this balanced chemical equation?

$$CaCO_3 + 2\,HCl \rightarrow CaCl_2 + CO_2 + H_2O$$

Solution

Our strategy will be to convert from moles of HCl to moles of CO_2 and then from moles of CO_2 to grams of CO_2. We will need the molar mass of CO_2, which is 44.01 g/mol. Performing these two conversions in a single-line gives 46.0 g of CO_2:

$$2.09\ \text{mol}\ HCl \times \underbrace{\frac{1\ \text{mol}\ CO_2}{2\ \text{mol}\ HCl}}_{\text{from the coefficients of the balanced equation}} \times \frac{44.01\ \text{g}\ CO_2}{1\ \text{mol}\ CO_2} = 46.0\ \text{g}\ CO_2$$

The molar ratio between CO_2 and HCl comes from the balanced chemical equation.

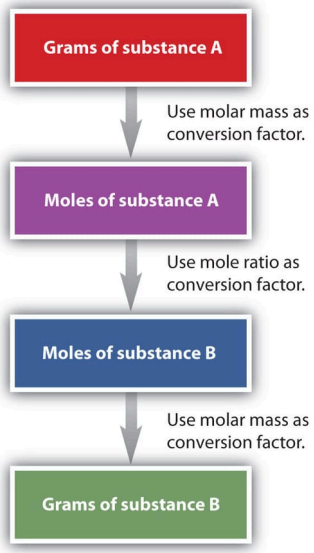
Exercise

How many grams of glucose ($C_6H_{12}O_6$) are produced if 17.3 mol of H_2O are reacted according to this balanced chemical equation?

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

Answer available at the end of this section.

It is a small step from mole-mass calculations to mass-mass calculations. If we start with a known mass of one substance in a chemical reaction (instead of a known number of moles), we can calculate the corresponding masses of other substances in the reaction. The first step in this case is to convert the known mass into moles, using the substance's molar mass as the conversion factor. Then—and only then—we use the balanced chemical equation to construct a conversion factor to convert that quantity to moles of another substance, which in turn can be converted to a corresponding mass. Sequentially, the process is as follows:



This three-part process can be carried out in three discrete steps or combined into a single calculation that contains three conversion factors. The following example illustrates both techniques.

Example 6.4.2: Chlorination of Carbon

Methane can react with elemental chlorine to make carbon tetrachloride (CCl_4). The balanced chemical equation is as follows:

$$CH_4 + 4\,Cl_2 \rightarrow CCl_4 + 4\,HCl$$

How many grams of HCl are produced by the reaction of 100.0 g of CH_4?

Solution

First, let us work the problem in stepwise fashion. We begin by converting the mass of CH_4 to moles of CH_4, using the molar mass of CH_4 (16.05 g/mol) as the conversion factor:

$$100.0\text{ g } CH_4 \times \frac{1\text{ mol } CH_4}{16.05\text{ g } CH_4} = 6.231\text{ mol } CH_4$$

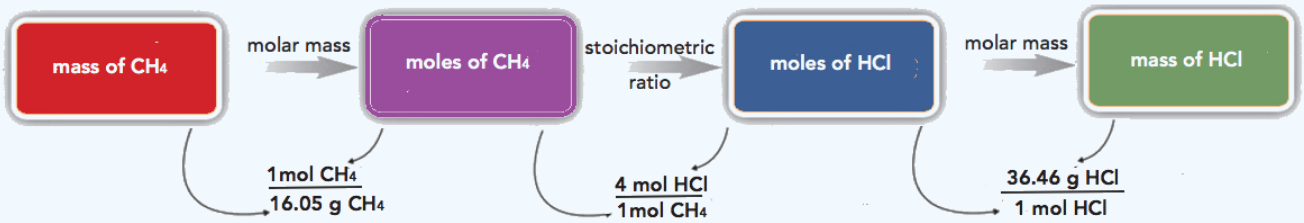
Note that we inverted the molar mass so that the gram units cancel, giving us an answer in moles. Next, we use the balanced chemical equation to determine the ratio of moles CCl_4 and moles HCl and convert our first result into moles of HCl:

$$6.231 \text{ mol } CH_4 \times \frac{4 \text{ mol HCl}}{1 \text{ mol } CH_4} = 24.92 \text{ mol HCl}$$

Finally, we use the molar mass of HCl (36.46 g/mol) as a conversion factor to calculate the mass of 24.92 mol of HCl:

$$24.92 \text{ mol HCl} \times \frac{36.46 \text{ g HCl}}{1 \text{ mol HCl}} = 908.5 \text{ g HCl}$$

In each step, we have limited the answer to the proper number of significant figures. If desired, we can do all three conversions on a single line:



$$100.0 \text{ g } CH_4 \times \frac{1 \text{ mol } CH_4}{16.05 \text{ g } CH_4} \times \frac{4 \text{ mol HCl}}{1 \text{ mol } CH_4} \times \frac{36.46 \text{ g HCl}}{1 \text{ mol HCl}} = 908.7 \text{ g HCl}$$

This final answer is slightly different from our first answer because only the final answer is restricted to the proper number of significant figures. In the first answer, we limited each intermediate quantity to the proper number of significant figures. As you can see, both answers are essentially the same.

Exercise 6.4.2: Oxidation of Propanal

The oxidation of propanal (CH_3CH_2CHO) to propionic acid (CH_3CH_2COOH) has the following chemical equation:

$$CH_3CH_2CHO + 2K_2Cr_2O_7 \rightarrow CH_3CH_2COOH + \text{other products}$$

How many grams of propionic acid are produced by the reaction of 135.8 g of $K_2Cr_2O_7$?

Answer available at the end of this section.

To Your Health: The Synthesis of Taxol

Taxol is a powerful anticancer drug that was originally extracted from the Pacific yew tree (*Taxus brevifolia*). As you can see from the accompanying figure, taxol is a very complicated molecule, with a molecular formula of $C_{47}H_{51}NO_{14}$. Isolating taxol from its natural source presents certain challenges, mainly that the Pacific yew is a slow-growing tree, and the equivalent of six trees must be harvested to provide enough taxol to treat a single patient. Although related species of yew trees also produce taxol in small amounts, there is significant interest in synthesizing this complex molecule in the laboratory.

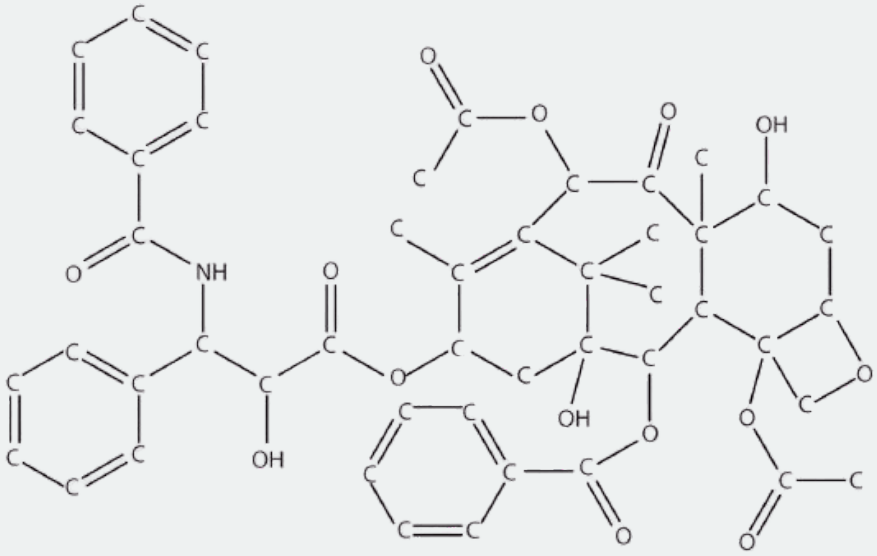


Figure 6.4.1 The Structure of the Cancer Drug Taxol. Because of the complexity of the molecule, hydrogen atoms are not shown, but they are present on every atom to give the atom the correct number of covalent bonds (four bonds for each carbon atom).

After a 20-year effort, two research groups announced the complete laboratory synthesis of taxol in 1994. However, each synthesis required over 30 separate chemical reactions, with an overall efficiency of less than 0.05%. To put this in perspective, to obtain a single 300 mg dose of taxol, you would have to begin with 600 g of starting material. To treat the 26,000 women who are diagnosed with ovarian cancer each year with one dose, almost 16,000 kg (over 17 tons) of starting material must be converted to taxol. Taxol is also used to treat breast cancer, with which 200,000 women in the United States are diagnosed every year. This only increases the amount of starting material needed.

Clearly, there is intense interest in increasing the overall efficiency of the taxol synthesis. An improved synthesis not only will be easier but also will produce less waste materials, which will allow more people to take advantage of this potentially life-saving drug.

Key Takeaway

- A balanced chemical equation can be used to relate masses or moles of different substances in a reaction.

Answers

Exercise

$$17.3\ \text{mol}\ H_2O \times \frac{1\ \text{mol}\ C_6H_{12}O_6}{6\ \text{mol}\ H_2O} \times \frac{180.18\ \text{g}\ C_6H_{12}O_6}{1\ \text{mol}\ C_6H_{12}O_6} = 520\ \text{g}\ C_6H_{12}O_6$$

Exercise 6.4.2: Oxidation of Propanal

$$135.8\ \text{g}\ K_2Cr_2O_7 \times \frac{1\ \text{mol}\ K_2Cr_2O_7}{294.20\ \text{g}\ K_2Cr_2O_7} \times \frac{1\ \text{mol}\ CH_3CH_2COOH}{2\ \text{mol}\ K_2Cr_2O_7} \times \frac{74.09\ \text{g}\ CH_3CH_2COOH}{1\ \text{mol}\ CH_3CH_2COOH} = 17.10\ \text{g}\ CH_3CH_2COOH$$

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6.5: Limiting Reagent and Percent Yield

Learning Objectives

- Define and determine theoretical yields, actual yields, and percent yields.
- Identify a limiting reagent from a set of reactants.
- Calculate how much product will be produced from the limiting reagent.
- Calculate how much reactant(s) remains when the reaction is complete.

Yield

In all the previous calculations we have performed involving balanced chemical equations, we made two assumptions:

1. The reaction goes exactly as written.
2. The reaction proceeds completely.

In reality, such things as side reactions occur that make some chemical reactions rather messy. For example, in the actual combustion of some carbon-containing compounds, such as methane, some CO is produced as well as CO_2. However, we will continue to ignore side reactions, unless otherwise noted. The second assumption, that the reaction proceeds completely, is more troublesome. Many chemical reactions do not proceed to completion as written, for a variety of reasons. When we calculate an amount of product assuming that all the reactant reacts, we calculate the **theoretical yield**, an amount that is theoretically produced as calculated using the balanced chemical reaction.

In many cases, however, this is not what really happens. In many cases, less—sometimes, much less—of a product is made during the course of a chemical reaction. The amount that is actually produced in a reaction is called the **actual yield**. By definition, the actual yield is less than or equal to the theoretical yield. If it is not, then an error has been made.

Both theoretical yields and actual yields are expressed in units of moles or grams. It is also common to see something called a percent yield. The **percent yield** is a comparison between the actual yield and the theoretical yield and is defined as

$$\text{percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% \tag{6.5.1}$$

It does not matter whether the actual and theoretical yields are expressed in moles or grams, as long as they are expressed in the same units. However, the percent yield always has units of percent. Proper percent yields are between 0% and 100%. In the laboratory, a student will occasionally obtain a yield that appears to be greater than 100%. This usually happens when the product is impure or is wet with a solvent such as water. If this is not the case, then the student must have made an error in weighing either the reactants or the products. The law of conservation of mass applies even to undergraduate chemistry laboratory experiments. A 100% yield means that everything worked perfectly, and the chemist obtained all the product that could have been produced. Anyone who has tried to do something as simple as fill a salt shaker or add oil to a car's engine without spilling knows the unlikelihood of a 100% yield. At the other extreme, a yield of 0% means that no product was obtained. A percent yield of 80%–90% is usually considered good to excellent; a yield of 50% is only fair. In part because of the problems and costs of waste disposal, industrial production facilities face considerable pressures to optimize the yields of products and make them as close to 100% as possible.

Example 6.5.1:

A worker reacts 30.5 g of Zn with nitric acid and evaporates the remaining water to obtain 65.2 g of $Zn(NO_3)_2$. What are the theoretical yield, the actual yield, and the percent yield?

$$\mathrm{Zn\,(s) + 2\,HNO_3\,(aq) \longrightarrow Zn(NO_3)_2\,(aq) + H_2\,(g)}$$

Solution

A mass-mass calculation can be performed to determine the theoretical yield. We need the molar masses of Zn (65.39 g/mol) and $Zn(NO_3)_2$ (189.41 g/mol). In three steps, the mass-mass calculation is:

$$30.5\ \cancel{g\ Zn} \times \frac{1\ \cancel{mol\ Zn}}{65.39\ \cancel{g\ Zn}} \times \frac{1\ \cancel{mol\ Zn(NO_3)_2}}{1\ \cancel{mol\ Zn}} \times \frac{189.41\ g\ Zn(NO_3)_2}{1\ \cancel{mol\ Zn(NO_3)_2}} = 88.3\ g\ Zn(NO_3)_2$$

Thus, the theoretical yield is 88.3 g of $Zn(NO_3)_2$. The actual yield is the amount that was actually made, which was 65.2 g of $Zn(NO_3)_2$. To calculate the percent yield, we take the actual yield and divide it by the theoretical yield and multiply by 100 (Equation 6.5.1):

$$\frac{65.2\ g\ Zn(NO_3)_2}{88.3\ g\ Zn(NO_3)_2} \times 100\% = 73.8\%$$

The worker achieved almost three-fourths of the possible yield.

Exercise 6.5.1

A synthesis produced 2.05 g of NH_3 from 16.5 g of N_2. What is the theoretical yield and the percent yield?

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

*Technically, this is a reversible reaction (with double arrows), but for this exercise consider it irreversible (single arrow).

Answer

theoretical yield = 20.1 g; percent yield = 10.2%

Chemistry is Everywhere: Actual Yields in Drug Synthesis and Purification

Many drugs are the product of several steps of chemical synthesis. Each step typically occurs with less than 100% yield, so the overall percent yield might be very small. The general rule is that the overall percent yield is the product of the percent yields of the individual synthesis steps. For a drug synthesis that has many steps, the overall percent yield can be very tiny, which is one factor in the huge cost of some drugs. For example, if a 10-step synthesis has a percent yield of 90% for each step, the overall yield for the entire synthesis is only 35%. Many scientists work every day trying to improve percent yields of the steps in the synthesis to decrease costs, improve profits, and minimize waste.

Even purifications of complex molecules into drug-quality purity are subject to percent yields. Consider the purification of impure albuterol. Albuterol ($C_{13}H_{21}NO_2$; accompanying figure) is an inhaled drug used to treat asthma, bronchitis, and other obstructive pulmonary diseases. It is synthesized from norepinephrine, a naturally occurring hormone and neurotransmitter. Its initial synthesis makes very impure albuterol that is purified in five chemical steps. The details of the steps do not concern us; only the percent yields do:

impure albuterol → intermediate A	percent yield = 70%
intermediate A → intermediate B	percent yield = 100%
intermediate B → intermediate C	percent yield = 40%
intermediate C → intermediate D	percent yield = 72%
intermediate D → purified albuterol	percent yield = 35%
overall percent yield = 70% × 100% × 40% × 72% × 35% = 7.5%	

That is, only about *one-fourteenth* of the original material was turned into the purified drug. This demonstrates one reason why some drugs are so expensive—a lot of material is lost in making a high-purity pharmaceutical.



Figure 6.5.1 A child using an albuterol inhaler, the container of albuterol medication, and a molecular model of the albuterol molecule. Source: Photo on far left © Thinkstock. Photo in center courtesy of Intropin, http://commons.wikimedia.org/wiki/Fi...te_%281%29.JPG.

Limiting Reagent

In all the examples discussed thus far, the reactants were assumed to be present in stoichiometric quantities. Consequently, none of the reactants was left over at the end of the reaction. This is often desirable, as in the case of a space shuttle, where excess oxygen or hydrogen was not only extra freight to be hauled into orbit but also an explosion hazard. More often, however, reactants are present in mole ratios that are not the same as the ratio of the coefficients in the balanced chemical equation. As a result, one or more of them will not be used up completely but will be left over when the reaction is completed. In this situation, the amount of product that can be obtained is limited by the amount of only one of the reactants. The reactant that restricts the amount of product obtained is called the limiting reactant. The reactant that remains after a reaction has gone to completion is in excess.

Consider a nonchemical example. Assume you have invited some friends for dinner and want to bake brownies for dessert. You find two boxes of brownie mix in your pantry and see that each package requires two eggs. The balanced equation for brownie preparation is thus

$$1\,\text{box mix} + 2\,\text{eggs} \rightarrow 1\,\text{batch brownies} \tag{6.5.2}$$

If you have a dozen eggs, which ingredient will determine the number of batches of brownies that you can prepare? Because each box of brownie mix requires two eggs and you have two boxes, you need four eggs. Twelve eggs is eight more eggs than you need. Although the ratio of eggs to boxes in is 2:1, the ratio in your possession is 6:1. Hence the eggs are the ingredient (reactant) present in excess, and the brownie mix is the limiting reactant. Even if you had a refrigerator full of eggs, you could make only two batches of brownies.

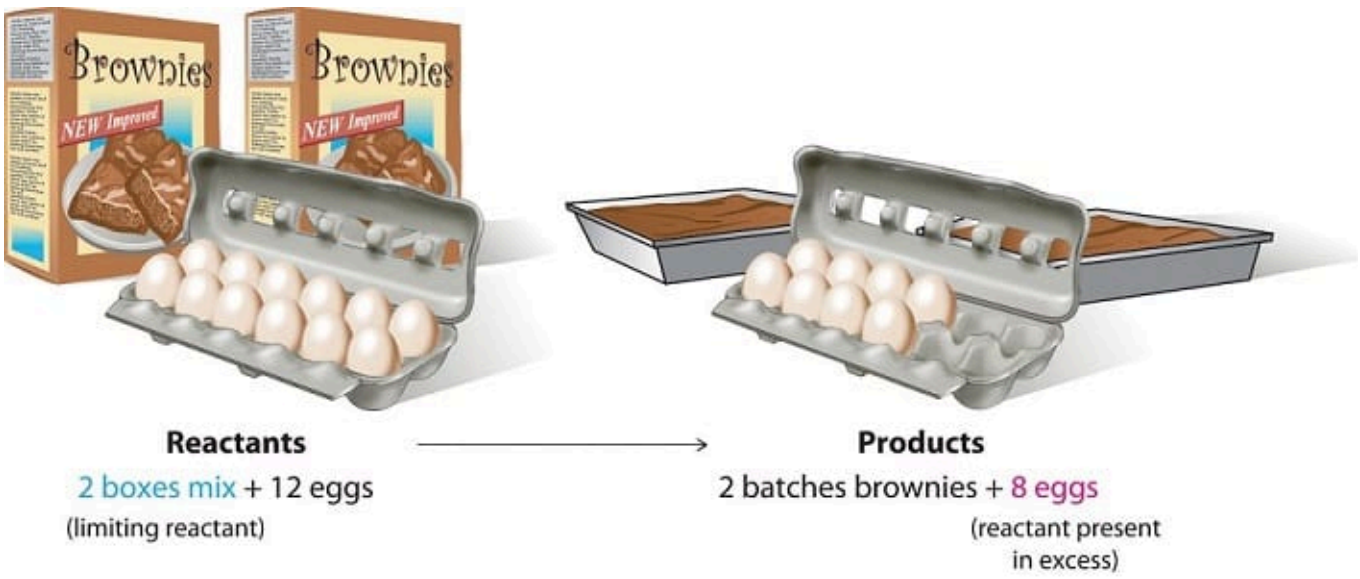


Figure 6.5.1: *The Concept of a Limiting Reactant in the Preparation of Brownies*

A similar situation exists for many chemical reactions: you usually run out of one reactant before all of the other reactant has reacted. The reactant you run out of is called the **limiting reagent**; the other reactant or reactants are considered to be *in excess*. A crucial skill in evaluating the conditions of a chemical process is to determine which reactant is the limiting reagent and which is in excess.

The key to recognizing which reactant is the limiting reagent is based on a mole-mass or mass-mass calculation: whichever reactant gives the *lesser* amount of product is the limiting reagent. What we need to do is determine an amount of one product (either moles or mass), assuming all of each reactant reacts. Whichever reactant gives the least amount of that particular product is the limiting reagent. It does not matter which product we use, as long as we use the same one each time. It does not matter whether we determine the number of moles or grams of that product; however, we will see shortly that knowing the final mass of product can be useful.

For example, consider this reaction:

$$4As(s) + 3O_2(g) \rightarrow 2As_2O_3(s)$$

Suppose we start a reaction with 50.0 g of As and 50.0 g of O_2. Which one is the limiting reagent? We need to perform two mole-mass calculations, each assuming that each reactant reacts completely. Then we compare the amount of the product produced by each and determine which is less.

The calculations are as follows:

$$50.0\ \cancel{g\,As} \times \frac{1\ \cancel{mol\,As}}{74.92\ \cancel{g\,As}} \times \frac{2\,mol\,As_2O_3}{4\ \cancel{mol\,As}} = 0.334\,mol\,As_2O_3$$

$$50.0\ \cancel{g\,O_2} \times \frac{1\ \cancel{mol\,O_2}}{32.00\ \cancel{g\,O_2}} \times \frac{2\,mol\,As_2O_3}{3\ \cancel{mol\,O_2}} = 1.04\,mol\,As_2O_3$$

Comparing these two answers, it is clear that 0.334 mol of As_2O_3 is less than 1.04 mol of As_2O_3, so arsenic is the limiting reagent. If this reaction is performed under these initial conditions, the arsenic will run out before the oxygen runs out. We say that the oxygen is "in excess."

Identifying the limiting reagent, then, is straightforward. However, there are usually two associated questions: (1) what mass of product (or products) is then actually formed? and (2) what mass of what reactant is left over? The first question is straightforward to answer: simply perform a conversion from the number of moles of product formed to its mass, using its molar mass. For As_2O_3, the molar mass is 197.84 g/mol; knowing that we will form 0.334 mol of As_2O_3 under the given conditions, we will get

$$0.334\ \cancel{mol\,As_2O_3} \times \frac{197.84\,g\,As_2}{1\ \cancel{mol\,As_2O_3}} = 66.1\,g\,As_2O_3$$

The second question is somewhat more convoluted to answer. First, we must do a mass-mass calculation relating the limiting reagent (here, As) to the other reagent (O_2). Once we determine the mass of O_2 that reacted, we subtract that from the original amount to determine the amount left over. According to the mass-mass calculation,

$$50.0\ \cancel{g\,As} \times \frac{1\ \cancel{mol\,As}}{74.92\ \cancel{g\,As}} \times \frac{3\ \cancel{mol\,O_2}}{4\ \cancel{mol\,As}} \times \frac{32.00\,g\,O_2}{1\ \cancel{mol\,O_2}} = 16.0\,g\,O_2\ reacted$$

Because we reacted 16.0 g of our original O_2, we subtract that from the original amount, 50.0 g, to get the mass of O_2 remaining:

50.0 g O_2 – 16.0 g O_2 reacted = 34.0 g O_2 left over

You must remember to perform this final subtraction to determine the amount remaining; a common error is to report the 16.0 g

as the amount remaining.

Example 6.5.1:

A 5.00 g quantity of Rb is combined with 3.44 g of $MgCl_2$ according to this chemical reaction:

$$2Rb(s) + MgCl_2(s) \rightarrow Mg(s) + 2RbCl(s)$$

What mass of Mg is formed, and what mass of what reactant is left over?

Solution

Because the question asks what mass of magnesium is formed, we can perform two mass-mass calculations and determine which amount is less.

$$5.00\ \cancel{g\ Rb} \times \frac{1\ \cancel{mol\ Rb}}{85.47\ \cancel{g\ Rb}} \times \frac{1\ \cancel{mol\ Mg}}{2\ \cancel{mol\ Rb}} \times \frac{24.31\ g\ Mg}{1\ \cancel{mol\ Mg}} = 0.711\ g\ Mg$$

$$3.44\ \cancel{g\ MgCl_2} \times \frac{1\ \cancel{mol\ MgCl_2}}{95.21\ \cancel{g\ MgCl_2}} \times \frac{1\ \cancel{mol\ Mg}}{1\ \cancel{mol\ MgCl_2}} \times \frac{24.31\ g\ Mg}{1\ \cancel{mol\ Mg}} = 0.878\ g\ Mg$$

The 0.711 g of Mg is the lesser quantity, so the associated reactant—5.00 g of Rb—is the limiting reagent. To determine how much of the other reactant is left, we have to do one more mass-mass calculation to determine what mass of $MgCl_2$ reacted with the 5.00 g of Rb, and then subtract the amount reacted from the original amount.

$$5.00\ \cancel{g\ Rb} \times \frac{1\ \cancel{mol\ Rb}}{85.47\ \cancel{g\ Rb}} \times \frac{1\ \cancel{mol\ MgCl_2}}{2\ \cancel{mol\ Rb}} \times \frac{95.21\ g\ Mg}{1\ \cancel{mol\ MgCl_2}} = 2.78\ g\ MgCl_2\ \ reacted$$

Because we started with 3.44 g of $MgCl_2$, we have

3.44 g $MgCl_2$ – 2.78 g $MgCl_2$ reacted = 0.66 g $MgCl_2$ left

Exercise 6.5.1

Given the initial amounts listed, what is the limiting reagent, and what is the mass of the leftover reagent?

$$\underbrace{22.7\ g}_{MgO(s)} + \underbrace{17.9\ g}_{H_2S} \rightarrow MgS(s) + H_2O(l)$$

Answer available at the end of this section.

Summary

Theoretical yield is the calculated yield using the balanced chemical reaction. Actual yield is what is actually obtained in a chemical reaction. Percent yield is a comparison of the actual yield with the theoretical yield.

The limiting reagent is the reactant that produces the least amount of product. Mass-mass calculations can determine how much product is produced and how much of the other reactants remain.

Answers

Exercise 6.5.1

H_2S is the limiting reagent; 1.5 g of MgO are left over.

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7: CHEMICAL REACTIONS - ENERGY, RATES, AND EQUILIBRIUM

7.1: Energy and Chemical Bonds

7.2: Heat Changes during Chemical Reactions

7.3: Exothermic and Endothermic Reactions

7.4: Why Do Chemical Reactions Occur? Free Energy

7.5: How Do Chemical Reactions Occur? Reaction Rates

7.6: Effects of Temperature, Concentration, and Catalysts on Reaction Rates

7.7: Reversible Reactions and Chemical Equilibrium

7.8: Equilibrium Equations and Equilibrium Constants

7.9: Le Chatelier's Principle- The Effect of Changing Conditions on Equilibria

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7.1: Energy and Chemical Bonds

Learning Objectives

- Define energy and distinguish the different types of energy, potential and kinetic.

Chemical changes and their accompanying changes in *energy* are important parts of our everyday world (Figure 7.1.1). The macronutrients in food (proteins, fats, and carbohydrates) undergo metabolic reactions that provide the energy to keep our bodies functioning. We burn a variety of fuels (gasoline, natural gas, coal) to produce energy for transportation, heating, and the generation of electricity. Industrial chemical reactions use enormous amounts of energy to produce raw materials (such as iron and aluminum). Energy is then used to manufacture those raw materials into useful products, such as cars, skyscrapers, and bridges.



Figure 7.1.1: The energy involved in chemical changes is important to our daily lives: (a) A cheeseburger for lunch provides the energy you need to get through the rest of the day; (b) the combustion of gasoline provides the energy that moves your car (and you) between home, work, and school; and (c) coke, a processed form of coal, provides the energy needed to convert iron ore into iron, which is essential for making many of the products we use daily. (credit a: modification of work by "Pink Sherbet Photography"/Flickr; credit b: modification of work by Jeffery Turner).

Over 90% of the energy we use comes originally from the sun. Every day, the sun provides the earth with almost 10,000 times the amount of energy necessary to meet all of the world's energy needs for that day. Our challenge is to find ways to convert and store incoming solar energy so that it can be used in reactions or chemical processes that are both convenient and nonpolluting. Plants and many bacteria capture solar energy through photosynthesis. We release the energy stored in plants when we burn wood or plant products such as ethanol. We also use this energy to fuel our bodies by eating food that comes directly from plants or from animals that got their energy by eating plants. Burning coal and petroleum also releases stored solar energy: These fuels are fossilized plant and animal matter.

Energy

Energy can be defined as the capacity to supply heat or do work. One type of work (w) is the process of causing matter to move against an opposing force. For example, we do work when we inflate a bicycle tire—we move matter (the air in the pump) against the opposing force of the air surrounding the tire.

Like matter, energy comes in different types. One scheme classifies energy into two types: **potential energy**, the energy an object has because of its relative position, composition, or condition, often referred to as *stored energy*, and **kinetic energy**, the energy that an object possesses because of its motion. Water at the top of a waterfall or dam has potential energy because of its position; when it flows downward through generators, it has kinetic energy that can be used to do work and produce electricity in a hydroelectric plant (Figure 7.1.2). A battery has potential energy because the chemicals within it can produce electricity that can do work.



Figure 7.1.2: (a) Water that is higher in elevation, for example, at the top of Victoria Falls, has a higher potential energy than water at a lower elevation. As the water falls, some of its potential energy is converted into kinetic energy. (b) If the water flows through generators at the bottom of a dam, such as the Hoover Dam shown here, its kinetic energy is converted into electrical energy. (credit a: modification of work by Steve Jurvetson; credit b: modification of work by "curimedia"/Wikimedia commons).

Energy can be converted from one form into another, but all of the energy present before a change occurs always exists in some form after the change is completed. This observation is expressed in the law of conservation of energy: during a chemical or physical change, energy can be neither created nor destroyed, although it can be changed in form. (This is also one version of the first law of thermodynamics, as you will learn later.)

When one substance is converted into another, there is always an associated conversion of one form of energy into another. **Heat** is usually released or absorbed, but sometimes the conversion involves light, electrical energy, or some other form of energy. For example, chemical energy (a type of potential energy) is stored in the molecules that compose gasoline. When gasoline is combusted within the cylinders of a car's engine, the rapidly expanding gaseous products of this chemical reaction generate mechanical energy (a type of kinetic energy) when they move the cylinders' pistons.

According to the law of conservation of matter (seen in an earlier chapter), there is no detectable change in the total amount of matter during a chemical change. When chemical reactions occur, the energy changes are relatively modest and the mass changes are too small to measure, so the laws of conservation of matter and energy hold well. However, in nuclear reactions, the energy changes are much larger (by factors of a million or so), the mass changes are measurable, and matter-energy conversions are significant. This will be examined in more detail in a later chapter on nuclear chemistry. To encompass both chemical and nuclear changes, we combine these laws into one statement: The total quantity of matter and energy in the universe is fixed.

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7.2: Heat Changes during Chemical Reactions

Learning Objectives

- Define *bond dissociation energy*.
- Determine if a chemical process is exothermic or endothermic.

A general statement, based on countless observations over centuries of study, is that all objects tend to move spontaneously to a position of minimum energy unless acted on by some other force or object.

Bond Dissociation Energy

Atoms bond together to form compounds because in doing so they attain lower energies than they possess as individual atoms. A quantity of energy, equal to the difference between the energies of the bonded atoms and the energies of the separated atoms, is released, usually as heat. That is, the bonded atoms have a lower energy than the individual atoms do. *When atoms combine to make a compound, energy is always given off, and the compound has a lower overall energy.* In making compounds, atoms act like a basketball on a playground slide; they move in the direction of decreasing energy.

We can reverse the process by putting energy into a molecule, which causes its bonds to break, separating the molecule into individual atoms. Bonds between certain specific elements usually have a characteristic energy, called the **bond dissociation energy**, that is needed to break the bond. The same amount of energy was liberated when the atoms made the chemical bond in the first place. The term bond dissociation energy is usually used to describe the *strength* of interactions between atoms that make covalent bonds. A C–C bond has an approximate bond energy of 80 kcal/mol, while a C=C has a bond energy of about 145 kcal/mol. The C=C bond is stronger than C-C (as discussed in relation to bond length in Section 4.4). For atoms in ionic compounds attracted by opposite charges, the term lattice energy is used. For now, we will deal with covalent bonds in molecules.

Although each molecule has its own characteristic bond dissociation energy, some generalizations are possible. For example, although the exact value of a C–H bond energy depends on the particular molecule, all C–H bonds have a bond energy of roughly the same value because they are all C–H bonds. It takes roughly 100 kcal of energy to break 1 mol of C–H bonds, so we speak of the bond dissociation energy of a C–H bond as being about 100 kcal/mol. Table 7.2.1 lists the approximate bond dissociation energies of various covalent bonds.

Table 7.2.1: Approximate Bond Dissociation Energies

Bond	Bond Dissociation Energy (kcal/mol)
C–H	100
C–O	86
C=O	190
C–N	70
C–C	85
C=C	145
C≡C	200
N–H	93
H–H	105
Br-Br	46
Cl–Cl	58
O–H	110

Bond	Bond Dissociation Energy (kcal/mol)
O=O	119
H–Br	87
H–Cl	103

When a chemical reaction occurs, the atoms in the reactants rearrange their chemical bonds to make products. The new arrangement of bonds does not have the same total energy as the bonds in the reactants. Therefore, when chemical reactions occur, *there will always be an accompanying energy change*. The energy change, for a given reaction can be calculated using the bond dissociation energy values from Table 7.2.1.

Enthalpy Change or Heat of Reaction, Δ*H*

During a chemical reaction, bonds are broken and new bonds are formed. Breaking chemical bonds is **endothermic**, a process that requires an input of energy or absorption of heat. The reverse process of bond breaking is bond formation, which is **exothermic**, meaning it releases energy or gives off heat. The bond dissociation energy values listed in the above table give the amount of energy required to break a specific bond. When that same bond is reformed, an identical amount of energy is released. The numerical *value* of energy is the same for breaking and forming a bond, but the sign, or *direction* of the process is different. The overall energy change of a specific bond breaking and reforming would be zero, in other words energy is neither created or destroyed, following the law of conservation of energy.

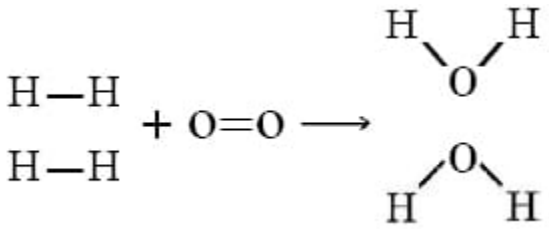
In a chemical reaction, the bonds breaking are often different than the bonds reforming, sometimes there is more heat absorbed (more bonds are broken) and sometimes more heat is released (more bonds are formed). The measured *difference* between the total heat absorbed and the total heat released during a chemical reaction (performed at constant pressure) is called the **heat of reaction** or **enthalpy change**, and is represented by the symbol Δ*H* (where the Δ stands for change and the H represents enthalpy).

$$\text{enthalpy change} \approx \Sigma\ (\text{bond dissociation energies}_{reactants}) - \Sigma\ (\text{bond dissociation energies}_{products}) \tag{7.2.1}$$

The ≈ sign is used because we are adding together *average* bond dissociation energies; hence this approach does not give exact values for the enthalpy change, Δ*H*.

Let's consider the reaction of 2 mols of hydrogen gas (H_2) with 1 mol of oxygen gas (O_2) to give 2 mol water:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \tag{7.2.2}$$



H–H = 105 kcal/mol O=O = 119 kcal/mol O–H = 110 kcal/mol

In this reaction, 2 H–H bonds and 1 O=O bonds from the reactant side are broken, while 4 O–H bonds (two for each H_2O) are formed on the product side. The energy changes can be tabulated and calculated as follows:

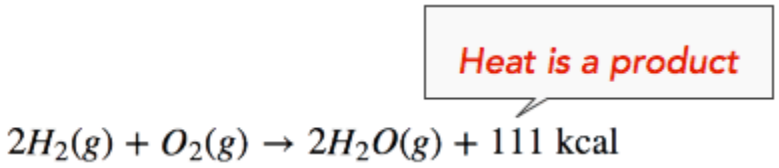
Reactant Bond Dissociation Energy (kcal/mol)		Product Bond Dissociation Energy (kcal/mol)	
2 H–H	2 mol x 105 kcal/mol = 210 kcal	4 O–H	4 mols x 110 kcal/mol = 440 kcal
1 O=O	1 mol x 119 kcal/mol = 119 kcal		
	Total = 329 kcal		**Total** = 440 kcal

$$\Delta H \approx \Sigma \text{ (bond dissociation energies}_{reactants}) - \Sigma \text{ (bond dissociation energies}_{products}) \quad (7.2.3)$$

$$\Delta H \approx 329 \text{ kcal} - 440 \text{ kcal} \quad (7.2.4)$$

$$\Delta H \approx -111 \text{ kcal} \quad (7.2.5)$$

The enthalpy change (ΔH) of the reaction is approximately –111 kcal/mol. This means that bonds in the products (440 kcal) are stronger than the bonds in the reactants (329 kcal) by about 111 kcal/mol. Because the bonds in the products are stronger than those in the reactants, the reaction releases more energy than it absorbs. This excess energy is **released** as heat, so the reaction is **exothermic**. Hence, we can re-write the reaction with the heat released (111 kcal) on the **product side** of the equation, as follows:



We can also re-write the reaction equation with the ΔH information (see below). Note that an **exothermic** reaction has a **negative ΔH** value.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \qquad \Delta H = -111 \text{ kcal} \quad (7.2.6)$$

Example 7.2.1

What is the enthalpy change for this reaction? Is the reaction exothermic or endothermic?

$$H_2(g) + Br_2(g) \rightarrow 2HBr(g) \quad (7.2.7)$$

Solution

Step 1- First look at the equation and identify which bonds exist on in the reactants (bonds broken).

- one H-H bond and
- one Br-Br bond

Step 2- Do the same for the products (bonds formed)

- two H-Br bonds

Step 3- Identify the bond dissociation energies of these bonds from Table 7.2.1:

- H-H bonds: 105 kcal/mol
- Br-Br bonds: 46 kcal/mol

Step 4- Set up the table (see below) and apply the formula for enthalpy change.

Reactant Bond Dissociation Energy (kcal/mol)		**Product Bond Dissociation Energy (kcal/mol)**	
1 H–H	1 mol x 105 kcal/mol = 105 kcal	2 H–*Br*	2 mols x 87 kcal/mol = 174 kcal
1 Br–Br	1 mol x 46 kcal/mol = 46 kcal		
	Total = 151 kcal		**Total** = 174 kcal

$$\Delta H \approx 151 \text{ kcal} - 174 \text{ kcal} \quad (7.2.8)$$

$$\Delta H \approx -23 \text{ kcal} \quad (7.2.9)$$

Step 5- Since ΔH is negative (−23 kcal), the reaction is *exothermic*.

Exercise 7.2.1

Using the bond dissociation energies given in the chart above, find the enthalpy change for the thermal decomposition of water:

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g) \tag{7.2.10}$$

Is the reaction written above exothermic or endothermic? Explain.

Answer available at the end of this section.

Answers

Exercise 7.2.1

ΔH = −43 kcal

Since ΔH is negative (−43 kcal), the reaction is *exothermic*.

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7.3: Exothermic and Endothermic Reactions

Learning Objectives

- Use bond dissociation energies to calculate enthalpy change or heat of reaction.
- Determine if a chemical process is exothermic or endothermic.

Endothermic and Exothermic Reactions

Endothermic and exothermic reactions can be thought of as having energy as either a reactant of the reaction or a product. Endothermic reactions *require* energy, so energy is a reactant. Heat flows from the surroundings to the system (reaction mixture) and the enthalpy of the system increases (ΔH is positive). As discussed in the previous section, heat is released (considered a product) in an exothermic reaction, and the enthalpy of the system decreases (ΔH is negative).

In the course of an endothermic process, the system gains heat from the surroundings and so the temperature of the surroundings decreases (gets cold). A chemical reaction is exothermic if heat is released by the system into the surroundings. Because the surroundings is gaining heat from the system, the temperature of the surroundings increases. See Figure $7.3.1$.

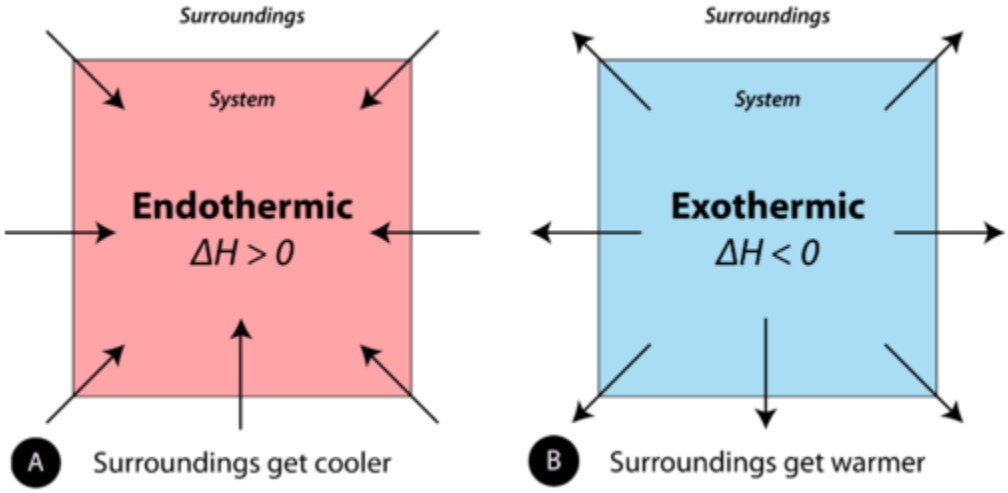
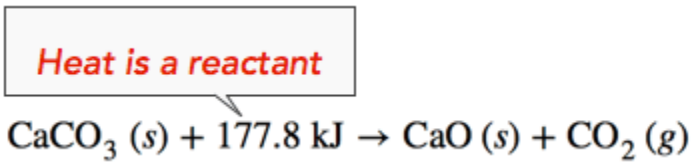


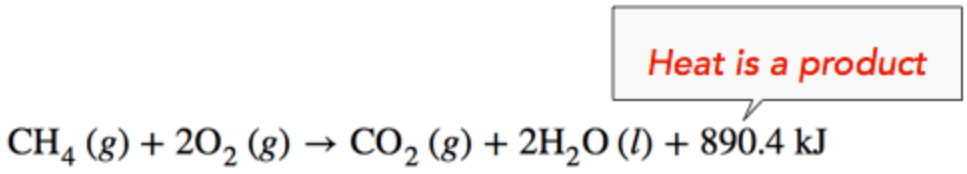
Figure $7.3.1$: (A) Endothermic reaction. (B) Exothermic reaction.

Endothermic Reaction: When $1\ \text{mol}$ of calcium carbonate decomposes into $1\ \text{mol}$ of calcium oxide and $1\ \text{mol}$ of carbon dioxide, $177.8\ \text{kJ}$ of heat is absorbed. Because the heat is absorbed by the system, the $177.8\ \text{kJ}$ is written as a *reactant*. The ΔH is *positive* for an endothermic reaction.



$$\text{CaCO}_3\,(s) \rightarrow \text{CaO}\,(s) + \text{CO}_2\,(g) \quad \Delta H = +177.8\ \text{kJ} \tag{7.3.1}$$

Exothermic Reaction: When methane gas is combusted, heat is released, making the reaction exothermic. Specifically, the combustion of $1\ \text{mol}$ of methane releases 890.4 kilojoules of heat energy. This information can be shown as part of the balanced equation in two ways. First, the amount of heat released can be written in the product side of the reaction. Another way is to write the ΔH information with a *negative* sign, $-890.4\ \text{kJ}$.



$$\mathrm{CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l)} \quad \Delta H = -890.4\ \mathrm{kJ} \tag{7.3.2}$$

Example 7.3.1

Is each chemical reaction exothermic or endothermic?

a. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell) + 213$ kcal
b. $N_2(g) + O_2(g) + 45$ kcal $\rightarrow 2NO(g)$

Solution

a. Because energy (213 kcal) is a product, energy is given off by the reaction. Therefore, this reaction is exothermic.
b. Because energy (45 kcal) is a reactant, energy is absorbed by the reaction. Therefore, this reaction is endothermic.

Exercise 7.3.1

Is each chemical reaction exothermic or endothermic?

a. $H_2(g) + F_2(g) \rightarrow 2HF\,(g) + 130$ kcal
b. $2C(s) + H_2(g) + 5.3$ kcal $\rightarrow C_2H_2(g)$

Answer available at the end of this section.

Energy Diagrams

Endothermic and exothermic reactions can be visually represented by *energy-level diagrams* like the ones in Figure 7.3.2. In endothermic reactions, the reactants have higher bond energy (*stronger bonds*) than the products. Strong bonds have lower potential energy than weak bonds. Hence, the energy of the reactants is lower than that of the products. This type of reaction is represented by an "uphill" energy-level diagram shown in Figure 7.3.2*A*. For an endothermic chemical reaction to proceed, the reactants must absorb energy from their environment to be converted to products.

In an exothermic reaction, the bonds in the product have higher bond energy (stronger bonds) than the reactants. In other words, the energy of the products is lower than the energy of the reactants, hence is energetically downhill, shown in Figure 7.3.2*B*. Energy is given off as reactants are converted to products. The energy given off is usually in the form of heat (although a few reactions give off energy as light). In the course of an exothermic reaction, heat flows from the system to its surroundings, and thus, gets warm.

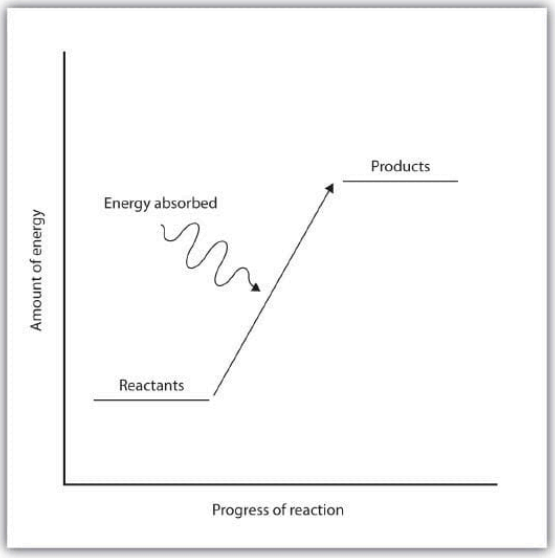


Figure $7.3.2A$: Endothermic Reactions

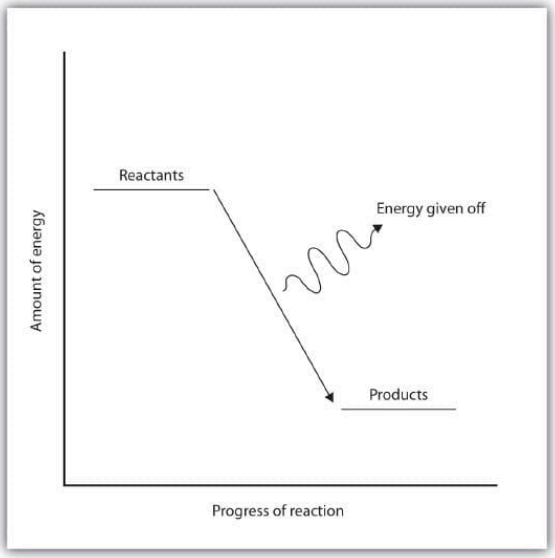


Figure $7.3.2B$: Exothermic Reactions

Table $7.3.1$*: Endothermic and Exothermic Reactions*

Endothermic Reactions	Exothermic Reactions
Heat is absorbed by reactants to form products.	Heat is released.
Heat is absorbed from the surroundings; as a result, the surroundings get cold.	Heat is released by the reaction to surroundings; surroundings feel hot.
ΔH_{rxn} is positive	ΔH_{rxn} is negative
The bonds broken in the reactants are stronger than the bonds formed in the products.	The bonds formed in the products are stronger than the bonds broken in the reactants.
The reactants are lower in energy than the products.	The products are lower in energy than the reactants.
Represented by an "uphill" energy diagram.	Represented by an "downhill" energy diagram

Concept Review Exercises

1. What is the connection between energy and chemical bonds?
2. Why does energy change during the course of a chemical reaction?
3. Two different reactions are performed in two identical test tubes. In reaction A, the test tube becomes very warm as the reaction occurs. In reaction B, the test tube becomes cold. Which reaction is endothermic and which is exothermic? Explain.
4. Classify "burning paper" as endothermic or exothermic processes.

Answers

1. Chemical bonds have a certain energy that is dependent on the elements in the bond and the number of bonds between the atoms.
2. Energy changes because bonds rearrange to make new bonds with different energies.
3. Reaction A is exothermic because heat is leaving the system making the test tube feel hot. Reaction B is endothermic because heat is being absorbed by the system making the test tube feel cold.
4. "Burning paper" is exothermic because burning (also known as combustion) releases heat

Key Takeaways

- Atoms are held together by a certain amount of energy called bond energy.
- Energy is required to break bonds. Energy is released when chemical bonds are formed because atoms become more stable.
- Chemical processes are labeled as exothermic or endothermic based on whether they give off or absorb energy, respectively.

Answers

Exercise 7.3.1

a. The energy (130 kcal) is produced, hence the reaction is exothermic

b. The energy (5.3 kcal) is supplied or absorbed to react, hence, the reaction is endothermic

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7.4: Why Do Chemical Reactions Occur? Free Energy

Learning Outcomes

- Describe the meaning of a spontaneous reaction in terms of enthalpy and entropy changes.
- Define free energy.
- Determine the spontaneity of a reaction based on the value of its change in free energy at high and low temperatures.

Spontaneous Reactions

A **spontaneous reaction** *is a reaction that favors the formation of products at the conditions under which the reaction is occurring*. A roaring bonfire (see Figure 7.4.1 below) is an example of a spontaneous reaction. A fire is *exothermic*, which means a decrease in the energy of the system as energy is released to the surroundings as heat. The products of a fire are composed mostly of gases such as carbon dioxide and water vapor, so the entropy of the system increases during most combustion reactions. This combination of a decrease in energy and an increase in entropy means that combustion reactions occur spontaneously.



Figure 7.4.1: Combustion reactions, such as this fire, are spontaneous reactions. Once the reaction begins, it continues on its own until one of the reactants (fuel or oxygen) is gone.

A **nonspontaneous reaction** *is a reaction that does not favor the formation of products at the given set of conditions*. In order for a reaction to be nonspontaneous, one or both of the driving forces must favor the reactants over the products. In other words, the reaction is endothermic, is accompanied by a decrease in entropy, or both. Out atmosphere is composed primarily of a mixture of nitrogen and oxygen gases. One could write an equation showing these gases undergoing a chemical reaction to form nitrogen monoxide.

$$\mathrm{N_2}\,(g) + \mathrm{O_2}\,(g) \rightarrow 2\mathrm{NO}\,(g) \tag{7.4.1}$$

Fortunately, this reaction is nonspontaneous at normal temperatures and pressures, it is a highly endothermic reaction. However, nitrogen monoxide is capable of being produced at very high temperatures, and this reaction has been observed to occur as a result of lightning strikes.

One must be careful not to confuse the term spontaneous with the notion that a reaction occurs rapidly. A spontaneous reaction is one in which product formation is favored, even if the reaction is extremely slow. You do not have to worry about a piece of paper on your desk suddenly bursting into flames, although its combustion is a spontaneous reaction. What is missing is the required

activation energy to get the reaction started. If the paper were to be heated to a high enough temperature, it would begin to burn, at which point the reaction would proceed spontaneously until completion.

Entropy as a Driving Force

An example of a very simple spontaneous process is that of a melting ice cube. Energy is transferred from the room to the ice cube, causing it to change from the solid to the liquid state.

$$\mathrm{H_2O}\,(s) + 6.01\ \mathrm{kJ} \rightarrow \mathrm{H_2O}\,(l) \tag{7.4.2}$$

The solid state of water, ice, is highly *ordered* because its molecules are fixed in place. The melting process frees the water molecules from their hydrogen-bonded network and allows them a greater degree of movement. Water is more *disordered* than ice. The change from the solid to the liquid state of any substance corresponds to an increase in the disorder of the system.

The tendency in nature for systems to proceed toward a state of greater disorder or randomness is called **entropy**, which is symbolized by S, and expressed in units of Joules per mole-kelvin, $\mathrm{J/(mol \cdot K)}$. Larger values of S indicate that the particles in a substance have more disorder or randomness. In the example above, the particles in the ice cube (solid water) have lower freedom of motion, they are less random. As the ice melts to liquid water, the particles become more disordered and entropy increases. If the liquid water was heated further, the particles would even gain more freedom of motion, become more disordered, and eventually change to a gas, which has even higher entropy.

Chemical reactions also tend to proceed in such a way as to increase the total entropy of the system, measured by the **entropy change (ΔS)** between reactants and products. How can you tell if a certain reaction shows an increase or a decrease in entropy? The states of the reactants and produces provide certain clues. The general cases below illustrate entropy at the molecular level.

1. For a given substance, the entropy of the liquid state is greater than the entropy of the solid state. Likewise, the entropy of the gas is greater than the entropy of the liquid. Therefore, entropy increases in processes in which solid or liquid reactants form gaseous products. Entropy also increases when solid reactants form liquid products.
2. Entropy increases when a substance is broken up into multiple parts. The process of dissolving increases entropy because the solute particles become separated from one another when a solution is formed.
3. Entropy increases as temperature increases. An increase in temperature means that the particles of the substance have greater kinetic energy. The faster moving particles have more disorder than particles that are moving more slowly at a lower temperature.
4. Entropy generally increases in reactions in which the total number of product molecules is greater than the total number of reactant molecules. An exception to this rule is when nongaseous products are formed from gaseous reactants.

The examples below will serve to illustrate how the entropy change in a reaction can be predicted.

$$\mathrm{Cl_2}\,(g) \rightarrow \mathrm{Cl_2}\,(l) \tag{7.4.3}$$

The entropy is decreasing because a gas is becoming a liquid.

$$\mathrm{CaCO_3}\,(s) \rightarrow \mathrm{CaO}\,(s) + \mathrm{CO_2}\,(g) \tag{7.4.4}$$

The entropy is increasing because a gas is being produced, and the number of molecules is increasing.

$$\mathrm{N_2}\,(g) + 3\mathrm{H_2}\,(g) \rightarrow 2\mathrm{NH_3}\,(g) \tag{7.4.5}$$

The entropy is decreasing because four total reactant molecules are forming two total product molecules. All are gases.

$$\mathrm{AgNO_3}\,(aq) + \mathrm{NaCl}\,(aq) \rightarrow \mathrm{NaNO_3}\,(aq) + \mathrm{AgCl}\,(s) \tag{7.4.6}$$

The entropy is decreasing because a solid is formed from aqueous reactants.

$$\mathrm{H_2}\,(g) + \mathrm{Cl_2}\,(g) \rightarrow 2\mathrm{HCl}\,(g) \tag{7.4.7}$$

The entropy change is unknown (but likely not zero) because there are equal numbers of molecules on both sides of the equation, and all are gases.

Gibbs Free Energy

Many chemical reactions and physical processes release energy that can be used to do other things. When the fuel in a car is burned, some of the released energy is used to power the vehicle. **Free energy** *is energy that is available to do work*. Spontaneous reactions release free energy as they proceed. The determining factors for spontaneity of a reaction depend on both the *enthalpy* and *entropy* changes that occur for the system. The **free energy change (ΔG)** of a reaction is a mathematical combination of the enthalpy change and the entropy change.

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \tag{7.4.8}$$

The symbol for free energy is G, in honor of American scientist Josiah Gibbs (1839 - 1903), who made many contributions to thermodynamics. The change in Gibbs free energy is equal to the change in enthalpy minus the mathematical product of the change in entropy multiplied by the Kelvin temperature. Each thermodynamic quantity in the equation is for substances in their standard states, as indicated by the $^{\circ}$ superscripts.

A spontaneous reaction is one that releases free energy, and so the sign of ΔG must be negative. Since both ΔH and ΔS can be either positive or negative, depending on the characteristics of the particular reaction, there are four different possible combinations. The outcomes for ΔG based on the signs of ΔH and ΔS are outlined in the table below. Recall that $-\Delta \mathrm{H}$ indicates that the reaction is exothermic and a $+\Delta \mathrm{H}$ means the reaction is endothermic. For entropy, $+\Delta \mathrm{S}$ means the entropy is increasing and the system is becoming more disordered. A $-\Delta \mathrm{S}$ means that entropy is decreasing and the system is becoming less disordered (more ordered).

> A process that releases free energy, ($-\Delta G$), is said to be ***exergonic***. Processes that require free energy ($+\Delta G$), are ***endergonic***. These terms are used when considering chemical reactions that occur in living systems.

Table 7.4.1: Enthalpy, Entropy, and Free Energy Changes.

ΔH	ΔS	ΔG
negative	positive	always negative
positive	positive	negative at higher temperatures, positive at lower temperatures
negative	negative	negative at lower temperatures, positive at higher temperatures
positive	negative	always positive

Keep in mind that the temperature in the Gibbs free energy equation is the Kelvin temperature, so it can only have a positive value. When ΔH is negative and ΔS is positive, the sign of ΔG will always be negative, and the reaction will be spontaneous at all temperatures. This corresponds to both driving forces being in favor of product formation. When ΔH is positive and ΔS is negative, the sign of ΔG will always be positive, and the reaction can never be spontaneous. This corresponds to both driving forces working against product formation.

When one driving force favors the reaction, but the other does not, it is the temperature that determines the sign of ΔG. Consider first an endothermic reaction (positive ΔH) that also displays an increase in entropy (positive ΔS). It is the entropy term that favors the reaction. Therefore, as the temperature increases, the $T\Delta S$ term in the Gibbs free energy equation will begin to predominate and ΔG will become negative. A common example of a process which falls into this category is the melting of ice (see figure below). At a relatively low temperature (below $273\ \mathrm{K}$), the melting is not spontaneous because the positive ΔH term "outweighs" the $T\Delta S$ term. When the temperature rises above $273\ \mathrm{K}$, the process becomes spontaneous because the larger T value has tipped the sign of ΔG over to being negative.



Figure 7.4.2: Ice melts spontaneously only when the temperature is above $0^{\circ}\mathrm{C}$. The increase in entropy is then able to drive the unfavorable endothermic process.

When the reaction is exothermic (negative ΔH) but undergoes a decrease in entropy (negative ΔS), it is the enthalpy term which favors the reaction. In this case, a spontaneous reaction is dependent upon the $T\Delta S$ term being small relative to the ΔH term, so that ΔG is negative. The freezing of water is an example of this type of process. It is spontaneous only at a relatively low temperature. Above $273.\ \mathrm{K}$, the larger $T\Delta S$ value causes the sign of ΔG to be positive, and freezing does not occur.

Contributors and Attributions

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7.5: How Do Chemical Reactions Occur? Reaction Rates

Learning Outcomes

- Define reaction rate.
- Explain the concept of activation energy.
- Label a diagram with reactants, products, enthalpy of forward and reverse reactions, activation energy of forward and reverse reactions, and activated complex.

Chemical kinetics is the study of the rates of chemical reactions. In this lesson, you will learn how to express the rate of a chemical reaction and about various factors that influence reaction rates.

Expressing Reaction Rate

Chemical reactions vary widely in the speeds with which they occur. Some reactions occur very quickly. It a lighted match is brought into contact with lighter fluid or another flammable liquid, it erupts into flame instantly and burns fast. Other reactions occur very slowly. A container of milk in the refrigerator will be good to drink for weeks before it begins to turn sour. Millions of years were required for dead plants under Earth's surface to accumulate and eventually turn into fossil fuels such as coal and oil.

Chemists need to be concerned with the rates at which chemical reactions occur. Rate is another word for speed. If a sprinter takes 11.0 seconds (s) to run a 100 meter (\left(m \right)\) dash, his rate or speed is given by the distance traveled divided by the time (see figure below).

$$\text{speed} = \frac{\text{distance}}{\text{time}} = \frac{100\ \text{m}}{11.0\ \text{s}} = 9.09\ \text{m/s} \tag{7.5.1}$$

The sprinter's average running rate for the race is $9.09\ \text{m/s}$. We say that it is his average rate because he did not run at that speed for the entire race. At the very beginning of the race, while coming from a standstill, his rate must be slower until he is able to get up to his top speed. His top speed must the be greater than $9.09\ \text{m/s}$ so that taken over the entire race, the average ends up at $9.09\ \text{m/s}$.



Figure $7.5.1$: Usain Bolt set the world record for the 100 meter dash in 2009 with a time of 9.58 seconds. His average running rate over the course of this race was $10.4\ \text{m/s}$, or $23.4\ \text{mph}$.

Chemical reactions can't be measured in units of meters per second, as that would not make any sense. A **reaction rate** *is the*

change in concentration of a reactant or product with time. Suppose that a simple reaction were to take place in which a 1.00 molar (M) aqueous solution of substance A was converted to substance B.

$$\mathrm{A}\,(aq) \rightarrow \mathrm{B}\,(aq) \tag{7.5.2}$$

Suppose that after 20.0 seconds, the concentration of A had dropped from $1.00\ \mathrm{M}$ to $0.72\ \mathrm{M}$ as it was being converted to substance B. We can express the rate of this reaction as the change in concentration of A divided by the time.

$$\text{rate} = -\frac{\Delta\,[\mathrm{A}]}{\Delta t} = -\frac{[\mathrm{A}]_{\text{final}} - [\mathrm{A}]_{\text{initial}}}{\Delta t} \tag{7.5.3}$$

A bracket around a symbol or formula means the concentration in molarity of that substance. The change in concentration of A is its final concentration minus its initial concentration. Because the concentration of A is decreasing over time, the negative sign is used. Thus, the rate for the reaction is positive, and the units are molarity per second or $\mathrm{M/s}$.

$$\text{rate} = -\frac{0.72\ \mathrm{M} - 1.00\ \mathrm{M}}{20.0\ \mathrm{s}} = -\frac{-0.28\ \mathrm{M}}{20.0\ \mathrm{s}} = 0.041\ \mathrm{M/s} \tag{7.5.4}$$

Over the first 20.0 seconds of this reaction, the molarity of A decreases by an average rate of $0.041\ \mathrm{M}$ every second. In summary, the rate of a chemical reaction is measured by the change in concentration over time for a reactant or product. The unit of measurement for a reaction rate is molarity per second $(\mathrm{M/s})$.

Collision Theory

The behavior of the reactant atoms, molecules, or ions is responsible for the rates of a given chemical reaction. **Collision theory** *is a set of principles based around the idea that reactant particles form products when they collide with one another, but only when those collisions have enough kinetic energy and the correct orientation to cause a reaction*. Particles that lack the necessary kinetic energy may collide, but the particles will simply bounce off one another unchanged. The figure below illustrates the difference. In the first collision, the particles bounce off one another, and no rearrangement of atoms has occurred. The second collision occurs with greater kinetic energy, and so the bond between the two red atoms breaks. One red atom bonds with the other molecule as one product, while the single red atom is the other produce. The first collision is called an ineffective collision, while the second collision is called an effective collision.

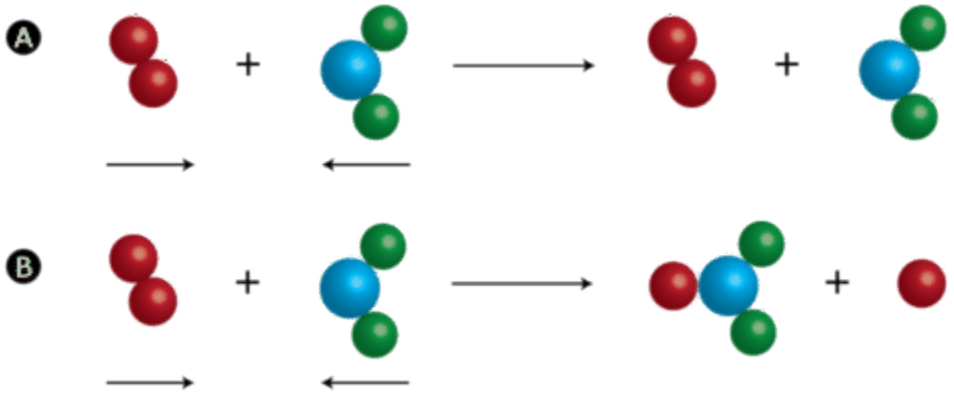


Figure 7.5.2: (A) An ineffective collision is one that does not result in product formation. (B) An effective collision is one in which chemical bonds are broken, and a product is formed.

Supplying reactant particles with energy causes the bonds between the atoms to vibrate with a greater frequency. This increase in vibrational energy makes a chemical bond more likely to break and a chemical reaction more likely to occur when those particles collide with other particles. Additionally, more energetic particles have more forceful collisions, which also increases the likelihood that a rearrangement of atoms will take place. The **activation energy** *for a reaction is the minimum energy that colliding particles must have in order to undergo a reaction*. Some reactions occur readily at room temperature because most of the reacting particles already have the requisite activation energy at that temperature. Other reactions only occur when heated because the particles do not have enough energy to react unless more is provided by an external source of heat.

Potential Energy Diagrams

Then energy changes that occur during a chemical reaction can be shown in a diagram called a potential energy diagram, sometimes called a reaction progress curve. A **potential energy diagram** *shows the change in the potential energy of a system as reactants are converted into products*. The figure below shows basic potential energy diagrams for an endothermic (left) and an exothermic (right) reaction. Recall that the enthalpy change (ΔH) is positive for an endothermic reaction and negative for an exothermic reaction. This can be seen in the potential energy diagrams. The total potential energy of the system increases for the endothermic reaction as the system absorbs energy from the surroundings. The total potential energy of the system decreases for the exothermic reaction as the system releases energy to the surroundings.

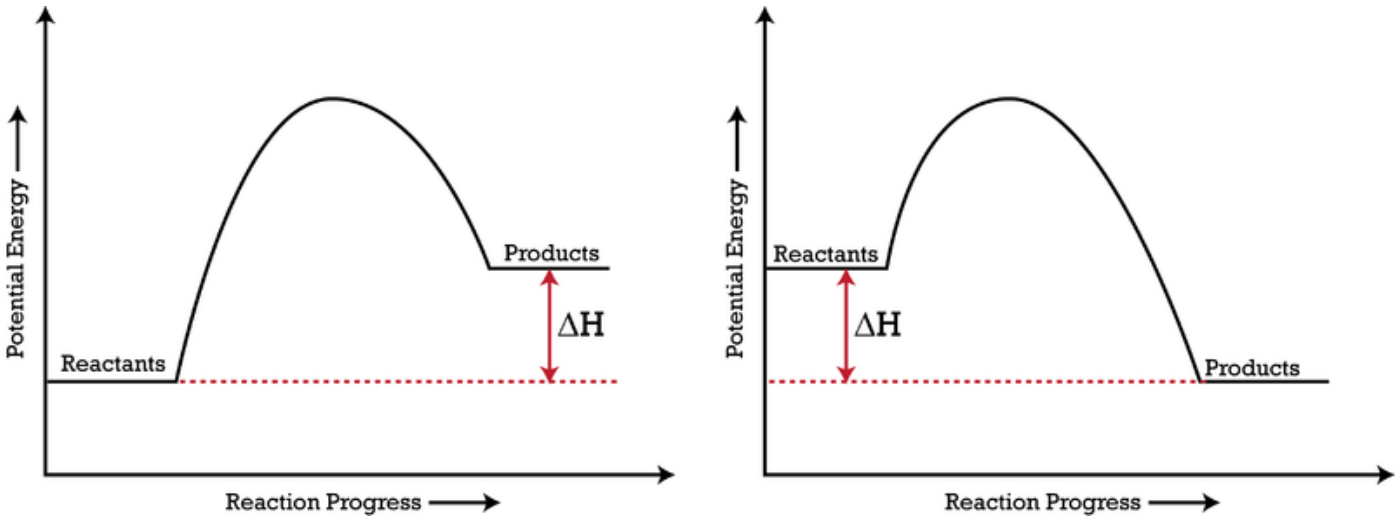


Figure 7.5.3: A potential energy diagram shows the total potential energy of a reacting system as the reaction proceeds. (Left) In an endothermic reaction, the energy of the products is greater than the energy of the reactants, and ΔH is positive. (Right) In an exothermic reaction, the energy of the products is lower than the energy of the reactants, and ΔH is negative.

The activation energy for a reaction is illustrated in the potential energy diagram by the height of the hill between the reactants and the products. For this reason, the activation energy of a reaction is sometimes referred to as the activation energy barrier. Reacting particles must have enough energy so that when they collide, they can overcome this barrier (see figure below).

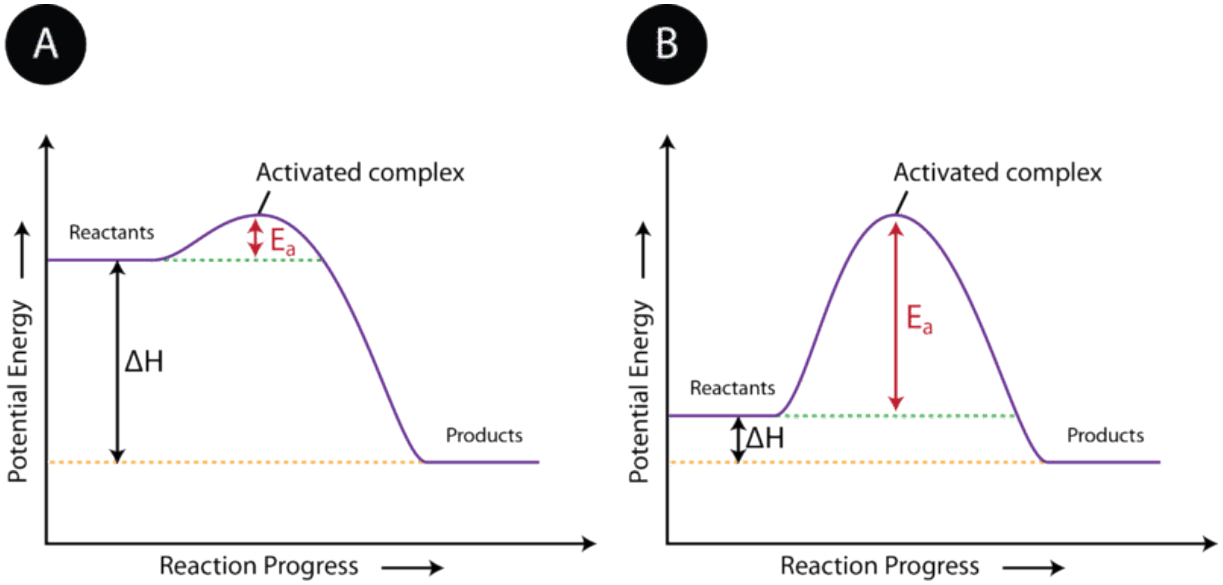


Figure 7.5.4: The activation energy (E_a) of a reaction is the barrier that must be overcome in order for the reactants to become products. (A) The activation energy is low, meaning that the reaction is likely to be fast. (B) The activation energy is high, meaning that the reaction is likely to be slow.

As discussed earlier, reactant particles sometimes collide with one another and yet remain unchanged by the collision. Other

times, the collision leads to the formation of products. The state of the particles that is in between the reactants and products is called the activated complex. An **activated complex** *is an unstable arrangement of atoms that exists momentarily at the peak of the activation energy barrier*. Because of its high energy, the activated complex exists only for an extremely short period of time (about 10^{-13} s). The activated complex is equally likely to either reform the original reactants or go on to form the products. The figure below shows the formation of a possible activated complex between colliding hydrogen and oxygen molecules. Because of their unstable nature and brief existence, very little is known about the exact structures of most activated complexes.

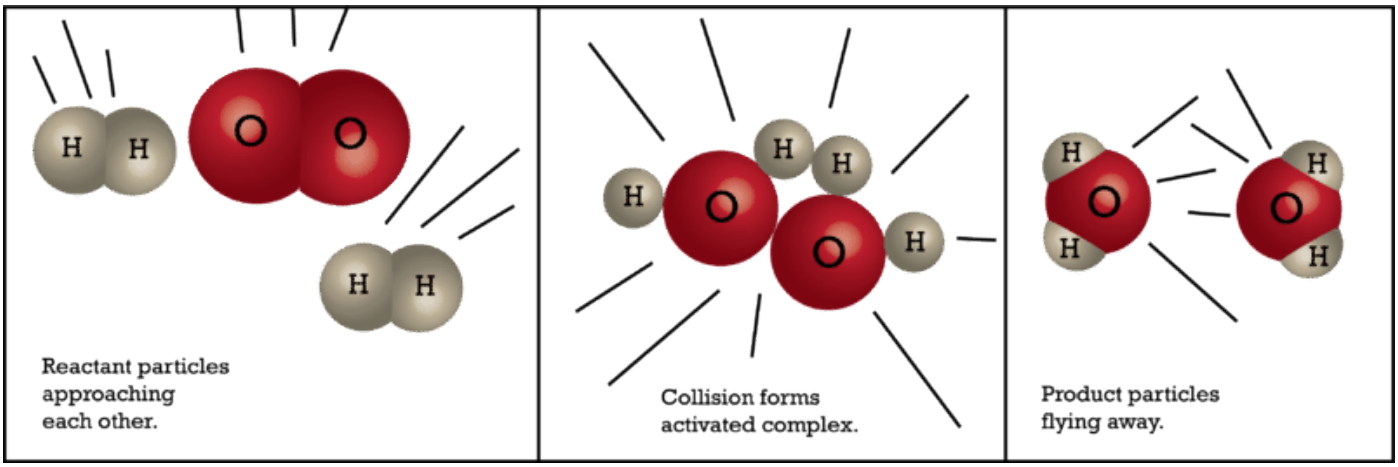


Figure 7.5.5: An activated complex is a short-lived state in which the colliding particles are at the peak of the potential energy curve.

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7.6: Effects of Temperature, Concentration, and Catalysts on Reaction Rates

Learning Outcomes

- Describe how temperatures, concentration of reactant, and a catalyst affect the reaction rate.

By their nature, some reactions occur very quickly, while others are very slow. However, certain changes in the reaction conditions can have an effect on the rate of a given chemical reaction. Collision theory can be utilized to explain these rate effects.

Concentration

Increasing the concentration of one or more of the reacting substances generally increases the reaction rate. When more particles are present in a given amount of space, a greater number of collisions will naturally occur between those particles. Since the rate of a reaction is dependent on the frequency of collisions between the reactants, the rate increases as the concentration increases.

Temperature

Raising the temperature of a chemical reaction results in a higher reaction rate. When the reactant particles are heated, they move faster and faster, resulting in a greater frequency of collisions. An even more important effect of the temperature increase is that the collisions occur with a greater force, which means the reactants are more likely to surmount the activation energy barrier and go on to form products. Increasing the temperature of a reaction increases not only the frequency of collisions, but also the percentage of those collisions that are effective, resulting in an increased reaction rate.

Paper is certainly a highly combustible material, but paper does not burn at room temperature because the activation energy for the reaction is too high. The vast majority of collisions between oxygen molecules and the paper are ineffective. However, when the paper is heated by the flame from a match, it reaches a point where the molecules now have enough energy to react. The reaction is very exothermic, so the heat released by the initial reaction will provide enough energy to allow the reaction to continue, even if the match is removed. The paper continues to burn rapidly until it is gone.

Catalysts

The rates of some chemical reactions can be increased dramatically by introducing certain other substances into the reaction mixture. Hydrogen peroxide is used as a disinfectant for scrapes and cuts, and it can be found in many medicine cabinets as a 3% aqueous solution. Hydrogen peroxide naturally decomposes to produce water and oxygen gas, but the reaction is very slow. A bottle of hydrogen peroxide will last for several years before it needs to be replaced. However, the addition of just a small amount of manganese (IV) oxide to hydrogen peroxide will cause it to decompose completely in just a matter of minutes. A **catalyst** *is a substance that increases the rate of a chemical reaction without being used up in the reaction.* It accomplishes this task by providing an alternate reaction pathway that has a lower activation energy barrier. After the reaction occurs, a catalyst returns to its original state, so catalysts can be used over and over again. Because it is neither a reactant nor a product, a catalyst is shown in a chemical equation by being written above the yield arrow.

$$2\mathrm{H_2O_2}\,(aq) \overset{\mathrm{MnO_2}}{\rightarrow} 2\mathrm{H_2O}\,(l) + \mathrm{O_2}\,(g) \tag{7.6.1}$$

A catalyst works by changing the mechanism of the reaction, which can be though of as the specific set of smaller steps by which the reactants become products. The important point is that the use of a catalyst lowers the overall activation energy of the reaction (see figure below). With a lower activation energy barrier, a greater percentage of reactant molecules are able to have effective collisions, and the reaction rate increases.

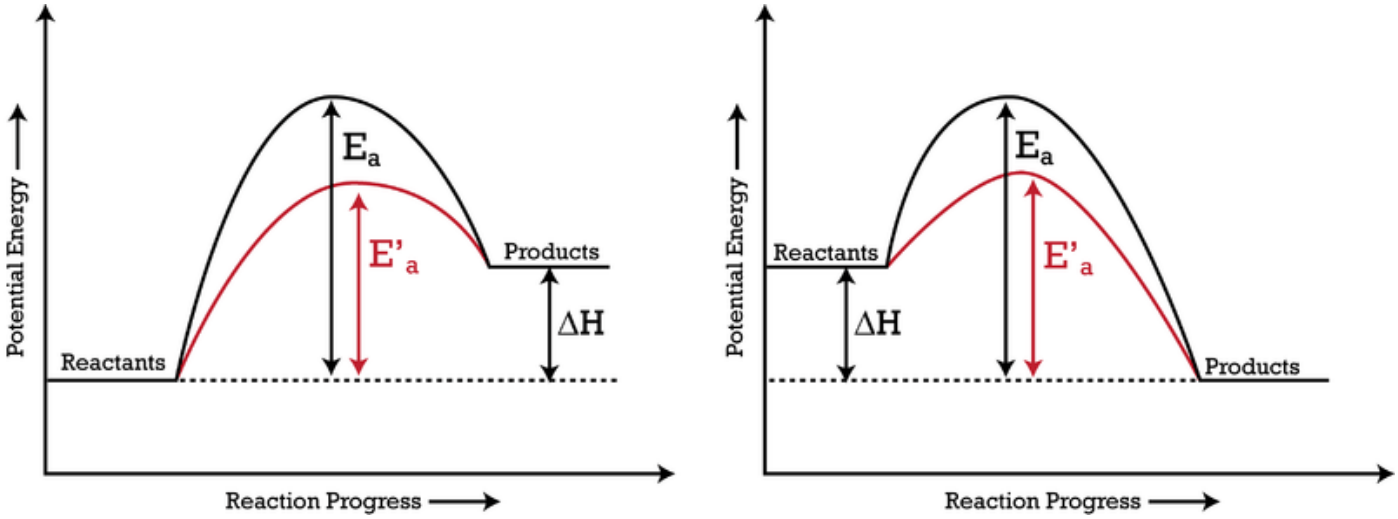


Figure 7.6.7: The addition of a catalyst to a reaction lowers the activation energy, increasing the rate of the reaction. The activation energy of the uncatalyzed reaction is shown by E_a, while the catalyzed reaction is shown by E'_a. The heat of reaction (ΔH) is unchanged by the presence of the catalyst.

Catalysts are extremely important parts of many chemical reactions. Enzymes in your body act as nature's catalysts, allowing important biochemical reactions to occur at reasonable rates. Chemical companies constantly search for new and better catalysts to make reactions go faster and thus make the company more profitable.

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7.7: Reversible Reactions and Chemical Equilibrium

Learning Objectives

- Define chemical equilibrium.
- Recognize chemical equilibrium as a dynamic process.

Consider the following reaction occurring in a closed container (so that no material can go in or out):

$$H2 + I2 \rightarrow 2HI$$

This is simply the reaction between elemental hydrogen and elemental iodine to make hydrogen iodide. The way the equation is written, we are led to believe that the reaction goes to completion, that all the H2 and the I2 react to make HI.

However, this is not the case because it is a **reversible reaction**, meaning it can go in either direction. As soon as there is enough product formed, the HI can react and the reverse chemical reaction occurs essentially "undoing" the first reaction:

$$2HI \rightarrow H2 + I2$$

Eventually, the reverse reaction proceeds so quickly that it matches the speed of the forward reaction. When that happens, the concentration of the reactants and products remains constant, there is no further change; the reaction has reached **chemical equilibrium** (sometimes just spoken as *equilibrium*; plural *equilibria*), the point at which the forward and reverse processes balance each other's progress.

Because two opposing processes are occurring at once, it is conventional to represent an equilibrium using a double arrow, like this:

$$H_2 + I_2 \rightleftharpoons 2HI$$

The double arrow implies that the reaction is going in both directions. Note that the reaction must still be balanced.

Example 7.7.1

Write the equilibrium equation that exists between calcium carbonate as a reactant and calcium oxide and carbon dioxide as products.

Solution

As this is an equilibrium situation, a double arrow is used. The equilibrium equation is written as follows:

$$CaCO_3 + \rightleftharpoons CaO + CO_2$$

Exercise 7.7.1

Write the equilibrium equation between elemental hydrogen and elemental oxygen as reactants and water as the product.

Answer available at the end of this section.

One thing to note about equilibrium is that the reactions do not stop; both the forward reaction and the reverse reaction continue to occur. They both occur at the same rate, so any overall change by one reaction is canceled by the reverse reaction. We say that chemical equilibrium is *dynamic*, rather than static. Also, because both reactions are occurring simultaneously, the equilibrium can be written backward. For example, representing an equilibrium as

$$H_2 + I_2 \rightleftharpoons 2HI$$

is the same thing as representing the same equilibrium as

$$2HI \rightleftharpoons H_2 + I_2$$

The reaction must be at equilibrium for this to be the case, however.

Key Takeaways

- Chemical reactions eventually reach equilibrium, a point at which forward and reverse reactions balance each other's progress.
- Chemical equilibria are dynamic: the chemical reactions are always occurring; they just cancel each other's progress.

Answers

Exercise 7.7.1

$$2H_2 + O_2 + \rightleftharpoons 2H_2O$$

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7.8: Equilibrium Equations and Equilibrium Constants

Learning Objectives

- Define the equilibrium constant.
- Construct an equilibrium constant expression for a chemical reaction.

In the mid 1860s, Norwegian scientists C. M. Guldberg and P. Waage noted a peculiar relationship between the amounts of reactants and products in an equilibrium. No matter how many reactants they started with, a certain ratio of reactants and products was achieved at equilibrium. Today, we call this observation the **law of mass action**. It relates the amounts of reactants and products at equilibrium for a chemical reaction. For a general chemical reaction occurring in solution,

$$aA + bB \rightleftharpoons cC + dD$$

the **equilibrium constant**, also known as K_{eq}, is defined by the following expression:

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

where [A] is the molar concentration of species A at equilibrium, and so forth. The coefficients *a*, *b*, *c*, and *d* in the chemical equation become exponents in the expression for K_{eq}. The K_{eq} is a characteristic numerical value for a given reaction at a given temperature; that is, each chemical reaction has its own characteristic K_{eq}. The concentration of each reactant and product in a chemical reaction at equilibrium is *related*; the concentrations cannot be random values, but they depend on each other. The numerator of the expression for K_{eq} has the concentrations of every product (however many products there are), while the denominator of the expression for K_{eq} has the concentrations of every reactant, leading to the common *products over reactants* definition for the K_{eq}.

Let us consider a simple example. Suppose we have this equilibrium:

$$A \rightleftharpoons B$$

There is one reactant, one product, and the coefficients on each are just 1 (assumed, not written). The K_{eq} expression for this equilibrium is

$$K_{eq} = \frac{[B]}{[A]}$$

(Exponents of 1 on each concentration are understood.) Suppose the numerical value of K_{eq} for this chemical reaction is 2.0. If [B] = 4.0 M, then [A] must equal 2.0 M so that the value of the fraction equals 2.0:

$$K_{eq} = \frac{[B]}{[A]} = \frac{4.0}{2.0} = 2.0$$

By convention, the units are understood to be M and are omitted from the K_{eq} expression. Suppose [B] were 6.0 M. For the K_{eq} value to remain constant (it is, after all, called the equilibrium *constant*), then [A] would have to be 3.0 M at equilibrium:

$$K_{eq} = \frac{[B]}{[A]} = \frac{6.0}{3.0} = 2.0$$

If [A] were *not* equal to 3.0 M, the reaction would not be at equilibrium, and a net reaction would occur until that ratio was indeed 2.0. At that point, the reaction is at equilibrium, and any net change would cease. (Recall, however, that the forward and reverse reactions do not stop because chemical equilibrium is dynamic.)

The issue is the same with more complex expressions for the K_{eq}; only the mathematics become more complex. Generally speaking, given a value for the K_{eq} and all but one concentration at equilibrium, the missing concentration can be calculated.

Example 7.8.1

Given the following reaction:

$$\mathrm{H_2 + I_2 \rightleftharpoons 2\,HI} \tag{7.8.1}$$

If the equilibrium [HI] is 0.75 M and the equilibrium [H2] is 0.20 M, what is the equilibrium [I2] if the K_{eq} is 0.40?

Solution

We start by writing the K_{eq} expression. Using the *products over reactants* approach, the K_{eq} expression is as follows:

$$K_{eq} = \frac{[HI]^2}{[H_2][I_2]}$$

Note that [HI] is squared because of the coefficient 2 in the balanced chemical equation. Substituting for the equilibrium [H2] and [HI] and for the given value of K_{eq}:

$$0.40 = \frac{(0.75)^2}{(0.20)[I_2]}$$

To solve for [I2], we have to do some algebraic rearrangement: divide the 0.40 into both sides of the equation and multiply both sides of the equation by [I2]. This brings [I2] into the numerator of the left side and the 0.40 into the denominator of the right side:

$$[I_2] = \frac{(0.75)^2}{(0.20)(0.40)}$$

Solving,

[I2] = 7.0 M

The concentration unit is assumed to be molarity. This value for [I2] can be easily verified by substituting 0.75, 0.20, and 7.0 into the expression for K_{eq} and evaluating: you should get 0.40, the numerical value of K_{eq} (and you do).

Exercise 7.8.1

Given the following reaction:

$$\mathrm{H_2 + I_2 \rightleftharpoons 2\,HI} \tag{7.8.2}$$

If the equilibrium [HI] is 0.060 M and the equilibrium [I2] is 0.90 M, what is the equilibrium [H2] if the K_{eq} is 0.40?

Answer available at the end of this section.

In some types of equilibrium problems, square roots, cube roots, or even higher roots need to be analyzed to determine a final answer. Make sure you know how to perform such operations on your calculator; if you do not know, ask your instructor for assistance.

Example 7.8.2

The following reaction is at equilibrium:

$$\mathrm{N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3} \tag{7.8.3}$$

The K_{eq} at a particular temperature is 13.7. If the equilibrium [N_2] is 1.88 M and the equilibrium [NH_3] is 6.62 M, what is the equilibrium [H_2]?

Solution

We start by writing the K_{eq} expression from the balanced chemical equation:

$$K_{eq} = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

Substituting for the known equilibrium concentrations and the K_{eq}, this becomes

$$13.7 = \frac{(6.62)^2}{(1.88)[H_2]^3}$$

Rearranging algebraically and then evaluating the numerical expression, we get

$$[H_2]^3 = \frac{(6.62)^2}{(1.88)(13.7)} = 1.7015219754$$

To solve for [H_2], we need to take the cube root of the equation. Performing this operation, we get

[H_2] = 1.19 M

You should verify that this is correct using your own calculator to confirm that you know how to do a cube root correctly.

Exercise 7.8.2

The following reaction is at equilibrium:

$$\mathrm{N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3} \tag{7.8.4}$$

The K_{eq} at a particular temperature is 13.7. If the equilibrium [N_2] is 0.055 M and the equilibrium [H_2] is 1.62 M, what is the equilibrium [NH_3]?

Answer available at the end of this section.

The K_{eq} was defined earlier in terms of concentrations. For gas-phase reactions, the K_{eq} can also be defined in terms of the partial pressures of the reactants and products, P_i. For the gas-phase reaction

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

the pressure-based equilibrium constant, K_P, is defined as follows:

$$K_P = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

where P_A is the partial pressure of substance A at equilibrium in atmospheres, and so forth. As with the concentration-based equilibrium constant, the units are omitted when substituting into the expression for K_P.

Example 7.8.3

What is the K_P for this reaction, given the equilibrium partial pressures of 0.664 atm for NO_2 and 1.09 for N_2O_4?

$$\mathrm{2\,NO_2\,(g) \rightleftharpoons N_2O_4\,(g)} \tag{7.8.5}$$

Solution

Write the K_P expression for this reaction:

$$K_P = \frac{P_{N_2O_4}}{P_{NO_2}^2}$$

Then substitute the equilibrium partial pressures into the expression and evaluate:

$$K_P = \frac{(1.09)}{(0.664)^2} = 2.47$$

Exercise 7.8.3

What is the K_P for this reaction, given the equilibrium partial pressures of 0.44 atm for H_2, 0.22 atm for Cl_2, and 2.98 atm for HCl?

$$\mathrm{H_2 + Cl_2 \rightleftharpoons 2\,HCl} \tag{7.8.6}$$

Answer available at the end of this section.

There is a simple relationship between K_{eq} (based on concentration units) and K_P (based on pressure units):

$$K_P = K_{eq} \cdot (RT)^{\Delta n}$$

where R is the ideal gas law constant (in units of L·atm/mol·K), T is the absolute temperature, and Δn is the change in the number of moles of gas in the balanced chemical equation, defined as $n_{gas,prods} - n_{gas,rcts}$. Note that this equation implies that if the number of moles of gas are the same in reactants and products, $K_{eq} = K_P$.

Example 7.8.4

What is the K_P at 25°C for this reaction if the K_{eq} is 4.2×10^{-2}?

$$\mathrm{N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3} \tag{7.8.7}$$

Solution

Before we use the relevant equation, we need to do two things: convert the temperature to kelvins and determine Δn. Converting the temperature is easy:

$T = 25 + 273 = 298$ K

To determine the change in the number of moles of gas, take the number of moles of gaseous products and subtract the number of moles of gaseous reactants. There are 2 mol of gas as product and 4 mol of gas of reactant:

$\Delta n = 2 - 4 = -2$ mol

Note that Δn is negative. Now we can substitute into our equation, using $R = 0.08205$ L·atm/mol·K. The units are omitted for clarity:

$K_P = (4.2 \times 10^{-2})(0.08205)(298)^{-2}$

Solving,

$K_P = 7.0 \times 10^{-5}$

Exercise 7.8.4

What is the K_P at 25°C for this reaction if the K_{eq} is 98.3?,-

$$\mathrm{I_2\,(g) \rightleftharpoons 2\,I\,(g)} \tag{7.8.8}$$

Answer available at the end of this section.

Finally, we recognize that many chemical reactions involve substances in the solid or liquid phases. For example, a particular chemical reaction is represented as follows:

$$\mathrm{2\,NaHCO_3\,(s) \rightleftharpoons Na_2CO_3\,(s) + CO_2\,(g) + H_2O\,(l)} \tag{7.8.9}$$

This chemical equation includes all three phases of matter. This kind of equilibrium is called a **heterogeneous equilibrium** because there is more than one phase present.

The rule for heterogeneous equilibria is as follows: *Do not include the concentrations of pure solids and pure liquids in* K_{eq} *expressions*. Only partial pressures for gas-phase substances or concentrations in solutions are included in the expressions of equilibrium constants. As such, the equilibrium constant expression for this reaction would simply be

$$K_P = P_{CO_2}$$

because the two solids and one liquid would not appear in the expression.

Key Takeaways

- Every chemical equilibrium can be characterized by an equilibrium constant, known as K_{eq}.
- The K_{eq} and K_P expressions are formulated as amounts of products divided by amounts of reactants; each amount (either a concentration or a pressure) is raised to the power of its coefficient in the balanced chemical equation.
- Solids and liquids do not appear in the expression for the equilibrium constant.

Answers

Exercise 7.8.1
0.010 M

Exercise 7.8.2
1.79 M

Exercise 7.8.3
91.7

.Exercise 7.8.4
2.40×10^3

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7.9: Le Chatelier's Principle- The Effect of Changing Conditions on Equilibria

Learning Objectives

- Define *Le Chatelier's principle*.
- Predict the direction of shift for an equilibrium under stress.

Once equilibrium is established, the reaction is over, right? Not exactly. An experimenter has some ability to affect the equilibrium.

Chemical equilibria can be shifted by changing the conditions that the system experiences. We say that we "stress" the equilibrium. When we stress the equilibrium, the chemical reaction is no longer at equilibrium, and the reaction starts to move back toward equilibrium in such a way as to decrease the stress. The formal statement is called **Le Chatelier's principle**: If an equilibrium is stressed, then the reaction shifts to reduce the stress.

Effect of Changes in Concentration

There are several ways to stress an equilibrium. One way is to add or remove a product or a reactant in a chemical reaction at equilibrium. When additional reactant is added, the equilibrium shifts to reduce this stress: it makes more product. When additional product is added, the equilibrium shifts to reactants to reduce the stress. If reactant or product is removed, the equilibrium shifts to make more reactant or product, respectively, to make up for the loss.

Example 7.9.1

Given this reaction at equilibrium:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

In which direction—toward reactants or toward products-—does the reaction shift if the equilibrium is stressed by each change?

1. H_2 is added.
2. NH_3 is added.
3. NH_3 is removed.

Solution

1. If H_2 is added, there is now more reactant, so the reaction will shift toward products to reduce the added H_2.
2. If NH_3 is added, there is now more product, so the reaction will shift toward reactants to reduce the added NH_3.
3. If NH_3 is removed, there is now less product, so the reaction will shift toward products to replace the product removed.

Exercise 7.9.1

Given this reaction at equilibrium:

$$CO(g) + Br_2(g) \rightleftharpoons COBr_2(g)$$

In which direction—toward reactants or toward products—does the reaction shift if the equilibrium is stressed by each change?

1. Br_2 is removed.
2. $COBr_2$ is added.

Answers

1. toward reactants
2. toward reactants

It is worth noting that when reactants or products are added or removed, *the value of the* K_{eq} *does not change*. The chemical reaction simply shifts, in a predictable fashion, to reestablish concentrations so that the K_{eq} expression reverts to the correct value.

Effect of Changes in Pressure and Temperature

How does an equilibrium react to a change in *pressure*? Pressure changes do not markedly affect the solid or liquid phases. However, pressure strongly impacts the gas phase. Le Chatelier's principle implies that a pressure increase shifts an equilibrium to the side of the reaction with the fewer number of moles of gas, while a pressure decrease shifts an equilibrium to the side of the reaction with the greater number of moles of gas. If the number of moles of gas is the same on both sides of the reaction, pressure has no effect.

Example 7.9.2

What is the effect on this equilibrium if pressure is increased?

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Solution

According to Le Chatelier's principle, if pressure is increased, then the equilibrium shifts to the side with the fewer number of moles of gas. This particular reaction shows a total of 4 mol of gas as reactants and 2 mol of gas as products, so the reaction shifts toward the products side.

Exercise 7.9.2

What is the effect on this equilibrium if pressure is decreased?

$$3O_2(g) \rightleftharpoons 2O_3(g)$$

Answer available at the end of this section.

What is the effect of *temperature* changes on an equilibrium? It depends on whether the reaction is endothermic or exothermic. Recall that *endothermic* means that energy is absorbed by a chemical reaction, while *exothermic* means that energy is given off by the reaction. As such, energy can be thought of as a reactant or a product, respectively, of a reaction:

endothermic reaction: energy + reactants → products

exothermic reaction: reactants → products + energy

Because temperature is a measure of the energy of the system, increasing temperature can be thought of as adding energy. The reaction will react as if a reactant or a product is being added and will act accordingly by shifting to the other side. For example, if the temperature is increased for an endothermic reaction, essentially a reactant is being added, so the equilibrium shifts toward products. Decreasing the temperature is equivalent to decreasing a reactant (for endothermic reactions) or a product (for

exothermic reactions), and the equilibrium shifts accordingly.

Example 7.9.3

Predict the effect of increasing the temperature on this equilibrium.

$$PCl_3 + Cl_2 \rightleftharpoons PCl_5 + 60kJ$$

Solution

Because energy is listed as a product, it is being produced, so the reaction is exothermic. If the temperature is increasing, a product is being added to the equilibrium, so the equilibrium shifts to minimize the addition of extra product: it shifts back toward reactants.

Exercise 7.9.3

Predict the effect of decreasing the temperature on this equilibrium.

$$N_2O_4 + 57kJ \rightleftharpoons 2NO_2$$

Answer available at the end of this section.

In the case of temperature, the value of the equilibrium has changed because the K_{eq} is dependent on temperature. That is why equilibria shift with changes in temperature.

A **catalyst** is a substance that increases the speed of a reaction. Overall, a catalyst is not a reactant and is not used up, but it still affects how fast a reaction proceeds. However, a catalyst does not affect the extent or position of a reaction at equilibrium. It helps a reaction achieve equilibrium faster.

Chemistry is Everywhere: Equilibria in the Garden

Hydrangeas are common flowering plants around the world. Although many hydrangeas are white, there is one common species (*Hydrangea macrophylla*) whose flowers can be either red or blue, as shown in the accompanying figure. How is it that a plant can have different colored flowers like this?



Figure 7.9.1 Garden Equilibria © Thinkstock. This species of hydrangea has flowers that can be either red or blue. Why the color difference?

Interestingly, the color of the flowers is due to the acidity of the soil that the hydrangea is planted in. An astute gardener can adjust the pH of the soil and actually change the color of the flowers. However, it is not the H^+ or OH^- ions that affect the color of the flowers. Rather, it is the presence of aluminum that causes the color change.

The solubility of aluminum in soil, and the ability of plants to absorb it, is dependent upon the acidity of the soil. If the soil is relatively acidic, the aluminum is more soluble, and plants can absorb it more easily. Under these conditions, hydrangea flowers are blue, as Al ions interact with anthocyanin pigments in the plant. In more basic soils, aluminum is less soluble, and under these conditions the hydrangea flowers are red. Gardeners who change the pH of their soils to change the color of their hydrangea flowers are therefore employing Le Chatelier's principle: the amount of acid in the soil changes the equilibrium of aluminum solubility, which in turn affects the color of the flowers.

Key Takeaways

- Le Chatelier's principle addresses how an equilibrium shifts when the conditions of an equilibrium are changed.
- The direction of shift can be predicted for changes in concentrations, temperature, or pressure.
- Catalysts do not affect the position of an equilibrium; they help reactions achieve equilibrium faster.

Exercise 7.9.1

1. Define *Le Chatelier's principle*.
2. What is meant by a stress? What are some of the ways an equilibrium can be stressed?
3. Given this equilibrium, predict the direction of shift for each stress.

$$H_2(g) + I_2(s) + 53kJ \rightleftharpoons 2HI(g)$$

   a. decreased temperature
   b. increased pressure
   c. removal of HI
4. Given this equilibrium, predict the direction of shift for each stress.

$$H_2(g) + F_2(g) \rightleftharpoons 2HF(g) + 546kJ$$

   a. increased temperature
   b. addition of H_2
   c. decreased pressure
5. Given this equilibrium, predict the direction of shift for each stress.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + 196kJ$$

   a. removal of SO_3
   b. addition of O_2
   c. decreased temperature
6. Given this equilibrium, predict the direction of shift for each stress.

$$CO_2(g) + C(s) + 171kJ \rightleftharpoons 2CO(g)$$

   a. addition of CO
   b. increased pressure
   c. addition of a catalyst
7. The synthesis of NH_3 uses this chemical reaction.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 92kJ$$

   Identify three stresses that can be imposed on the equilibrium to maximize the amount of NH_3.
8. The synthesis of $CaCO_3$ uses this chemical reaction.

$$CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s) + 180kJ$$

   Identify three stresses that can be imposed on the equilibrium to maximize the amount of $CaCO_3$.

Answers

1. When an equilibrium is stressed, the equilibrium shifts to minimize that stress.
2.
3. a. toward reactants

- toward reactants
- toward products
-
- a. toward products
  b. toward products
  c. toward products
-
- increased pressure, decreased temperature, removal of NH_3

Answers

Exercise 7.9.2

Reaction shifts toward reactants.

Exercise 7.9.3

Equilibrium shifts toward reactants.

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8: GASES, LIQUIDS, AND SOLIDS

8.1: States of Matter and Their Changes

8.2: Intermolecular Forces

8.3: Gases and the Kinetic-Molecular Theory

8.4: Pressure

8.5: Boyle's Law - The Relation between Volume and Pressure

8.6: Charles's Law- The Relation between Volume and Temperature

8.7: Gay-Lussac's Law- The Relationship Between Pressure and Temperature

8.8: The Combined Gas Law

8.9: Avogadro's Law - The Relation between Volume and Molar Amount

8.10: The Ideal Gas Law

8.11: Partial Pressure and Dalton's Law

8.12: Liquids

8.13: Solids

8.14: Changes of State Calculations

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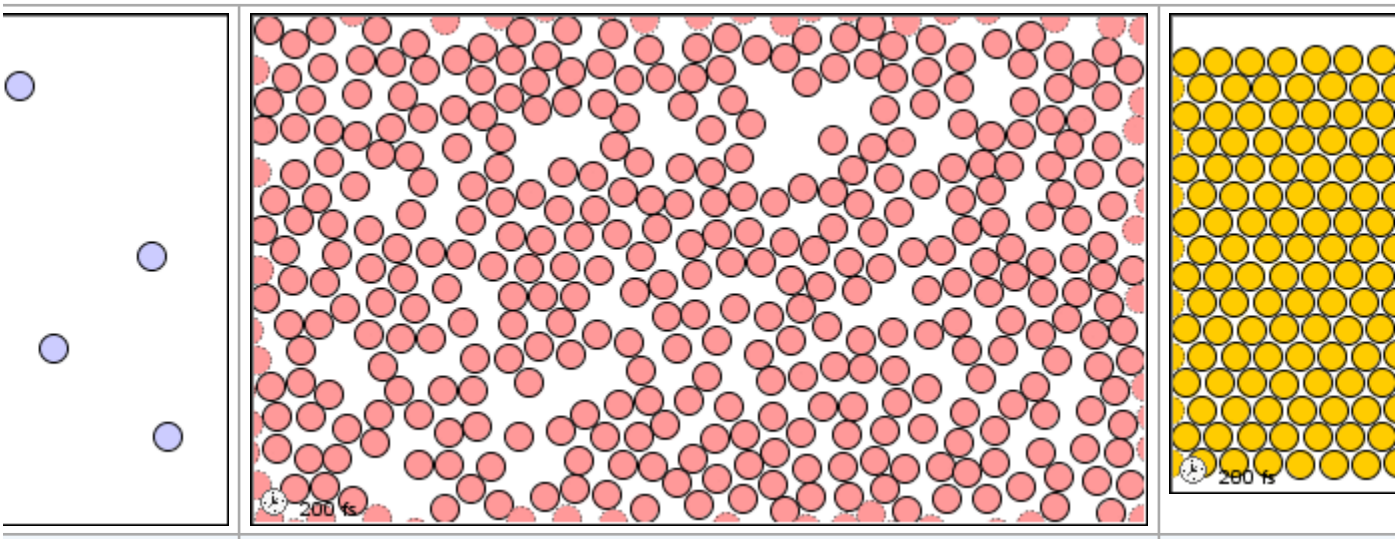
8.1: States of Matter and Their Changes

Learning Objectives

- Review the states of matter and their properties
- Describe how change in temperature will affect the state of matter.

Previously, you were introduced to the three states, also called phases, of matter; solid, liquid, and gas. A phase is a certain form of matter that includes a specific set of physical properties. That is, the atoms, the molecules, or the ions that make up the phase do so in a consistent manner throughout the phase. Science recognizes three stable phases: the ***solid*** *phase*, in which individual particles can be thought of as in contact and held in place; the ***liquid*** *phase*, in which individual particles are in contact but moving with respect to each other; and the ***gas*** *phase*, in which individual particles are separated from each other by relatively large distances (see Figure 8.1.1).

The *state* of a substance depends on the balance between the *kinetic energy* of the individual particles (molecules or atoms) and the attractive forces between molecules, called *intermolecular forces*. The kinetic energy keeps the molecules apart and moving around, and is a function of the temperature of the substance. The intermolecular forces draw the particles together. A discussed previously, gasses are very sensitive to temperatures and pressure. However, these also affect liquids and solids too. Heating and cooling can change the *kinetic energy* of the particles in a substance, and so, we can change the physical state of a substance by heating or cooling it. Increasing the pressure on a substance forces the molecules closer together, which *increases* the strength of intermolecular forces.



(b) as a liquid

Figure 8.1.1: Molecular level picture of gases, liquids and solids.

We take advantage of changes between the gas, liquid, and solid states to cool a drink with ice cubes (solid to liquid), cool our bodies by perspiration (liquid to gas), and cool food inside a refrigerator (gas to liquid and vice versa). We use dry ice, which is solid CO_2, as a refrigerant (solid to gas), and we make artificial snow for skiing and snowboarding by transforming a liquid to a solid. In this section, we examine what happens when any of the three forms of matter is converted to either of the other two. These **changes of state** are often called phase changes. The six most common phase changes are shown in Figure 8.1.2.

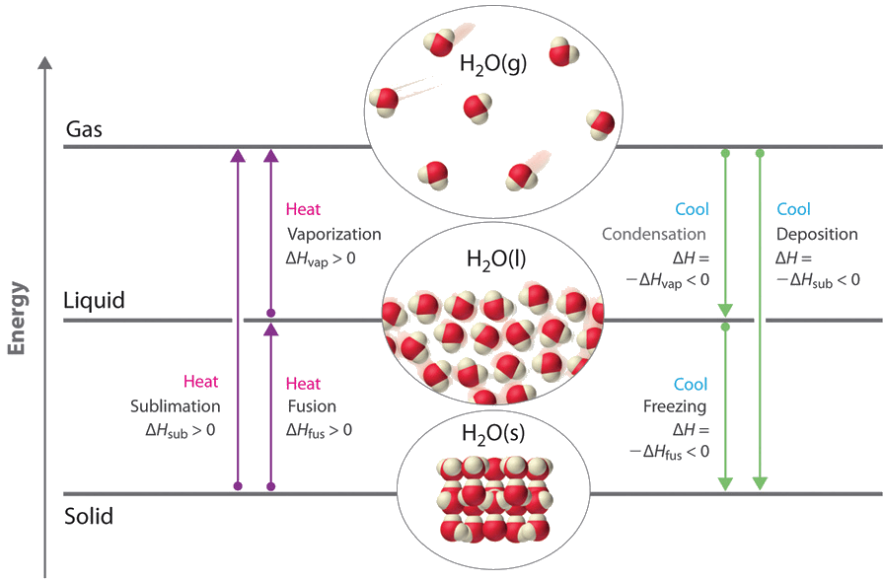


Figure 8.1.2: Enthalpy changes that accompany phase transitions are indicated by purple and green arrows. (CC BY-SA-NC; anoymous)

Energy Changes That Accompany Phase Changes

Phase changes are *always* accompanied by a change in the enthalpy, ΔH, of a system. For example, converting a liquid, in which the molecules are close together, to a gas, in which the molecules are, on average, far apart, requires an input of energy (heat) to give the molecules enough kinetic energy to allow them to overcome the intermolecular attractive forces. The stronger the attractive forces, the more energy is needed to overcome them. Solids, which are highly ordered, have the strongest intermolecular interactions, whereas gases, which are very disordered, have the weakest. Thus any transition from a more ordered to a less ordered state (solid to liquid, liquid to gas, or solid to gas) requires an input of energy; the ΔH is positive (endothermic). Conversely, any transition from a less ordered to a more ordered state (liquid to solid, gas to liquid, or gas to solid) releases energy; the ΔH is negative (exothermic). The energy change associated with each common phase change is shown in Figure 8.1.2 .

> ΔH is positive for any transition from a more ordered to a less ordered state and negative for a transition from a less ordered to a more ordered state.

Previously, we defined the enthalpy changes associated with various chemical and physical processes. The molar **enthalpy of fusion** (ΔH_{fus}), is the energy required to convert a solid to a liquid, a process known as fusion (or melting). As noted above, the process of melting requires energy and therefore, the (ΔH_{fus}) is positive. The reverse process of freezing would release energy making the (ΔH_{fus}) negative. The molar **enthalpy of vaporization** (ΔH_{vap}), is the energy required to convert a liquid to a gas, known as vaporization. Melting points, enthalpies of fusion, boiling points, and enthalpies of vaporization for selected compounds are listed in Table 8.1.1.

Table 8.1.1: Melting and Boiling Points and Enthalpies of Fusion and Vaporization for Selected Substances. Values given under 1 atm. of external pressure.

Substance	Melting Point (°C)	ΔH_{fus} (kJ/mol)	Boiling Point (°C)	ΔH_{vap} (kJ/mol)
N_2	−210.0	0.71	−195.8	5.6
HCl	−114.2	2.00	−85.1	16.2
Br_2	−7.2	10.6	58.8	30.0
CCl_4	−22.6	2.56	76.8	29.8
CH_3CH_2OH (ethanol)	−114.1	4.93	78.3	38.6
$CH_3(CH_2)_4CH_3$ (*n*-hexane)	−95.4	13.1	68.7	28.9
H_2O	0	6.01	100	40.7

Substance	Melting Point (°C)	ΔH_{fus} (kJ/mol)	Boiling Point (°C)	ΔH_{vap} (kJ/mol)
Na	97.8	2.6	883	97.4
NaF	996	33.4	1704	176.1

The substances with the highest melting points usually have the highest enthalpies of fusion; they tend to be ionic compounds that are held together by very strong electrostatic interactions. Substances with high boiling points are those with strong intermolecular interactions that must be overcome to convert a liquid to a gas, resulting in high enthalpies of vaporization. The enthalpy of vaporization of a given substance is much greater than its enthalpy of fusion because it takes more energy to completely separate molecules (conversion from a liquid to a gas) than to enable them only to move past one another freely (conversion from a solid to a liquid).

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8.2: Intermolecular Forces

Learning Objective

- Identify the different types of intermolecular forces.
- Relate the physical properties of a substance to the strength of attractive forces.

Why does a substance exist as a solid, liquid, or a gas at specific temperatures? Why do some substances evaporate quickly or melt more easily? These questions can be answered by considering the balance between the energy of the particles and **intermolecular forces** (or intermolecular interactions) between the particles. If the forces between particles are strong enough, the substance is a liquid or, if stronger, a solid. If the forces between particles are weak and sufficient energy is present, the particles separate from each other, so the gas phase is the preferred phase. The energy of the particles is mostly determined by temperature, so temperature is the main variable that determines what phase is stable at any given point.

There are three types of intermolecular forces: *London Dispersion, dipole-dipole, and hydrogen bonding*, collectively termed van der Waals forces, that will be introduced below.

London Dispersion Forces

There are forces between all molecules that are caused by electrons being in different places in a molecule at any one time, which sets up a temporary separation of charge (a temporary dipole moment) that disappears almost as soon as it appears. These very weak intermolecular interactions are called **dispersion forces** (or **London dispersion forces**, named for the physicist Fritz London, who first described this force in the early 1900s).

Dispersion forces that develop between atoms in different molecules can attract the two molecules to each other. The forces are relatively weak, however, and become significant only when the molecules are very close. **Larger and heavier atoms and molecules** exhibit **stronger dispersion forces** than do smaller and lighter atoms and molecules. F_2 and Cl_2 are gases at room temperature (reflecting weaker attractive forces); Br_2 is a liquid, and I_2 is a solid (reflecting stronger attractive forces). Trends in observed melting and boiling points for the halogens clearly demonstrate this effect, as seen in Table 8.2.1.

Table 8.2.1: ***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
bromine, Br_2	160 g/mol	114 pm	266 K	332 K
iodine, I_2	254 g/mol	133 pm	387 K	457 K
astatine, At_2	420 g/mol	150 pm	575 K	610 K

The increase in melting and boiling points with increasing atomic/molecular size may be rationalized by considering how the strength of dispersion forces is affected by the electronic structure of the atoms or molecules in the substance. In a larger atom, the valence electrons are, on average, farther from the nuclei than in a smaller atom. Thus, they are less tightly held and can more easily form the temporary dipoles that produce the attraction. The measure of how easy or difficult it is for another electrostatic charge (for example, a nearby ion or polar molecule) to distort a molecule's charge distribution (its electron cloud) is known as **polarizability**. A molecule that has a charge cloud that is easily distorted is said to be very polarizable and will have large

dispersion forces; one with a charge cloud that is difficult to distort is not very polarizable and will have small dispersion forces.

Example 8.2.1

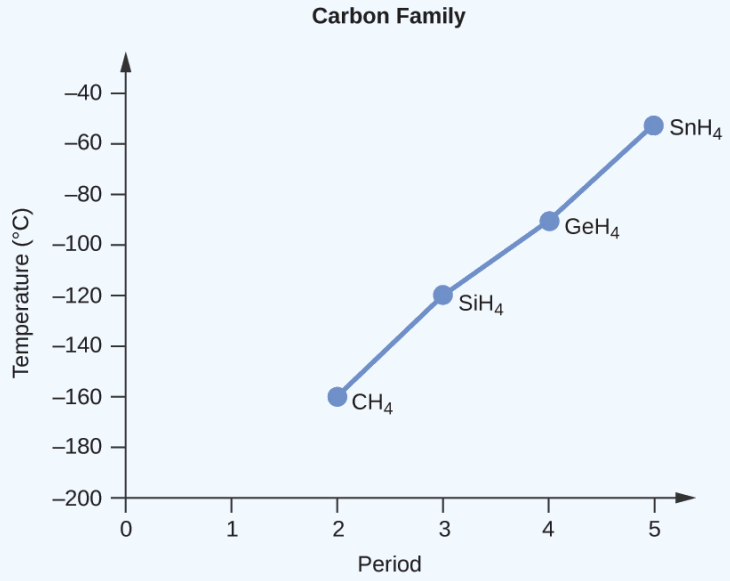
Order the following compounds of a group 14 element and hydrogen from lowest to highest boiling point: CH_4, SiH_4, GeH_4, and SnH_4. Explain your reasoning.

Solution

Applying the skills acquired in the chapter on chemical bonding and molecular geometry, all of these compounds are predicted to be nonpolar, so they may experience only dispersion forces: the smaller the molecule, the less polarizable and the weaker the dispersion forces; the larger the molecule, the larger the dispersion forces. The molar masses of CH_4, SiH_4, GeH_4, and SnH_4 are approximately 16 g/mol, 32 g/mol, 77 g/mol, and 123 g/mol, respectively. Therefore, CH_4 is expected to have the lowest boiling point and SnH_4 the highest boiling point. The ordering from lowest to highest boiling point is expected to be

$CH_4 < SiH_4 < GeH_4 < SnH_4$

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



Exercise 8.2.1

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

Answer available at the end of this section.

Answer available at the end of this section.

Dipole-Dipole Intermolecular Forces

Recall that a polar molecule will have a net unequal distribution of electrons in its covalent bonds resulting in a partial positive charge on one side of the molecule and a partial negative charge on the other side of the molecule—a separation of charge called a ***dipole***. The electrostatic attraction between oppositely charged ends of polar molecules are called **dipole-dipole interactions**, (as illustrated in Figure 8.2.1). Dipole-dipole attractions are between permanent dipoles and are therefore generally *stronger* than

dispersion forces, which are between temporary dipoles. Thus, a polar molecule such as CH_2Cl_2 has a significantly higher boiling point (313 K, or 40°C) than a nonpolar molecule like CF_4 (145 K, or –128°C), even though it has a lower molar mass (85 g/mol vs. 88 g/mol).

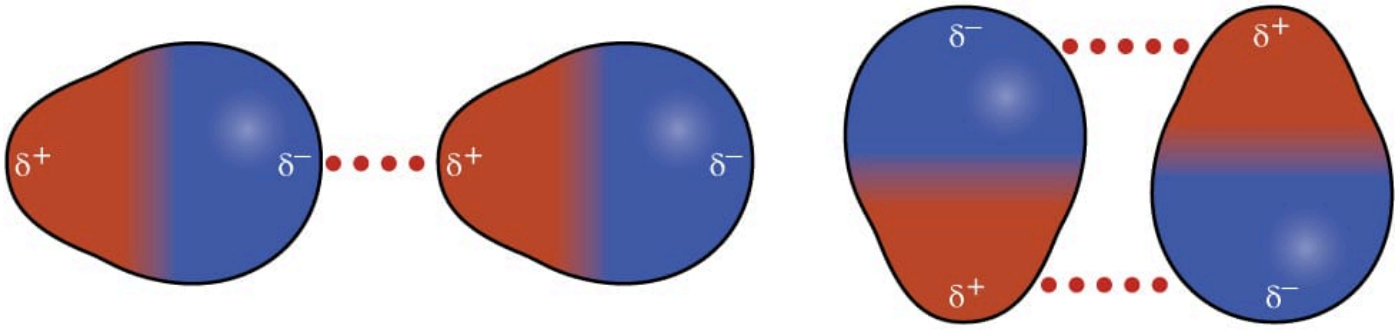


Figure 8.2.1: This image illustrates a dipole-dipole interaction, two arrangements of polar molecules that allow an attraction between the partial negative end of one molecule and the partial positive end of another.

Example 8.2.2

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.

Exercise 8.2.2

Predict which will have the higher boiling point: ICl or $\mathrm{Br_2}$. Explain your reasoning.

Answer available at the end of this section.

Hydrogen Bonds

An unusually strong form of dipole-dipole interaction is called **hydrogen bonding**. Hydrogen bonding is found in molecules with an H atom bonded to an N atom, an O atom, or an F atom. Such covalent bonds are very polar, and the dipole-dipole interaction between these bonds in two or more molecules is strong enough to create a new category of intermolecular force. Hydrogen bonding is the reason water has unusual properties. For such a small molecule (its molar mass is only 18 g/mol), H_2O has relatively high melting and boiling points. Its boiling point is 373 K (100°C), while the boiling point of a similar molecule, H_2S, is 233 K (–60°C). This is because H_2O molecules experience hydrogen bonding, while H_2S molecules do not. This strong attraction between H_2O molecules requires additional energy to separate the molecules in the condensed phase, so its boiling point is higher than would be expected. Hydrogen bonding is also responsible for water's ability as a solvent, its high heat capacity, and its ability to expand when freezing; the molecules line up in such a way that there is extra space between the molecules, increasing its volume in the solid state (Figure 8.2.2).

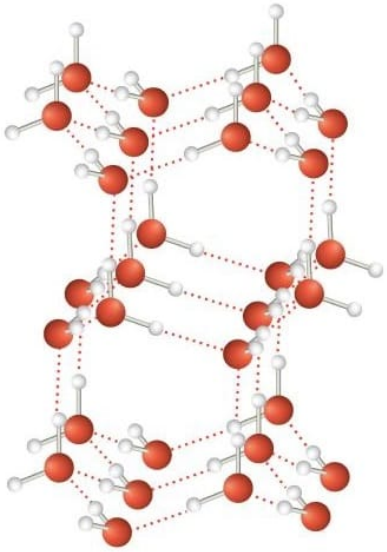


Figure 8.2.2: Hydrogen Bonding. When water solidifies, hydrogen bonding between the molecules forces the molecules to line up in a way that creates empty space between the molecules, increasing the overall volume of the solid. This is why ice is less dense than liquid water.

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

Hydrogen Bonding and DNA

Deoxyribonucleic acid (DNA) is found in every living organism and contains the genetic information that determines the organism’s characteristics, provides the blueprint for making the proteins necessary for life, and serves as a template to pass this information on to the organism’s offspring. A DNA molecule consists of two (anti-)parallel chains of repeating nucleotides, which form its well-known double helical structure, as shown in Figure 8.2.3.

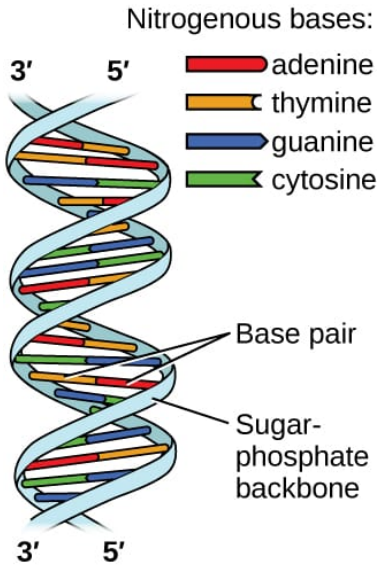


Figure 8.2.3: Two separate DNA molecules form a double-stranded helix in which the molecules are held together via hydrogen bonding. (credit: modification of work by Jerome Walker, Dennis Myts)

Each nucleotide contains a (deoxyribose) sugar bound to a phosphate group on one side, and one of four nitrogenous bases on the other. Two of the bases, cytosine (C) and thymine (T), are single-ringed structures known as pyrimidines. The other two, adenine (A) and guanine (G), are double-ringed structures called purines. These bases form complementary base pairs consisting

of one purine and one pyrimidine, with adenine pairing with thymine, and cytosine with guanine. Each base pair is held together by hydrogen bonding. A and T share two hydrogen bonds, C and G share three, and both pairings have a similar shape and structure Figure 8.2.4

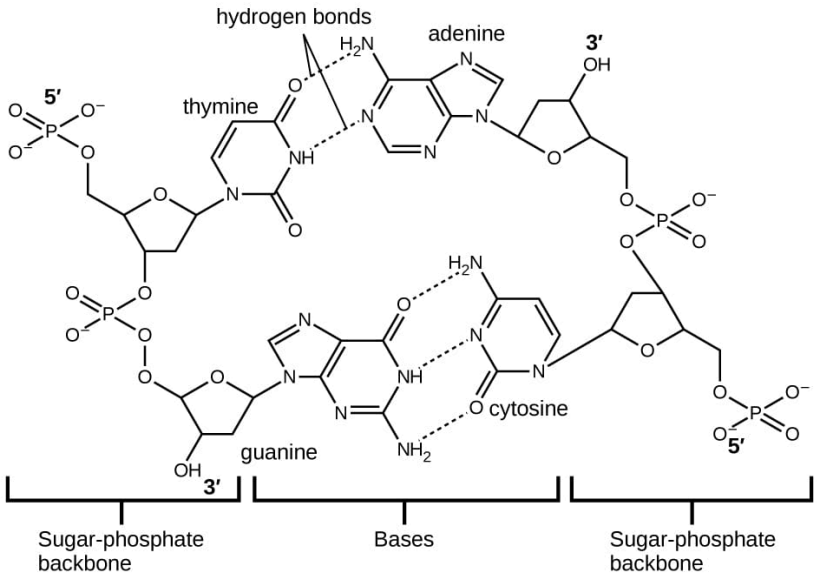


Figure 8.2.4: The geometries of the base molecules result in maximum hydrogen bonding between adenine and thymine (AT) and between guanine and cytosine (GC), so-called "complementary base pairs."

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

Applications: Geckos and Intermolecular Forces

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

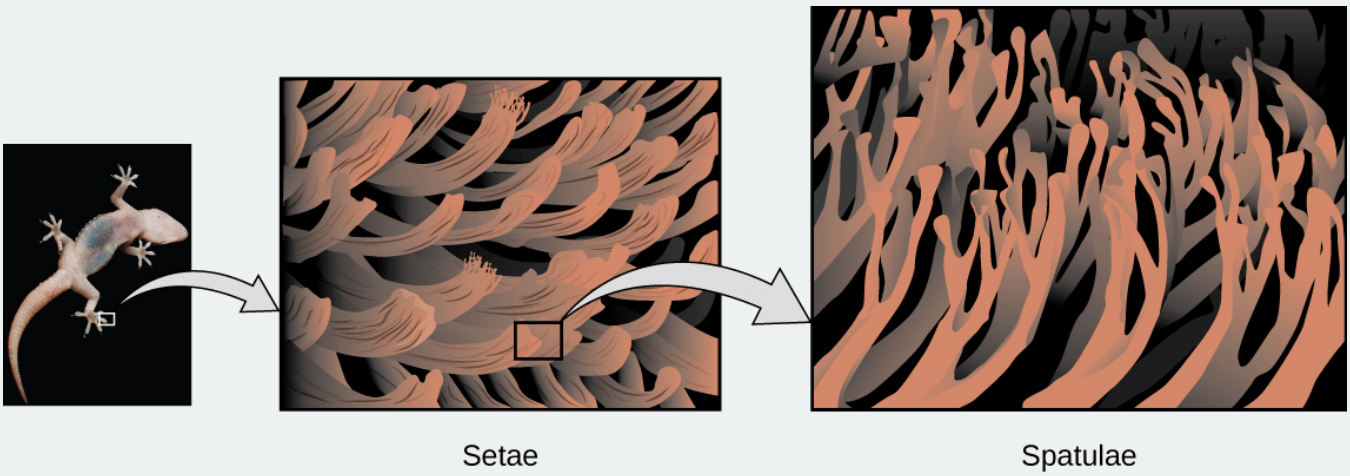


Figure 8.2.12: *Geckos' toes contain large numbers of tiny hairs (setae), which branch into many triangular tips (spatulae). Geckos adhere to surfaces because of van der Waals attractions between the surface and a gecko's millions of spatulae. By changing how the spatulae contact the surface, geckos can turn their stickiness "on" and "off." (credit photo: modification of work by "JC*+A!"/Flickr)*

Geckos' toes are covered with hundreds of thousands of tiny hairs known as *setae*, with each seta, in turn, branching into hundreds of tiny, flat, triangular tips called *spatulae*. The huge numbers of spatulae on its setae provide a gecko, shown in Figure 8.1.12, with a large total surface area for sticking to a surface. In 2000, Kellar Autumn, who leads a multi-institutional gecko research team, found that geckos adhered equally well to both polar silicon dioxide and nonpolar gallium arsenide. This proved that geckos stick to surfaces because of dispersion forces—weak intermolecular attractions arising from temporary, synchronized charge distributions between adjacent molecules. Although dispersion forces are very weak, the total attraction over millions of spatulae is large enough to support many times the gecko's weight.

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

Boiling Points and Bonding Types

In order for a substance to enter the gas phase, its particles must completely overcome the intermolecular forces holding them together. Therefore, a comparison of boiling points is essentially equivalent to comparing the strengths of the attractive intermolecular forces exhibited by the individual molecules. For small molecular compounds, London dispersion forces are the weakest intermolecular forces. Dipole-dipole forces are somewhat stronger, and hydrogen bonding is a particularly strong form of dipole-dipole interaction. However, when the mass of a nonpolar molecule is sufficiently large, its dispersion forces can be stronger than the dipole-dipole forces in a lighter polar molecule. Thus, nonpolar Cl_2 has a higher boiling point than polar HCl.

Table 8.2.3: Intermolecular Forces and Boiling Points

Substance	Strongest Intermolecular Force	Boiling Point (°C)
H_2	dispersion	-253
Ne	dispersion	-246
O_2	dispersion	-183
Cl_2	dispersion	-34
HCl	dipole-dipole	-85
HBr	dipole-dipole	-66
H_2S	dipole-dipole	-61
NH_3	hydrogen bonding	-33
HF	hydrogen bonding	20
H_2O	hydrogen bonding	100

Example 8.2.3

Consider the compounds dimethylether (CH_3OCH_3), ethanol (CH_3CH_2OH), and propane ($CH_3CH_2CH_3$). Their boiling points, not necessarily in order, are −42.1 °C, −24.8 °C, and 78.4 °C. Match each compound with its boiling point. Explain your reasoning.

Solution

The shapes of CH_3OCH_3, CH_3CH_2OH, and $CH_3CH_2CH_3$ are similar, as are their molar masses (46 g/mol, 46 g/mol, and 44 g/mol, respectively), so they will exhibit similar dispersion forces. Since $CH_3CH_2CH_3$ is nonpolar, it may exhibit *only* dispersion forces. Because CH_3OCH_3 is polar, it will also experience dipole-dipole attractions. Finally, CH_3CH_2OH has an –OH group,

and so it will experience the uniquely strong dipole-dipole attraction known as hydrogen bonding. So the ordering in terms of strength of IMFs, and thus boiling points, is $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CH_2OH$. The boiling point of propane is –42.1 °C, the boiling point of dimethylether is –24.8 °C, and the boiling point of ethanol is 78.5 °C.

Exercise 8.2.3

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 available at the end of this section.

Example 8.2.4: Intermolecular Forces

What intermolecular forces besides dispersion forces, if any, exist in each substance? Are any of these substances solids at room temperature?

a. potassium chloride (KCl)
b. ethanol (C_2H_5OH)
c. bromine (Br_2)

Solution

a. Potassium chloride is composed of ions, so the intermolecular interaction in potassium chloride is ionic forces. Because ionic interactions are strong, it might be expected that potassium chloride is a solid at room temperature.
b. Ethanol has a hydrogen atom attached to an oxygen atom, so it would experience hydrogen bonding. If the hydrogen bonding is strong enough, ethanol might be a solid at room temperature, but it is difficult to know for certain. (Ethanol is actually a liquid at room temperature.)
c. Elemental bromine has two bromine atoms covalently bonded to each other. Because the atoms on either side of the covalent bond are the same, the electrons in the covalent bond are shared equally, and the bond is a nonpolar covalent bond. Thus, diatomic bromine does not have any intermolecular forces other than dispersion forces. It is unlikely to be a solid at room temperature unless the dispersion forces are strong enough. Bromine is a liquid at room temperature.

Exercise 8.2.4

What intermolecular forces besides dispersion forces, if any, exist in each substance? Are any of these substances solids at room temperature?

a. methylamine (CH_3NH_2)
b. calcium sulfate ($CaSO_4$)
c. carbon monoxide (CO)

Answer available at the end of this section.

Concept Review Exercise

1. What types of intermolecular interactions can exist in compounds?

2. What is the difference between covalent network and covalent molecular compounds?

Answer

1. ionic bonding, network covalent, dispersion forces, dipole-dipole interactions, and hydrogen bonding.

2. Covalent network compounds contain atoms that are covalently bonded to other individual atoms in a giant 3-dimensional network. Covalent molecular compounds contain individual molecules that are attracted to one another through dispersion, dipole-dipole or hydrogen bonding.

Key Takeaways

- A phase is a form of matter that has the same physical properties throughout.
- Molecules interact with each other through various forces: dipole-dipole interactions, hydrogen bonding, and dispersion forces.
- Dipole-dipole attractions result from the electrostatic attraction of the partial negative end of one dipolar molecule for the partial positive end of another.
- Hydrogen bonds are a special type of dipole-dipole attraction that results when hydrogen is bonded to one of the three most electronegative elements: F, O, or N.
- The temporary dipole that results from the motion of the electrons in an atom can induce a dipole in an adjacent atom and give rise to the London dispersion force. London forces increase with increasing molecular size.

Exercises

1. List the three common phases in the order you are likely to find them—from lowest temperature to highest temperature.

2. List the three common phases in the order they exist from lowest energy to highest energy.

3. List these intermolecular interactions from weakest to strongest: London forces, hydrogen bonding, and ionic interactions.

4. List these intermolecular interactions from weakest to strongest: covalent network bonding, dipole-dipole interactions, and dispersion forces.

5. What type of intermolecular interaction is predominate in each substance?

    a. water (H_2O)
    b. sodium sulfate (Na_2SO_4)
    c. decane ($C_{10}H_{22}$)

6. What type of intermolecular interaction is predominate in each substance?

    a. diamond (C, crystal)
    b. helium (He)
    c. ammonia (NH_3)

7. Explain how a molecule like carbon dioxide (CO_2) can have polar covalent bonds but be nonpolar overall.

8. Sulfur dioxide (SO_2) has a formula similar to that of carbon dioxide (see Exercise 7) but is a polar molecule overall. What can you conclude about the shape of the SO_2 molecule?

9. What are some of the physical properties of substances that experience covalent network bonding?

10. What are some of the physical properties of substances that experience only dispersion forces?

Answers

1. solid, liquid, and gas

2. solid, liquid, and gas

3. London forces, hydrogen bonding, and ionic interactions

4. dispersion, dipole-dipole, network covalent

5. a. hydrogen bonding
   b. ionic interactions
   c. dispersion forces

6. a. network covalent
b. dispersion
c. hydrogen bonding

7. The two covalent bonds are oriented in such a way that their dipoles cancel out.

8. SO_2 is not a linear molecule. It has a bent or V-shape.

9. very hard, high melting point

10. very soft, very low melting point

Answers

Exercise 8.2.1

Exercise 8.2.1

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

$$C_2H_6 < C_3H_8 < C_4H_{10}.$$

Exercise 8.2.2

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.

Exercise 8.2.3

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

Exercise 8.2.4

a. dipole-dipole, hydrogen bonding

b. ionic forces (solid at room temperature)

c. dipole-dipole

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8.3: Gases and the Kinetic-Molecular Theory

Learning Objectives

- State the major concepts behind the kinetic theory of gases.
- Relate the general properties of gases to the kinetic theory.

Gases were among the first substances studied in terms of the modern scientific method, which was developed in the 1600s. It did not take long to recognize that gases all shared certain physical behaviors, suggesting that all gases could be described by one all-encompassing theory. Today, that theory is the **kinetic theory of gases**. The kinetic theory of gases is based on the following statements:

1. Gases consist of tiny particles of matter that are in constant motion.
2. Gas particles are constantly colliding with each other and the walls of a container. These collisions are elastic—that is, there is no net loss of energy from the collisions.
3. Gas particles are separated by large distances, with the size of a gas particle tiny compared to the distances that separate them.
4. There are no interactive forces (i.e., attraction or repulsion) between the particles of a gas.
5. The average speed of gas particles is dependent on the temperature of the gas.

Figure 8.3.1 shows a representation of how we mentally picture the gas phase.

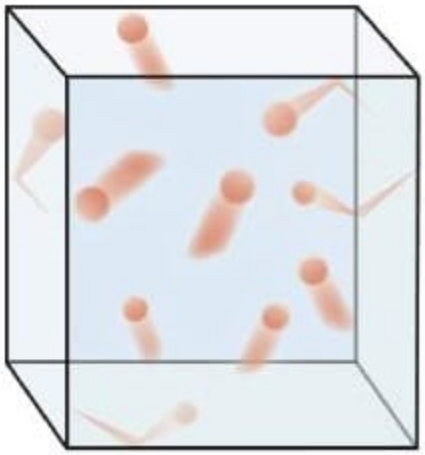


Figure 8.3.1: The Kinetic Theory of Gases. The kinetic theory of gases describes this state of matter as composed of tiny particles in constant motion, with a lot of distance between the particles.

This model of gases explains some of the physical properties of gases. Because most of a gas is empty space, a gas has a low density and can expand or contract under the appropriate influence. The fact that gas particles are in constant motion means that two or more gases will always mix, as the particles from the individual gases move and collide with each other.

An **ideal gas** is a gas that exactly follows the statements of the kinetic theory. Unfortunately, *real gases* are not ideal. Many gases deviate slightly from agreeing perfectly with the kinetic theory of gases. However, most gases adhere to the statements, and the kinetic theory of gases is well accepted by the scientific community.

- The physical behavior of gases is explained by the kinetic theory of gases.
- An ideal gas adheres exactly to the kinetic theory of gases.

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8.4: Pressure

Learning Objectives

- To describe and measure the pressure of a gas.

At the macroscopic level, a complete physical description of a sample of a gas requires four quantities: *temperature* (expressed in kelvins), *volume* (expressed in liters), *amount* (expressed in moles), and *pressure* (in atmospheres). As we explain in this section, these variables are *not* independent. If we know the values of any *three* of these quantities, we can calculate the fourth and thereby obtain a full physical description of the gas. Temperature, volume, and amount have been discussed in previous chapters. We now discuss pressure and its units of measurement.

Units of Pressure

Any object, whether it is your computer, a person, or a sample of gas, exerts a force on any surface with which it comes in contact. The air in a balloon, for example, exerts a force against the interior surface of the balloon, and a liquid injected into a mold exerts a force against the interior surface of the mold, just as a chair exerts a force against the floor because of its mass and the effects of gravity. If the air in a balloon is heated, the increased kinetic energy of the gas eventually causes the balloon to burst because of the increased pressure (an increase in the collisions between gas molecules) inside the balloon. Pressure (P) is defined as the amount of force (F) per unit area (A):

$$P = \frac{F}{A}$$

Pressure is dependent on *both* the force exerted *and* the size of the area to which the force is applied. We know from experience that applying the same force to a smaller area produces a higher pressure. When we use a hose to wash a car, for example, we can increase the pressure of the water by reducing the size of the opening of the hose with a thumb.

The units of pressure are derived from the units used to measure force and area. The SI unit for pressure, derived from the SI units for force (newtons) and area (square meters), is the newton per square meter (N/m^2), which is called the **Pascal (Pa)**, after the French mathematician Blaise Pascal (1623–1662):

$$1\ \text{Pa} = 1\ \text{N/m}^2 \tag{8.4.1}$$

Example 8.4.1

Assuming a paperback book has a mass of 2.00 kg, a length of 27.0 cm, a width of 21.0 cm, and a thickness of 4.5 cm, what pressure does it exert on a surface if it is

a. lying flat?
b. standing on edge in a bookcase?

Given: mass and dimensions of object

Asked for: pressure

Strategy:

A. Calculate the force exerted by the book and then compute the area that is in contact with a surface.
B. Substitute these two values into Equation ??? to find the pressure exerted on the surface in each orientation.

Solution:

The force exerted by the book does *not* depend on its orientation. Recall that the force exerted by an object is $F = ma$, where m is its mass and a is its acceleration. In Earth's gravitational field, the acceleration is due to gravity (9.8067 m/s^2 at Earth's surface). In SI units, the force exerted by the book is therefore

$$F = ma = 2.00\ \text{kg} \times 9.8067 \frac{\text{m}}{\text{s}^2} = 19.6 \frac{\text{kg} \cdot \text{m}}{\text{s}^2} = 19.6\ \text{N}$$

A We calculated the force as 19.6 N. When the book is lying flat, the area is

$$A = 0.270\ \text{m} \times 0.210\ \text{m} = 0.0567\ \text{m}^2.$$

B The pressure exerted by the text lying flat is thus

$$P = \frac{F}{A} = \frac{19.6\ \text{N}}{0.0567\ \text{m}^2} = 3.46 \times 10^2 \text{Pa}$$

A If the book is standing on its end, the force remains the same, but the area decreases:

$$\text{A} = 21.0\ \text{cm} \times 4.5\ \text{cm} = 0.210\ \text{m} \times 0.045\ \text{m} = 9.5 \times 10^{-3}\ \text{m}^2$$

B The pressure exerted by the text lying flat is thus

$$P = \frac{19.6\ \text{N}}{9.5 \times 10^{-3}\ \text{m}^2} = 2.06 \times 10^3\ \text{Pa}$$

Exercise 8.4.1

What pressure does a 60.0 kg student exert on the floor

a. when standing flat-footed in the laboratory in a pair of tennis shoes (the surface area of the soles is approximately 180 cm^2)?
b. as she steps heel-first onto a dance floor wearing high-heeled shoes (the area of the heel = 1.0 cm^2)?

Answer a available at the end of this section.

Atmospheric Pressure

Just as we exert pressure on a surface because of gravity, so does our atmosphere. We live at the bottom of an ocean of gases that becomes progressively less dense with increasing altitude. Approximately 99% of the mass of the atmosphere lies within 30 km of Earth's surface, and half of it is within the first 5.5 km (Figure 8.4.1). Every point on Earth's surface experiences a net pressure called *atmospheric pressure*. The pressure exerted by the atmosphere is considerable: a 1.0 m^2 column, measured from sea level to the top of the atmosphere, has a mass of about 10,000 kg, which gives a pressure of about 100 kPa.

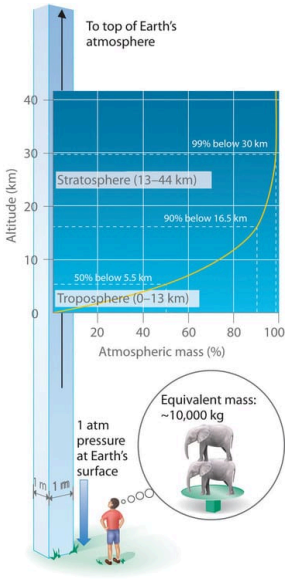


Figure 8.4.1: Atmospheric Pressure. Each square meter of Earth's surface supports a column of air that is more than 200 km high and weighs about 10,000 kg at Earth's surface, resulting in a pressure at the surface of 1.01×10^5 N/m^2. This corresponds to a pressure of 101 kPa = 760 mmHg = 1 atm.

Atmospheric pressure can be measured using a barometer, a device invented in 1643 by one of Galileo's students, Evangelista Torricelli (1608–1647). A barometer may be constructed from a long glass tube that is closed at one end. It is filled with mercury and placed upside down in a dish of mercury without allowing any air to enter the tube. Some of the mercury will run out of the tube, but a relatively tall column remains inside (Figure 8.4.2). Why doesn't all the mercury run out? Gravity is certainly exerting a downward force on the mercury in the tube, but it is opposed by the pressure of the atmosphere pushing down on the surface of the mercury in the dish, which has the net effect of pushing the mercury up into the tube. Because there is no air above the mercury inside the tube in a properly filled barometer (it contains a vacuum), there is no pressure pushing down on the column. Thus the mercury runs out of the tube until the pressure exerted by the mercury column itself exactly balances the pressure of the atmosphere.

Under normal weather conditions at sea level, the two forces are balanced when the top of the mercury column is approximately 760 mm above the level of the mercury in the dish, as shown in Figure 8.4.2. This value varies with meteorological conditions and altitude. In Denver, Colorado, for example, at an elevation of about 1 mile, or 1609 m (5280 ft), the height of the mercury column is 630 mm rather than 760 mm.

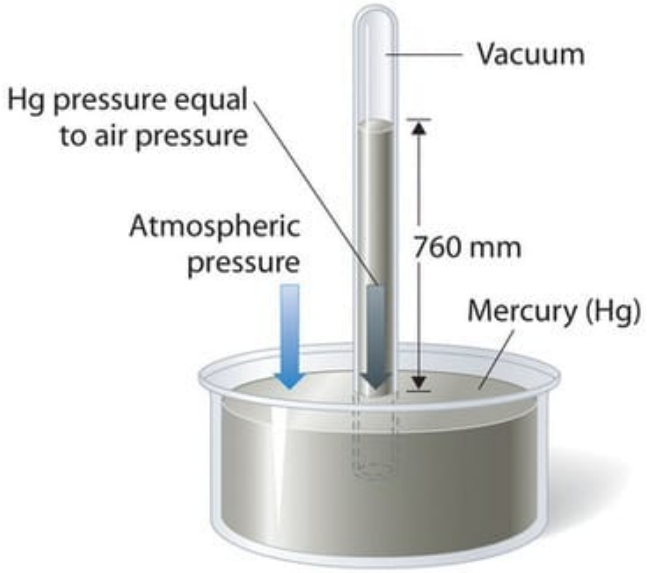


Figure 8.4.2: A Mercury Barometer. The pressure exerted by the atmosphere on the surface of the pool of mercury supports a column of mercury in the tube that is about 760 mm tall. Because the boiling point of mercury is quite high (356.73°C), there is very little mercury vapor in the space above the mercury column.

Mercury barometers have been used to measure barometric pressure for so long that they have their own unit for pressure: the millimeter of mercury (mmHg), often called the torr, after Torricelli. Standard barometric pressure is the barometric pressure required to support a column of mercury exactly 760 mm tall; this pressure is also referred to as 1 atmosphere (atm). These units are also related to the pascal:

$$1 \text{ atm} = 760\ mmHg \tag{8.4.2}$$
$$= 760\ torr \tag{8.4.3}$$
$$= 1.01325 \times 10^5\ Pa \tag{8.4.4}$$
$$= 101.325\ kPa \tag{8.4.5}$$

Thus a pressure of 1 atm equals 760 mmHg exactly.

We are so accustomed to living under this pressure that we never notice it. Instead, what we notice are *changes* in the pressure, such as when our ears pop in fast elevators in skyscrapers or in airplanes during rapid changes in altitude. We make use of barometric pressure in many ways. We can use a drinking straw because sucking on it removes air and thereby reduces the pressure inside the straw. The barometric pressure pushing down on the liquid in the glass then forces the liquid up the straw.

Example 8.4.2: Barometric Pressure

One of the authors visited Rocky Mountain National Park several years ago. After departing from an airport at sea level in the eastern United States, he arrived in Denver (altitude 5280 ft), rented a car, and drove to the top of the highway outside Estes Park (elevation 14,000 ft). He noticed that even slight exertion was very difficult at this altitude, where the barometric pressure is only 454 mmHg. Convert this pressure to

a. atmospheres (atm).
b. bar.

Given: pressure in millimeters of mercury

Asked for: pressure in atmospheres and bar

Strategy:

Use the conversion factors in Equation 8.4.5 to convert from millimeters of mercury to atmospheres and kilopascals.

Solution:

From Equation 8.4.5, we have 1 atm = 760 mmHg = 101.325 kPa. The pressure at 14,000 ft in atm is thus

$$P = 454 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} \tag{8.4.6}$$
$$= 0.597 \ atm$$

The pressure in bar is given by

$$P = 0.597 \text{ atm} \times \frac{1.01325 \text{ bar}}{1 \text{ atm}} \tag{8.4.7}$$
$$= 0.605 \ bar$$

Exercise 8.4.2: Barometric Pressure

Mt. Everest, at 29,028 ft above sea level, is the world's tallest mountain. The normal barometric pressure at this altitude is about 0.308 atm. Convert this pressure to

a. millimeters of mercury.
b. bar.

Answer a available at the end of this section.

Barometers measure atmospheric pressure, but **manometers** measure the pressures of samples of gases contained in an apparatus. The key feature of a manometer is a U-shaped tube containing mercury (or occasionally another nonvolatile liquid). A closed-end manometer is shown schematically in part (a) in Figure 8.4.3. When the bulb contains no gas (i.e., when its interior is a near vacuum), the heights of the two columns of mercury are the same because the space above the mercury on the left is a near vacuum (it contains only traces of mercury vapor). If a gas is released into the bulb on the right, it will exert a pressure on the mercury in the right column, and the two columns of mercury will no longer be the same height. The *difference* between the heights of the two columns is equal to the pressure of the gas.

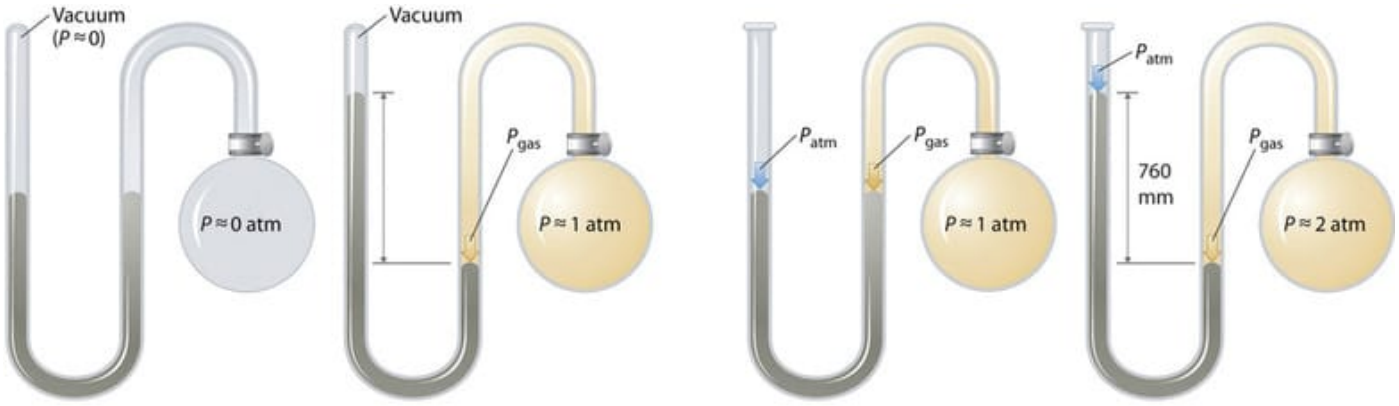


Figure 8.4.3: The Two Types of Manometer. (a) In a closed-end manometer, the space above the mercury column on the left (the reference arm) is essentially a vacuum ($P \approx 0$), and the difference in the heights of the two columns gives the pressure of the gas contained in the bulb directly. (b) In an open-end manometer, the left (reference) arm is open to the atmosphere ($P \approx 1$ atm), and the difference in the heights of the two columns gives the *difference* between barometric pressure and the pressure of the gas in the bulb.

If the tube is open to the atmosphere instead of closed, as in the open-end manometer shown in part (b) in Figure 8.4.3, then the two columns of mercury have the same height only if the gas in the bulb has a pressure equal to the barometric pressure. If the gas in the bulb has a *higher* pressure, the mercury in the open tube will be forced up by the gas pushing down on the mercury in the other arm of the U-shaped tube. The pressure of the gas in the bulb is therefore the sum of the barometric pressure (measured with a barometer) and the difference in the heights of the two columns. If the gas in the bulb has a pressure *less* than that of the atmosphere, then the height of the mercury will be greater in the arm attached to the bulb. In this case, the pressure

of the gas in the bulb is the barometric pressure minus the difference in the heights of the two columns.

Summary

Pressure is defined as the force exerted per unit area; it can be measured using a barometer or manometer. Four quantities must be known for a complete physical description of a sample of a gas: *temperature*, *volume*, *amount*, and *pressure*. **Pressure** is force per unit area of surface; the SI unit for pressure is the **pascal (Pa)**, defined as 1 newton per square meter (N/m^2). The pressure exerted by an object is proportional to the force it exerts and inversely proportional to the area on which the force is exerted. The pressure exerted by Earth's atmosphere, called *barometric pressure*, is about 101 kPa or 14.7 $lb/in.^2$ at sea level. barometric pressure can be measured with a **barometer**, a closed, inverted tube filled with mercury. The height of the mercury column is proportional to barometric pressure, which is often reported in units of **millimeters of mercury (mmHg)**, also called **torr**. **Standard barometric pressure**, the pressure required to support a column of mercury 760 mm tall, is yet another unit of pressure: 1 **atmosphere (atm)**. A **manometer** is an apparatus used to measure the pressure of a sample of a gas.

Answers

Exercise 8.4.1

3.27×10^4 Pa

5.9×10^6 Pa

Exercise 8.4.2**: Barometric Pressure**

234 mmHg;

0.312 bar

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8.5: Boyle’s Law - The Relation between Volume and Pressure

Learning Objectives

- Define the relationship between gas volume and pressure, Boyle's Law.
- Use Boyle's Law to calculate changes in pressure or volume of a gas.

When seventeenth-century scientists began studying the physical properties of gases, they noticed some simple relationships between some of the measurable properties of the gas. Take pressure (*P*) and volume (*V*), for example. Scientists noted that for a given amount of a gas (usually expressed in units of moles [*n*]), if the temperature (*T*) of the gas was kept constant, pressure and volume were related: As one increases, the other decreases. As one decreases, the other increases. We say that pressure and volume are *inversely related*.

There is more to it, however: pressure and volume of a given amount of gas at constant temperature are *numerically* related. If you take the pressure value and multiply it by the volume value, the product is a constant (*k*) for a given amount of gas at a constant temperature:

$$P \times V = k \; (at \; constant \; n \; and \; T)$$

If either volume or pressure changes while amount and temperature stay the same, then the other property must change so that the product of the two properties still equals that same constant. That is, if the original conditions are labeled P_1 and V_1 and the new conditions are labeled P_2 and V_2, we have

$$P_1V_1 = k = P_2V_2$$

where the properties are assumed to be multiplied together. Leaving out the middle part, we have simply

$$P_1V_1 = P_2V_2 \; (at \; constant \; n \; and \; T)$$

This equation is an example of a gas law. A **gas law** is a simple mathematical formula that allows you to model, or predict, the behavior of a gas. This particular gas law is called **Boyle's law**, after the English scientist Robert Boyle, who first announced it in 1662. Figure $8.5.1$ shows two representations of how Boyle's law works.

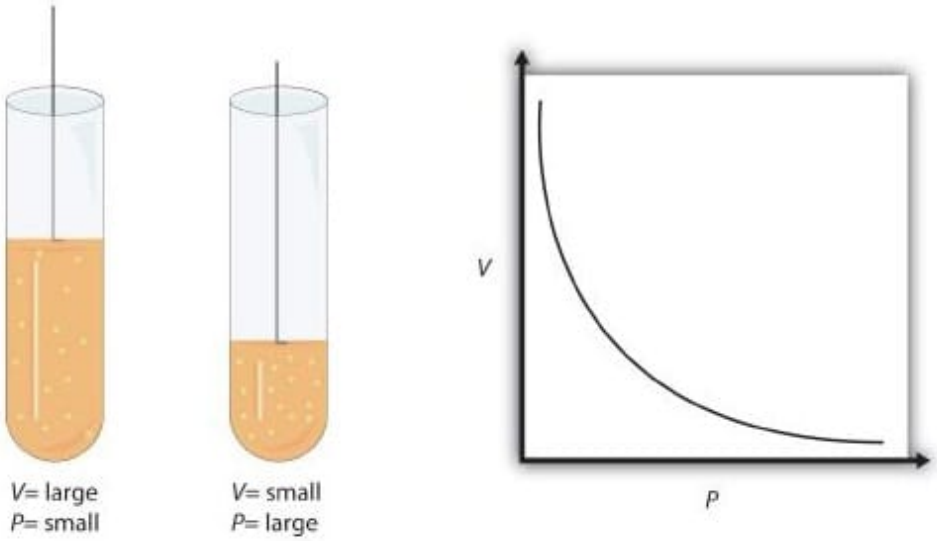


Figure 8.5.1: Boyle's Law. A piston having a certain pressure and volume (left piston) will have half the volume when its pressure is twice as much (right piston). One can also plot P versus V for a given amount of gas at a certain temperature; such a plot will look like the graph on the right.

Boyle's law is an example of a second type of mathematical problem we see in chemistry—one based on a mathematical formula. Tactics for working with mathematical formulas are different from tactics for working with conversion factors. First, most of the questions you will have to answer using formulas are word-type questions, so the first step is to identify what quantities are known and assign them to variables. Second, in most formulas, some mathematical rearrangements (i.e., algebra) must be performed to solve for an unknown variable. The rule is that to find the value of the unknown variable, you must mathematically isolate the unknown variable *by itself and in the numerator* of one side of the equation. Finally, units must be consistent. For example, in Boyle's law there are two pressure variables; they must have the same unit. There are also two volume variables; they also must have the same unit. In most cases, it won't matter *what* the unit is, but the unit must be the *same* on both sides of the equation.

Example 8.5.1

A sample of gas has an initial pressure of 2.44 atm and an initial volume of 4.01 L. Its pressure changes to 1.93 atm. What is the new volume if temperature and amount are kept constant?

Solution

First, determine what quantities we are given. We are given an initial pressure and an initial volume, so let these values be P_1 and V_1:

$$P_1 = 2.44 \text{ atm and } V_1 = 4.01 \text{ L}$$

We are given another quantity, final pressure of 1.93 atm, but not a final volume. This final volume is the variable we will solve for.

$$P_2 = 1.93 \text{ atm and } V_2 = ? \text{ L}$$

Substituting these values into Boyle's law, we get

$$(2.44 \text{ atm})(4.01 \text{ L}) = (1.93 \text{ atm})V_2$$

To solve for the unknown variable, we isolate it by dividing both sides of the equation by 1.93 atm—both the number *and* the unit:

$$\frac{(2.44\,atm)(4.01\,L)}{1.93\,atm} = \frac{(1.93\,atm)\,V_2}{1.93\,atm}$$

Note that, on the left side of the equation, the unit *atm* is in the numerator and the denominator of the fraction. They cancel algebraically, just as a number would. On the right side, the unit *atm* and the number 1.93 are in the numerator and the denominator, so the entire quantity cancels:

$$\frac{(2.44\ \cancel{atm}\ )(4.01\,L)}{1.93\ \cancel{atm}} = \frac{(1.93\ \cancel{atm}\ )\,V_2}{1.93\ \cancel{atm}}$$

What we have left is

$$\frac{(2.44)(4.01\,L)}{1.93} = V_2$$

Now we simply multiply and divide the numbers together and combine the answer with the L unit, which is a unit of volume. Doing so, we get $V_2 = 5.07\ L$

Does this answer make sense? We know that pressure and volume are inversely related; as one decreases, the other increases. Pressure is decreasing (from 2.44 atm to 1.93 atm), so volume should be increasing to compensate, and it is (from 4.01 L to 5.07 L). So the answer makes sense based on Boyle's law.

Exercise 8.5.1

If P_1 = 334 torr, V_1 = 37.8 mL, and P_2 = 102 torr, what is V_2?

Answer available at the end of this section.

As mentioned, you can use any units for pressure or volume, but both pressures must be expressed in the same units, and both volumes must be expressed in the same units.

Example 8.5.2

A sample of gas has an initial pressure of 722 torr and an initial volume of 88.8 mL. Its volume changes to 0.663 L. What is the new pressure?

Solution

We can still use Boyle's law to answer this, but now the two volume quantities have different units. It does not matter which unit we change, as long as we perform the conversion correctly. Let us change the 0.663 L to milliliters:

$$0.663\,L \times \frac{1000\,ml}{1\,L} = 663\,ml$$

Now that both volume quantities have the same units, we can substitute into Boyle's law:

$$(722\,torr)(88.8\,ml) = P_2(663\,ml)$$

$$\frac{(722\,torr)(88.8)\,ml}{(663\,ml)} = P_2$$

The mL units cancel, and we multiply and divide the numbers to get P_2 = 96.7 torr

The volume is increasing, and the pressure is decreasing, which is as expected for Boyle's law.

Exercise 8.5.2

If V_1 = 456 mL, P_1 = 308 torr, and P_2 = 1.55 atm, what is V_2?

Answer available at the end of this section.

To Your Health: Breathing and Boyle's Law

What do you do about 20 times per minute for your whole life, without break, and often without even being aware of it? The answer, of course, is respiration, or breathing. How does it work? It turns out that the gas laws apply here. Your lungs take in gas that your body needs (oxygen) and get rid of waste gas (carbon dioxide). Lungs are made of spongy, stretchy tissue that expands and contracts while you breathe. When you inhale, your diaphragm and intercostal muscles (the muscles between your ribs) contract, expanding your chest cavity and making your lung volume larger. The increase in volume leads to a decrease in pressure (Boyle's law). This causes air to flow into the lungs (from high pressure to low pressure). When you exhale, the process reverses: Your diaphragm and rib muscles relax, your chest cavity contracts, and your lung volume decreases, causing the pressure to increase (Boyle's law again), and air flows out of the lungs (from high pressure to low pressure). You then breathe in and out again, and again, repeating this Boyle's law cycle for the rest of your life (Figure 8.5.2).

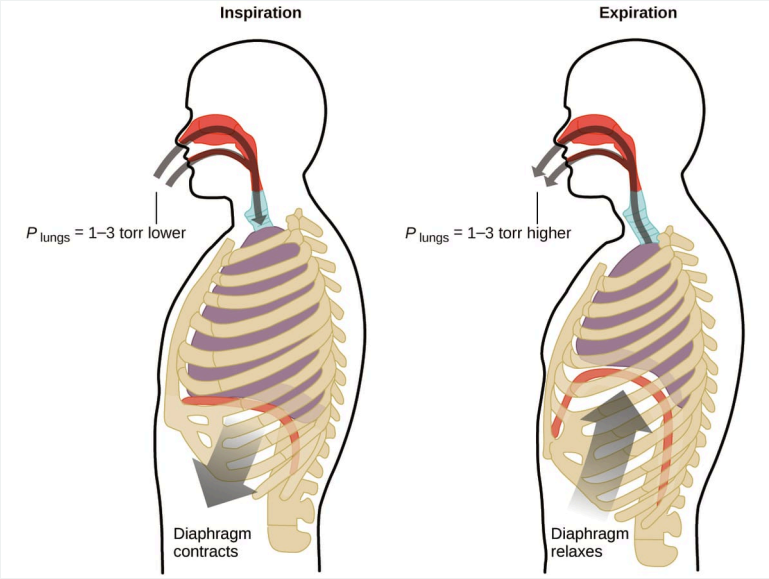


Figure 8.5.2: Breathing occurs because expanding and contracting lung volume creates small pressure differences between your lungs and your surroundings, causing air to be drawn into and forced out of your lungs.

This figure contains two diagrams of a cross section of the human head and torso. The first diagram on the left is labeled "Inspiration." It shows curved arrows in gray proceeding through the nasal passages and mouth to the lungs. An arrow points downward from the diaphragm, which is relatively flat, just beneath the lungs. This arrow is labeled "Diaphragm contracts." At the entrance to the mouth and nasal passages, a label of P subscript lungs equals 1 dash 3 torr lower" is provided. The second, similar diagram, which is labeled "Expiration," reverses the direction of both arrows. Arrows extend from the lungs out through the nasal passages and mouth. Similarly, an arrow points up to the diaphragm, showing a curved diaphragm and lungs reduced in size from the previous image. This arrow is labeled "Diaphragm relaxes." At the entrance to the mouth and nasal passages, a label of P subscript lungs equals 1 dash 3 torr higher" is provided.

Summary

- The behavior of gases can be modeled with gas laws.
- Boyle's law relates a gas's pressure and volume at constant temperature and amount.

Answers

Exercise 8.5.1

124 mL

Exercise 8.5.2

119 mL

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8.6: Charles's Law- The Relation between Volume and Temperature

Learning Objectives

- Define the relationship between gas temperature and volume, Charles's Law.
- Use Charles's Law to calculate changes in temperature or volume of a gas.

In addition to pressure and volume, another measurable characteristics of a gas is temperature (*T*). Perhaps one can vary the temperature of a gas sample and note what effect it has on the other properties of the gas. Early scientists did just this, discovering that if the amount of a gas and its pressure are kept constant, then changing the temperature changes the volume (*V*). As temperature increases, volume increases; as temperature decreases, volume decreases. We say that these two characteristics are *directly related*.

Kelvin Temperature Scale

A mathematical relationship between *V* and *T* should be possible except for one thought: what temperature scale should we use? We know from previous chapters that scientists uses several possible temperature scales. Experiments show that the volume of a gas is related to its absolute temperature in **Kelvin**, *not its temperature in degrees Celsius*. If the temperature of a gas is expressed in Kelvins, then experiments show that the *ratio* of volume to temperature is a constant (*k*):

$$\frac{V}{T} = k$$

Charles's Law

We can modify this equation as we modified Boyle's law: the initial conditions V_1 and T_1 have a certain value, and the value must be the same when the conditions of the gas are changed to some new conditions V_2 and T_2, as long as pressure and the amount of the gas remain constant. Thus, we have another gas law:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \; (at\ constant\ P\ and\ n)$$

This gas law is commonly referred to as **Charles's law**, after the French scientist Jacques Charles, who performed experiments on gases in the 1780s. The tactics for using this mathematical formula are similar to those for Boyle's law. To determine an unknown quantity, use algebra to isolate the unknown variable by itself and in the numerator; the units of similar variables must be the same. But we add one more tactic: all temperatures must be expressed in the absolute temperature scale (Kelvin). As a reminder, we review the conversion between the absolute temperature scale and the Celsius temperature scale:

$$K = °C + 273$$

where K represents the temperature in kelvins, and °C represents the temperature in degrees Celsius.

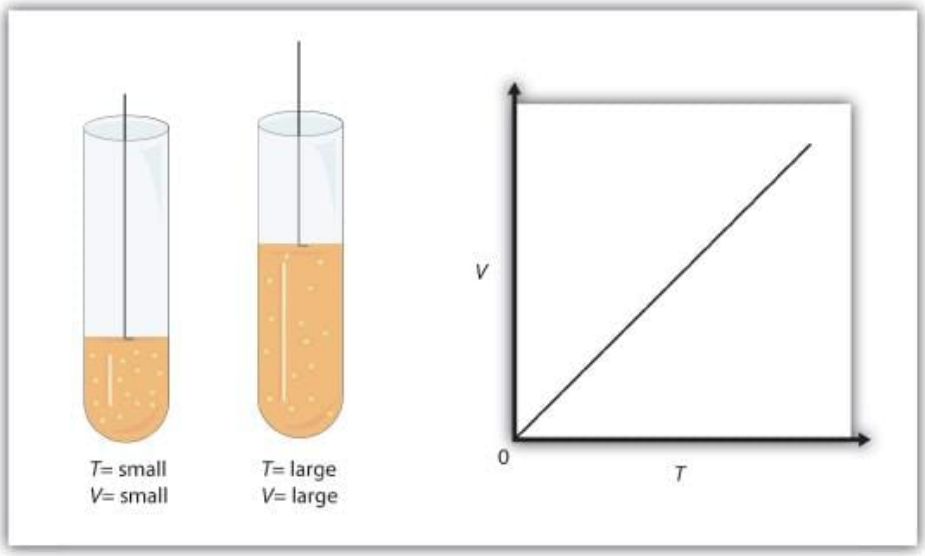


Figure 8.6.1: Charles's Law. A piston having a certain volume and temperature (left piston) will have twice the volume when its temperature is twice as much (right piston). One can also plot V versus T for a given amount of gas at a certain pressure; such a plot will look like the graph on the right.

Example 8.6.1

A sample of gas has an initial volume of 34.8 mL and an initial temperature of 315 K. What is the new volume if the temperature is increased to 559 K? Assume constant pressure and amount for the gas.

Solution

First, we assign the given values to their variables. The initial volume is V_1, so V_1 = 34.8 mL, and the initial temperature is T_1, so T_1 = 315 K. The temperature is increased to 559 K, so the final temperature T_2 = 559 K. We note that the temperatures are already given in kelvins, so we do not need to convert the temperatures. Substituting into the expression for Charles's law yields

$$\frac{34.8\,ml}{315\,K} = \frac{V_2}{559\,K}$$

We solve for V_2 by algebraically isolating the V_2 variable on one side of the equation. We do this by multiplying both sides of the equation by 559 K (number and unit). When we do this, the temperature unit cancels on the left side, while the entire 559 K cancels on the right side:

$$\frac{(559\,\cancel{K})(34.8\,ml)}{315\,\cancel{K}} = \frac{V_2(\,\cancel{559\,K}\,)}{\cancel{559\,K}}$$

The expression simplifies to

$$\frac{(559)(34.8\,ml)}{315} = V_2$$

By multiplying and dividing the numbers, we see that the only remaining unit is mL, so our final answer is

V_2 = 61.8 mL

Does this answer make sense? We know that as temperature increases, volume increases. Here, the temperature is increasing from 315 K to 559 K, so the volume should also increase, which it does.

Exercise 8.6.1

If V_1 = 3.77 L and T_1 = 255 K, what is V_2 if T_2 = 123 K?

Answer

1.82 L

It is more mathematically complicated if a final temperature must be calculated because the *T* variable is in the denominator of Charles's law. There are several mathematical ways to work this, but perhaps the simplest way is to take the reciprocal of Charles's law. That is, rather than write it as

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

write the equation as

$$\frac{T_1}{V_1} = \frac{T_2}{V_2}$$

It is still an equality and a correct form of Charles's law, but now the temperature variable is in the numerator, and the algebra required to predict a final temperature is simpler.

Example 8.6.2

A sample of a gas has an initial volume of 34.8 L and an initial temperature of −67°C. What must the temperature of the gas be for its volume to be 25.0 L?

Solution

Here, we are looking for a final temperature, so we will use the reciprocal form of Charles's law. However, the initial temperature is given in degrees Celsius, not kelvins. We must convert the initial temperature to kelvins:

−67°C + 273 = 206 K

In using the gas law, we must use T_1 = 206 K as the temperature. Substituting into the reciprocal form of Charles's law, we get

$$\frac{206\ K}{34.8\ L} = \frac{T_2}{25.0\ L}$$

Bringing the 25.0 L quantity over to the other side of the equation, we get

$$\frac{(25.0\ \cancel{L})(206\ K)}{34.8\ \cancel{L}} = T_2$$

The L units cancel, so our final answer is T_2 = 148 K

This is also equal to −125°C. As temperature decreases, volume decreases, which it does in this example.

Exercise 8.6.2

If V_1 = 623 mL, T_1 = 255°C, and V_2 = 277 mL, what is T_2?

Answer available at the end of this section.

Summary

- Charles's law relates a gas's volume and temperature at constant pressure and amount.
- In gas laws, temperatures must always be expressed in kelvins.

Answers

Exercise 8.6.2

235 K, or −38°C

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8.7: Gay-Lussac's Law- The Relationship Between Pressure and Temperature

Learning Objectives

- Define the relationship between gas pressure and temperature, Gay-Lussac's Law.

A third gas law may be derived as a corollary to Boyle's and Charles's laws. Suppose we double the thermodynamic temperature of a sample of gas. According to Charles's law, the volume should double. Now, how much pressure would be required at the higher temperature to return the gas to its original volume? According to Boyle's law, we would have to double the pressure to halve the volume. Thus, if the volume of gas is to remain the same, doubling the temperature will require doubling the pressure. This law was first stated by the Frenchman Joseph Gay-Lussac (1778 to 1850). According to **Gay-Lussac's law**, *for a given amount of gas held at constant volume, the pressure is proportional to the absolute temperature*. Mathematically,

$$P \propto T \text{ or } P = k \times T \text{ or } \frac{P}{T} = k$$

where $\propto$ means "is proportional to," and *k* is a proportionality constant that depends on the identity, amount, and volume of the gas.

In terms of two sets of data: $\frac{P_1}{T_1} = \frac{P_2}{T_2}$. This equation is useful for pressure-temperature calculations for a confined gas at constant volume. Note that temperatures must be on the kelvin scale for any gas law calculations (0 on the kelvin scale and the lowest possible temperature is called absolute zero). (Also note that there are at least three ways we can describe how the pressure of a gas changes as its temperature changes: We can use a table of values, a graph, or a mathematical equation.)

Gay-Lussac's law tells us that it may be dangerous to heat a gas in a closed container. The increased pressure might cause the container to explode, as you can see in the video below. The video shows very, very cold nitrogen gas in a bottle being warmed by the air. Since the bottle's volume is relatively constant, as the temperature of the nitrogen gas (formed when the liquid nitrogen boils) increases, so does the pressure inside the bottle until, finally, BOOM!

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Example 8.7.1: Temperature

A container is designed to hold a pressure of 2.5 atm. The volume of the container is 20.0 cm^3, and it is filled with air at room temperature (20°C) and normal atmospheric pressure. Would it be safe to throw the container into a fire where temperatures of 600°C would be reached?

Solution

Using the common-sense method, we realize that the pressure will increase at the higher temperature, and so:

$$P_2 = 1.0 \text{ atm } \times \frac{(273.15 + 600) \text{ K}}{(273.15 + 20) \text{ K}} = 3.0 \text{ atm}$$

This would exceed the safe strength of the container. Note that the volume of the container was not needed to solve the problem.

This concept works in reverse, as well. For instance, if we subject a gas to lower temperatures than their initial state, the external atmosphere can actually force the container to shrink. The following video demonstrates how a sample of hot gas, when cooled will collapse a container. A syringe barrel is filled with hot steam (vaporized water) and a plunger placed to cap off the end. The syringe is then placed in a beaker of ice water to cool the internal gas. When the temperature of the water vapor decreases, the pressure exerted by the vapor decreases as well. This leads to a difference in pressure between the vapor inside the barrel and the atmosphere. Atmospheric pressure then pushes the plunger into the barrel.

Summary

- Gay-Lussac's law relates a gas's temperature and pressure at constant volume and amount.
- In gas laws, temperatures must always be expressed in kelvins.

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8.8: The Combined Gas Law

Learning Objectives

- Use the combined gas law to determine the relationships between pressure, volume, and temperature of a gas.

One thing we notice about all gas laws, collectively, is that volume and pressure are always in the numerator, and temperature is always in the denominator. This suggests that we can propose a gas law that combines pressure, volume, and temperature. This gas law is known as the **combined gas law**, and its mathematical form is:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \; at \; constant \; n$$

This allows us to follow changes in all three major properties of a gas. Again, the usual warnings apply about how to solve for an unknown algebraically (isolate it on one side of the equation in the numerator), units (they must be the same for the two similar variables of each type), and units of temperature must be in kelvins.

Notice that each of the previous gas laws introduced, can be derived from the combined gas law:

At constant T, $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ *gives* Boyle's Law: $P_1V_1 = P_2V_2$

At constant P, $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ *gives* Charles's Law: $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

At constant V, $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ *gives* Gay-Lussac's Law: $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

In other words, if you know the equation for the combined gas law, you can calculate relationships between pressure, volume, or temperature of a fixed amount of gas.

Example 8.8.2

A sample of gas at an initial volume of 8.33 L, an initial pressure of 1.82 atm, and an initial temperature of 286 K simultaneously changes its temperature to 355 K and its volume to 5.72 L. What is the final pressure of the gas?

Solution

We can use the combined gas law directly; all the units are consistent with each other, and the temperatures are given in Kelvin. Substituting,

$$\frac{(1.82\,atm)(8.33\,L)}{286\,K} = \frac{P_2(5.72\,L)}{355\,K}$$

We rearrange this to isolate the *P*2 variable all by itself. When we do so, certain units cancel:

$$\frac{(1.82\,atm)(8.33\,\cancel{L})(355\,\cancel{K})}{(286\,\cancel{K})(5.72\,\cancel{L})} = P_2$$

Multiplying and dividing all the numbers, we get

$$P_2 = 3.29\,atm$$

Ultimately, the pressure increased, which would have been difficult to predict because two properties of the gas were changing.

Exercise 8.8.2

If P_1 = 662 torr, V_1 = 46.7 mL, T_1 = 266 K, P_2 = 409 torr, and T_2 = 371 K, what is V_2?

Answer available at the end of this section.

Summary

- There are gas laws that relate any two physical properties of a gas.
- The combined gas law relates pressure, volume, and temperature of a gas.

Contributors

Answers

Exercise 8.8.2

105 mL

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8.9: Avogadro's Law - The Relation between Volume and Molar Amount

Learning Objectives

- Describe the relationship between the amount and volume of a gas, Avogadro's Law.
- Define the conditions of standard temperature and pressure.

The Relationship between Amount and Volume: Avogadro's Law

We can demonstrate the relationship between the volume and the amount of a gas by filling a balloon; as we add more gas, the balloon gets larger. The specific quantitative relationship was discovered by the Italian chemist Amedeo Avogadro, who recognized the importance of Gay-Lussac's work on combining volumes of gases. In 1811, Avogadro postulated that, at the same temperature and pressure, equal volumes of gases contain the same number of gaseous particles (Figure 8.9.1). This is the historic "Avogadro's hypothesis."

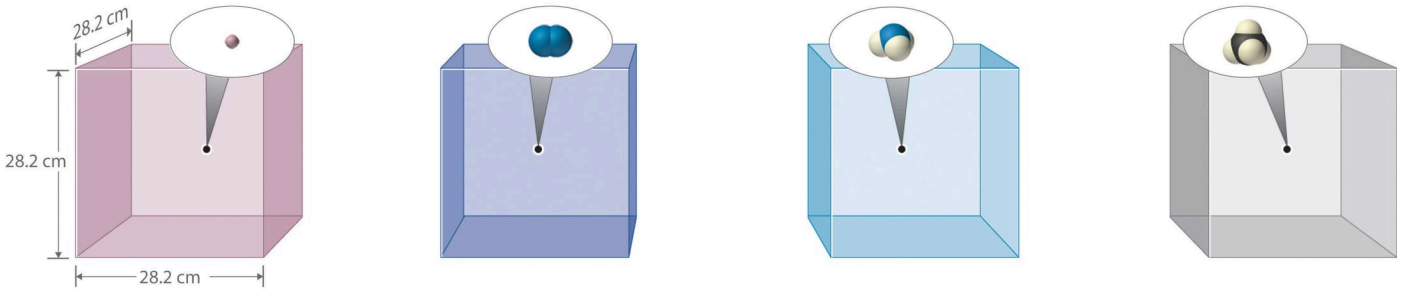


Figure 8.9.1: Avogadro's Hypothesis. Equal volumes of four different gases at the same temperature and pressure contain the same number of gaseous particles. Because the molar mass of each gas is different, the *mass* of each gas sample is different even though all contain 1 mol of gas (CC BY-SA-NC; anonymous).

Because the number of particles is related to the number of moles (1 mol = 6.022 × 10^{23} particles), **Avogadro's law** essentially states that equal volumes of different gases, at the same temperature and pressure, contain the same *amount* (moles, particles) of gas. *At constant temperature and pressure, the volume (V) of a sample of gas is directly proportional to the number of moles (n) of gas in the sample.* Stated mathematically,

$$V \propto n \text{ or } V = k \times n \text{ or } \frac{V}{n} = k$$

where $\propto$ means "is proportional to," and *k* is a proportionality constant that is the same for all gases.

In terms of two sets of data: $\frac{V_1}{n_1} = \frac{V_2}{n_2}$.

This relationship is valid for most gases at relatively low pressures, but deviations from strict linearity are observed at elevated pressures. Mathematical relationships can also be determined for the other variable pairs, such as *P* versus *n*, and *n* versus *T*.

> Visit this interactive PhET simulation to investigate the relationships between pressure, volume, temperature, and amount of gas. Use the simulation to examine the effect of changing one parameter on another while holding the other

parameters constant (as described in the preceding sections on the various gas laws).

Standard Temperature and Pressure

It should be obvious by now that some physical properties of gases depend strongly on the conditions. What we need is a set of standard conditions so that properties of gases can be properly compared to each other. **Standard Temperature and Pressure (STP)** is defined as exactly 100 kPa of pressure (0.986 atm) and 273 K (0°C). For simplicity, we will use 1 atm as standard pressure. Defining STP allows us to more directly compare the properties of gases that differ from one another.

One property shared among gases is a molar volume. The **molar volume** is the volume of 1 mol of a gas. At STP, the molar volume of a gas can be easily determined by using the ideal gas law:

$$(1\,atm)V = (1\,mol)\left(0.08205\frac{L.atm}{mol.K}\right)(273\,K)$$

All the units cancel except for L, the unit of volume. So V = 22.4 L

Note that we have not specified the identity of the gas; we have specified only that the pressure is 1 atm and the temperature is 273 K. This makes for a very useful approximation: *any gas at STP has a volume of 22.4 L per mole of gas*; that is, the molar volume at STP is 22.4 L/mol (Figure 8.9.1). This molar volume makes a useful conversion factor in stoichiometry problems if the conditions are at STP. If the conditions are not at STP, a molar volume of 22.4 L/mol is not applicable. However, if the conditions are at STP, the combined gas law can be used to calculate what the volume of the gas would be if at STP; then the 22.4 L/mol molar volume can be used.

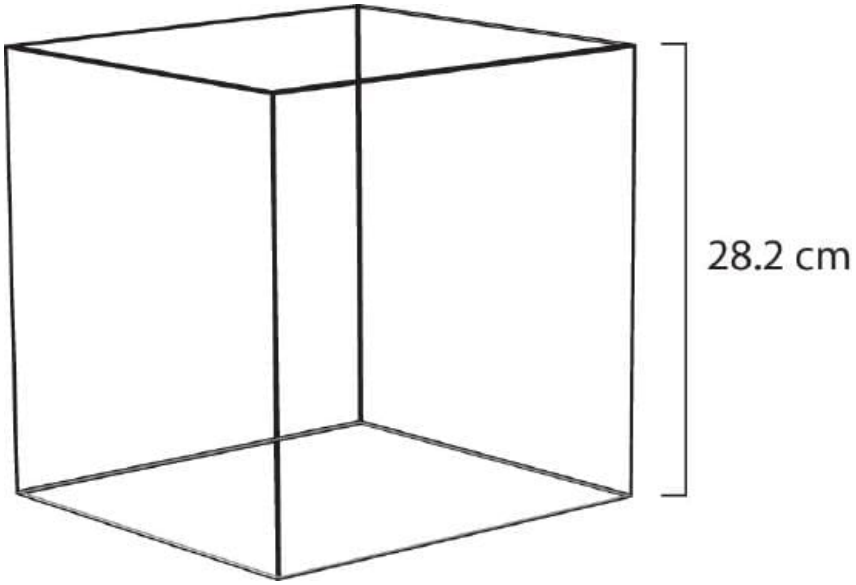


Figure 8.9.1: Molar Volume. A mole of gas at STP occupies 22.4 L, the volume of a cube that is 28.2 cm on a side.

Example 8.9.4

How many moles of Ar are present in 38.7 L at STP?

Solution

We can use the molar volume, 22.4 L/mol, as a conversion factor, but we need to reverse the fraction so that the L units cancel and mol units are introduced. It is a one-step conversion:

$$38.7 \cancel{L} \times \frac{1\,mol}{22.4 \cancel{L}} = 1.73\,mol$$

Exercise 8.9.4

What volume does 4.87 mol of Kr have at STP?

Answer available at the end of this section.

Example 8.9.5

What volume of $\mathrm{H_2}$ is produced at STP when 55.8 g of Zn metal react with excess HCl?

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

Solution

This is a stoichiometry problem with a twist: we need to use the molar volume of a gas at STP to determine the final answer. The first part of the calculation is the same as in a previous example:

$$55.8 \cancel{g\,Zn} \times \frac{1 \cancel{mol\,Zn}}{65.41 \cancel{g\,Zn}} \times \frac{1\,mol\,H_2}{1 \cancel{mol\,Zn}} = 0.853\,H_2$$

Now we can use the molar volume, 22.4 L/mol, because the gas is at STP:

$$0.853 \cancel{mol\,H_2} \times \frac{22.4\,L}{1 \cancel{mol\,H_2}} = 19.1\,L\,H_2$$

Alternatively, we could have applied the molar volume as a third conversion factor in the original stoichiometry calculation.

Exercise 8.9.5

What volume of HCl is generated if 3.44 g of $\mathrm{Cl_2}$ are reacted at STP?

$$\mathrm{H_2\,(g) + Cl_2\,(g) \longrightarrow 2\,HCl\,(g)}$$

Answer available at the end of this section.

Summary

- Avogadro's law states that the volume of gas is directly proportional to the number of moles of gas.
- Standard temperature and pressure (STP) are a useful set of benchmark conditions to compare other properties of gases.
- At STP, gases have a volume of 22.4 L per mole.

Answers

Exercise 8.9.4

109 L

Exercise 8.9.5

2.17 L

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8.10: The Ideal Gas Law

Learning Objectives

- Describe the ideal gas law.
- Use the ideal gas law to calculate pressure, volume, temperature, or moles of an ideal gas.

So far, the gas laws we have considered have all required that the gas change its conditions; then we can predict a resulting change in one of its properties. Are there any gas laws that relate the physical properties of a gas at any given time? Consider a further extension of the combined gas law to include *n*. By analogy to Avogadro's law, *n* is positioned in the denominator of the fraction, opposite the volume. So,

$$\frac{PV}{nT} = constant$$

Because pressure, volume, temperature, and amount are the only four independent physical properties of a gas, the constant in the above equation is truly a constant. Indeed, because we do not need to specify the identity of a gas to apply the gas laws, this constant is the same for all gases. We define this constant with the symbol *R*, so the previous equation is written as

$$\frac{PV}{nT} = R$$

which is usually rearranged as

$$PV = nRT$$

This equation is called the **ideal gas law**. It relates the four independent properties of a gas at any time. The constant \(*R*\) is called the **ideal gas law constant**. Its value depends on the units used to express pressure and volume.

Table 8.10.1*: Values of the Ideal Gas Law Constant lists the numerical values of* R.

Numerical Value	Units
0.08205	$\frac{L \cdot atm}{mol \cdot K}$
62.36	$\frac{L \cdot torr}{mol \cdot K} = \frac{L \cdot mmHg}{mol \cdot K}$
8.314	$\frac{J}{mol \cdot K}$

The ideal gas law is used like any other gas law, with attention paid to the unit and expression of the temperature in kelvin. However, *the ideal gas law does not require a change in the conditions of a gas sample*. The ideal gas law implies that if you know any three of the physical properties of a gas, you can calculate the fourth property.

Example 8.10.1

A 4.22 mol sample of Ar has a pressure of 1.21 atm and a temperature of 34°C. What is its volume?

Solution

The first step is to convert temperature to kelvins:

$$34 + 273 = 307\,\mathrm{K}$$

Now we can substitute the conditions into the ideal gas law:

$$(1.21atm)(V) = (4.22\,mol)\left(0.08205\frac{L.atm}{mol.K}\right)(307\,K)$$

The *atm* unit is in the numerator of both sides, so it cancels. On the right side of the equation, the *mol* and *K* units appear in the numerator and the denominator, so they cancel as well. The only unit remaining is *L*, which is the unit of volume that we are looking for. We isolate the volume variable by dividing both sides of the equation by 1.21:

$$V = \frac{(4.22)(0.08205)(307)}{1.21}L$$

Then solving for volume, we get *V* = 87.9 L

Exercise 8.10.1

A 0.0997 mol sample of O_2 has a pressure of 0.692 atm and a temperature of 333 K. What is its volume?

Answer available at the end of this section.

Example 8.10.2

At a given temperature, 0.00332 g of Hg in the gas phase has a pressure of 0.00120 mmHg and a volume of 435 L. What is its temperature?

Solution

We are not given the number of moles of Hg directly, but we are given a mass. We can use the molar mass of Hg to convert to the number of moles.

$$0.00332\,\cancel{g\,Hg} \times \frac{1\,mol\,Hg}{200.59\,\cancel{g\,Hg}} = 0.0000165\,mol = 1.65 \times 10^{-5} mol$$

Pressure is given in units of millimeters of mercury. We can either convert this to atmospheres or use the value of the ideal gas constant that includes the mmHg unit. We will take the second option. Substituting into the ideal gas law,

$$(0.00332\,mm\,Hg)(435\,L) = (1.65 \times 10^{-5} mol)(62.36\frac{L.mmHg}{mol.K})T$$

The mmHg, L, and mol units cancel, leaving the K unit, the unit of temperature. Isolating *T* on one side, we get

$$T = \frac{(0.00332)(435)}{(1.65 \times 10^{-5})(62.36)}K$$

Then solving for K, we get *T* = 1,404 K.

Exercise 8.10.2

For a 0.00554 mol sample of H_2, *P* = 23.44 torr and *T* = 557 K. What is its volume?

Answer available at the end of this section.

The ideal gas law can also be used in stoichiometry problems.

Example 8.10.3

What volume of $\mathrm{H_2}$ is produced at 299 K and 1.07 atm when 55.8 g of Zn metal react with excess HCl?

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

Solution

Here we have a stoichiometry problem where we need to find the number of moles of H2 produced. Then we can use the ideal gas law, with the given temperature and pressure, to determine the volume of gas produced. First, the number of moles of H2 is calculated:

$$55.8\ \cancel{g\,Zn} \times \frac{1\ \cancel{mol\,Zn}}{65.41\ \cancel{g\,Zn}} \times \frac{1\,mol\,H_2}{1\ \cancel{mol\,Zn}} = 0.853\,H_2$$

Now that we know the number of moles of gas, we can use the ideal gas law to determine the volume, given the other conditions:

$$(1.07atm)V = (0.853\,mol)\left(0.08205\frac{L.atm}{mol.K}\right)(299\,K)$$

All the units cancel except for L, for volume, which means *V* = 19.6 L

Exercise 8.10.3

What pressure of HCl is generated if 3.44 g of $\mathrm{Cl_2}$ are reacted in 4.55 L at 455 K?

$$\mathrm{H_2\,(g) + Cl_2\,(g) \longrightarrow 2\,HCl\,(g)}$$

Answer available at the end of this section.

Summary

- The ideal gas law relates the four independent physical properties of a gas at any time.
- The ideal gas law can be used in stoichiometry problems with chemical reactions that involve gases.

Answers

Exercise 8.10.1
3.94 L

Exercise 8.10.2
8.21 L

Exercise 8.10.3
0.796 atm

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8.11: Partial Pressure and Dalton's Law

Learning Objective

- Define Dalton's law of partial pressures.
- Use Dalton's law to calculate partial pressure of a gas in a mixture.

One of the properties of gases is that they mix with each other. When they do so, they become a solution—a homogeneous mixture. Some of the properties of gas mixtures are easy to determine if we know the composition of the gases in the mix.

In gas mixtures, each component in the gas phase can be treated separately because, according to the kinetic theory of gases, there are little to no attractive or repulsive forces between particles. Each component of a gas mixture shares the same temperature and volume, (remember that gases expand to fill the volume of their container; gases in a mixture continue to do that as well). However, each individual gas will have its *own pressure* within a mixture. This is called the **partial pressure** of a gas, P_i. Partial pressures are expressed in torr, millimeters of mercury, or atmospheres like any other gas pressure; however, we use the term *pressure* when talking about pure gases and the term *partial pressure* when we are talking about the individual gas components in a mixture.

Dalton's law of partial pressures states that the total pressure of a gas mixture, P_{tot}, is equal to the sum of the partial pressures of the components, P_i:

which is expressed algebraically as

$$P_{total} = P_1 + P_2 + P_3... = \sum_i P_i$$

or, equivalently

$$P_{total} = \frac{RT}{V} \sum_i n_i$$

where i counts over all gases in mixture.

Although this law may seem trivial, it reinforces the idea that gases behave independently of each other.

Example 8.11.1

A mixture of H_2 at 2.33 atm and N_2 at 0.77 atm is in a container. What is the total pressure in the container?

Solution

Dalton's law of partial pressures states that the total pressure is equal to the sum of the partial pressures. We simply add the two pressures together:

P_{tot} = 2.33 atm + 0.77 atm = 3.10 atm

Exercise 8.11.1

N_2 and O_2. In 760 torr of air, the partial pressure of N_2 is 608 torr. What is the partial pressure of O_2?

Answer available at the end of this section.

Example 8.11.2

A 2.00 L container with 2.50 atm of H_2 is connected to a 5.00 L container with 1.90 atm of O_2 inside. The containers are opened, and the gases mix. What is the final pressure inside the containers?

Solution

Because gases act independently of each other, we can determine the resulting final pressures using Boyle's law and then add the two resulting pressures together to get the final pressure. The total final volume is 2.00 L + 5.00 L = 7.00 L. First, we use Boyle's law to determine the final pressure of H_2:

$$(2.50 \text{ atm})(2.00 \text{ L}) = P_2(7.00 \text{ L})$$

Solving for P_2, we get P_2 = 0.714 atm = partial pressure of H_2.

Now we do that same thing for the O_2:

$$(1.90 \text{ atm})(5.00 \text{ L}) = P_2(7.00 \text{ L}) P_2 = 1.36 \text{ atm} = \text{partial pressure of } O_2$$

The total pressure is the sum of the two resulting partial pressures:

$$P_{tot} = 0.714 \text{ atm} + 1.36 \text{ atm} = 2.07 \text{ atm}$$

Exercise 8.11.2

If 0.75 atm of He in a 2.00 L container is connected to a 3.00 L container with 0.35 atm of Ne and the containers are opened, what is the resulting total pressure?

Answer available at the end of this section.

Dalton's law states that in a gas mixture (P_{total}) each gas will exert a pressure independent of the other gases (P_n) and each gas will behave as if it alone occupies the total volume. By extension, the partial pressure of each gas can be calculated by multiplying the total pressure (P_{total}) by the gas percentage (%).

$$P_{Total} = P_1 + P_2 + P_3 + P_4 + ... + P_n$$

or

$$P_n = \frac{n}{P_{Total}}$$

Table 8.11.1: Partial Pressures for the gases in air on a typical day

Gas	Partial Pressure (mm Hg)	Percentage (%)
Nitrogen, (N_2\)	P_{N_2} = 594	78
Oxygen, O_2	P_{O_2}= 160	21
Carbon Dioxide, CO_2	P_{CO_2} = 0.25	0.033
Water Vapor, H_2O	P_{H_2O} = 5.7	0.75
Other trace gases	P_{Other} = 0.05	0.22
Total air	P_{Total} = 760	1

Application of Dalton's Law: Collecting Gases over Water

A common laboratory method of collecting the gaseous product of a chemical reaction is to conduct it into an inverted tube or bottle filled with water, the opening of which is immersed in a larger container of water. This arrangement is called a *pneumatic trough*, and was widely used in the early days of chemistry. As the gas enters the bottle it displaces the water and becomes trapped in the upper part.

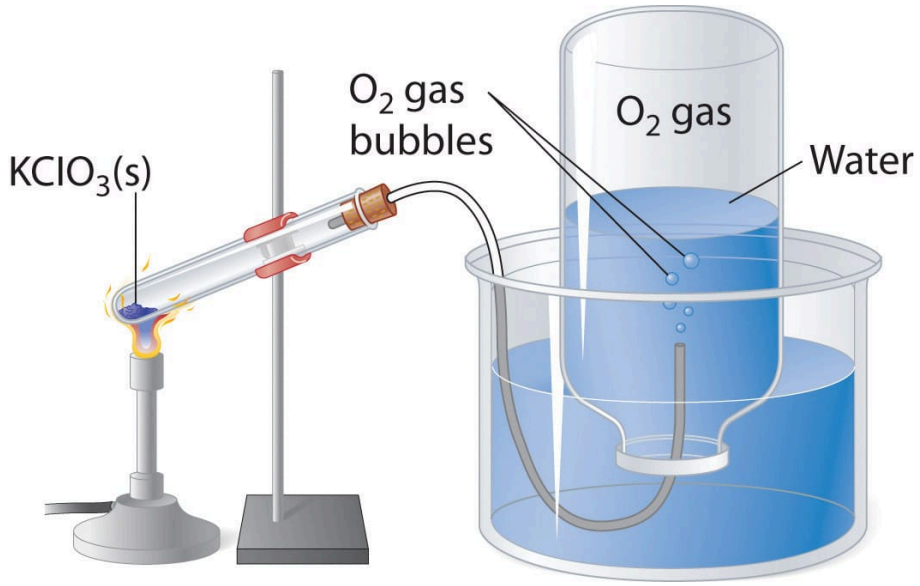


Figure 8.11.1:An Apparatus for Collecting Gases by the Displacement of Water

The volume of the gas can be observed by means of a calibrated scale on the bottle, but what about its pressure? The total pressure confining the gas is just that of the atmosphere transmitting its force through the water. (An exact calculation would also have to take into account the height of the water column in the inverted tube.) But liquid water itself is always in equilibrium with its vapor, so the space in the top of the tube is a mixture of two gases: the gas being collected, and gaseous H_2O. The partial pressure of H_2O is known as the vapor pressure of water and it depends on the temperature. In order to determine the quantity of gas we have collected, we must use Dalton's Law to find the partial pressure of that gas.

Example 8.11.3

Oxygen gas was collected over water as shown above. The atmospheric pressure was 754 torr, the temperature was 22°C, and the volume of the gas was 155 mL. The vapor pressure of water at 22°C is 19.8 torr. Use this information to estimate the number of moles of O_2 produced.

Solution

From Dalton's law,

$$P_{O_2} = P_{total} – P_{H_2O} = 754 – 19.8 = 734\ torr = 0.966\ atm$$

Now use the Ideal Gas Law to convert to moles

$$n = \frac{PV}{RT} = \frac{(0.966\ atm)(0.155\ L)}{(0.082\ Latmmol^{-1}K^{-1})(295\ K)} = 0.00619\ mol$$

Exercise 8.11.3

CO_2, generated by the decomposition of $CaCO_3$, is collected in a 3.50 L container over water. If the temperature is 50°C and the total pressure inside the container is 833 torr, how many moles of CO_2 were generated?

Answer available at the end of this section.

Food and Drink Application: Carbonated Beverages

Carbonated beverages—sodas, beer, sparkling wines—have one thing in common: they have CO_2 gas dissolved in them in such sufficient quantities that it affects the drinking experience. Most people find the drinking experience pleasant—indeed, in the United States alone, over 1.5×10^9 gal of soda are consumed each year, which is almost 50 gal per person! This figure does not include other types of carbonated beverages, so the total consumption is probably significantly higher.

All carbonated beverages are made in one of two ways. First, the flat beverage is subjected to a high pressure of CO_2 gas, which forces the gas into solution. The carbonated beverage is then packaged in a tightly-sealed package (usually a bottle or a can) and sold. When the container is opened, the CO_2 pressure is released, resulting in the well-known *hiss* of an opening container, and CO_2 bubbles come out of solution. This must be done with care: if the CO_2 comes out too violently, a mess can occur!



Figure 8.11.1: Carbonated beverage. If you are not careful opening a container of a carbonated beverage, you can make a mess, as the CO_2 comes out of solution suddenly. (Unsplash License; Tina Vanhove via Unsplash)

The second way a beverage can become carbonated is by the ingestion of sugar by yeast, which then generates CO_2 as a digestion product. This process is called *fermentation*. The overall reaction is

$$C_6H_{12}O_6\,(aq) \longrightarrow 2\,C_2H_5OH\,(aq) + 2\,CO_2\,(aq)$$

When this process occurs in a closed container, the CO_2 produced dissolves in the liquid, only to be released from solution when the container is opened. Most fine sparkling wines and champagnes are turned into carbonated beverages this way. Less-expensive sparkling wines are made like sodas and beer, with exposure to high pressures of CO_2 gas.

Summary

- The pressure of a gas in a gas mixture is termed the *partial pressure*.
- Dalton's law of partial pressure says that the total pressure in a gas mixture is the sum of the individual partial pressures.

Answers

Exercise 8.11.1

152 torr

Exercise 8.11.2

0.51 atm

Exercise 8.11.3

0.129 mol

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8.12: Liquids

Learning Objective

- Define the vapor pressure of liquids.
- Explain the origin of both surface tension and capillary action.

There are some properties that all liquids, including water, have. All liquids have a certain portion of particles with enough energy to enter the gas phase, and if these particles are at the surface of the liquid, they do so (Figure 8.12.1). The formation of a gas from a liquid at temperatures below the boiling point is called **evaporation**. At these temperatures, the material in the gas phase is called **vapor**, rather than gas; the term *gas* is reserved for when the gas phase is the stable phase.

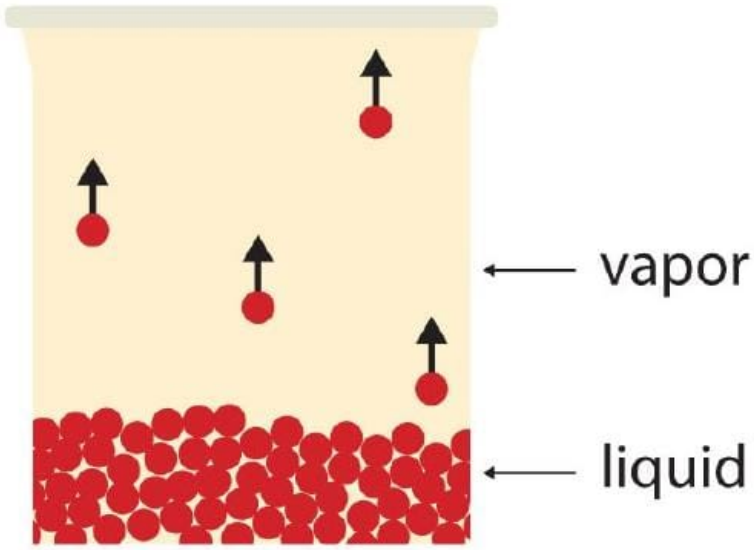


Figure 8.12.1: Evaporation. Some particles of a liquid have enough energy to escape the liquid phase to become a vapor.

If the available volume is large enough, eventually all the liquid will become vapor. But if the available volume is not enough, eventually some of the vapor particles will reenter the liquid phase (Figure 8.12.2 Equilibrium). At some point, the number of particles entering the vapor phase will equal the number of particles leaving the vapor phase, so there is no net change in the amount of vapor in the system. We say that the system is *at equilibrium*. The partial pressure of the vapor at equilibrium is called the **vapor pressure** of the liquid.

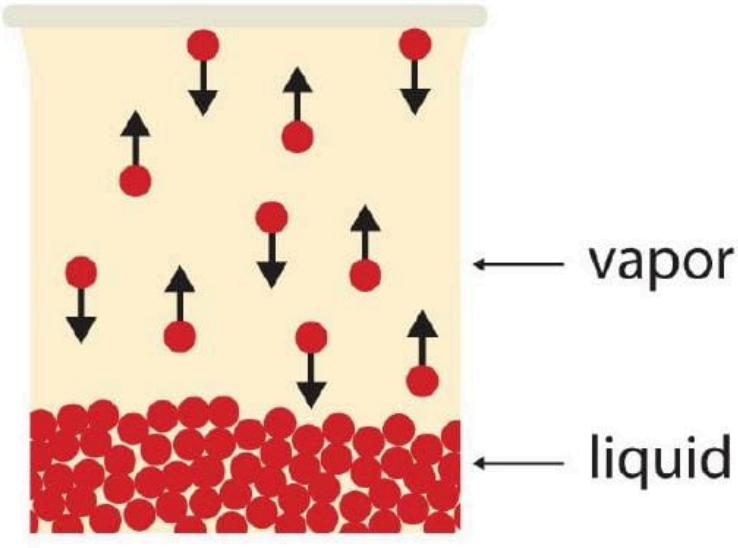


Figure 8.12.2: Equilibrium. At some point, the number of particles entering the vapor phase will be balanced by the number of particles returning to the liquid. This point is called equilibrium.

Understand that the liquid has not stopped evaporating. The reverse process—condensation—is occurring as fast as evaporation, so there is no net change in the amount of vapor in the system. The term *dynamic equilibrium* represents a situation in which a process still occurs, but the opposite process also occurs at the same rate, so that there is no net change in the system.

The vapor pressure for a substance is dependent on the temperature of the substance; as the temperature increases, so does the vapor pressure. Figure 8.12.3 - Plots of Vapor Pressure versus Temperature for Several Liquids, is a plot of vapor pressure versus temperature for several liquids. Having defined vapor pressure, we can also redefine the boiling point of a liquid: the temperature at which the vapor pressure of a liquid equals the surrounding environmental pressure. The **normal boiling point**, then, is the temperature at which the vapor pressure is 760 torr, or exactly 1 atm. Thus boiling points vary with surrounding pressure, a fact that can have large implications on cooking foods at lower- or higher-than-normal elevations. Atmospheric pressure varies significantly with altitude.

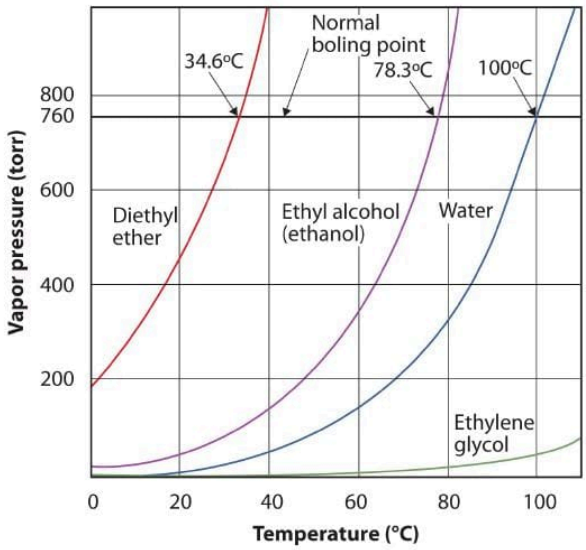


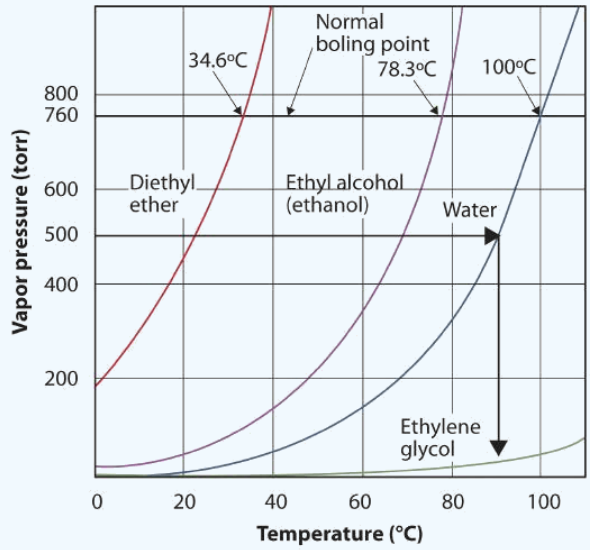
Figure 8.12.3: Plots of Vapor Pressure versus Temperature for Several Liquids. The vapor pressure of a liquid depends on the identity of the liquid and the temperature, as this plot shows.

Example 8.12.1

Use Figure 8.12.3 to estimate the boiling point of water at 500 torr, which is the approximate atmospheric pressure at the top of Mount Everest.

Solution

See the accompanying figure. Five hundred torr is between 400 and 600, so we extend a line from that point on the *y*-axis across to the curve for water and then drop it down to the *x*-axis to read the associated temperature. It looks like the point on the water vapor pressure curve corresponds to a temperature of about 90°C, so we conclude that the boiling point of water at 500 torr is 90°C.



By reading the graph properly, you can estimate the boiling point of a liquid at different temperatures.

Exercise 8.12.1

Use Figure 8.12.3 to estimate the boiling point of ethanol at 400 torr.

Answer available at the end of this section.

The vapor pressure curve for water is not exactly zero at the melting point 0°C. Even ice has a vapor pressure—that is why it sublimes over time. However, the vapor pressures of solids are typically much lower than that of liquids. At –1°C, the vapor pressure of ice is 4.2 torr. At a freezer temperature of 0°F (–17°C), the vapor pressure of ice is only 1.0 torr; so-called deep freezers can get down to –23°C, where the vapor pressure of ice is only 0.6 torr.

All liquids share some other properties as well. **Surface tension** is an effect caused by an imbalance of forces on the atoms at the surface of a liquid, as shown in Figure 8.12.4. The blue particle in the bulk of the liquid experiences intermolecular forces from all around, as illustrated by the arrows. However, the yellow particle on the surface does not experience any forces above it because there are no particles above it. This leads to an imbalance of forces, called surface tension.

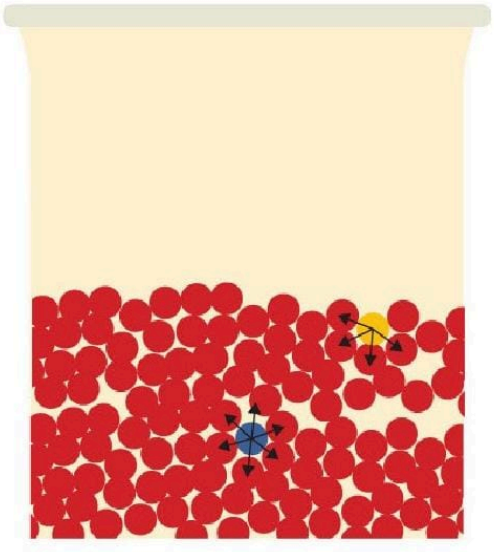


Figure 8.12.4 Surface Tension. Surface tension comes from the fact that particles at the surface of a liquid do not experience interactions from all directions, leading to an imbalance of forces on the surface.

Surface tension is responsible for several well-known behaviors of liquids, including water. Liquids with high surface tension tend to bead up when present in small amounts (Figure 8.12.5).



Figure 8.12.5 Effects of Surface Tension © Thinkstock. Water on the surface of this apple beads up due to the effect of surface tension.

Surface tension causes liquids to form spheres in free fall or zero gravity. Surface tension is also responsible for the fact that small insects can "walk" on water. Because of surface tension, it takes energy to break the surface of a liquid, and if an object (such as an insect) is light enough, there is not enough force due to gravity for the object to break through the surface, so the object stays on top of the water (Figure 8.12.6). Carefully done, this phenomenon can also be illustrated with a thin razor blade or a paper clip.



Figure 8.12.6 Walking on Water. Small insects can actually walk on top of water because of surface tension effects. (Unsplash License; Miguel Alcântara via unsplash)

The fact that small droplets of water bead up on surfaces does not mean that water—or any other liquid—does not interact with other substances. Sometimes the attraction can be very strong. **Adhesion** is the tendency of a substance to interact with other substances because of intermolecular forces, while **cohesion** is the tendency of a substance to interact with itself. If cohesive forces within a liquid are stronger than adhesive forces between a liquid and another substance, then the liquid tends to keep to itself; it will bead up. However, if adhesive forces between a liquid and another substance are stronger than cohesive forces, then the liquid will spread out over the other substance, trying to maximize the interface between the other substance and the liquid. It is said that the liquid *wets* the other substance.

Adhesion and cohesion are important for other phenomena as well. In particular, if adhesive forces are strong, then when a liquid is introduced to a small-diameter tube of another substance, the liquid will move up or down in the tube, as if ignoring gravity.

Because tiny tubes are called capillaries, this phenomenon is called **capillary action.** For example, one type of capillary action, *capillary rise*, is seen when water or water-based liquids rise up in thin glass tubes (like the capillaries sometimes used in blood tests), forming an upwardly curved surface called a **meniscus**. Capillary action is also responsible for the "wicking" effect that towels and sponges use to dry wet objects; the matting of fibers forms tiny capillaries that have good adhesion with water. Cotton is a good material for this; polyester and other synthetic fabrics do not display similar capillary action, which is why you seldom find rayon bath towels. A similar effect is observed with liquid fuels or melted wax and their wicks. Capillary action is thought to be at least partially responsible for transporting water from the roots to the tops of trees, even tall ones.

On the other hand, some liquids have stronger cohesive forces than adhesive forces. In this case, in the presence of a capillary, the liquid is forced down from its surface; this is an example of a type of capillary action called *capillary depression*. In this case, the meniscus curves downward. Mercury has very strong cohesive forces; when a capillary is placed in a pool of mercury, the surface of the mercury liquid is depressed (Figure 8.12.7).



Figure 8.12.7: Capillary Action. (a) Capillary rise is seen when adhesion is strong, such as with water in a thin glass tube. (b) Capillary depression is seen when cohesive forces are stronger than adhesive forces, such as with mercury and thin glass tubes.

Chemistry is Everywhere: Waxing a Car

Responsible car owners are encouraged to wax their cars regularly. In addition to making the car look nicer, it also helps protect the surface, especially if the surface is metal. Why?

The answer has to do with cohesion and adhesion (and, to a lesser extent, rust). Water is an important factor in the rusting of iron, sometimes used extensively in outer car bodies. Keeping water away from the metal is one way to minimize rusting. A coat of paint helps with this. However, dirty or scratched paint can attract water, and adhesive forces will allow the water to wet the surface, maximizing its contact with the metal and promoting rust.



Figure 8.12.8: Waxing a car. Droplets of water on a freshly waxed car do not wet the car well because of low adhesion between water and the waxed surface. This helps protect the car from rust. (Unsplash License; Yuvraj Singh via Unspash)

Wax is composed of long hydrocarbon molecules that do not interact well with water. (Hydrocarbons are compounds with C and H atoms; for more information on hydrocarbons, see Chapter 16). That is, a thin layer of wax will not be wetted by water. A freshly waxed car has low adhesive forces with water, so water beads up on the surface, as a consequence of its cohesion and surface tension. This minimizes the contact between water and metal, thus minimizing rust.

Summary

- All liquids evaporate.
- If volume is limited, evaporation eventually reaches a dynamic equilibrium, and a constant vapor pressure is maintained.
- All liquids experience surface tension, an imbalance of forces at the surface of the liquid.
- All liquids experience capillary action, demonstrating either capillary rise or capillary depression in the presence of other substances.

Answers

Exercise 8.12.1

about 65°C

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8.13: Solids

Learning Objective

- Describe the general properties of a solid.
- Describe the six different types of solids.

A solid is like a liquid in that particles are in contact with one another. Solids are unlike liquids in that the intermolecular forces are strong enough to hold the particles in place. At low enough temperatures, all substances are solids (helium is the lone exception), but the temperature at which the solid state becomes the stable phase varies widely among substances, from 20 K (−253°C) for hydrogen to over 3,900 K (3,600°C) for carbon.

The solid phase has several characteristics. First, solids maintain their shape. They do not fill their entire containers like gases do, and they do not adopt the shape of their containers like liquids do. They cannot be easily compressed like gases can, and they have relatively high densities.

Solids may also demonstrate a variety of properties. For example, many metals can be beaten into thin sheets or drawn into wires, while compounds such as NaCl will shatter if they are struck. Some metals, such as sodium and potassium, are rather soft, while others, such as diamond, are very hard and can easily scratch other substances. Appearances differ as well: most metals are shiny and silvery, but sulfur (a nonmetal) is yellow, and ionic compounds can take on a rainbow of colors. Solid metals conduct electricity and heat, while ionic solids do not. Many solids are opaque, but some are transparent. Some dissolve in water, but some do not. Figure 8.13.1, shows two solids that exemplify the similar and dissimilar properties of solids.



Figure 8.13.1: Properties of Solids. (a) Sodium metal is silvery, soft, opaque, and conducts electricity and heat well. (b) NaCl is transparent, hard, colorless, and does not conduct electricity or heat well in the solid state. These two substances illustrate the range of properties that solids can have. Source: Photo on left courtesy of Images of Elements, http://images-of-elements.com/sodium.php. Photo on right courtesy of Choba Poncho, commons.wikimedia.org/wiki/File:Sodiumchloride_crystal_01.jpg.

Solids can have a wide variety of physical properties. We will review the different types of solids and the bonding that gives them their properties.

First, we must distinguish between two general types of solids. An **amorphous solid** is a solid with no long-term structure or repetition. Examples include glass and many plastics, both of which are composed of long chains of molecules with no order from one molecule to the next. A **crystalline solid** is a solid that has a regular, repeating three-dimensional structure. A crystal of NaCl (Figure 8.13.1) is one example: at the atomic level, NaCl is composed of a regular three-dimensional array of Na^+ ions and Cl^- ions.

There is only one type of amorphous solid. However, there are several different types of crystalline solids, depending on the identity of the units that compose the crystal.

An **ionic solid** is a crystalline solid composed of ions (even if the ions are polyatomic). NaCl is an example of an ionic solid (Figure 8.13.2 - An Ionic Solid). The Na^+ ions and Cl^- ions alternate in three dimensions, repeating a pattern that goes on throughout the sample. The ions are held together by the attraction of opposite charges—a very strong force. Hence most ionic solids have relatively high melting points; for example, the melting point of NaCl is 801°C. Ionic solids are typically very brittle. To break them, the very strong ionic attractions need to be broken; a displacement of only about 1×10^{-10} m will move ions next to ions of the same charge, which results in repulsion. Ionic solids do not conduct electricity in their solid state; however, in the liquid state and when dissolved in some solvent, they do conduct electricity. This fact originally promoted the idea that some substances exist as ionic particles.

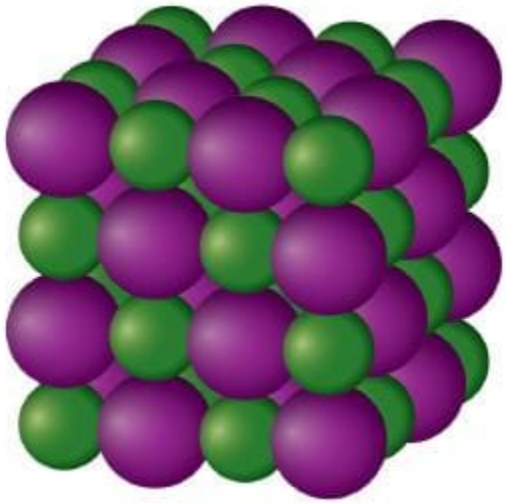


Figure 8.13.2: An Ionic Solid. NaCl is a solid composed of a three-dimensional array of alternating Na^+ ions (green) and Cl^- ions (purple) held together by the attraction of opposite charges.

A **molecular solid** is a crystalline solid whose components are covalently bonded molecules. Many molecular substances, especially when carefully solidified from the liquid state, form solids where the molecules line up with a regular fashion similar to an ionic crystal, but they are composed of molecules instead of ions. Because the intermolecular forces between molecules are typically less strong than in ionic solids, molecular solids typically melt at lower temperatures and are softer than ionic solids. Ice is an example of a molecular solid. In the solid state, the molecules line up in a regular pattern (Figure 8.13.3). Some very large molecules, such as biological molecules, will form crystals only if they are very carefully solidified from the liquid state or, more often, from a dissolved state; otherwise, they will form amorphous solids.

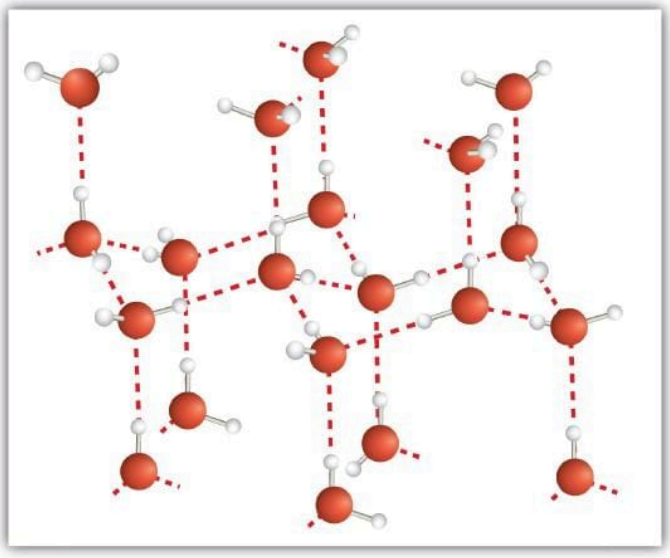


Figure 8.13.3: Molecular Solids. Water molecules line up in a regular pattern to form molecular solids. The dotted lines show how the polar O–H covalent bonds in one molecule engage in hydrogen bonding with other molecules. The O atoms are red, and the H atoms are white.

Some solids are composed of atoms of one or more elements that are covalently bonded together in a seemingly never-ending fashion. Such solids are called **covalent network solids**. Each piece of the substance is essentially one huge molecule, as the covalent bonding in the crystal extends throughout the entire crystal. The two most commonly known covalent network solids are carbon in its diamond form and silicon dioxide (SiO_2). Figure 8.13.4 - Covalent Network Solids, shows the bonding in a covalent network solid. Generally, covalent network solids are poor conductors of electricity, although their ability to conduct heat is variable: diamond is one of the most thermally conductive substances known, while SiO_2 is about 100 times less thermally conductive. Most covalent network solids are very hard, as exemplified by diamond, which is the hardest known substance. Covalent network solids have high melting points by virtue of their network of covalent bonds, all of which would have to be broken for them to transform into a liquid. Indeed, covalent network solids are among the highest-melting substances known: the melting point of diamond is over 3,500°C, while the melting point of SiO_2 is around 1,650°C. These characteristics are explained by the network of covalent bonds throughout the sample.

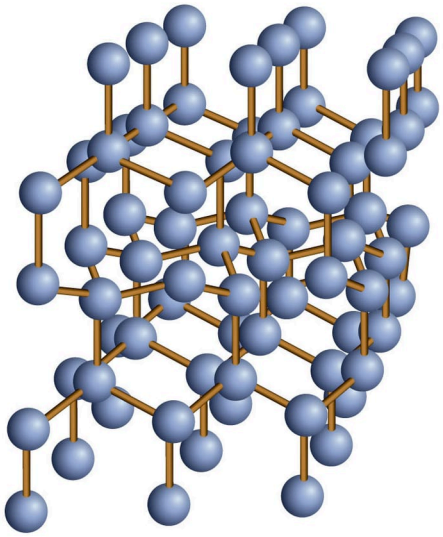


Figure 8.13.4: Covalent Network Solids. Diamond is a covalent network solid, with each C atom making four covalent bonds to four other C atoms. A diamond is essentially one huge molecule.

A **metallic solid** is a solid with the characteristic properties of a metal: shiny and silvery in color and a good conductor of heat and electricity. A metallic solid can also be hammered into sheets and pulled into wires. A metallic solid exhibits metallic bonding,

a type of intermolecular interaction caused by the sharing of the s valence electrons by all atoms in the sample. It is the sharing of these valence electrons that explains the ability of metals to conduct electricity and heat well. It is also relatively easy for metals to lose these valence electrons, which explains why metallic elements usually form cations when they make compounds.

Example 8.13.1

Predict the type of crystal exhibited by each solid.

a. MgO
b. Ag
c. CO_2

Solution

a. A combination of a metal and a nonmetal makes an ionic compound, so MgO would exist as ionic crystals in the solid state.
b. Silver is a metal, so it would exist as a metallic solid in the solid state.
c. CO_2 is a covalently bonded molecular compound. In the solid state, it would form molecular crystals. (You can actually see the crystals in dry ice with the naked eye.)

Exercise 8.13.1

Predict the type of crystal exhibited by each solid.

a. I_2
b. $Ca(NO_3)_2$

Answers

a. molecular crystals
b. ionic crystals

Food and Drink Application: The Rocks We Eat

The foods and beverages we eat and drink all have different phases: solid, liquid, and gas. (How do we ingest gases? Carbonated beverages have gas, which sometimes cause a person to belch.) However, among the solids we eat, three in particular are, or are produced from, rocks. Yes, rocks!

The first one is NaCl, or common salt. Salt is the only solid that we ingest that is actually mined as a rock (hence the term *rock salt*; it really is a rock). Salt provides both Na^+ ions and Cl^- ions, both of which are necessary for good health. Salt preserves food, a function that was much more important before the days of modern food preparation and storage. The fact that saltiness is one of the major tastes the tongue can detect suggests a strong evolutionary link between ingesting salt and survival. There is some concern today that there is too much salt in the diet; it is estimated that the average person consumes at least three times as much salt daily as is necessary for proper bodily function.

The other two rocks we eat are related: sodium bicarbonate ($NaHCO_3$) and sodium carbonate (Na_2CO_3). However, we do not mine these substances directly from the ground; we mine trona, whose chemical formula is $Na_3H(CO_3)_2$. This substance is dissolved in water and treated with CO_2 gas to make either Na_2CO_3 or $NaHCO_3$. Another process, called the Solvay process, is also used to make Na_2CO_3. In the Solvay process, NH_3 and CO_2 are added to solutions of NaCl to make $NaHCO_3$ and NH_4Cl; the $NaHCO_3$ precipitates and is heated to produce Na_2CO_3. Either way, we get these two products from the ground (i.e., rocks).

$NaHCO_3$ is also known as baking soda, which is used in many baked goods. Na_2CO_3 is used in foods to regulate the acid balance. It is also used in laundry (where it is called washing soda) to interact with other ions in water that tend to reduce detergent efficiency.



Figure 8.13.5: Salt Mining © Thinkstock. Salt mining can be at the surface or below ground. Here salt is mined from surface deposits. Part of the processing facility can be seen in the background.

Summary

- Solids can be divided into amorphous solids and crystalline solids.
- Crystalline solids can be ionic, molecular, covalent network, or metallic.

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8.14: Changes of State Calculations

Learning Objectives

- Define enthalpy of fusion and enthalpy of vaporization.
- Calculate the energy changes that accompany phase changes.
- Interpret heating and cooling curves.

Everyday we take advantage of changes between the gas, liquid, and solid states to cool a drink with ice cubes (solid to liquid), cool our bodies by perspiration (liquid to gas), and cool food inside a refrigerator (gas to liquid and vice versa). We use dry ice, which is solid CO_2, as a refrigerant (solid to gas), and we make artificial snow for skiing and snowboarding by transforming a liquid to a solid. In this section, we examine the changes in energy that occur during these changes in state or phase changes.

As introduced in an earlier section, changes of state involve changes in enthalpy ΔH, or changes in energy. Melting (changing a solid to liquid) and evaporating (changing a liquid to a gas) are both *endothermic* processes, requiring the addition of heat to break the intermolecular interactions between molecules. The reverse processes, condensation (changing a gas to a liquid) and freezing (changing a liquid to a solid), are both *exothermic*, meaning heat is given off or released when intermolecular interactions are reformed. The specific amount of energy absorbed or released when one gram of substance changes between a solid and a liquid (at the melting point) is called the **enthalpy of fusion** or heat of fusion, (ΔH_{fus}). At the boiling point, when one gram of substance changes between a liquid and a gas, the energy change is called the **enthalpy of vaporization** or heat of vaporization, (ΔH_{vap}).

Heating Curves

It is important to understand the difference between the energy associated with changes in temperature and changes in state where the temperature remains constant. This difference is most clearly depicted in a **heating curve**, which is a plot of the temperature versus heating time (or heat added). The heating curve in figure $8.14.1$ is the temperature change for a 75 g sample of water as heat is added over time. The sample is initially solid (ice) at 1 atm and –23°C; as heat is added, the *temperature* of the ice increases linearly with time. The slope of the line depends on both the mass of the ice and the specific heat (C_S) of ice, which is the amount of energy (in Joules or calories) required to raise the temperature of 1 g of ice by 1°C. As the temperature increases, the water molecules in the ice crystal absorb more and more energy and vibrate more vigorously. At the melting point, they have enough kinetic energy to overcome attractive forces and move with respect to one another. As more heat is added, the temperature of the system does *not* increase further but remains constant at 0°C until all the ice has melted. Once all the ice has been converted to liquid water, the temperature of the water again begins to increase. Now, however, the temperature increases more slowly than before because the specific heat capacity of liquid water is *greater* than that of solid water. When the temperature of the water reaches 100°C, the water begins to boil. Here, too, the temperature remains constant at 100°C until all the water has been converted to steam. At this point, the temperature again begins to rise, but at a *faster* rate than seen in the other phases because the heat capacity of steam is *less* than that of ice or water.

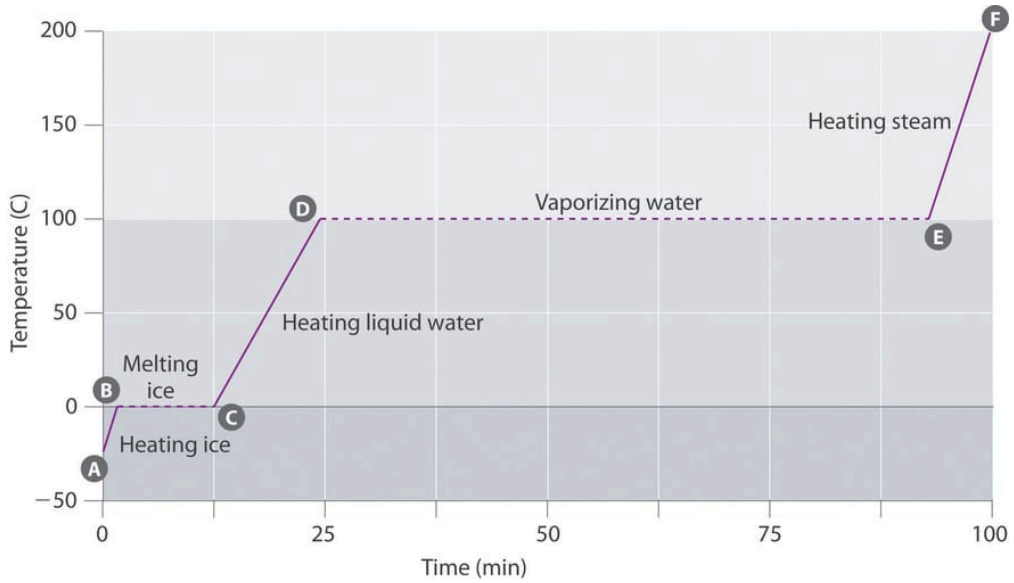


Figure 8.14.1: A Heating Curve for Water. This plot of temperature shows what happens to a 75 g sample of ice initially at 1 atm and –23°C as heat is added at a constant rate: A–B: heating solid ice; B–C: melting ice; C–D: heating liquid water; D–E: vaporizing water; E–F: heating steam.

It is worth noting again that *the temperature of a system does not change during a phase change*. In this example, as long as even a tiny amount of ice is present, the temperature of the system remains at 0°C during the melting process, and as long as even a small amount of liquid water is present, the temperature of the system remains at 100°C during the boiling process. The rate at which heat is added does *not* affect the temperature of the ice/water or water/steam mixture because the added heat is being used exclusively to overcome the attractive forces that hold the more condensed phase together. Many cooks think that food will cook faster if the heat is turned up higher so that the water boils more rapidly. Instead, the pot of water will boil to dryness sooner, but the temperature of the water does not depend on how vigorously it boils.

> The temperature of a sample does not change during a phase change.

If heat is added at a constant rate, as in Figure 8.14.1, then the length of the horizontal lines, which represents the time during which the temperature does not change, is directly proportional to the magnitude of the enthalpies associated with the phase changes. In Figure 8.14.1, the horizontal line at 100°C is much longer than the line at 0°C because the enthalpy of vaporization of water is several times greater than the enthalpy of fusion.

A superheated liquid is a sample of a liquid at the temperature and pressure at which it should be a gas. Superheated liquids are not stable; the liquid will eventually boil, sometimes violently. The phenomenon of superheating causes “bumping” when a liquid is heated in the laboratory. When a test tube containing water is heated over a Bunsen burner, for example, one portion of the liquid can easily become too hot. When the superheated liquid converts to a gas, it can push or “bump” the rest of the liquid out of the test tube. Placing a stirring rod or a small piece of ceramic (a “boiling chip”) in the test tube allows bubbles of vapor to form on the surface of the object so the liquid boils instead of becoming superheated. Superheating is the reason a liquid heated in a smooth cup in a microwave oven may not boil until the cup is moved, when the motion of the cup allows bubbles to form.

Cooling Curves

The **cooling curve**, in Figure 8.14.2 plots temperature versus time as a 75 g sample of steam, initially at 1 atm and 200°C, is cooled (heat is released). Although we might expect the cooling curve to be the mirror image of the heating curve in Figure 8.14.1, the cooling curve is *not* an identical mirror image. As heat is removed from the steam, the temperature falls until it reaches 100°C. At this temperature, the steam begins to condense to liquid water. No further temperature change occurs until all the steam is converted to the liquid; then the temperature again decreases as the water is cooled. We might expect to reach another plateau at 0°C, where the water is converted to ice; in reality, however, this does not always occur. Instead, the temperature often drops below the freezing point for some time, as shown by the little dip in the cooling curve below 0°C. This region corresponds to an unstable form of the liquid, a supercooled liquid. If the liquid is allowed to stand, if cooling is continued, or if a small crystal of the solid phase is added (a seed crystal), the supercooled liquid will convert to a solid, sometimes quite suddenly. As the water freezes, the temperature increases slightly due to the heat evolved during the freezing process and then holds constant at the melting point as the rest of the water freezes. Subsequently, the temperature of the ice decreases again as more heat is removed

from the system.

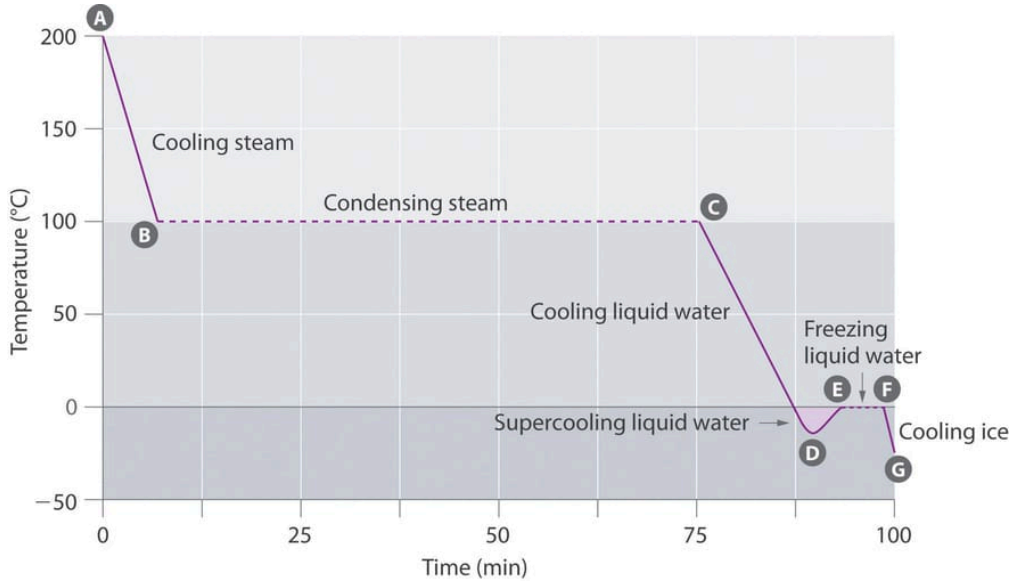


Figure 8.14.2: A Cooling Curve for Water. This plot of temperature shows what happens to a 75 g sample of steam initially at 1 atm and 200°C as heat is removed at a constant rate: A–B: cooling steam; B–C: condensing steam; C–D: cooling liquid water to give a supercooled liquid; D–E: warming the liquid as it begins to freeze; E–F: freezing liquid water; F–G: cooling ice.

Supercooling effects have a huge impact on Earth's climate. For example, supercooling of water droplets in clouds can prevent the clouds from releasing precipitation over regions that are persistently arid as a result. Clouds consist of tiny droplets of water, which in principle should be dense enough to fall as rain. In fact, however, the droplets must aggregate to reach a certain size before they can fall to the ground. Usually a small particle (a *nucleus*) is required for the droplets to aggregate; the nucleus can be a dust particle, an ice crystal, or a particle of silver iodide dispersed in a cloud during *seeding* (a method of inducing rain). Unfortunately, the small droplets of water generally remain as a supercooled liquid down to about –10°C, rather than freezing into ice crystals that are more suitable nuclei for raindrop formation. One approach to producing rainfall from an existing cloud is to cool the water droplets so that they crystallize to provide nuclei around which raindrops can grow. This is best done by dispersing small granules of solid CO_2 (dry ice) into the cloud from an airplane. Solid CO_2 sublimes directly to the gas at pressures of 1 atm or lower, and the enthalpy of sublimation is substantial (25.3 kJ/mol). As the CO_2 sublimes, it absorbs heat from the cloud, often with the desired results.

YouTube Video

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A Video Discussing the Thermodynamics of Phase Changes. Video Source: The Thermodynamics of Phase Changes, YouTube(opens in new window) [youtu.be]

Example 8.14.1: Cooling Tea

If a 50.0 g ice cube at 0.0°C is added to 500 mL of tea at 20.0°C, what is the temperature of the tea when the ice cube has just melted? Assume that no heat is transferred to or from the surroundings. The density of water (and iced tea) is 1.00 g/mL over the range 0°C–20°C, the specific heats of liquid water and ice are 4.184 J/(g•°C) and 2.062 J/(g•°C), respectively, and the enthalpy of fusion of ice is 6.01 kJ/mol.

Given: mass, volume, initial temperature, density, specific heats, and ΔH_{fus}

Asked for: final temperature

Strategy

Substitute the given values into the general equation relating heat gained (by the ice) to heat lost (by the tea) to obtain the final temperature of the mixture.

Solution

When two substances or objects at different temperatures are brought into contact, heat will flow from the warmer one to the cooler. The amount of heat that flows is given by

$$q = mC_s\Delta T$$

where q is heat, m is mass, C_s is the specific heat, and ΔT is the temperature change. Eventually, the temperatures of the two substances will become equal at a value somewhere between their initial temperatures. Calculating the temperature of iced tea after adding an ice cube is slightly more complicated. The general equation relating heat gained and heat lost is still valid, but in this case we also have to take into account the amount of heat required to melt the ice cube from ice at 0.0°C to liquid water at 0.0°C.

The amount of heat gained by the ice cube as it melts is determined by its enthalpy of fusion in kJ/mol:

$$q = n\Delta H_{fus}$$

For our 50.0 g ice cube:

$$\begin{aligned} q_{ice} &= 50.0g \cdot \frac{1\,mol}{18.02\,g} \cdot 6.01\,kJ/mol \\ &= 16.7\,kJ \end{aligned}$$

Thus, when the ice cube has just melted, it has absorbed 16.7 kJ of heat from the tea. We can then substitute this value into the first equation to determine the change in temperature of the tea:

$$q_{tea} = -16,700J = 500mL \cdot \frac{1.00\,g}{1\,mL} \cdot 4.184J/(g\,\bullet°C)\Delta T$$

$$\Delta T = -7.98°C = T_f - T_i$$

$$T_f = 12.02°C$$

This would be the temperature of the tea when the ice cube has just finished melting; however, this leaves the melted ice still at 0.0°C. We might more practically want to know what the final temperature of the mixture of tea will be once the melted ice has come to thermal equilibrium with the tea. To determine this, we can add one more step to the calculation by plugging in to the general equation relating heat gained and heat lost again:

$$\begin{aligned} q_{ice} &= -q_{tea} \\ q_{ice} &= m_{ice}C_s\Delta T = 50.0g \cdot 4.184J/(g\,\bullet°C) \cdot (T_f - 0.0°C) \\ &= 209.2J/°C \cdot T_f \end{aligned}$$

$$q_{tea} = m_{tea}C_s\Delta T = 500g \cdot 4.184J/(g\,\bullet°C) \cdot (T_f - 12.02°C) = 2092J/°C \cdot T_f - 25,150J$$

$$209.2J/°C \cdot T_f = -2092J/°C \cdot T_f + 25,150J$$

$$2301.2J/°C \cdot T_f = 25,150J$$

$$T_f = 10.9°C$$

The final temperature is in between the initial temperatures of the tea (12.02 °C) and the melted ice (0.0 °C), so this answer makes sense. In this example, the tea loses much more heat in melting the ice than in mixing with the cold water, showing the importance of accounting for the heat of phase changes!

Exercise 8.14.1: Death by Freezing

Suppose you are overtaken by a blizzard while ski touring and you take refuge in a tent. You are thirsty, but you forgot to bring liquid water. You have a choice of eating a few handfuls of snow (say 400 g) at –5.0°C immediately to quench your thirst or setting up your propane stove, melting the snow, and heating the water to body temperature before drinking it. You recall that the survival guide you leafed through at the hotel said something about not eating snow, but you cannot remember why—after all, it's just frozen water. To understand the guide's recommendation, calculate the amount of heat that your body will have to supply to bring 400 g of snow at –5.0°C to your body's internal temperature of 37°C. Use the data in Example 8.14.1

Answer available at the end of this section.

Sublimation

There is also a phase change where a solid goes directly to a gas:

$$\text{solid} \rightarrow \text{gas} \tag{8.14.1}$$

This phase change is called *sublimation*. Each substance has a characteristic heat of sublimation associated with this process. For example, the heat of sublimation (ΔH_{sub}) of H_2O is 620 cal/g.

We encounter sublimation in several ways. You may already be familiar with dry ice, which is simply solid carbon dioxide (CO_2). At –78.5°C (–109°F), solid carbon dioxide sublimes, changing directly from the solid phase to the gas phase:

$$\mathrm{CO_2(s)} \xrightarrow{-78.5^\circ\mathrm{C}} \mathrm{CO_2(g)} \tag{8.14.2}$$

Solid carbon dioxide is called dry ice because it does not pass through the liquid phase. Instead, it does directly to the gas phase. (Carbon dioxide *can* exist as liquid but only under high pressure.) Dry ice has many practical uses, including the long-term preservation of medical samples.

Even at temperatures below 0°C, solid H_2O will slowly sublime. For example, a thin layer of snow or frost on the ground may slowly disappear as the solid H_2O sublimes, even though the outside temperature may be below the freezing point of water. Similarly, ice cubes in a freezer may get smaller over time. Although frozen, the solid water slowly sublimes, redepositing on the colder cooling elements of the freezer, which necessitates periodic defrosting (frost-free freezers minimize this redeposition). Lowering the temperature in a freezer will reduce the need to defrost as often.

Under similar circumstances, water will also sublime from frozen foods (e.g., meats or vegetables), giving them an unattractive, mottled appearance called freezer burn. It is not really a "burn," and the food has not necessarily gone bad, although it looks unappetizing. Freezer burn can be minimized by lowering a freezer's temperature and by wrapping foods tightly so water does not have any space to sublime into.

Summary

- Phase changes are associated with energy changes.
- The enthalpy of fusion, ΔH_{fus}, is the energy absorbed or released when a substance changes between a solid and a liquid.
- The enthalpy of vaporization, ΔH_{vap}, is the energy absorbed or released when a substance changes between a liquid and a gas.
- Heating and cooling curves are useful tools to show how temperature, energy, and phases are related.

Answers

Exercise 8.14.1**: Death by Freezing**

200 kJ (4.1 kJ to bring the ice from –5.0°C to 0.0°C, 133.6 kJ to melt the ice at 0.0°C, and 61.9 kJ to bring the water from 0.0°C to 37°C), which is energy that would not have been expended had you first melted the snow.

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9: SOLUTIONS

9.1: Mixtures and Solutions

9.2: The Solution Process

9.3: Solubility

9.4: The Effect of Temperature on Solubility

9.5: The Effect of Pressure on Solubility - Henry's Law

9.6: Units of Concentration

9.7: Dilution

9.8: Ions in Solution - Electrolytes

9.9: Properties of Solutions

9.10: Osmosis and Osmotic Pressure

9.11: Dialysis

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9.1: Mixtures and Solutions

Learning Objectives

- Describe the difference between homogenous and heterogenous mixtures.
- Distinguish a homogenous mixture as a solution or colloid.

As introduced previously, *mixtures* are combinations of two or more substances that each retain their individual physical properties. A mixture can be classified as either *heterogenous* or *homogenous*. In a heterogeneous mixture, the composition is *not* uniform throughout the sample, and sometimes the individual substances that make up the mixture can be differentiated by eye. Trail mix, salad, and blood (which is also called a suspension) are examples of heterogenous mixtures. Homogenous mixtures are uniform and have the same composition throughout. Air, simple syrup, and seawater are examples of homogenous mixtures.

Homogenous mixtures can be further classified, based on the *size* of their particles, as solutions or colloids. **Solutions** are composed of particles the size of an ion or small molecule, ~0.1-2.0 nm. The examples provided above are all considered solutions; air is a solution of small gas molecules, simple syrup is a solution of sucrose in water, and seawater is a solution of ions and water. Homogenous mixtures with larger particles, ~2.0-500 nm, are classified as **colloids**. Milk, fog, and butter are all considered colloids. Mixtures with particles larger than 500 nm are called **suspensions** and are considered to be heterogenous mixtures in which the particles will settle upon standing. Many medications are classified as suspensions that need to be re-mixed before taking in order to redistribute the particles throughout the mixture. Some examples and distinguishing characteristics of solutions, colloids, and suspensions are listed in Table 9.1.1 below.

Table 9.1.1: Properties of Liquid Solutions, Colloids, and Suspensions

Type of Mixture	Approximate Size of Particles (nm)	Characteristic Properties	Examples
solution	< 2	not filterable; does not separate on standing; does not scatter visible light	air, white wine, gasoline, salt water
colloid	2–500	scatters visible light; translucent or opaque; not filterable; does not separate on standing	smoke, fog, ink, milk, butter, cheese
suspension	500–1000	cloudy or opaque; filterable; separates on standing	muddy water, hot cocoa, blood, paint

The major component of a solution, called the **solvent**, is typically the same phase as the solution itself. Each minor component of a solution (and there may be more than one) is called the **solute**. In most of the solutions we will describe in this textbook, there will be no ambiguity about whether a component is the solvent or the solute. For example, in a solution of salt in water, the solute is salt, and solvent is water.

Solutions come in all phases, and the solvent and the solute do not have to be in the same phase to form a solution (such as salt and water). For example, air is a gaseous solution of about 80% nitrogen and about 20% oxygen, with some other gases present in much smaller amounts. An alloy is a solid solution consisting of a metal (like iron) with some other metals or nonmetals dissolved in it. Steel, an alloy of iron and carbon and small amounts of other metals, is an example of a solid solution. Table 9.1.2 lists some common types of solutions, with examples of each.

Table 9.1.2: Types of Solutions

Solvent Phase	Solute Phase	Example
gas	gas	air
liquid	gas	carbonated beverages
liquid	liquid	ethanol (C_2H_5OH) in H_2O (alcoholic beverages)
liquid	solid	saltwater

Solvent Phase	Solute Phase	Example
solid	gas	H_2 gas absorbed by Pd metal
solid	liquid	Hg(ℓ) in dental fillings
solid	solid	steel alloys

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9.2: The Solution Process

Learning Objectives

- Predict solubility based on interactions between solute and solvent.

What occurs at the molecular level to cause a solute to dissolve in a solvent? The answer depends in part on the strength of attractions between solute and solvent particles. A good rule of thumb is to use is *like dissolves like*, which means that substances must have similar intermolecular attractions to form solutions.

A substance can *dissolve* in a solvent, and form a solution, if the solute and solvent are *attracted* to each other. For example, water molecules that are held together by hydrogen bonding will dissolve solutes that can also hydrogen bond, like ethanol (CH_3CH_2OH). The new hydrogen bonds between the water and the ethanol molecules (solvent-solute attractions) are nearly as strong as the hydrogen bonds in water (solvent-solvent) and ethanol (solute-solute) alone, making the process of solution formation (also called dissolution or dissolving) favorable.

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, are surrounded by solvent molecules. (Gaseous solutes already have their constituent particles separated, but the concept of being surrounded by solvent particles still applies.) This process is called **solvation** and is illustrated in Figure 9.2.1. When the solvent is water, the word **hydration**, rather than solvation, is used.

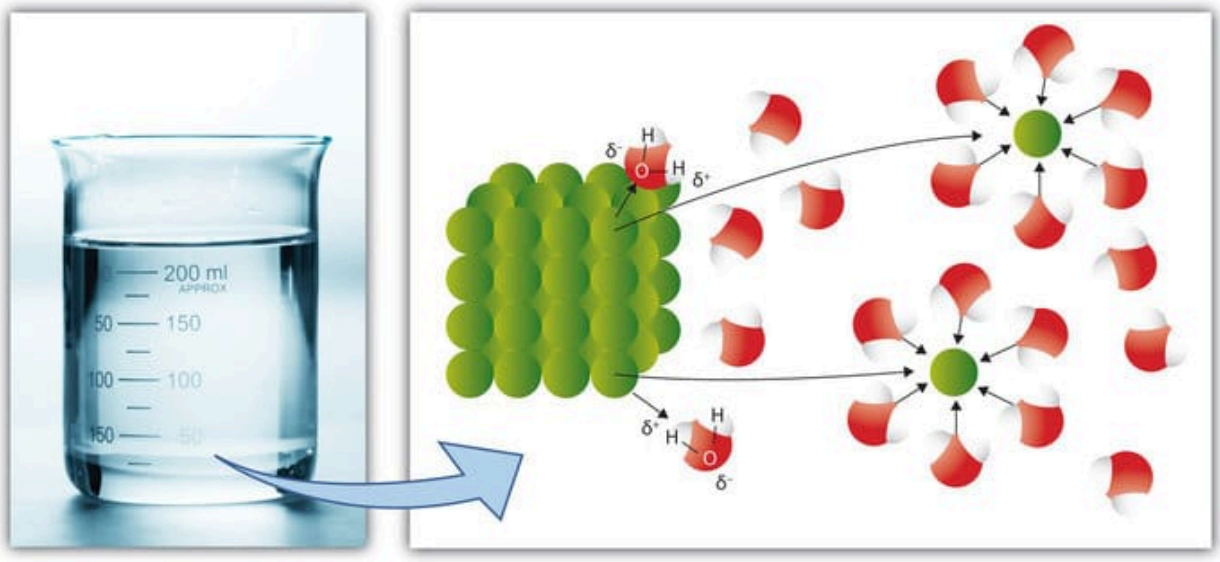


Figure 9.2.1: Solvation. When a solute dissolves, the individual particles of solute become surrounded by solvent particles. Eventually the particle detaches from the remaining solute, surrounded by solvent molecules in solution. Source: Photo © Thinkstock

When a solute and solvent that do not have similar intermolecular interactions are mixed, a solution is not formed because the solute-solute or solvent-solvent attractions are stronger than any favorable interactions between solute and solvent. For example when water and oil are mixed, stay in separate layers, i.e., they will not mix to yield solutions and the water molecules remain hydrogen bonded to water molecules while the oil molecules stay together (Figure 9.2.2). Hydrogen bonding is the dominant intermolecular attractive force present in liquid water; the nonpolar hydrocarbon molecules of cooking oils are not capable of hydrogen bonding, instead being held together by dispersion forces. Forming an oil-water solution would require overcoming the very strong hydrogen bonding in water, as well as the significantly strong dispersion forces between the relatively large oil molecules. And, since the polar water molecules and nonpolar oil molecules would not experience very strong intermolecular attraction, very little energy would be released by solvation.



Figure 9.2.2: A mixture of nonpolar cooking oil and polar water does not yield a solution. (credit: Gautam Dogra).

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. The positively charged cations are attracted to the neg and anions of an ionic solute separate when the solute dissolves. This process is referred to as **dissociation** (Figure 9.2.1).

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

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

Example 9.2.1

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

1. potassium chloride (KCl)
2. fructose ($C_6H_{12}O_6$)
3. isopropyl alcohol [$CH_3CH(OH)CH_3$]
4. magnesium hydroxide [$Mg(OH)_2$]

Solution

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

1. Potassium chloride is an ionic compound; therefore, when it dissolves, its ions separate, making it an electrolyte.
2. Fructose is a sugar similar to glucose. (In fact, it has the same molecular formula as glucose.) Because it is a molecular compound, we expect it to be a nonelectrolyte.

3. Isopropyl alcohol is an organic molecule containing the alcohol functional group. The bonding in the compound is all covalent, so when isopropyl alcohol dissolves, it separates into individual molecules but not ions. Thus, it is a nonelectrolyte
4. Magnesium hydroxide is an ionic compound, so when it dissolves it dissociates. Thus, magnesium hydroxide is an electrolyte.

Exercise 9.2.1

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

a. acetone (CH_3COCH_3)
b. iron(III) nitrate [$Fe(NO_3)_3$]
c. elemental bromine (Br_2)
d. sodium hydroxide (NaOH)

Answer available at the end of this section.

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.

Concept Review Exercise

1. Explain how the solvation process describes the dissolution of a solute in a solvent.

Answer

1. Each particle of the solute is surrounded by particles of the solvent, carrying the solute from its original phase.

Key Takeaway

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

Exercises

1. Describe what happens when an ionic solute like Na_2SO_4 dissolves in a polar solvent.
2. Describe what happens when a molecular solute like sucrose ($C_{12}H_{22}O_{11}$) dissolves in a polar solvent.
3. Classify each substance as an electrolyte or a nonelectrolyte. Each substance dissolves in H_2O to some extent.
   a. NH_4NO_3
   b. CO_2
   c. NH_2CONH_2

d. HCl

4. Classify each substance as an electrolyte or a nonelectrolyte. Each substance dissolves in H_2O to some extent.

a. $CH_3CH_2CH_2OH$
b. $Ca(CH_3CO_2)_2$
c. I_2
d. KOH

5. Will solutions of each solute conduct electricity when dissolved?

a. $AgNO_3$
b. $CHCl_3$
c. $BaCl_2$
d. Li_2O

6. Will solutions of each solute conduct electricity when dissolved?

a. CH_3COCH_3
b. $N(CH_3)_3$
c. $CH_3CO_2C_2H_5$
d. $FeCl_2$

Answers

1. Each ion of the ionic solute is surrounded by particles of solvent, carrying the ion from its associated crystal.

2. Each sucrose molecule is surrounded by solvent molecules (attracted to each other via intermolecular forces of attraction).

3. a. electrolyte
b. nonelectrolyte
c. nonelectrolyte
d. electrolyte

4.

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

5.

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

6.

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

Answers

Exercise 9.2.1

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

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9.3: Solubility

Learning Objectives

- Describe solutions as saturated or unsaturated by understanding solubility.

To define a solution precisely, we need to state its concentration: how much solute is dissolved in a certain amount of solvent. Words such as *dilute* or *concentrated* are used to describe solutions that have a little or a lot of dissolved solute, respectively, but these are relative terms whose meanings depend on various factors.

Solubility

There is usually a limit to how much solute will dissolve in a given amount of solvent. This limit is called the **solubility** of the solute. Some solutes have a very small solubility, while other solutes are soluble in all proportions. Table 9.3.1 lists the solubilities of various solutes in water. Solubilities vary with temperature, so Table 9.3.1 includes the temperature at which the solubility was determined.

Table 9.3.1: Solubilities of Various Solutes in Water at 25°C (Except as Noted)

Substance	Solubility (g in 100 mL of H_2O)
AgCl(s)	0.019
$C_6H_6(\ell)$ (benzene)	0.178
$CH_4(g)$	0.0023
$CO_2(g)$	0.150
$CaCO_3(s)$	0.058
$CaF_2(s)$	0.0016
$Ca(NO_3)_2(s)$	143.9
$C_6H_{12}O_6$ (glucose)	120.3 (at 30°C)
KBr(s)	67.8
$MgCO_3(s)$	2.20
NaCl(s)	36.0
$NaHCO_3(s)$	8.41
$C_{12}H_{22}O_{11}$ (sucrose)	204.0 (at 20°C)

If a solution contains so much solute that its solubility limit is reached, the solution is said to be **saturated**, and its concentration is known from information contained in Table 9.3.1. If a solution contains less solute than the solubility limit, it is **unsaturated**. Under special circumstances, more solute can be dissolved even after the normal solubility limit is reached; such solutions are called ***supersaturated*** and are not stable. If the solute is solid, excess solute can easily recrystallize. If the solute is a gas, it can bubble out of solution uncontrollably, like what happens when you shake a soda can and then immediately open it.

Most solutions we encounter are unsaturated, so knowing the solubility of the solute does not accurately express the amount of solute in these solutions. There are several common ways of specifying the concentration of a solution that will be discussed in later sections.

Solution Equilibrium

When a solute dissolves, its individual atoms, molecules, or ions interact with the solvent, become solvated, and are able to diffuse independently throughout the solution (Figure $9.3.1a$). This is not, however, a unidirectional process. If the molecule or ion happens to collide with the surface of a particle of the undissolved solute, it may adhere to the particle in a process called crystallization. The **equilibrium** between dissolution and crystallization continue as long as excess solid is present, resulting in a dynamic equilibrium analogous to the equilibrium that maintains the vapor pressure of a liquid. We can represent these opposing processes as follows:

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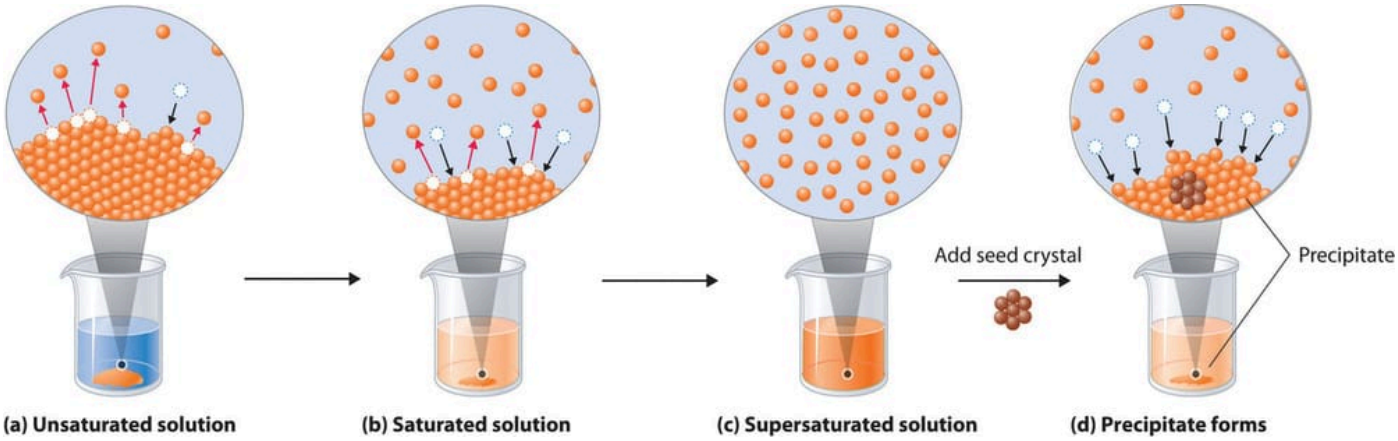


Figure $9.3.1$: Dissolution and Precipitation. (a) When a solid is added to a solvent in which it is soluble, solute particles leave the surface of the solid and become solvated by the solvent, initially forming an unsaturated solution. (b) When the maximum possible amount of solute has dissolved, the solution becomes saturated. If excess solute is present, the rate at which solute particles leave the surface of the solid equals the rate at which they return to the surface of the solid. (c) A supersaturated solution can usually be formed from a saturated solution by filtering off the excess solute and lowering the temperature. (d) When a seed crystal of the solute is added to a supersaturated solution, solute particles leave the solution and form a crystalline precipitate.

Starting on the left the solution starts are unsaturated, then saturated, then supersaturated, when seed crystal is added a precipitate forms.

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9.4: The Effect of Temperature on Solubility

Learning Objectives

- Describe how temperature affects solubility of different types of solute.

The solubility of the majority of solid substances increases as the temperature increases. However, the effect is difficult to predict and varies widely from one solute to another. The temperature dependence of solubility can be visualized with the help of a **solubility curve**, a graph of the solubility vs. temperature (Figure $9.4.1$ below).

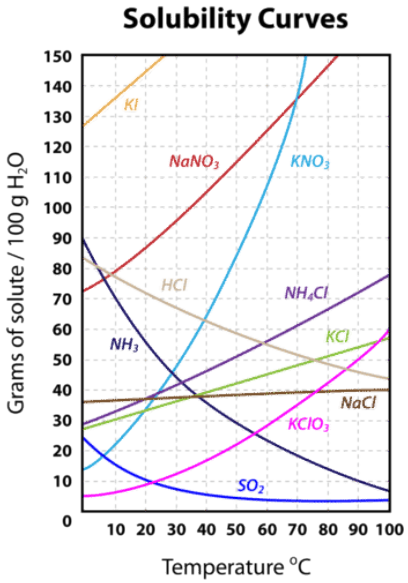


Figure $9.4.1$: A solubility curve is a graph of the solubility of a substance as a function of temperature.

Notice how the temperature dependence of NaCl is fairly flat, meaning that an increase in temperature has relatively little effect on the solubility of NaCl. The curve for $\mathrm{KNO_3}$, on the other hand, is very steep, and so an increase in temperature dramatically increases the solubility of $\mathrm{KNO_3}$.

Several substances—HCl, $\mathrm{NH_3}$, and $\mathrm{SO_2}$—have solubility that decreases as temperature increases. They are all gases at standard pressure. When a solvent with a gas dissolved in it is heated, the kinetic energy of both the solvent and solute increase. As the kinetic energy of the gaseous solute increases, its molecules have a greater tendency to escape the attraction of the solvent molecules and return to the gas phase. Therefore, the solubility of a gas decreases as the temperature increases.

Solubility curves can be used to determine if a given solution is *saturated* or *unsaturated*. Suppose that $80\ \mathrm{g}$ of $\mathrm{KNO_3}$ is added to $100\ \mathrm{g}$ of water at $30\ ^\circ\mathrm{C}$. According to the solubility curve in Figure $9.4.1$, approximately $48\ \mathrm{g}$ of $\mathrm{KNO_3}$ will dissolve at $30\ ^\circ\mathrm{C}$. This means that the solution will be saturated since $48\ \mathrm{g}$ is less than $80\ \mathrm{g}$. We can also determine that there will be $80 - 48 = 32\ \mathrm{g}$ of undissolved $\mathrm{KNO_3}$ remaining at the bottom of the container. In a second scenario, suppose that this saturated solution is heated to $60\ ^\circ\mathrm{C}$. According to the curve, the solubility of $\mathrm{KNO_3}$ at $60\ ^\circ\mathrm{C}$ is about $107\ \mathrm{g}$. The solution, in this case, is unsaturated since it contains only the original $80\ \mathrm{g}$ of dissolved solute. Suppose in a third case, that the solution is cooled all the way down to $0\ ^\circ\mathrm{C}$. The solubility at $0\ ^\circ\mathrm{C}$ is about $14\ \mathrm{g}$, meaning that $80 - 14 = 66\ \mathrm{g}$ of the $\mathrm{KNO_3}$ will recrystallize.

Supersaturated Solutions

Some solutes, such as sodium acetate, do not recrystallize easily. Suppose an exactly saturated solution of sodium acetate is prepared at $50\ ^\circ\mathrm{C}$. As it cools back to room temperature, no crystals appear in the solution, even though the solubility of sodium acetate is lower at room temperature. A **supersaturated solution** is a solution that contains more than the maximum amount of solute that is capable of being dissolved at a given temperature. The recrystallization of the excess dissolved solute in a

supersaturated solution can be initiated by the addition of a tiny crystal of solute, called a seed crystal. The seed crystal provides a nucleation site on which the excess dissolved crystals can begin to grow. Recrystallization from a supersaturated solution is typically very fast.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Chemistry in Everyday Life: Handwarmers

Recrystallization of excess solute from a supersaturated solution usually gives off energy as heat. Commercial heat packs, such as the one in Figure 9.4.2, containing supersaturated sodium acetate ($NaC_2H_3O_2$) take advantage of this phenomenon. You can probably find them at your local drugstore.



Figure 9.4.2: This hand warmer produces heat when the sodium acetate in a supersaturated solution precipitates. Precipitation of the solute is initiated by a mechanical shockwave generated when the flexible metal disk within the solution is "clicked." (credit: modification of work by "Velela"/Wikimedia Commons)

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9.5: The Effect of Pressure on Solubility - Henry's Law

Learning Objectives

- Describe how pressure affects concentration of a solute in a solution.

Pressure has very little effect on the solubility of solids or liquids, but has a significant effect on the solubility of gases. Gas solubility increases as the partial pressure of a gas above the liquid increases. Suppose a certain volume of water is in a closed container with the space above it occupied by carbon dioxide gas at standard pressure. Some of the $\mathrm{CO_2}$ molecules come into contact with the surface of the water and dissolve into the liquid. Now suppose that more $\mathrm{CO_2}$ is added to the space above the container, causing a pressure increase. In this case, more $\mathrm{CO_2}$ molecules are in contact with the water and so more of them dissolve. Thus, the solubility increases as the pressure increases. As with a solid, the $\mathrm{CO_2}$ that is undissolved reaches an equilibrium with the dissolved $\mathrm{CO_2}$, represented by the equation:

$$\mathrm{CO_2}\,(g) \rightleftharpoons \mathrm{CO_2}\,(aq)$$

At equilibrium, the rate of gaseous $\mathrm{CO_2}$ dissolution is equal to the rate of dissolved $\mathrm{CO_2}$ coming out of the solution.

When carbonated beverages are packaged, they are done so under high $\mathrm{CO_2}$ pressure so that a large amount of carbon dioxide dissolves in the liquid. When the bottle is open, the equilibrium is disrupted because the $\mathrm{CO_2}$ pressure above the liquid decreases. Immediately, bubbles of $\mathrm{CO_2}$ rapidly exit the solution and escape out of the top of the open bottle, see Figure $9.5.1$. The amount of dissolved $\mathrm{CO_2}$ decreases. If the bottle is left open for an extended period of time, the beverage becomes "flat" as more and more $\mathrm{CO_2}$ comes out of the liquid.

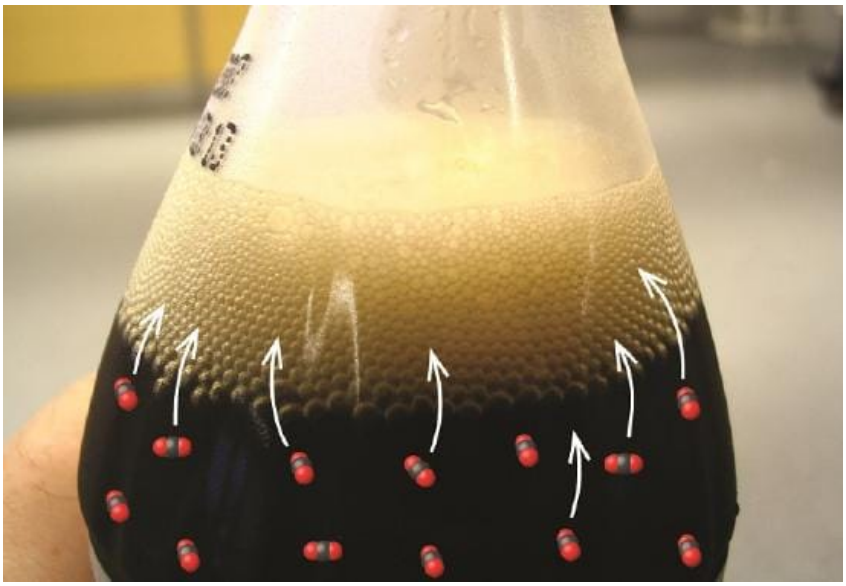


Figure $9.5.1$: Opening the bottle of carbonated beverage reduces the pressure of the gaseous carbon dioxide above the beverage. The solubility of CO_2 is thus lowered, and some dissolved carbon dioxide may be seen leaving the solution as small gas bubbles. (credit: modification of work by Derrick Coetzee)

The relationship of gas solubility to pressure is described by Henry's law, named after English chemist William Henry (1774-1836). **Henry's Law** states that the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the liquid. Henry's law can be written as follows:

$$\frac{C_1}{P_1} = \frac{C_2}{P_2} = k$$

C_1 and P_1 are the concentration and the pressure at an initial set of conditions; C_2 and P_2 are the concentration and pressure at

another changed set of conditions; k is a constant at a constant temperature. The solubility of a gas is typically reported in $\mathrm{g/L}$.

Example 9.5.1

The solubility of a certain gas in water is $0.745\ \mathrm{g/L}$ at standard pressure. What is its solubility when the pressure above the solution is raised to $4.50\ \mathrm{atm}$? The temperature is constant at $20^{\circ}\mathrm{C}$.

Solution

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

Known

- $C_1 = 0.745\ \mathrm{g/L}$
- $P_1 = 1.00\ \mathrm{atm}$
- $P_2 = 4.50\ \mathrm{atm}$

Unknown

Substitute into Henry's law and solve for C_2.

Step 2: Solve.

$$C_2 = \frac{C_1 \times P_2}{P_1} = \frac{0.745\ \mathrm{g/L} \times 4.50\ \mathrm{atm}}{1.00\ \mathrm{atm}} = 3.35\ \mathrm{g/L}$$

Step 3: Think about your result.

The solubility is increased to 4.5 times its original value, according to the direct relationship.

Exercise 9.5.1

Exposing a 100.0 mL sample of water at 0 °C to an atmosphere containing a gaseous solute at 20.26 kPa (152 torr) resulted in the dissolution of 1.45×10^{-3} g of the solute. Use Henry's law to determine the solubility of this gaseous solute when its pressure is 101.3 kPa (760 torr).

Answer available at the end of this section.

Case Study: Decompression Sickness ("The Bends")

Decompression sickness (DCS), or "the bends," is an effect of the increased pressure of the air inhaled by scuba divers when swimming underwater at considerable depths. In addition to the pressure exerted by the atmosphere, divers are subjected to additional pressure due to the water above them, experiencing an increase of approximately 1 atm for each 10 m of depth. Therefore, the air inhaled by a diver while submerged contains gases at the corresponding higher ambient pressure, and the concentrations of the gases dissolved in the diver's blood are proportionally higher per Henry's law.

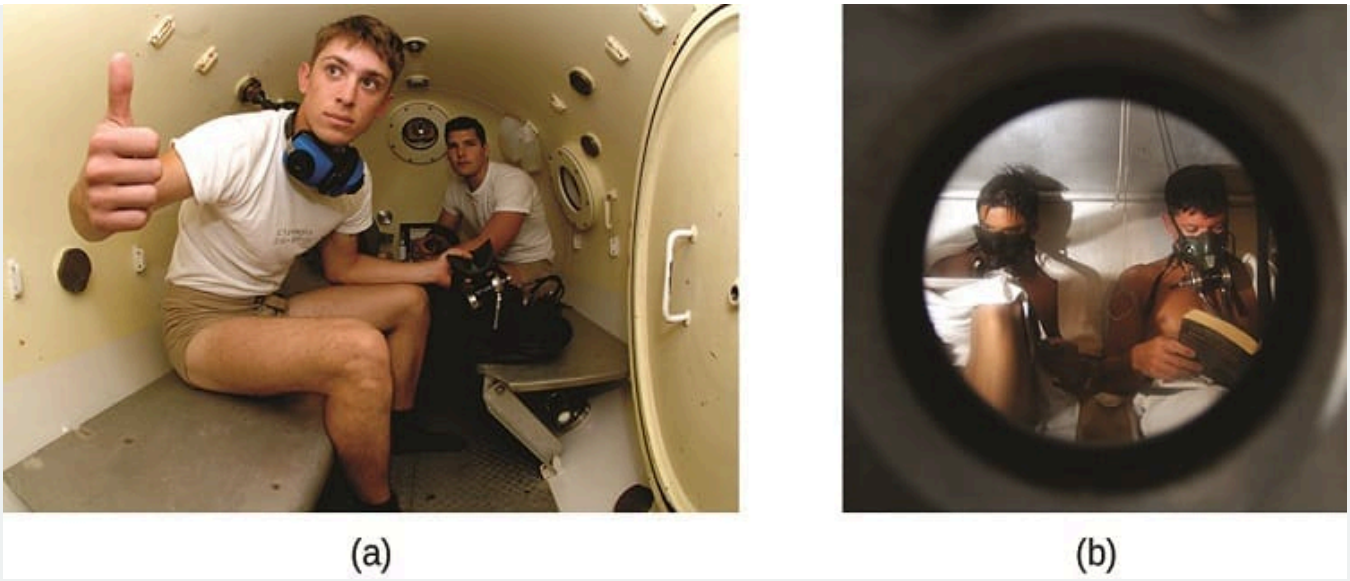


Figure 9.5.4: (a) US Navy divers undergo training in a recompression chamber. (b) Divers receive hyperbaric oxygen therapy.

Two photos are shown. The first shows two people seated in a steel chamber on benches that run length of the chamber on each side. The chamber has a couple of small circular windows and an open hatch-type door. One of the two people is giving a thumbs up gesture. The second image provides a view through a small, circular window. Inside the two people can be seen with masks over their mouths and noses. The people appear to be reading.

As the diver ascends to the surface of the water, the ambient pressure decreases and the dissolved gases becomes less soluble. If the ascent is too rapid, the gases escaping from the diver's blood may form bubbles that can cause a variety of symptoms ranging from rashes and joint pain to paralysis and death. To avoid DCS, divers must ascend from depths at relatively slow speeds (10 or 20 m/min) or otherwise make several decompression stops, pausing for several minutes at given depths during the ascent. When these preventive measures are unsuccessful, divers with DCS are often provided hyperbaric oxygen therapy in pressurized vessels called decompression (or recompression) chambers (Figure 9.5.4).

Answers

Exercise 9.5.1

7.25×10^{-3} g in 100.0 mL or 0.0725 g/L

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9.6: Units of Concentration

Learning Objectives

- Calculate concentration of a solution using different units.
- Use concentration units to calculate the amount of solute in a solution.
- Use molarity to determine quantities in chemical reactions.

Percent Concentrations

There are several ways of expressing the concentration of a solution by using a percentage. The **mass/mass percent** (% m/m) is defined as the mass of a solute divided by the mass of a solution times 100:

$$\%\ \mathrm{m/m} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

If you can measure the masses of the solute and the solution, determining the mass/mass percent is easy. Each mass must be expressed in the same units to determine the proper concentration.

Example 9.6.1

A saline solution with a mass of 355 g has 36.5 g of NaCl dissolved in it. What is the mass/mass percent concentration of the solution?

Solution

We can substitute the quantities given in the equation for mass/mass percent:

$$\%\ \mathrm{m/m} = \frac{36.5\ \mathrm{g}}{355\ \mathrm{g}} \times 100\% = 10.3\%$$

Exercise 9.6.1

A dextrose (also called D-glucose, $C_6H_{12}O_6$) solution with a mass of 2.00×10^2 g has 15.8 g of dextrose dissolved in it. What is the mass/mass percent concentration of the solution?

Answer available at the end of this section.

For gases and liquids, volumes are relatively easy to measure, so the concentration of a liquid or a gas solution can be expressed as a **volume/volume percent** (% v/v): the volume of a solute divided by the volume of a solution times 100:

$$\%\ \mathrm{v/v} = \frac{\text{volume of solute}}{\text{volume of solution}} \times 100\%$$

Again, the units of the solute and the solution must be the same. A hybrid concentration unit, **mass/volume percent** (% m/v), is commonly used for intravenous (IV) fluids (Figure 9.6.1). It is defined as the mass in grams of a solute, divided by volume in milliliters of solution times 100:

$$\%\ \mathrm{m/v} = \frac{\text{mass of solute (g)}}{\text{volume of solution (mL)}} \times 100\%$$



Figure 9.6.1: Mass/Volume Percent.The 0.9% NaCl concentration on this IV bag is mass/volume percent (left). Such solution is used for other purposes and available in bottles (right). Figures used with permission from Wikipedia

Using Percent Concentration in Calculations

The percent concentration can be used to produce a conversion factor between the amount of solute and the amount of solution. As such, concentrations can be useful in a variety of stoichiometry problems as discussed in Chapter 6. In many cases, it is best to use the original definition of the concentration unit; it is that definition that provides the conversion factor.

As an example, if the given concentration is 5% *v/v* alcohol, this means that there are 5 mL of alcohol dissolved in every 100 mL solution.

5 mL alcohol = 100 mL solution

The two possible conversion factors are written as follows:

$$\frac{5\text{ mL alcohol}}{100\text{ mL solution}} \text{ or } \frac{100\text{ mL solution}}{5\text{ mL alcohol}}$$

Use the first conversion factor to convert from a given amount of solution to amount of solute. The second conversion factor is used to convert from a given amount of solute to amount of solution. Given any two quantities in any percent composition, the

third quantity can be calculated, as the following example illustrates.

Example 9.6.2

A sample of 45.0% v/v solution of ethanol (C_2H_5OH) in water has a volume of 115 mL. What volume of ethanol solute does the sample contain?

Solution

A percentage concentration is simply the number of parts of solute per 100 parts of solution. Thus, the percent concentration of 45.0% v/v implies the following:

$$45.0\%\ \text{v/v} \rightarrow \frac{45\ \text{mL}\ C_2H_5OH}{100\ \text{mL solution}}$$

That is, there are 45 mL of C_2H_5OH for every 100 mL of solution. We can use this fraction as a conversion factor to determine the amount of C_2H_5OH in 115 mL of solution:

$$115\ \text{mL solution} \times \frac{45\ \text{mL}\ C_2H_5OH}{100\ \text{mL solution}} = 51.8\ \text{mL}\ C_2H_5OH$$

Exercise 9.6.2

What volume of a 12.75% m/v solution of glucose ($C_6H_{12}O_6$) in water is needed to obtain 50.0 g of $C_6H_{12}O_6$?

Answer available at the end of this section.

Example 9.6.3

A normal saline IV solution contains 9.0 g of NaCl in every liter of solution. What is the mass/volume percent of normal saline?

Solution

We can use the definition of mass/volume percent, but first we have to express the volume in milliliter units:

1 L = 1,000 mL

Because this is an exact relationship, it does not affect the significant figures of our result.

$$\%\ \text{m/v} = \frac{9.0\ \text{g NaCl}}{1,000\ \text{mL solution}} \times 100\% = 0.90\%\ \text{m/v}$$

Exercise 9.6.3

The chlorine bleach that you might find in your laundry room is typically composed of 27.0 g of sodium hypochlorite (NaOCl), dissolved to make 500.0 mL of solution. What is the mass/volume percent of the bleach?

Answer available at the end of this section.

Parts per Million (ppm) and Parts per Billion (ppb)

In addition to percentage units, the units for expressing the concentration of extremely dilute solutions are parts per million (ppm) and parts per billion (ppb). Both of these units are mass based and are defined as follows:

$$\text{ppm} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 1,000,000$$

$$\text{ppb} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 1,000,000,000$$

Similar to parts per million and parts per billion, related units include parts per thousand (ppth) and parts per trillion (ppt).

Concentrations of *trace elements* in the body—elements that are present in extremely low concentrations but are nonetheless necessary for life—are commonly expressed in parts per million or parts per billion. Concentrations of poisons and pollutants are also described in these units. For example, cobalt is present in the body at a concentration of 21 ppb, while the State of Oregon's Department of Agriculture limits the concentration of arsenic in fertilizers to 9 ppm.

In aqueous solutions, 1 ppm is essentially equal to 1 mg/L, and 1 ppb is equivalent to 1 µg/L.

Example 9.6.4

If the concentration of cobalt in a human body is 21 ppb, what mass in grams of Co is present in a body having a mass of 70.0 kg?

Solution

A concentration of 21 ppb means "21 g of solute per 1,000,000,000 g of solution." Written as a **conversion factor,** this concentration of Co is as follows:

$$21 \text{ ppb Co} \rightarrow \frac{21 \text{ g Co}}{1,000,000,000 \text{ g solution}}$$

We can use this as a conversion factor, but first we must convert 70.0 kg to gram units:

$$70.0 \text{ kg} \times \frac{1,000 \text{ g}}{1 \text{ kg}} = 7.00 \times 10^4 \text{ g}$$

Now we determine the amount of Co:

$$7.00 \times 10^4 \text{ g solution} \times \frac{21 \text{ g Co}}{1,000,000,000 \text{ g solution}} = 0.0015 \text{ g Co}$$

This is only 1.5 mg.

Exercise 9.6.4

An 85 kg body contains 0.012 g of Ni. What is the concentration of Ni in parts per million?

Answer available at the end of this section.

Mole/Volume Concentration: Molarity

Another way of expressing concentration is to give the number of moles of solute per unit volume of solution. Such concentration units are useful for discussing chemical reactions in which a solute is a product or a reactant. Molar mass can then be used as a conversion factor to convert amounts in moles to amounts in grams.

Molarity*(M)* is defined as the number of moles of a solute dissolved per liter of solution:

$$\text{molarity} = \frac{\text{number of moles of solute}}{\text{number of liters of solution}}$$

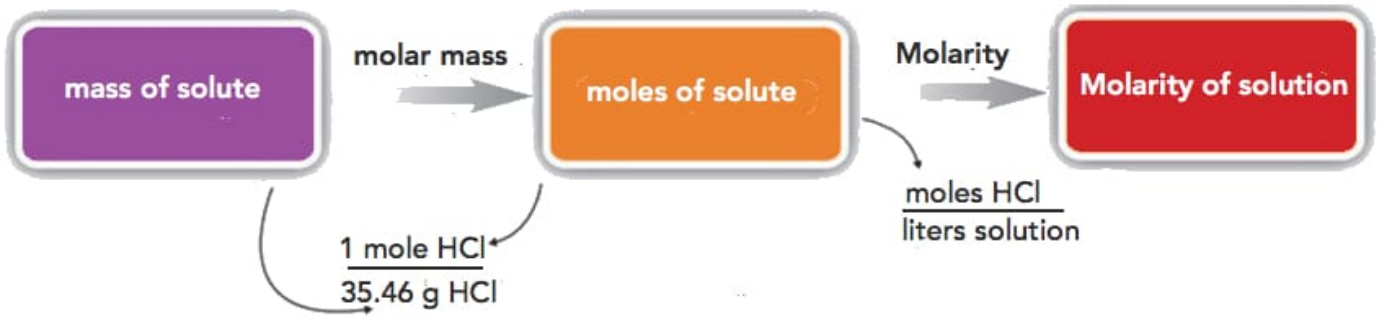
Molarity is abbreviated M (often referred to as “molar”), and the units are often abbreviated as mol/L. It is important to remember that “mol” in this expression refers to moles of solute and that “L” refers to liters of solution. For example, if you have 1.5 mol of NaCl dissolved in 0.500 L of solution, its molarity is therefore

$$\frac{1.5 \text{ mol NaCl}}{0.500 \text{ L solution}} = 3.0 \text{ M NaCl}$$

which is read as “three point oh molar sodium chloride.” Sometimes (aq) is added when the solvent is water, as in “3.0 M NaCl(aq).”

Before a molarity concentration can be calculated, the amount of the solute must be expressed in moles, and the volume of the solution must be expressed in liters.

If the quantity of the solute is given in mass units, you must convert mass units to mole units before using the definition of molarity to calculate concentration. For example, what is the molar concentration of a solution of 22.4 g of HCl dissolved in 1.56 L?



Step 1: convert the mass of solute to moles using the molar mass of HCl (36.46 g/mol):

$$22.4 \, \cancel{g HCl} \times \frac{1 \, mol \, HCl}{36.46 \, \cancel{g HCl}} = 0.614 \, mol \, HCl$$

Step 2: use the definition of molarity to determine the concentration:

$$M = \frac{0.614 \, mol \, HCl}{1.56 L \, solution} = 0.394 \, MHCl$$

Example 9.6.5

What is the molarity of an aqueous solution of 25.0 g of NaOH in 750 mL?

Solution

Before we substitute these quantities into the definition of molarity, we must convert them to the proper units. The mass of NaOH must be converted to moles of NaOH. The molar mass of NaOH is 40.00 g/mol:

$$25.0 \text{ g NaOH} \times \frac{1 \text{ mol NaOH}}{40.00 \text{ g NaOH}} = 0.625 \text{ mol NaOH}$$

Next, we convert the volume units from milliliters to liters:

$$750 \text{ mL} \times \frac{1 \text{ L}}{1,000 \text{ mL}} = 0.750 \text{ L}$$

Now that the quantities are expressed in the proper units, we can substitute them into the definition of molarity:

$$\text{M} = \frac{0.625\ \text{mol NaOH}}{0.750\ \text{L}} = 0.833\ \text{M NaOH}$$

Exercise 9.6.5

If a 350 mL cup of coffee contains 0.150 g of caffeine ($C_8H_{10}N_4O_2$), what is the molarity of this caffeine solution?

Answer available at the end of this section.

Using Molarity in Calculations

The definition of molarity can also be used to calculate a needed volume of solution, given its concentration and the number of moles desired, or the number of moles of solute (and subsequently, the mass of the solute), given its concentration and volume. As in the percent concentration, molarity can also be expressed as a conversion factor.

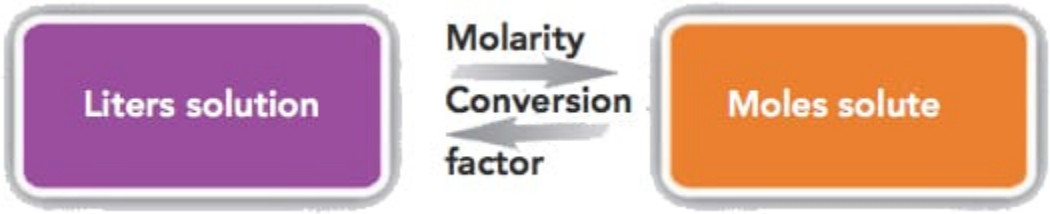
Molarity is defined as moles solute per liter solution. There is an understood 1 in the denominator of the conversion factor. For example, a 3.0 M solution of sucrose means that there are three moles of sucrose dissolved in every liter of solution. Mathematically, this is stated as follows:

3.0 moles sucrose = 1 L solution

Dividing both sides of this expression by either side, we generate two possible conversion factors:

$$\frac{3.0\ \text{mol sucrose}}{1\ \text{L solution}} \text{ or } \frac{1\ \text{L solution}}{3.0\ \text{mol sucrose}}$$

The first conversion factor can be used to convert from *volume (L) of solution to moles solute*, and the *second converts from moles of solute to volume (L) of solution*.



For example, suppose we are asked how many moles of sucrose are present in 0.108 L of a 3.0 M sucrose solution. The given volume (0.108 L) is multiplied by the first conversion factor to cancel the L units, and find that 0.32 moles of sucrose are present.

$$0.108\ \cancel{L\ solution} \times \frac{3.0\ mol\ sucrose}{1\ \cancel{L\ solution}} = 0.32\ mol\ sucrose$$

How many liters of 3.0 M sucrose solution are needed to obtain 4.88 mol of sucrose? In such a conversion, we multiply the given (4.88 moles sucrose) with the second conversion factor. This cancels the moles units and converts it to liters of solution.

$$4.88\ \cancel{mol\ sucrose} \times \frac{1\ L\ solution}{3.0\ \cancel{mol\ sucrose}} = 1.63\ L\ solution$$

Example 9.6.6

1. What volume of a 0.0753 M solution of dimethylamine [$(CH_3)_2NH$] is needed to obtain 0.450 mol of the compound?
2. Ethylene glycol ($C_2H_6O_2$) is mixed with water to make auto engine coolants. How many grams of $C_2H_6O_2$ are in 5.00 L of a 6.00 M aqueous solution?

Solution

1. To solve for the volume, multiply the "given" (0.450 mol of dimethylamine) with the molarity conversion factor (0.0753 M). Use the proper conversion factor to cancel the unit "mol" and get the unit volume (L) of solution:

$$0.450 \text{ mol dimethylamine} \times \frac{1 \text{ L solution}}{0.0753 \text{ mol dimethylamine}} = 5.98 \text{ L solution}$$

2. The strategy in solving this problem is to convert the given volume (5.00 L) using the 6.00 M (conversion factor) to solve for moles of ethylene glycol, which can then be converted to grams.

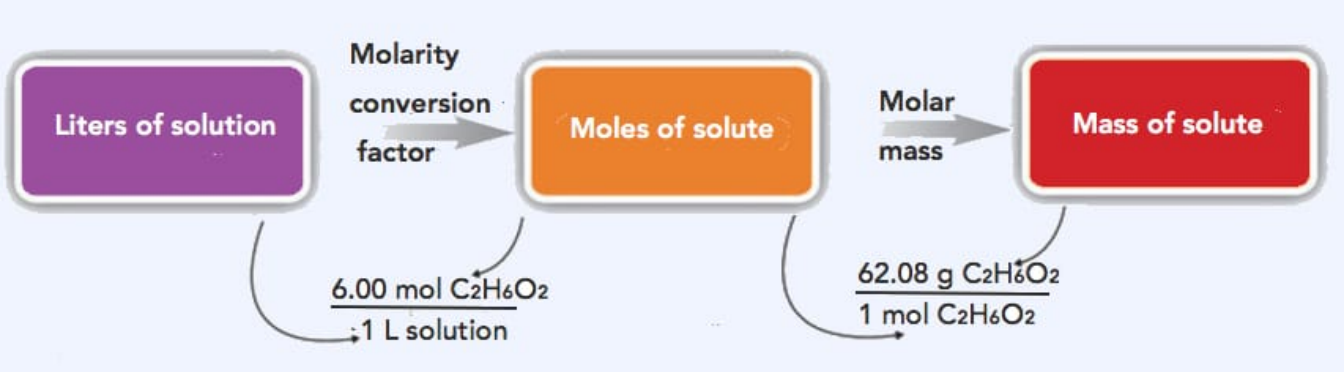
Step 1: Convert the given volume (5.00 L) to moles ethylene glycol.

$$5.00 \text{ L solution} \times \frac{6.00 \text{ mol } C_2H_6O_2}{1 \text{ L solution}} = 30.0 \text{ mol } C_2H_6O_2$$

Step 2: Convert 30.0 mols $C_2H_6O_2$ to grams $C_2H_6O_2$. Molar mass of $C_2H_6O_2$= 62.08 g/mol

$$30.0 \text{ mol } C_2H_6O_2 \times \frac{62.08 \text{ g } C_2H_6O_2}{1 \text{ mol } C_2H_6O_2} = 1,860 \text{ g } C_2H_6O_2$$

The same two-step problem can also be worked out in a single line, rather than as two separate steps, as follows:



$$5.00 \text{ L solution} \times \frac{6.00 \text{ mol } C_2H_6O_2}{1 \text{ L solution}} \times \frac{62.08 \text{ g } C_2H_6O_2}{1 \text{ mol } C_2H_6O_2} = 1,860 \text{ g } C_2H_6O_2$$

The final answer is rounded off to 3 significant figures. Thus, there are 1,860 g of $C_2H_6O_2$ in the specified amount of engine coolant.

Note: Dimethylamine has a “fishy” odor. In fact, organic compounds called amines cause the odor of decaying fish.

Exercise 9.6.6

a. What volume of a 0.0902 M solution of formic acid (HCOOH) is needed to obtain 0.888 mol of HCOOH?
b. Acetic acid ($HC_2H_3O_2$) is the acid in vinegar. How many grams of $HC_2H_3O_2$ are in 0.565 L of a 0.955 M solution?

Answer available at the end of this section.

Solution Stoichiometry

Of all the ways of expressing concentration, molarity is the one most commonly used in stoichiometry problems because it is directly related to the mole unit. Consider the following chemical equation:

$$HCl(aq) + NaOH(s) \rightarrow H_2O(\ell) + NaCl(aq)$$

Suppose we want to know how many liters of aqueous HCl solution will react with a given mass of NaOH. A typical approach to answering this question is as follows:

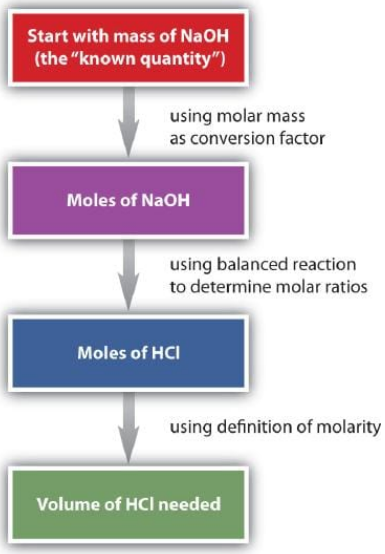


Figure 9.6.2: *Typical approach to solving Molarity problems*

In itself, each step is a straightforward conversion. It is the combination of the steps that is a powerful quantitative tool for problem solving.

Example 9.6.7

How many milliliters of a 2.75 M HCl solution are needed to react with 185 g of NaOH? The balanced chemical equation for this reaction is as follows:

$$HCl(aq) + NaOH(s) \rightarrow H_2O(\ell) + NaCl(aq)$$

Solution

We will follow the flowchart to answer this question. First, we convert the mass of NaOH to moles of NaOH using its molar mass, 40.00 g/mol:

$$185 \text{ g NaOH} \times \frac{1 \text{ mol NaOH}}{40.00 \text{ g NaOH}} = 4.63 \text{ mol NaOH}$$

Using the balanced chemical equation, we see that there is a one-to-one ratio of moles of HCl to moles of NaOH. We use this to determine the number of moles of HCl needed to react with the given amount of NaOH:

$$4.63 \text{ mol NaOH} \times \frac{1 \text{ mol HCl}}{1 \text{ mol NaOH}} = 4.63 \text{ mol HCl}$$

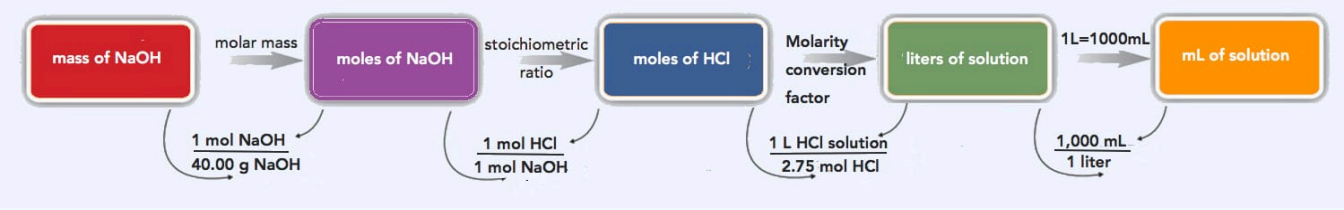
Finally, we use the definition of molarity to determine the volume of 2.75 M HCl needed:

$$2.75 \text{ M HCl} = \frac{4.63 \text{ mol HCl}}{\text{volume of HCl solution}}$$

$$\text{volume of HCl} = \frac{4.63 \text{ mol HCl}}{2.75 \text{ M HCl}} = 1.68 \text{ L} \times \frac{1,000 \text{ mL}}{1 \text{ L}} = 1,680 \text{ mL}$$

We need 1,680 mL of 2.75 M HCl to react with the NaOH.

The same multi-step problem can also be worked out in a single line, rather than as separate steps, as follows:



$$185 \text{ g NaOH} \times \frac{1 \text{ mol NaOH}}{40.00 \text{ g NaOH}} \times \frac{1 \text{ mol HCl}}{1 \text{ mol NaOH}} \times \frac{1 \text{ L HCl solution}}{2.75 \text{ mol HCl}} \times \frac{1000 \text{ mL HCl solution}}{1 \text{ L HCl solution}} = 1,680 \text{ mL HCl solution}$$

Our final answer (rounded off to three significant figures) is 1,680 mL HCl solution.

Exercise 9.6.7

How many milliliters of a 1.04 M H_2SO_4 solution are needed to react with 98.5 g of $Ca(OH)_2$? The balanced chemical equation for the reaction is as follows:

$$H_2SO_{4(aq)} + Ca(OH)_{2(s)} \rightarrow 2H_2O_{(\ell)} + CaSO_{4(aq)}$$

Answer available at the end of this section.

The generic steps for performing stoichiometry problems such as this are shown in Figure 9.6.3. You may want to consult this figure when working with solutions in chemical reactions. The double arrows in Figure 9.6.3 indicate that you can start at either end of the chart and, after a series of simple conversions, determine the quantity at the other end.

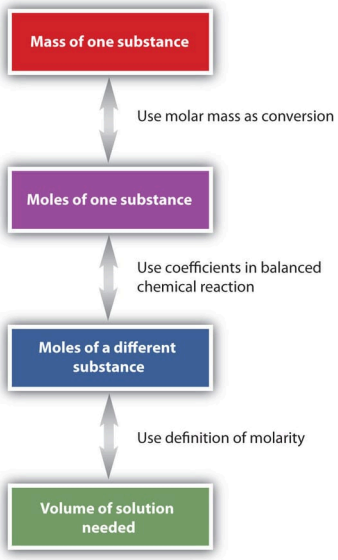


Figure 9.6.3: Diagram of Steps for Using Molarity in Stoichiometry Calculations. When using molarity in stoichiometry calculations, a specific sequence of steps usually leads you to the correct answer.

Solutions in Our Body

Many of the fluids found in our bodies are solutions. The solutes range from simple ionic compounds to complex proteins. Table 9.6.1 lists the typical concentrations of some of these solutes.

*Table 9.6.1: Approximate Concentrations of Various Solutes in Some Solutions in the Body**

Solution	Solute	Concentration (M)
blood plasma	Na^+	0.138
	K^+	0.005
	Ca^{2+}	0.004
	Mg^{2+}	0.003
	Cl^-	0.110
	HCO_3^-	0.030
stomach acid	HCl	0.10
urine	NaCl	0.15
	PO_4^{3-}	0.05
	NH_2CONH_2 (urea)	0.30
***Note: Concentrations are approximate and can vary widely.**		

Looking Closer: The Dose Makes the Poison

Why is it that we can drink 1 qt of water when we are thirsty and not be harmed, but if we ingest 0.5 g of arsenic, we might die? There is an old saying: *the dose makes the poison*. This means that what may be dangerous in some amounts may not be dangerous in other amounts.

Take arsenic, for example. Some studies show that arsenic deprivation limits the growth of animals such as chickens, goats, and pigs, suggesting that arsenic is actually an essential trace element in the diet. Humans are constantly exposed to tiny amounts of arsenic from the environment, so studies of completely arsenic-free humans are not available; if arsenic is an essential trace mineral in human diets, it is probably required on the order of 50 ppb or less. A toxic dose of arsenic corresponds to about 7,000 ppb and higher, which is over 140 times the trace amount that may be required by the body. Thus, arsenic is not poisonous in and of itself. Rather, it is the amount that is dangerous: the dose makes the poison.

Similarly, as much as water is needed to keep us alive, too much of it is also risky to our health. Drinking too much water too fast can lead to a condition called water intoxication, which may be fatal. The danger in water intoxication is not that water itself becomes toxic. It is that the ingestion of too much water too fast dilutes sodium ions, potassium ions, and other salts in the bloodstream to concentrations that are not high enough to support brain, muscle, and heart functions. Military personnel, endurance athletes, and even desert hikers are susceptible to water intoxication if they drink water but do not replenish the salts lost in sweat. As this example shows, even the right substances in the wrong amounts can be dangerous!

Answers

Exercise 9.6.1

7.90%

Exercise 9.6.2

$$50.0\text{ g } C_6H_12O_6 \times \frac{100\text{ mL solution}}{12.75\text{ g } C_6H_12O_6} = 392\text{ mL solution}$$

Exercise 9.6.3

$$\%\text{ m/v} = \frac{27.0\text{ g NaOCl}}{500.0\text{ mL solution}} \times 100\% = 5.40\%\text{ m/v}$$

Exercise 9.6.4

0.14 ppm

Exercise 9.6.5

0.00221 M

Exercise 9.6.6

a. 9.84 L

b. 32.4 g

Exercise 9.6.7

1,280 mL

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9.7: Dilution

Learning Objective

- Calculate the concentration of solutions prepared by dilution.

Often, a worker will need to change the concentration of a solution by changing the amount of solvent. **Dilution** is the *addition of solvent*, which decreases the concentration of the solute in the solution. **Concentration** is the *removal of solvent*, which increases the concentration of the solute in the solution. (Do not confuse the two uses of the word *concentration* here!)

In both dilution and concentration, the amount of solute stays the same. This gives us a way to calculate what the new solution volume must be for the desired concentration of solute. From the definition of molarity,

$$\text{molarity} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

we can solve for the number of moles of solute:

moles of solute = Molarity (mol/L) x Volume of solution (L)

A simpler way of writing this is to use M to represent molarity and V to represent volume. So the equation becomes

moles of solute = *M x V*

Because this quantity does not change before and after the change in concentration, the product *MV* must be the same before and after the concentration change. Using numbers to represent the initial and final conditions, we have

$$M_1V_1 = M_2V_2$$

as the dilution equation. The volumes must be expressed in the same units. Note that this equation gives only the initial and final conditions, not the amount of the change. The amount of change in volume is determined by subtraction.

9.7.1 Exam

If 25.0 mL of a 2.19 M solution are diluted to 72.8 mL, what is the final concentration?

Solution

It does not matter which set of conditions is labeled 1 or 2, as long as the conditions are paired together properly. Using the dilution equation, we have

(2.19 M)(25.0 mL) = M_2(72.8 mL)

Solving for the second concentration (noting that the milliliter units cancel),

M_2 = 0.752 M

The concentration of the solution has decreased. In going from 25.0 mL to 72.8 mL, 72.8 – 25.0 = 47.8 mL of solvent must be added.

9.7.1 Exerc

A 0.885 M solution of KBr whose initial volume is 76.5 mL has more water added until its concentration is 0.500 M. What is the new volume of the solution?

Answer available at the end of this section.

Concentrating solutions involves removing solvent. Usually this is done by evaporating or boiling, assuming that the heat of boiling does not affect the solute. The dilution equation is used in these circumstances as well.

Chemistry is Everywhere: Preparing IV Solutions

In a hospital emergency room, a physician orders an intravenous (IV) delivery of 100 mL of 0.5% KCl for a patient suffering from hypokalemia (low potassium levels). Does an aide run to a supply cabinet and take out an IV bag containing this concentration of KCl?

Not likely. It is more probable that the aide must make the proper solution from an IV bag of sterile solution and a more concentrated, sterile solution, called a *stock solution*, of KCl. The aide is expected to use a syringe to draw up some stock solution and inject it into the waiting IV bag and dilute it to the proper concentration. Thus the aide must perform a dilution calculation.



Figure 9.7.1 Preparing IV Solution © Thinkstock. Medical personnel commonly must perform dilutions for IV solutions.

If the stock solution is 10.0% KCl and the final volume and concentration need to be 100 mL and 0.50%, respectively, then it is easy to calculate how much stock solution to use:

$$(10\%)V_1 = (0.50\%)(100\text{ mL})V_1 = 5\text{ mL}$$

Of course, the addition of the stock solution affects the total volume of the diluted solution, but the final concentration is likely close enough even for medical purposes.

Medical and pharmaceutical personnel are constantly dealing with dosages that require concentration measurements and dilutions. It is an important responsibility: calculating the *wrong* dose can be useless, harmful, or even fatal!

Answers

135.4 mL

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9.8: Ions in Solution - Electrolytes

Learning Objectives

- Define solutes as strong electrolytes, weak electrolytes, or nonelectrolytes.
- Calculate equivalents for an ionic solute.

When some substances are dissolved in water, they undergo either a physical or a chemical change that yields ions in solution. These substances constitute an important class of compounds called electrolytes. Substances that do not yield ions when dissolved are called **nonelectrolytes**. If the physical or chemical process that generates the ions is essentially 100% efficient (all of the dissolved compound yields ions), then the substance is known as a **strong electrolyte**. If only a relatively small fraction of the dissolved substance undergoes the ion-producing process, it is called a **weak electrolyte**.

Substances may be identified as strong, weak, or nonelectrolytes by measuring the electrical conductance of an aqueous solution containing the substance. To conduct electricity, a substance must contain freely mobile, charged species. Most familiar is the conduction of electricity through metallic wires, in which case the mobile, charged entities are electrons. Solutions may also conduct electricity if they contain dissolved ions, with conductivity increasing as ion concentration increases. Applying a voltage to electrodes immersed in a solution permits assessment of the relative concentration of dissolved ions, either quantitatively, by measuring the electrical current flow, or qualitatively, by observing the brightness of a light bulb included in the circuit (Figure 9.8.1).

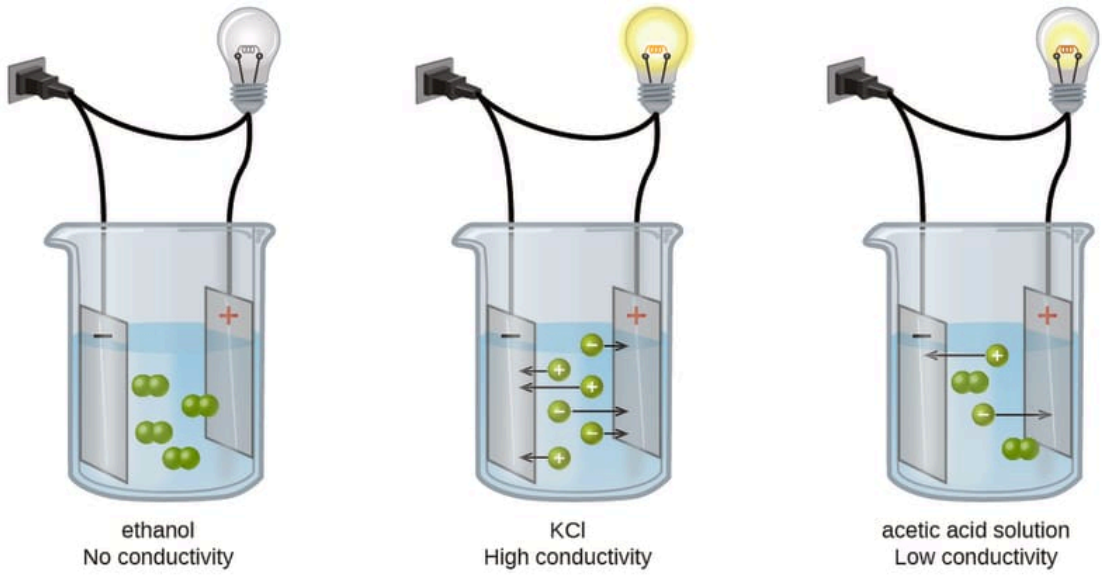


Figure 9.8.1: Solutions of nonelectrolytes such as ethanol do not contain dissolved ions and cannot conduct electricity. Solutions of electrolytes contain ions that permit the passage of electricity. The conductivity of an electrolyte solution is related to the strength of the electrolyte.

Ionic Electrolytes

Water and other polar molecules are attracted to ions, as shown in Figure 9.8.2. The electrostatic attraction between an ion and a molecule with a dipole is called an ion-dipole attraction. These attractions play an important role in the dissolution of ionic compounds in water.

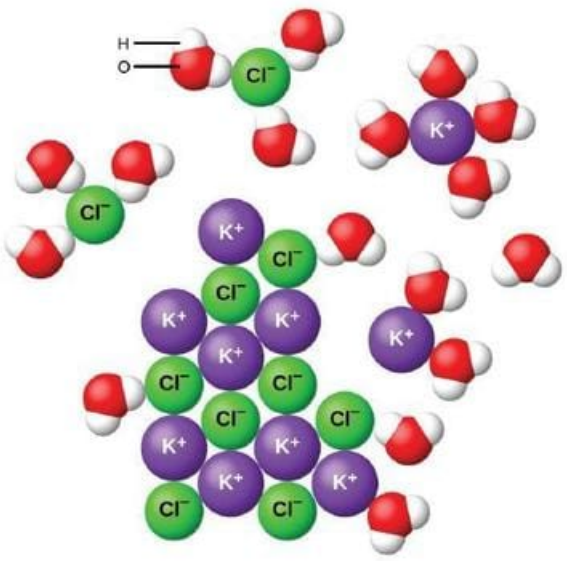


Figure 9.8.2: As potassium chloride (KCl) dissolves in water, the ions are hydrated. The polar water molecules are attracted by the charges on the K^+ and Cl^- ions. Water molecules in front of and behind the ions are not shown.

When ionic compounds dissolve in water, the ions in the solid separate and disperse uniformly throughout the solution because water molecules surround and solvate the ions, reducing the strong electrostatic forces between them. This process represents a physical change known as dissociation. Under most conditions, ionic compounds will dissociate nearly completely when dissolved, and so they are classified as strong electrolytes.

Let us consider what happens at the microscopic level when we add solid KCl to water. Ion-dipole forces attract the positive (hydrogen) end of the polar water molecules to the negative chloride ions at the surface of the solid, and they attract the negative (oxygen) ends to the positive potassium ions. The water molecules penetrate between individual K^+ and Cl^- ions and surround them, reducing the strong interionic forces that bind the ions together and letting them move off into solution as solvated ions, as Figure shows. The reduction of the electrostatic attraction permits the independent motion of each hydrated ion in a dilute solution, resulting in an increase in the disorder of the system as the ions change from their fixed and ordered positions in the crystal to mobile and much more disordered states in solution. This increased disorder is responsible for the dissolution of many ionic compounds, including KCl, which dissolve with absorption of heat.

In other cases, the electrostatic attractions between the ions in a crystal are so large, or the ion-dipole attractive forces between the ions and water molecules are so weak, that the increase in disorder cannot compensate for the energy required to separate the ions, and the crystal is insoluble. Such is the case for compounds such as calcium carbonate (limestone), calcium phosphate (the inorganic component of bone), and iron oxide (rust).

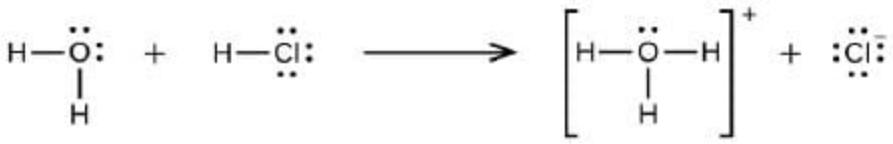
Covalent Electrolytes

Pure water is an extremely poor conductor of electricity because it is only very slightly ionized—only about two out of every 1 billion molecules ionize at 25 °C. Water ionizes when one molecule of water gives up a proton to another molecule of water, yielding hydronium and hydroxide ions.

$$\mathrm{H_2O\ (l)^+\ H_2O\,(l)\ \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq)} \tag{9.8.1}$$

In some cases, we find that solutions prepared from covalent compounds conduct electricity because the solute molecules react chemically with the solvent to produce ions. For example, pure hydrogen chloride is a gas consisting of covalent HCl molecules. This gas contains no ions. However, when we dissolve hydrogen chloride in water, we find that the solution is a very good conductor. The water molecules play an essential part in forming ions: Solutions of hydrogen chloride in many other solvents, such as benzene, do not conduct electricity and do not contain ions.

Hydrogen chloride is an *acid*, and so its molecules react with water, transferring H^+ ions to form hydronium ions (H_3O^+) and chloride ions (Cl^-):



This reaction is essentially 100% complete for HCl (i.e., it is a *strong acid* and, consequently, a strong electrolyte). Likewise, weak acids and bases that only react partially generate relatively low concentrations of ions when dissolved in water and are classified as weak electrolytes. Acids and bases will be explored further in a later chapter.

Equivalents

Concentrations of ionic solutes are occasionally expressed in units called equivalents (Eq). One equivalent equals 1 mol of positive or negative charge. Thus, 1 mol/L of $Na^+(aq)$ is also 1 Eq/L because sodium has a 1+ charge. A 1 mol/L solution of $Ca^{2+}(aq)$ ions has a concentration of 2 Eq/L because calcium has a 2+ charge. Dilute solutions may be expressed in milliequivalents (mEq)—for example, human blood plasma has a total concentration of about 150 mEq/L.

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9.9: Properties of Solutions

Learning Objectives

- To describe how the properties of solutions differ from those of pure solvents.

Solutions are likely to have properties similar to those of their major component—usually the solvent. However, some solution properties differ significantly from those of the solvent. Here, we will focus on liquid solutions that have a solid solute, but many of the effects we will discuss in this section are applicable to all solutions.

Colligative Properties

Solutes affect some properties of solutions that depend only on the concentration of the dissolved particles. These properties are called ***colligative properties***. Four important colligative properties that we will examine are **vapor pressure depression**, **boiling point elevation**, **freezing point depression**, and **osmotic pressure**.

Molecular compounds separate into individual molecules when they are dissolved, so for every 1 mol of molecules dissolved, we get 1 mol of particles. In contrast, ionic compounds separate into their constituent ions when they dissolve, so 1 mol of an ionic compound will produce more than 1 mol of dissolved particles. For example, every mole of NaCl that dissolves yields 1 mol of Na^+ ions and 1 mol of Cl^- ions, for a total of 2 mol of particles in solution. Thus, the effect on a solution's properties by dissolving NaCl may be twice as large as the effect of dissolving the same amount of moles of glucose ($C_6H_{12}O_6$).

Vapor Pressure Depression

All liquids evaporate. In fact, given enough volume, a liquid will turn completely into a vapor. If enough volume is not present, a liquid will evaporate only to the point where the rate of evaporation equals the rate of vapor condensing back into a liquid. The pressure of the vapor at this point is called the **vapor pressure** of the liquid.

The presence of a dissolved solid lowers the characteristic vapor pressure of a liquid so that it evaporates more slowly. (The exceptions to this statement are if the solute itself is a liquid or a gas, in which case the solute will also contribute something to the evaporation process. We will not discuss such solutions here.) This property is called vapor pressure depression and is depicted in Figure 9.9.1.

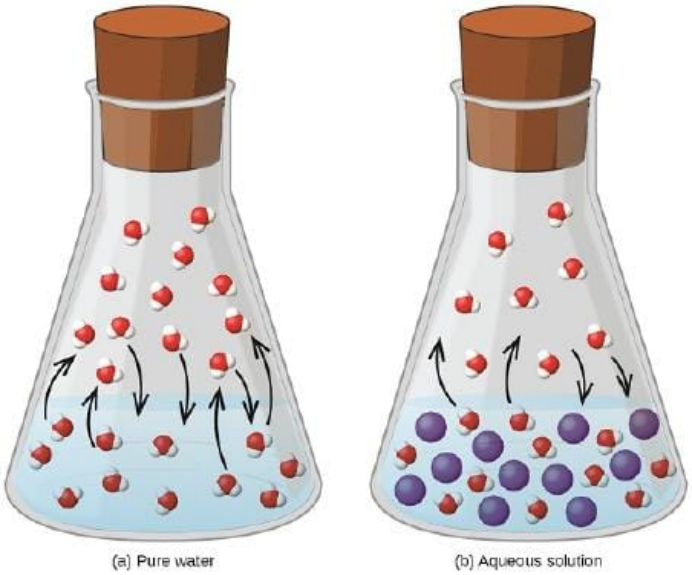


Figure 9.9.1: Vapor Pressure Depression. The presence of solute particles blocks some of the ability for liquid particles to evaporate. Thus, solutions of solid solutes typically have a lower vapor pressure than the pure solvent.

Boiling Point Elevation

A related property of solutions is that their boiling points are *higher* than the boiling point of the pure solvent. Because the presence of solute particles decreases the vapor pressure of the liquid solvent, a higher temperature is needed to reach the boiling point. This phenomenon is called boiling point elevation. For every mole of particles dissolved in a liter of water, the boiling point of water increases by about 0.51°C.

$$\Delta T_{boiling} = mol\ particles \times 0.51°C$$

The addition of one mole of sucrose (molecular compound) in one liter of water will raise the boiling point from 100°C to 100.51°C, but the addition of one mole of NaCl in one liter of water will raise the boiling point by 2 x 0.51°C = 1.02°C. Furthermore, the addition of one mole of $CaCl_2$ in one liter of water will raise the boiling point by 3 x 0.51°C = 1.53°C.

Everyday Application: Adding Salt to Pasta Water

When cooking dried pasta, many recipes call for salting the water before cooking the pasta. Some argue—with colligative properties on their side—that adding salt to the water raises the boiling point, thus cooking the pasta faster. Is there any truth to this?



Figure 9.9.2: Cooking dried pasta. Why do so many recipes call for adding salt to water when boiling pasta? Is it to raise the boiling temperature of the water? (Public Domain; Jan Vašek via pixabay)

In order to increase the boiling temperature of 4 L of water by 1.0°C, with the presumption that dried pasta cooks noticeably faster at 101°C than at 100°C (although a 1° difference may make only a negligible change in cooking times), over 1 lb of salt (~1 cup) would be needed. In your experience, do you add almost a cup of salt to a pot of water to make pasta? Certainly not! A few pinches, perhaps one-fourth of a teaspoon, but not almost a cup! It is obvious that the little amount of salt that most people add to their pasta water is not going to significantly raise the boiling point of the water.

So why do people add some salt to boiling water? There are several possible reasons, the most obvious of which is taste: adding salt adds a little bit of salt flavor to the pasta. It cannot be much because most of the salt remains in the water, not in the cooked pasta. However, it may be enough to detect with our taste buds. The other obvious reason is habit; recipes tell us to add salt, so we do, even if there is little scientific or culinary reason to do so.

Freezing Point Depression

The presence of solute particles has the opposite effect on the freezing point of a solution. When a solution freezes, only the solvent particles come together to form a solid phase, and the presence of solute particles interferes with that process. Therefore, for the liquid solvent to freeze, more energy must be removed from the solution, which lowers the temperature. Thus, solutions have lower freezing points than pure solvents do. This phenomenon is called freezing point depression. For every mole of particles in a liter of water, the freezing point decreases by about 1.86°C.

$$\Delta T_{freezing} = mol\ particles \times -1.86°C$$

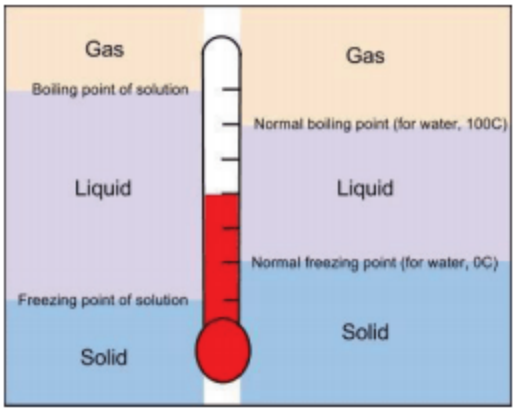


Figure 9.9.3: Comparison of boiling and freezing points of a pure liquid (right side) with a solution (left side).

Both boiling point elevation and freezing point depression have practical uses. For example, solutions of water and ethylene glycol ($C_2H_6O_2$) are used as coolants in automobile engines because the boiling point of such a solution is greater than 100°C, the normal boiling point of water. In winter, salts like NaCl and $CaCl_2$ are sprinkled on the ground to melt ice or keep ice from forming on roads and sidewalks (Figure 9.9.4). This is because the solution made by dissolving sodium chloride or calcium chloride in water has a lower freezing point than pure water, so the formation of ice is inhibited.



Figure 9.9.4: Effect of Freezing Point Depression. The salt sprinkled on this sidewalk makes the water on the sidewalk have a lower freezing point than pure water, so it does not freeze as easily. This makes walking on the sidewalk less hazardous in winter. © Thinkstock

Example 9.9.1

Which solution's freezing point deviates more from that of pure water—a 1 M solution of NaCl or a 1 M solution of $CaCl_2$?

Solution

Colligative properties depend on the number of dissolved particles, so the solution with the greater number of particles in solution will show the greatest deviation. When NaCl dissolves, it separates into two ions, Na^+ and Cl^-. But when $CaCl_2$ dissolves, it separates into three ions—one Ca^{2+} ion and two Cl^- ions. Thus, mole for mole, $CaCl_2$ will have 50% more impact on freezing point depression than NaCl.

Exercise 9.9.1

Which solution's boiling point deviates more from that of pure water—a 1 M solution of $CaCl_2$ or a 1 M solution of $MgSO_4$?

Answer available at the end of this section.

Example 9.9.2

Estimate the boiling point of 0.2 M $CaCl_2$ solution.

Solution

The boiling point increases 0.51°C for every mole of solute per liter of water. For this estimation, let's assume that 1 liter of solution is roughly the same volume as 1 liter of water. A 0.2 M $CaCl_2$ solution contains 0.2 moles of $CaCl_2$ solution formula units per liter of solution. Each $CaCl_2$ unit separates into three ions.

$$0.2 \text{ mol } CaCl_2 \times \frac{3 \text{ mol ions}}{1 \text{ mol } CaCl_2} \times \frac{0.51°C}{1 \text{ mol ion}} = 0.306°C$$

The normal boiling point of water is 100°C, so the boiling point of the solution is raised to 100.31°C.

Exercise 9.9.2

Estimate the freezing point of 0.3 M $CaCl_2$ solution.

Answer available at the end of this section.

Answer available at the end of this section.

Answers

Exercise 9.9.1

$CaCl_2$

Exercise 9.9.2

Exercise 9.9.2

–1.7°C

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9.10: Osmosis and Osmotic Pressure

Learning Objectives

- Describe osmosis and how it relates to osmotic pressure.

Osmotic Pressure

The last colligative property of solutions we will consider is a very important one for biological systems. It involves **osmosis**, the process by which solvent molecules can pass through certain membranes but solute particles cannot. When two solutions of different concentration are present on either side of these membranes (called *semipermeable membranes*), there is a tendency for solvent molecules to move from the more dilute solution to the more concentrated solution until the concentrations of the two solutions are equal. This tendency is called **osmotic pressure**. External pressure can be exerted on a solution to counter the flow of solvent; the pressure required to halt the osmosis of a solvent is equal to the osmotic pressure of the solution.

Consider the apparatus illustrated in Figure $9.10.1$, in which samples of pure solvent and a solution are separated by a membrane that only solvent molecules may permeate. Solvent molecules will diffuse across the membrane in both directions. Since the concentration of *solvent* is greater in the pure solvent than the solution, these molecules will diffuse from the solvent side of the membrane to the solution side at a faster rate than they will in the reverse direction. The result is a net transfer of solvent molecules from the pure solvent to the solution. Diffusion-driven transfer of solvent molecules through a semipermeable membrane is a process known as osmosis.

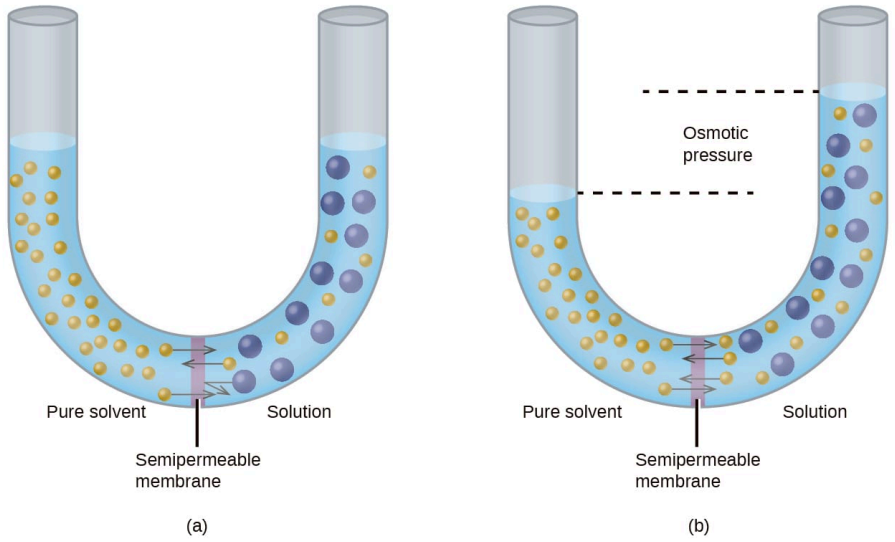


Figure $9.10.1$: Osmosis results in the transfer of solvent molecules from a sample of low (or zero) solute concentration to a sample of higher solute concentration.

When osmosis is carried out in an apparatus like that shown in Figure $9.10.1$, the volume of the solution increases as it becomes diluted by accumulation of solvent. This causes the level of the solution to rise, increasing its hydrostatic pressure (due to the weight of the column of solution in the tube) and resulting in a faster transfer of solvent molecules back to the pure solvent side. When the pressure reaches a value that yields a reverse solvent transfer rate equal to the osmosis rate, bulk transfer of solvent ceases. This pressure is called the osmotic pressure (π) of the solution. The osmotic pressure of a dilute solution can be determined in a similar way the pressure of an ideal gas is calculated using the ideal gas law:

$$\pi = \left(\frac{n}{V}\right) RT$$

where n is the number of moles of particles in solution, V is the volume, and R is the universal gas constant.

Osmolarity (osmol) is a way of reporting the total number of particles in a solution to determine osmotic pressure. It is defined as the molarity of a solute times the number of particles a formula unit of the solute makes when it dissolves (represented by i):

$$osmol = M \times i$$

If more than one solute is present in a solution, the individual osmolarities are additive to get the total osmolarity of the solution. Solutions that have the same osmolarity have the same osmotic pressure. If solutions of differing osmolarities are present on opposite sides of a semipermeable membrane, solvent will transfer from the lower-osmolarity solution to the higher-osmolarity solution. Counterpressure exerted on the high-osmolarity solution will reduce or halt the solvent transfer. An even higher pressure can be exerted to force solvent from the high-osmolarity solution to the low-osmolarity solution, a process called *reverse osmosis*. Reverse osmosis is used to make potable water from saltwater where sources of fresh water are scarce.

Example 9.10.1

A 0.50 M NaCl aqueous solution and a 0.30 M $Ca(NO_3)_2$ aqueous solution are placed on opposite sides of a semipermeable membrane. Determine the osmolarity of each solution and predict the direction of solvent flow.

Solution

The solvent will flow into the solution of higher osmolarity. The NaCl solute separates into two ions—Na^+ and Cl^-—when it dissolves, so its osmolarity is as follows:

$$\text{osmol (NaCl)} = 0.50\ \text{M} \times 2 = 1.0\ \text{osmol}$$

The $Ca(NO_3)_2$ solute separates into three ions—one Ca^{2+} and two NO_3^-—when it dissolves, so its osmolarity is as follows:

$$\text{osmol } [Ca(NO_3)_2] = 0.30\ \text{M} \times 3 = 0.90\ \text{osmol}$$

The osmolarity of the $Ca(NO_3)_2$ solution is lower than that of the NaCl solution, so water will transfer through the membrane from the $Ca(NO_3)_2$ solution to the NaCl solution.

Exercise 9.10.1

A 1.5 M $C_6H_{12}O_6$ aqueous solution and a 0.40 M $Al(NO_3)_3$ aqueous solution are placed on opposite sides of a semipermeable membrane. Determine the osmolarity of each solution and predict the direction of solvent flow.

Answer available at the end of this section.

Examples of osmosis are evident in many biological systems because cells are surrounded by semipermeable membranes. Carrots and celery that have become limp because they have lost water can be made crisp again by placing them in water. Water moves into the carrot or celery cells by osmosis. A cucumber placed in a concentrated salt solution loses water by osmosis and absorbs some salt to become a pickle. Osmosis can also affect animal cells. Solute concentrations are particularly important when solutions are injected into the body. Solutes in body cell fluids and blood serum give these solutions an osmotic pressure of approximately 7.7 atm. Solutions injected into the body must have the same osmotic pressure as blood serum; that is, they should be isotonic with blood serum. If a *less* concentrated solution, a **hypotonic** solution, is injected in sufficient quantity to dilute the blood serum, water from the diluted serum passes into the blood cells by osmosis, causing the cells to expand and rupture (Figure $9.10.2a$). This process is called hemolysis. When a *more* concentrated solution, a **hypertonic** solution, is injected, the cells lose water to the more concentrated solution, shrivel, and possibly die in a process called *crenation* (Figure $9.10.2c$). Only if red blood cells are placed in **isotonic** solutions that have the same osmolarity as exists inside the cells are they unaffected by negative effects of osmotic pressure (Figure $9.10.2b$). Glucose solutions of about 0.31 M, or sodium chloride (NaCl) solutions of about 0.16 M, are isotonic with blood plasma.

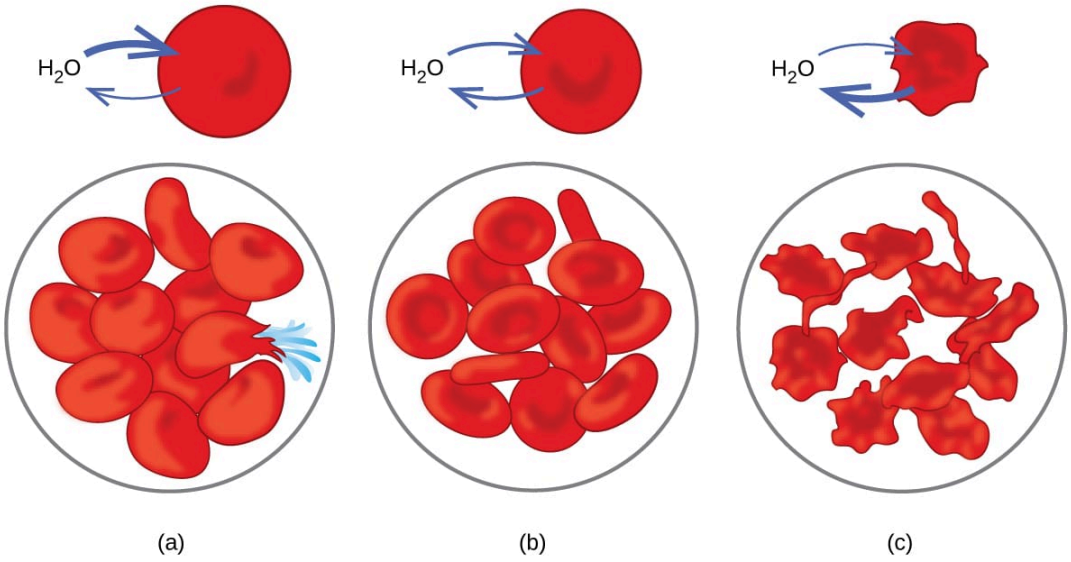


Figure 9.10.2: Red blood cell membranes are water permeable and will (a) swell and possibly rupture in a **hypotonic** solution; (b) maintain normal volume and shape in an **isotonic** solution; and (c) shrivel and possibly die in a **hypertonic** solution. (credit a/b/c: modifications of work by "LadyofHats"/Wikimedia commons)

Note: Isotonic Solutions for Red Blood Cells

The concentration of an red blood cell isotonic solution made with sodium chloride (NaCl) is half that of an isotonic solution made with glucose (0.16 M and 0.31 M respectively). This is because NaCl produces *two ions* when a formula unit dissolves, while molecular glucose produces only *one particle* when a formula unit dissolves. The osmolarities are therefore the same even though the concentrations of the two solutions are different.

isotonic NaCl solution: $osmol = 0.16\ M \times 2 = 0.32\ osmol/L$

isotonic glucose solution: $osmol = 0.31\ M \times 1 = 0.31\ osmol/L$

Osmotic pressure explains why you should not drink seawater if you are abandoned in a life raft in the middle of the ocean. Its osmolarity is about three times higher than most bodily fluids. You would actually become thirstier as water from your cells was drawn out to dilute the salty ocean water you ingested. Our bodies do a better job coping with hypotonic solutions than with hypertonic ones. The excess water is collected by our kidneys and excreted.

Osmotic pressure effects are used in the food industry to make pickles from cucumbers and other vegetables and in brining meat to make corned beef. It is also a factor in the mechanism of getting water from the roots to the tops of trees!

Answers

Exercise 9.10.1

osmol $C_6H_{12}O_6$ = 1.5; osmol $Al(NO_3)_3$ = 1.6

The solvent flows from $C_6H_{12}O_6$ solution (lower osmolarity) to $Al(NO_3)_3$ solution (higher osmolarity).

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9.11: Dialysis

Learning Objectives

- Understand the difference between dialysis and osmosis.

As introduced in a previous section, osmosis is the process by which s*olvent* particles can pass through a semipermeable membrane. **Dialysis** is similar to osmosis with the difference being that the pores in the semipermeable membranes are larger, thus allowing *both* solvent and small solute molecules to pass through. Larger solute particles, such as colloids and proteins, that cannot pass through the pores in the membrane are left behind. The size of the pores in the semipermeable membranes can be varied to allow for separation (or purification) of specific solute molecules from a solution based on their size. Biochemists and molecular biologists use dialysis to purify proteins from mixtures or to change the concentration of solute particles for different types of experiments, as illustrated in Figure 9.11.1.

Figure 9.11.1: Dialysis separates colloidal particles like protein and starch from water, small molecules, and ions. Source: Potcherboy at English Wikipedia / CC BY (https://creativecommons.org/licenses/by/3.0)

Role of dialysis in the human body

Kidneys filter the blood by dialysis, which occurs in tubular structures called nephrons (Figure 9.11.2. The nephrons filter the water, and small molecules, like glucose, amino acids, urea, and ions from the blood. Useful products and most of the water reabsorb later on, but urea and other waste products are excreted through urine. (You can read more about kidney structure and function here.)

Close up of a nephron and its place in the kidney. Labels on the kidney cross section show where unfiltered blood enters, filtered blood leaves, and urine exits. On the nephron, the glomerulus, tubule, and collecting duct are labeled along with where unfiltered blood enters, filtered blood exits, and urine exits.

Figure 9.11.2: Image of a close up nephron and its place in the kidney. Labels on the kidney cross section show where unfiltered blood enters, filtered blood leaves, and urine exits. On the nephron, the glomerulus, tubule, and collecting duct are labeled along with where unfiltered blood enters, filtered blood exits, and urine exits. (National Institute of Diabetes and Digestive and Kidney Diseases, National Institutes of Health. CC0 1.0)

The main function of the kidneys is to filter the blood to remove wastes and extra water, which are then expelled from the body as urine. Some diseases rob the kidneys of their ability to perform this function, causing a buildup of waste materials in the bloodstream. If a kidney transplant is not available or desirable, a procedure called dialysis can be used to remove waste materials and excess water from the blood.

In one form of dialysis, called **hemodialysis**, (see Figure 9.11.3), a patient's blood is passed though a length of tubing that travels through an *artificial kidney machine* (also called a *dialysis machine*). In the dialyser, a section of tubing composed of cellophane (a semipermeable membrane) is immersed in dialysate, a solution of sterile water, glucose, amino acids, and certain electrolytes. The osmotic pressure of the blood forces waste molecules, such as urea, and excess water through the membrane into the dialysate. Red and white blood cells are too large to pass through the membrane, so they remain in the blood. After being cleansed in this way, the blood is returned to the body.

Dialysis is a continuous process, as the osmosis of waste materials and excess water takes time. Typically, 5–10 lb of waste-containing fluid is removed in each dialysis session, which can last 2–8 hours and must be performed several times a week. Although some patients have been on dialysis for 30 or more years, dialysis is always a temporary solution because waste materials are constantly building up in the bloodstream. A more permanent solution is a kidney transplant.

undefined

Figure 9.11.3: Simplified hemodialysis circuit. (Yassine Mrabet, CC BY 3.0)

Career Connection: Dialysis Technician

Dialysis is a medical process of removing wastes and excess water from the blood by diffusion and ultrafiltration. When kidney function fails, dialysis must be done to artificially rid the body of wastes. This is a vital process to keep patients alive. In some cases, the patients undergo artificial dialysis until they are eligible for a kidney transplant. In others who are not candidates for kidney transplants, dialysis is a life-long necessity.

Dialysis technicians typically work in hospitals and clinics. While some roles in this field include equipment development and maintenance, most dialysis technicians work in direct patient care. Their on-the-job duties, which typically occur under the direct supervision of a registered nurse, focus on providing dialysis treatments. This can include reviewing patient history and current condition, assessing and responding to patient needs before and during treatment, and monitoring the dialysis process. Treatment may include taking and reporting a patient's vital signs and preparing solutions and equipment to ensure accurate and sterile procedures.

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10: ACIDS AND BASES

10.1: Acids and Bases Definitions
10.2: Acid and Base Strength
10.3: Acid Dissociation Constants
10.4: Water as Both an Acid and a Base
10.5: Measuring Acidity in Aqueous Solutions- The pH Scale
10.6: Working with pH
10.7: Acid and Base Equivalents
10.8: Some Common Acid-Base Reactions
10.9: Acidity and Basicity of Salt Solutions
10.10: Buffer Solutions
10.11: Titration

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10.1: Acids and Bases Definitions

Learning Objectives

- Identify an Arrhenius acid and an Arrhenius base.
- Identify a Brønsted-Lowry acid and a Brønsted-Lowry base.
- Identify conjugate acid-base pairs in an acid-base reaction.

There are three major classifications of substances known as acids or bases. The theory developed by Svante Arrhenius in 1883, the Arrhenius definition, states that an acid produces hydrogen ions, H^+, in solution and a base produces hydroxide ions, OH^-. Later, two more sophisticated and general theories were proposed. These theories are the Brønsted-Lowry and Lewis definitions of acids and bases. This section will cover the Arrhenius and Brønsted-Lowry theories; Lewis theory is discussed elsewhere.

The Arrhenius Theory of Acids and Bases

In 1884, the Swedish chemist Svante Arrhenius proposed two specific classifications of compounds, termed acids and bases. When dissolved in an aqueous solution, certain ions were released into the solution. An **Arrhenius acid** is a compound that *increases the concentration* of H^+ ions that are present when added to water. These H^+ ions form the **hydronium ion** (H_3O^+) when they combine with water molecules. This process is represented in a chemical equation by adding H_2O to the reactants side.

$$\mathrm{HCl\,(aq)} \rightarrow \mathrm{H^+\,(aq) + Cl^-\,(aq)} \tag{10.1.1}$$

In this reaction, hydrochloric acid (HCl) dissociates completely into hydrogen (H^+) and chloride (\Cl^{-}\) ions when dissolved in water, thereby releasing H^+ ions into solution. Formation of the hydronium ion equation:

$$\mathrm{HCl\,(aq) + H_2O(\ell) \rightarrow H_3O^+\,(aq) + Cl^-\,(aq)} \tag{10.1.2}$$

An **Arrhenius base** is a compound that *increases the concentration* of OH^- ions that are present when added to water. The dissociation is represented by the following equation:

$$\mathrm{NaOH\,(aq) \rightarrow Na^+\,(aq) + OH^-\,(aq)} \tag{10.1.3}$$

In this reaction, sodium hydroxide (NaOH) disassociates into sodium (Na^+) and hydroxide (OH^-) ions when dissolved in water, thereby releasing OH^- ions into solution.

Arrhenius acids are substances which produce hydrogen ions in solution and Arrhenius bases are substances which produce hydroxide ions in solution.

Limitations to the Arrhenius Theory

The Arrhenius theory has many more limitations than the other two theories. The theory does not explain the weak base ammonia (NH_3), which in the presence of water, releases hydroxide ions into solution, but does not contain OH^- itself. The Arrhenius definition of acid and base is also limited to aqueous (i.e., water) solutions.

The Brønsted-Lowry Theory of Acids and Bases

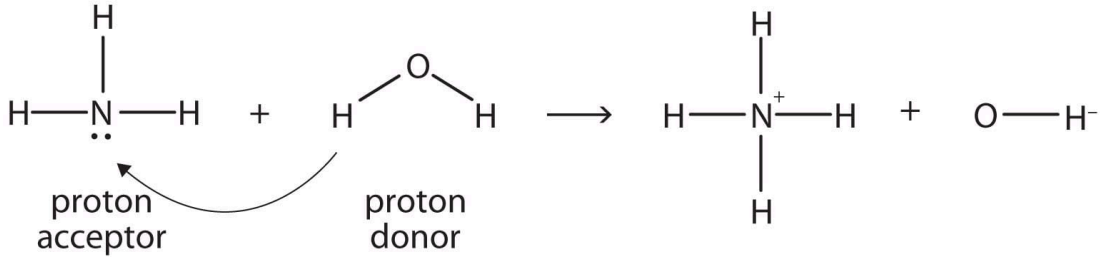
In 1923, Danish chemist Johannes Brønsted and English chemist Thomas Lowry independently proposed new definitions for acids and bases, ones that focus on proton transfer. A **Brønsted-Lowry acid** is any species that can donate a proton (H^+) to another molecule. A **Brønsted-Lowry base** is any species that can accept a proton from another molecule. In short, a Brønsted-Lowry acid is a proton donor, while a Brønsted-Lowry base is a proton acceptor.

A Brønsted-Lowry acid is a proton donor, while a Brønsted-Lowry base is a proton acceptor.

Let us use the reaction of ammonia in water to demonstrate the Brønsted-Lowry definitions of an acid and a base. Ammonia and water molecules are reactants, while the ammonium ion and the hydroxide ion are products:

$$\mathrm{NH_3\,(aq) + H_2O(\ell) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)} \tag{10.1.4}$$

What has happened in this reaction is that the original water molecule has donated a hydrogen ion to the original ammonia molecule, which in turn has accepted the hydrogen ion. We can illustrate this as follows:



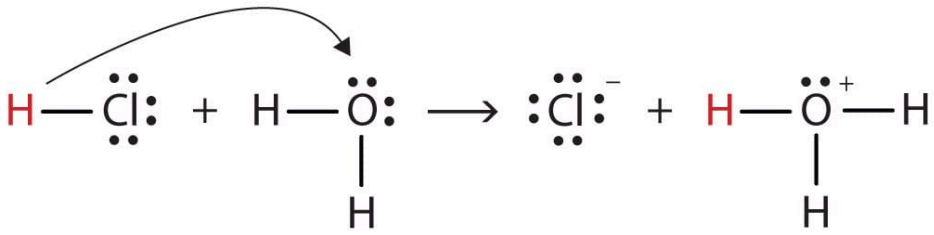
Because the water molecule *donates* a hydrogen ion to the ammonia, it is the Brønsted-Lowry acid, while the ammonia molecule—which *accepts* the hydrogen ion—is the Brønsted-Lowry base. Thus, ammonia acts as a base in both the Arrhenius sense and the Brønsted-Lowry sense.

Is an Arrhenius acid like hydrochloric acid still an acid in the Brønsted-Lowry sense? Yes, but it requires us to understand what really happens when HCl is dissolved in water. Recall that the hydrogen *atom* is a single proton surrounded by a single electron. To make the hydrogen ion, we remove the electron, leaving a bare proton. Do we really have bare protons floating around in aqueous solution? No, we do not. What really happens is that the H^+ ion attaches itself to H_2O to make H_3O^+, which is called the *hydronium ion*. For most purposes, H^+ and H_3O^+ represent the same species, but writing H_3O^+ instead of H^+ shows that we understand that there are no bare protons floating around in solution. Rather, these protons are actually attached to solvent molecules.

With this in mind, how do we define HCl as an acid in the Brønsted-Lowry sense? Consider what happens when HCl is dissolved in H_2O:

$$\mathrm{HCl\,(g) + H_2O(\ell)\ \rightarrow H_3O^+\,(aq)\ Cl^-\,(aq) + H_3O^+\,(aq)} \tag{10.1.5}$$

We can depict this process using Lewis electron dot diagrams:



Now we see that a hydrogen ion is transferred from the HCl molecule to the H_2O molecule to make chloride ions and hydronium ions. As the hydrogen ion donor, HCl acts as a Brønsted-Lowry acid; the hydrogen ion acceptor, H_2O is a Brønsted-Lowry base. So HCl is an acid not just in the Arrhenius sense, but also in the Brønsted-Lowry sense. Moreover, by the Brønsted-Lowry definitions, H_2O is a base in the formation of aqueous HCl. So the Brønsted-Lowry definitions of an acid and a base classify the dissolving of HCl in water as a reaction between an acid and a base—although the Arrhenius definition would not have labeled H_2O a base in

this circumstance.

Note: Acid and Base Definitions

- A Brønsted-Lowry acid is a proton (hydrogen ion) donor.
- A Brønsted-Lowry base is a proton (hydrogen ion) acceptor.
- **All** Arrhenius acids and bases are Brønsted-Lowry acids and bases as well. However, not all Brønsted-Lowry acids and bases are Arrhenius acids and bases.

Example 10.1.1

Aniline ($C_6H_5NH_2$) is slightly soluble in water. It has a nitrogen atom that can accept a hydrogen ion from a water molecule, just like the nitrogen atom in ammonia does. Write the chemical equation for this reaction and identify the Brønsted-Lowry acid and base.

Solution

$C_6H_5NH_2$ and H_2O are the reactants. When $C_6H_5NH_2$ accepts a proton from H_2O, it gains an extra H and a positive charge and leaves an OH^- ion behind. The reaction is as follows:

$$\mathrm{C_6H_5NH_2\,(aq) + H_2O(\ell) \rightleftharpoons C_6H_5NH_3{}^+\,(aq) + OH^-\,(aq)}$$

Because $C_6H_5NH_2$ accepts a proton, it is the Brønsted-Lowry base. The H_2O molecule, because it donates a proton, is the Brønsted-Lowry acid.

Exercise 10.1.1

Identify the Brønsted-Lowry acid and the Brønsted-Lowry base in this chemical equation.

$$\mathrm{H_2PO_4{}^- + H_2O \rightleftharpoons HPO_4{}^{2-} + H_3O^+} \tag{10.1.6}$$

Answer available at the end of this section.

Exercise 10.1.2

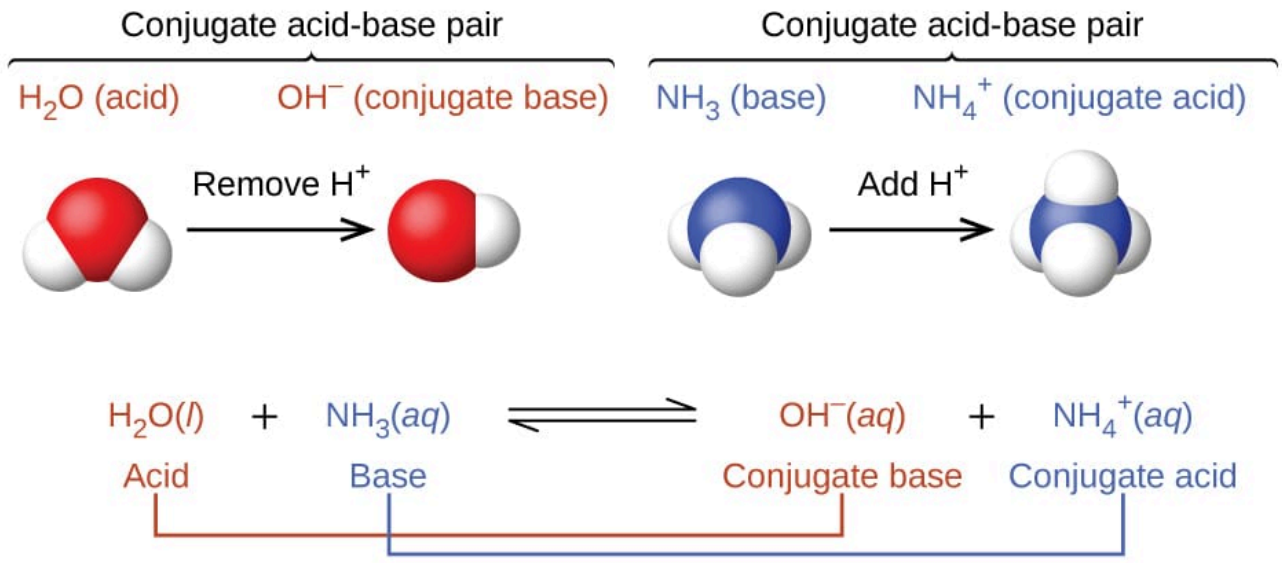
Which of the following compounds is a Bronsted-Lowry base?

a. HCl
b. HPO_4^{2-}
c. H_3PO_4
d. NH_4^+
e. $CH_3NH_3^+$

Answer available at the end of this section.

Conjugate Acid-Base Pair

In reality, all acid-base reactions involve the transfer of protons between acids and bases. For example, consider the acid-base reaction that takes place when ammonia is dissolved in water. A water molecule (functioning as an acid) transfers a proton to an ammonia molecule (functioning as a base), yielding the conjugate base of water, OH^-, and the conjugate acid of ammonia, NH_4^+ :



In the reaction of ammonia with water to give ammonium ions and hydroxide ions, ammonia acts as a base by accepting a proton from a water molecule, which in this case means that water is acting as an acid. In the reverse reaction, an ammonium ion acts as an acid by donating a proton to a hydroxide ion, and the hydroxide ion acts as a base. The conjugate acid–base pairs for this reaction are NH_4^+/NH_3 and H_2O/OH^-.

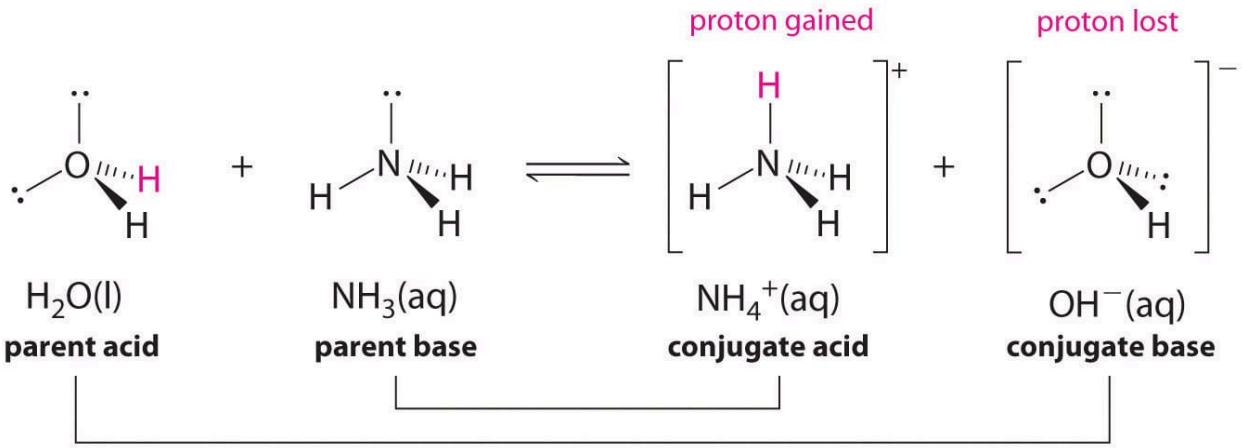


Figure 10.1.1. The pairing of parent acids and bases with conjugate acids and bases.

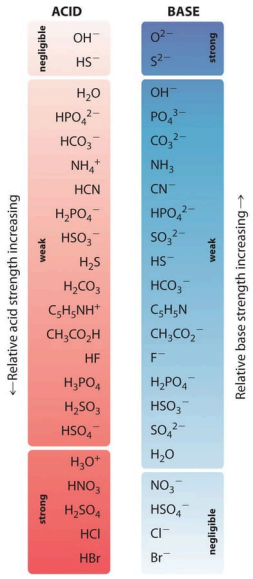


Figure 10.1.2: The Relative Strengths of Some Common Conjugate Acid-Base Pairs. The strongest acids are at the bottom left, and the strongest bases are at the top right. The conjugate base of a strong acid is a very weak base, and, conversely, the conjugate acid of a strong base is a very weak acid.

Example 10.1.2

Identify the conjugate acid-base pairs in this equilibrium.

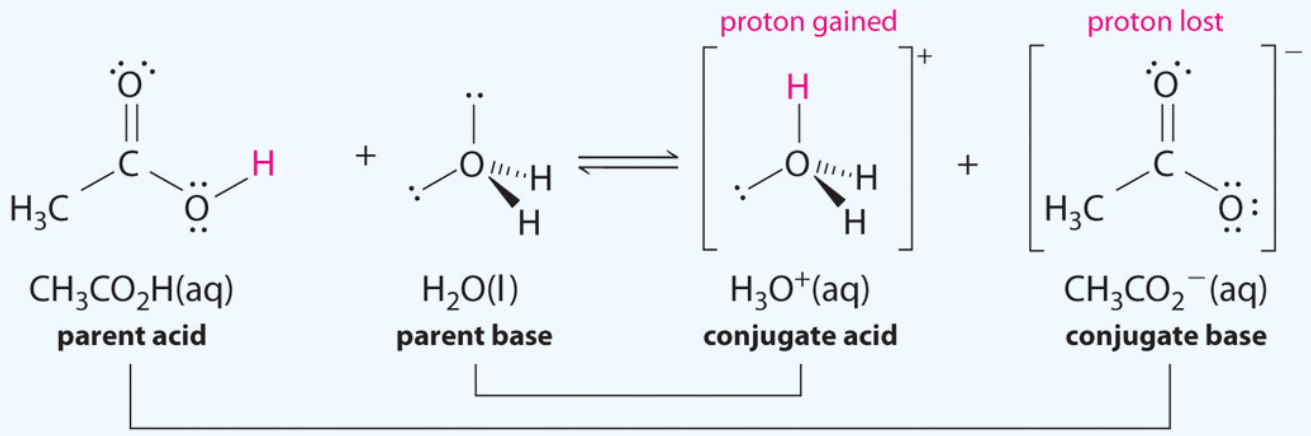
$$\mathrm{CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-}$$

Solution

Similarly, in the reaction of acetic acid with water, acetic acid **donates** a proton to water, which acts as the base. In the reverse reaction, H_3O^+ is the acid that donates a proton to the acetate ion, which acts as the base.

Once again, we have two conjugate acid-base pairs:

- the parent acid and its conjugate base ($CH_3CO_2H/CH_3CO_2^-$) and
- the parent base and its conjugate acid (H_3O^+/H_2O).



Example 10.1.3

Identify the conjugate acid-base pairs in this equilibrium.

$$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$$

Solution

One pair is H_2O and OH^-, where H_2O has one more H^+ and is the conjugate acid, while OH^- has one less H^+ and is the conjugate base.

The other pair consists of $(CH_3)_3N$ and $(CH_3)_3NH^+$, where $(CH_3)_3NH^+$ is the conjugate acid (it has an additional proton) and $(CH_3)_3N$ is the conjugate base.

Exercise 10.1.3

Identify the conjugate acid-base pairs in this equilibrium.

$$\mathrm{NH_2^- + H_2O \rightleftharpoons NH_3 + OH^-}$$

Answer available at the end of this section.

Contributions & Attributions

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Answers

Exercise 10.1.1

Brønsted-Lowry acid: $H_2PO_4^-$; Brønsted-Lowry base: H_2O

Exercise 10.1.2

A Brønsted-Lowry Base is a proton acceptor, which means it will take in an H^+. This eliminates HCl, $\mathrm{H_3PO_4}$, $\mathrm{NH_4^+}$ and $\mathrm{CH_3NH_3^+}$ because they are Bronsted-Lowry

acids. They all give away protons. In the case of $\mathrm{HPO_4^{2-}}$, consider the following equation:

$$\mathrm{HPO_4^{2-}(aq) + H_2O(l) \rightarrow PO_4^{3-}(aq) + H_3O^+(aq)}$$

Here, it is clear that HPO_4^{2-} is the acid since it donates a proton to water to make H_3O^+ and PO_4^{3-}. Now consider the following equation:

$$\mathrm{HPO_4^{2-}(aq) + H_2O(l) \rightarrow H_2PO_4^{-} + OH^-(aq)}$$

In this case, HPO_4^{2-} is the base since it accepts a proton from water to form $H_2PO_4^-$ and OH^-. Thus, HPO_4^{2-} is an acid and base together, making it amphoteric.

Since HPO_4^{2-} is the only compound from the options that can act as a base, the answer is **(b) HPO_4^{2-}.**

Exercise 10.1.3

H_2O (acid) and OH^- (base); NH_2^- (base) and NH_3 (acid)

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10.2: Acid and Base Strength

Learning Objectives

- Define a strong and a weak acid and base.
- Recognize an acid or a base as strong or weak.

Strong and Weak Acids

Except for their names and formulas, so far we have treated all acids as equals, especially in a chemical reaction. However, acids can be very different in a very important way. Consider $\mathrm{HCl(aq)}$. When HCl is dissolved in $\mathrm{H_2O}$, it completely **dissociates** (separates) into H^+(aq) and Cl^-(aq) ions; all the HCl molecules become ions:

$$\mathrm{HCl} \xrightarrow{100\,\%} \mathrm{H^+(aq) + Cl^-(aq)} \tag{10.2.1}$$

Any acid that dissociates 100% into ions is called a **strong acid**. If it does not dissociate 100%, it is a **weak acid**. $HC_2H_3O_2$ is an example of a weak acid:

$$HC_2H_3O_2 \xrightarrow{\sim 5\%} H^+(aq) + C_2H_3O_2^-(aq) \tag{10.2.2}$$

Because this reaction does not go 100% to completion, it is more appropriate to write it as **a reversible reaction**:

$$HC_2H_3O_2 \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq) \tag{10.2.3}$$

As it turns out, there are very few strong acids, which are given in Table 10.2.1. If an acid is not listed here, it is a weak acid. It may be 1% ionized or 99% ionized, but it is still classified as a weak acid.

Any acid that dissociates 100% into ions is called a strong acid. If it does not dissociate 100%, it is a weak acid.

Figure 10.2.1: Some of the common strong acids and bases are listed here.

Strong Acids		Strong Bases	
$\mathrm{HClO_4}$	perchloric acid	LiOH	lithium hydroxide
HCl	hydrochloric acid	NaOH	sodium hydroxide
HBr	hydrobromic acid	KOH	potassium hydroxide
HI	hydroiodic acid	$\mathrm{Ca(OH)_2}$	calcium hydroxide
$\mathrm{HNO_3}$	nitric acid	$\mathrm{Sr(OH)_2}$	strontium hydroxide
$\mathrm{H_2SO_4}$	sulfuric acid	$\mathrm{Ba(OH)_2}$	barium hydroxide

Strong and Weak Bases

The issue is similar with bases: a **strong base** is a base that is 100% ionized in solution. If it is less than 100% ionized in solution, it is a **weak base**. There are very few strong bases (Table 10.2.1); any base not listed is a weak base. All strong bases are OH^- compounds. So a base based on some other mechanism, such as NH_3 (which does not contain OH^- ions as part of its

formula), will be a weak base.

Example 10.2.1: Identifying Strong and Weak Acids and Bases

Identify each acid or base as strong or weak.

a. HCl
b. $Mg(OH)_2$
c. C_5H_5N

Solution

a. Because HCl is listed in Table 10.2.1, it is a strong acid.
b. Because $Mg(OH)_2$ is listed in Table 10.2.1, it is a strong base.
c. The nitrogen in C_5H_5N would act as a proton acceptor and therefore can be considered a base, but because it does not contain an OH compound, it cannot be considered a strong base; it is a weak base.

Exercise 10.2.1

Identify each acid or base as strong or weak.

a. RbOH
b. $\mathrm{HNO_2}$

Answer available at the end of this section.

Example 10.2.2: Characterizing Base Ionization

Write the balanced chemical equation for the dissociation of $Ca(OH)_2$ and indicate whether it proceeds 100% to products or not.

Solution

This is an ionic compound of Ca^{2+} ions and OH^- ions. When an ionic compound dissolves, it separates into its constituent ions:

$$\mathrm{Ca(OH)_2 \longrightarrow Ca^{2+}(aq) + 2\,OH^-(aq)}$$

Because $Ca(OH)_2$ is listed in Table 10.2.1, this reaction proceeds 100% to products.

Exercise 10.2.2

Write the balanced chemical equation for the dissociation of hydrazoic acid (HN_3) and indicate whether it proceeds 100% to products or not.

Answer a available at the end of this section.

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 [$\mathrm{HCl\,(aq)}$]. Vinegar has already been mentioned as a dilute solution of acetic acid [$\mathrm{HC_2H_3O_2\,(aq)}$]. In a medicine chest, one may find a bottle of vitamin C tablets; the chemical name of vitamin C is ascorbic acid ($\mathrm{HC_6H_7O_6}$).

One of the more familiar household bases is ammonia ($\mathrm{NH_3}$), which is found in numerous cleaning products. As we mentioned previously, ammonia is a base because it increases the hydroxide ion concentration by reacting with water:

$$\mathrm{NH_3\,(aq) + H_2O(\ell) \;\rightarrow NH_4^+\,(aq) + OH^-\,(aq)} \tag{10.2.4}$$

Many soaps are also slightly basic because they contain compounds that act as Brønsted-Lowry bases, accepting protons from water and forming excess hydroxide ions. This is one reason that soap solutions are slippery.



Figure 10.2.1: (left) Bottles of alkaline drain cleaners containing sodium hydroxide can dissolve greases and hair. (right) Chemical burns caused by sodium hydroxide solution photographed 44 hours after exposure. Figures used with permission from Wikipedia.

Perhaps the most dangerous household chemical is the lye-based drain cleaner. Lye is a common name for sodium hydroxide, although it is also used as a synonym for potassium hydroxide. Lye is an extremely caustic chemical that can react with grease, hair, food particles, and other substances that may build up and form a clog in a pipe. Unfortunately, lye can also attack tissues and other substances in our bodies. Thus, when we use lye-based drain cleaners, we must be very careful not to touch any of the solid drain cleaner or spill the water it was poured into. Safer, nonlye drain cleaners use peroxide compounds to react on the materials in the clog and clear the drain.

Chemical Equilibrium in Weak Acids and Bases

Ionization of weak acids or bases are reversible reactions, which means the forward and reverse reactions occur and eventually reach equilbrium. For example, the ionization of the weak acid $\mathrm{HC_2H_3O_2\,(aq)}$ is as follows:

$$\mathrm{HC_2H_3O_2\,(aq) + H_2O(\ell) \;\rightarrow H_3O^+\,(aq) + C_2H_3O_2^-\,(aq)} \tag{10.2.5}$$

The reverse process also begins to occur:

$$\mathrm{H_3O^+\,(aq) + C_2H_3O_2^-\,(aq) \;\rightarrow HC_2H_3O_2\,(aq) + H_2O(\ell)} \tag{10.2.6}$$

Eventually, there is a balance between the two opposing processes, and no additional change occurs. The chemical reaction is better represented at this point with a double arrow:

$$\mathrm{HC_2H_3O_2\,(aq) + H_2O(\ell) \rightleftharpoons H_3O^+\,(aq) + C_2H_3O_2^-\,(aq)} \tag{10.2.7}$$

The $\rightleftharpoons$ implies that both the forward and reverse reactions are occurring, and their effects cancel each other out. A process at this point is considered to be at **chemical equilibrium** (or equilibrium). It is important to note that the processes do not stop. They balance out each other so that there is no further net change; that is, chemical equilibrium is a *dynamic equilibrium*.

Example 10.2.3: Partial Ionization

Write the equilibrium chemical equation for the partial ionization of each weak acid or base.

a. $HNO_2(aq)$
b. $C_5H_5N(aq)$

Solution

a. $HNO_2(aq) + H_2O(\ell) \diamond NO_2^-(aq) + H_3O^+(aq)$
b. $C_5H_5N(aq) + H_2O(\ell) \diamond C_5H_5NH^+(aq) + OH^-(aq)$

Exercise 10.2.3

Write the equilibrium chemical equation for the partial ionization of each weak acid or base.

a. $HF_{(aq)}$
b. $AgOH_{(aq)}$
c. $CH_3NH_2(aq)$

Answer available at the end of this section.

Strengths of Conjugate Acid and Base Pairs

The extent to which an acid, HA, donates protons to water molecules depends on the strength of the conjugate base, $\mathrm{A^-}$, of the acid. If $\mathrm{A^-}$ is a strong base, any protons that are donated to water molecules are recaptured by $\mathrm{A^-}$. Thus there is relatively little $\mathrm{A^-}$ and $\mathrm{H_3O^+}$ in solution, and the acid, HA, is weak. If $\mathrm{A^-}$ is a weak base, water binds the protons more strongly, and the solution contains primarily $\mathrm{A^-}$ and $\mathrm{H_3O^+}$—the acid is strong. Strong acids form very weak conjugate bases, and weak acids form stronger conjugate bases (Figure 10.2.2).

The first six acids in Figure 10.2.2 are the most common strong acids. These acids are completely dissociated in aqueous solution. The conjugate bases of these acids are weaker bases than water. When one of these acids dissolves in water, their protons are completely transferred to water, the stronger base.

Those acids that lie between the hydronium ion and water in Figure 10.2.2 form conjugate bases that can compete with water for possession of a proton. Both hydronium ions and non-ionized acid molecules are present in equilibrium in a solution of one of these acids. Compounds that are weaker acids than water (those found below water in the column of acids) in Figure 10.2.2 exhibit no observable acidic behavior when dissolved in water. Their conjugate bases are stronger than the hydroxide ion, and if any conjugate base were formed, it would react with water to re-form the acid.

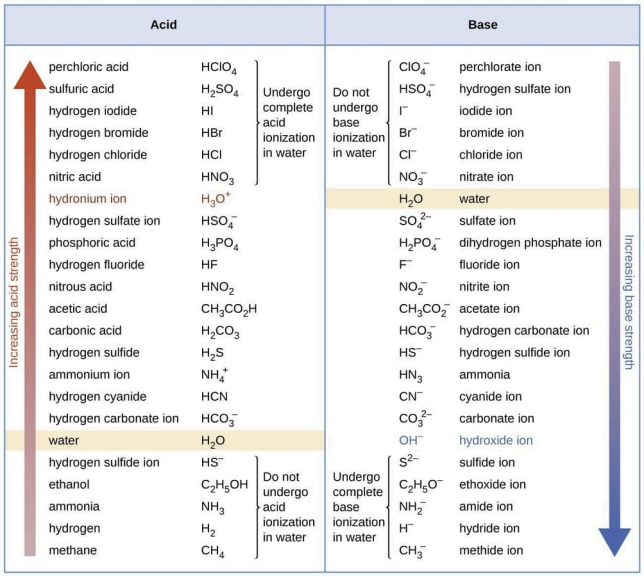


Figure 10.2.2: The chart shows the relative strengths of conjugate acid-base pairs.

The extent to which a base forms hydroxide ion in aqueous solution depends on the strength of the base relative to that of the hydroxide ion, as shown in the last column in Figure 10.2.2. A strong base, such as one of those lying below hydroxide ion, accepts protons from water to yield 100% of the conjugate acid and hydroxide ion. Those bases lying between water and hydroxide ion accept protons from water, but a mixture of the hydroxide ion and the base results. Bases that are weaker than water (those that lie above water in the column of bases) show no observable basic behavior in aqueous solution.

Key Takeaways

- Strong acids and bases are 100% ionized in aqueous solution.
- Weak acids and bases are less than 100% ionized in aqueous solution.

Answers

Exercise 10.2.1

a. strong base
b. weak acid

Exercise 10.2.2

The reaction is as follows:

$$\mathrm{HN_3} \longrightarrow \mathrm{H^+(aq) + N_3^-(aq)}$$

It does not proceed 100% to products because hydrazoic acid is not a strong acid.

Exercise 10.2.3

a. $HF(aq) + H_2O(\ell) \diamond F^-(aq) + H_3O^+(aq)$

b. $AgOH(aq) \diamond Ag^+(aq) + OH^-(aq)$

c. $CH_3NH_2(aq) + H_2O(\ell) \diamond CH_3NH_3^+(aq) + OH^-(aq)$

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10.3: Acid Dissociation Constants

Learning Objectives

- Write the acid dissociation constant (K_a) expression.
- Determine the relative strength of an acid using the (K_a) value.

The ionization for a general weak acid, HA, can be written as follows:

$$\mathrm{HA}\,(aq) \rightleftharpoons \mathrm{H^+}\,(aq) + \mathrm{A^-}\,(aq)$$

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.

$$K_\mathrm{a} = \frac{[\mathrm{H^+}]\,[\mathrm{A^-}]}{[\mathrm{HA}]}$$

The acid ionization represents the fraction of the original acid that has been *ionized* in solution. Therefore, the numerical value of K_a is a reflection of the strength of the acid. Weak acids with relatively higher K_a values are stronger than acids with relatively lower K_a values. Because strong acids are essentially 100% ionized, the concentration of the acid in the denominator is nearly zero and the K_a value approaches infinity. For this reason, K_a values are generally reported for weak acids only.

The table below is a listing of acid ionization constants for several acids. Note that polyprotic acids have a distinct ionization constant for each ionization step, with each successive ionization constant being smaller than the previous one.

Table $10.3.1$*: Acid Ionization Constants at* $25^\circ\mathrm{C}$

Name of Acid	Ionization Equation	K_a
Sulfuric acid	$\mathrm{H_2SO_4} \rightleftharpoons \mathrm{H^+} + \mathrm{HSO_4^-}$ $\mathrm{HSO_4} \rightleftharpoons \mathrm{H^+} + \mathrm{SO_4^{2-}}$	very large 1.3×10^{-2}
Hydrofluoric acid	$\mathrm{HF} \rightleftharpoons \mathrm{H^+} + \mathrm{F^-}$	7.1×10^{-4}
Nitrous acid	$\mathrm{HNO_2} \rightleftharpoons \mathrm{H^+} + \mathrm{NO_2^-}$	4.5×10^{-4}
Benzoic acid	$\mathrm{C_6H_5COOH} \rightleftharpoons \mathrm{H^+} + \mathrm{C_6H_5COO^-}$	6.5×10^{-5}
Acetic acid	$\mathrm{CH_3COOH} \rightleftharpoons \mathrm{H^+} + \mathrm{CH_3COO^-}$	1.8×10^{-5}
Carbonic acid	$\mathrm{H_2CO_3} \rightleftharpoons \mathrm{H^+} + \mathrm{HCO_3^-}$ $\mathrm{HCO_3^-} \rightleftharpoons \mathrm{H^+} + \mathrm{CO_3^{2-}}$	4.2×10^{-7} 4.8×10^{-11}

Hydrofluoric acid $HF_{(aq)}$ reacts directly with glass (very few chemicals react with glass). Hydrofluoric acid is used in glass etching.

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10.4: Water as Both an Acid and a Base

Learning Objectives

- To write chemical equations for water acting as an acid and as a base.
- Define and use the ion product constant for water, K_w, to calculate concentrations of $\mathrm{H_3O^+}$ and $\mathrm{OH^-}$ in aqueous solutions.

Water (H_2O) is an interesting compound in many respects. Here, we will consider its ability to behave as an acid or a base.

In some circumstances, a water molecule will accept a proton and thus act as a **Brønsted-Lowry base**. We saw an example in the dissolving of HCl in H_2O:

$$HCl + H_2O(\ell) \rightarrow H_3O^+(aq) + Cl^-(aq) \tag{10.4.1}$$

In other circumstances, a water molecule can donate a proton and thus act as a **Brønsted-Lowry acid**. For example, in the presence of the amide ion, a water molecule donates a proton, making ammonia as a product:

$$H_2O(\ell) + NH_2^-(aq) \rightarrow OH^-(aq) + NH_3(aq) \tag{10.4.2}$$

In this case, NH_2^- is a Brønsted-Lowry base (the proton acceptor).

So, depending on the circumstances, H_2O can act as either a Brønsted-Lowry acid or a Brønsted-Lowry base. Water is not the only substance that can react as an acid in some cases or a base in others, but it is certainly the most common example—and the most important one. A substance that can either donate or accept a proton, depending on the circumstances, is called an **amphiprotic** compound.

A water molecule can act as an acid or a base even in a sample of pure water. About 6 in every 100 million (6 in 10^8) water molecules undergo the following reaction:

$$H_2O(\ell) + H_2O(\ell) \rightarrow H_3O^+(aq) + OH^-(aq) \tag{10.4.3}$$

This process is called the **autoionization of water** (Figure 10.4.1) and occurs in every sample of water, whether it is pure or part of a solution. Autoionization occurs to some extent in any amphiprotic liquid. (For comparison, liquid ammonia undergoes autoionization as well, but only about 1 molecule in a million billion (1 in 10^{15}) reacts with another ammonia molecule.)

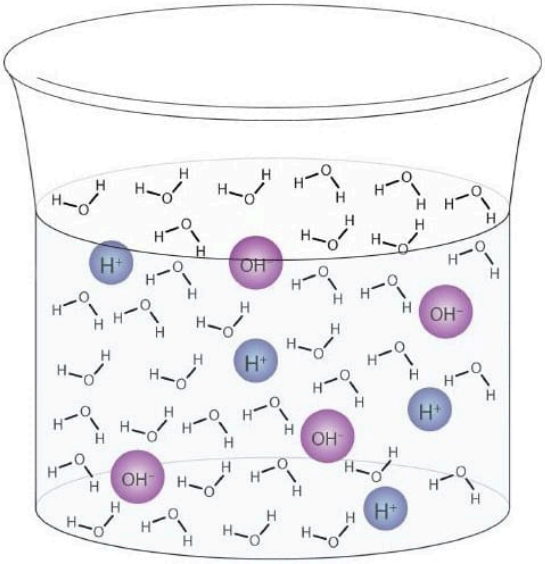


Figure 10.4.1 Autoionization. A small fraction of water molecules—approximately 6 in 100 million—ionize spontaneously into hydronium ions and hydroxide ions. This picture necessarily overrepresents the amount of autoionization that really occurs in pure water.

Example 10.4.1

Identify water as either a Brønsted-Lowry acid or a Brønsted-Lowry base.

1. $H_2O(\ell) + NO_2^-(aq) \rightarrow HNO_2(aq) + OH^-(aq)$
2. $HC_2H_3O_2(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + C_2H_3O_2^-(aq)$

Solution

1. In this reaction, the water molecule donates a proton to the NO_2^- ion, making $OH^-(aq)$. As the proton donor, H_2O acts as a Brønsted-Lowry acid.
2. In this reaction, the water molecule accepts a proton from $HC_2H_3O_2$, becoming $H_3O^+(aq)$. As the proton acceptor, H_2O is a Brønsted-Lowry base.

Exercise 10.4.2

Identify water as either a Brønsted-Lowry acid or a Brønsted-Lowry base.

1. $HCOOH(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + HCOO^-(aq)$
2. $H_2O(\ell) + PO_4^{3-}(aq) \rightarrow OH^-(aq) + HPO_4^{2-}(aq)$

Answer available at the end of this section.

Dissociation of Water

As we have already seen, H_2O can act as an acid or a base. Within any given sample of water, some H_2O molecules are acting as acids, and other H_2O molecules are acting as bases. The chemical equation is as follows:

$$\underbrace{H_2O}_{\text{acid}} + \underbrace{H_2O}_{\text{base}} \rightleftharpoons H_3O^+ + OH^- \tag{10.4.4}$$

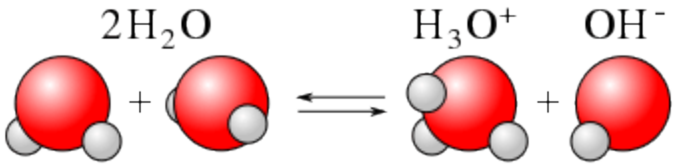


Figure 10.4.2: Autoionization of water, giving hydroxide and hydronium ions.

Similar to a weak acid, the autoionization of water is an equilibrium process, and is more properly written as follows:

$$\mathrm{H_2O}(\ell) + \mathrm{H_2O}(\ell) \rightleftharpoons \mathrm{H_3O^+}\,(\mathrm{aq}) + \mathrm{OH^-}\,(\mathrm{aq}) \tag{10.4.5}$$

We often use the simplified form of the reaction:

$$\mathrm{H_2O}\,(\mathrm{l}) \rightleftharpoons \mathrm{H^+}\,(\mathrm{aq}) + \mathrm{OH^-}\,(\mathrm{aq})$$

The equilibrium constant for the autoionization of water is referred to as the ion-product for water and is given the symbol K_w.

$$K_w = [\mathrm{H^+}][\mathrm{OH^-}]$$

The **ion-product constant for water (K_w)** is the mathematical product of the concentration of hydrogen ions and hydroxide ions. Note that H_2O is not included in the ion-product expression because it is a pure liquid. The value of K_w is very small, in accordance with a reaction that favors the reactants. At 25°C, the experimentally determined value of K_w in pure water is 1.0×10^{-14}.

$$K_w = [\mathrm{H^+}][\mathrm{OH^-}] = 1.0 \times 10^{-14}$$

In a sample of pure water, the concentrations of hydrogen and hydroxide ions are equal to one another. Pure water or any other aqueous solution in which this ratio holds is said to be *neutral*. To find the molarity of each ion, the square root of K_w is taken.

$$[\mathrm{H^+}] = [\mathrm{OH^-}] = 1.0\times10^{-7}$$

The product of these two concentrations is 1.0×10^{-14}

$$[\mathrm{H^+}]\times[\mathrm{OH^-}] = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

- For acids, the concentration of H^+ or $[H^+]$ is greater than 1.0×10^{-7} M
- For bases, the concentration of OH^- or $[OH^-]$ is greater than 1.0×10^{-7} M.

Aqueous HCl is an example of acidic solution. Hydrogen chloride (HCl) ionizes to produce H^+ and Cl^- ions upon dissolving in water. This increases the concentration of H^+ ions in the solution. According to Le Chatelier's principle, the equilibrium represented by

$$\mathrm{H_2O}\,(\mathrm{l}) \rightleftharpoons \mathrm{H^+}\,(\mathrm{aq}) + \mathrm{OH^-}\,(\mathrm{aq})$$

$$\mathrm{HCl}\,(\mathrm{g}) \longrightarrow \mathrm{H^+}\,(\mathrm{aq}) + \mathrm{Cl^-}\,(\mathrm{aq})$$

is forced to the left, towards the reactant. As a result, the concentration of the hydroxide ion decreases.

Now, consider KOH (aq), a **basic solution**. Solid potassium hydroxide (KOH) dissociates in water to yield potassium ions and hydroxide ions.

$$\mathrm{KOH(s)} \rightarrow \mathrm{K^+(aq)} + \mathrm{OH^-(aq)}$$

The increase in concentration of the OH^- ions will cause a decrease in the concentration of the H^+ ions.

No matter whether the aqueous solution is an acid, a base, or neutral:and the ion-product of $[H^+][OH^-]$ remains constant.

- For acidic solutions, $[H^+]$ is greater than $[OH^-]$.
- For basic solutions, [OH–] is greater than $[H^+]$.
- For neutral solutions, $[H_3O^+]$ = [OH–] = 1.0×10^{-7}M

This means that if you know $[H^+]$ for a solution, you can calculate what $[OH^-]$) has to be for the product to equal 1.0×10^{-14}, or if you know $[OH^-]$), you can calculate $[H^+]$. This also implies that as one concentration goes up, the other must go down to compensate so that their product always equals the value of K_w.

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \tag{10.4.6}$$

Example 10.4.2

Hydrochloric acid (HCl) is a strong acid, meaning it is 100% ionized in solution. What is the $[H^+]$ and the $[OH^-]$ in a solution of 2.0×10^{-3} M HCl?

Solution

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

Known

- [HCl] = 2.0×10^{-3} M
- Kw = 1.0×10^{-14}

Unknown

- $[H^+]$=?M
- $[OH^-]$=?M

Because HCl is 100% ionized, the concentration of H+ ions in solution will be equal to the original concentration of HCl. Each HCl molecule that was originally present ionizes into one H+ ion and one Cl– ion. The concentration of OH– can then be determined from the [H+] and Kw.

Step 2: Solve.

$$[H^+]=2.0\times10^{-3}\ M$$

$$Kw = [H^+][OH^-] = 1.0\times10^{-14}$$

$$[OH^-] = Kw/[H^+] = 1.0\times10^{-14}/2.0\times10^{-3} = 5.0\times10^{-12}\ M$$

Step 3: Think about your result.

The $[H^+]$ is much higher than the $[OH^-]$ because the solution is acidic. As with other equilibrium constants, the unit for Kw is customarily omitted.

Exercise 10.4.2

Sodium hydroxide (NaOH) is a strong base. What is the $[H^+]$ and the $[OH^-]$ in a 0.001 M NaOH solution at 25 °C?

Answer available at the end of this section.

Concept Review Exercises

1. Explain how water can act as an acid.
2. Explain how water can act as a base.

Answers

1. Under the right conditions, H_2O can donate a proton, making it a Brønsted-Lowry acid.
2. Under the right conditions, H_2O can accept a proton, making it a Brønsted-Lowry base.

Key Takeaway

- Water molecules can act as both an acid and a base, depending on the conditions.

Exercises

1. Is $H_2O(\ell)$ acting as an acid or a base?

   $H_2O(\ell) + NH_4^+(aq) \rightarrow H_3O^+(aq) + NH_3(aq)$

2. Is $H_2O(\ell)$ acting as an acid or a base?

   $CH_3^-(aq) + H_2O(\ell) \rightarrow CH_4(aq) + OH^-(aq)$

3. In the aqueous solutions of some salts, one of the ions from the salt can react with water molecules. In some $C_2H_3O_2^-$ solutions, the following reaction can occur:

   $C_2H_3O_2^-(aq) + H_2O(\ell) \rightarrow HC_2H_3O_2(aq) + OH^-(aq)$

   Is H_2O acting as an acid or a base in this reaction?

4. In the aqueous solutions of some salts, one of the ions from the salt can react with water molecules. In some NH_4^+ solutions, the following reaction can occur:

   $NH_4^+(aq) + H_2O \rightarrow NH_3(aq) + H_3O^+(aq)$

   Is H_2O acting as an acid or a base in this reaction?

5. Why is pure water considered neutral?

Answers

1. base
2. acid

3. acid
4. base

5. When water ionizes, equal amounts of H^+ (acid) and OH^- (base) are formed, so the solution is neither acidic nor basic: $H_2O(\ell) \rightarrow H^+(aq) + OH^-(aq)$

[SIDE NOTE: It is rare to truly have pure water. Water exposed to air will usually be slightly acidic because dissolved carbon dioxide gas, or carbonic acid, decreases the pH slightly below 7. Alternatively, dissolved minerals, like calcium carbonate

(limestone), can make water slightly basic.]

Answers

Exercise 10.4.2

1. H_2O acts as the proton acceptor (Brønsted-Lowry base)
2. H_2O acts as the proton donor (Brønsted-Lowry acid)

Exercise 10.4.2

$[OH^-]$ = 0.001M or 1 x 10^{-3}M; $[H^+]$=1×10^{-11}M.

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10.5: Measuring Acidity in Aqueous Solutions- The pH Scale

Learning Objectives

- Define the pH scale and use it to describe acids and bases.
- Calculate the pH of a solution from $[H_3O^+]$ and $[OH^-]$.

Knowing the amount of acid and base in solutions is extremely important for a wide variety of applications ranging from brewing beer or wine to studying the effects of ocean acidification to health and medicine. Scientists are good at calculating and measuring the concentration of hydronium in a solution, however, there is a more convenient way to make comparisons between solutions – *the pH scale*.

The pH Scale

One qualitative measure of the strength of an acid or a base solution is the pH scale, which is based on the concentration of the hydronium (or hydrogen) ion in aqueous solution.

$$pH = -\log[H^+]$$

or

$$pH = -\log[H_3O^+]$$

Figure $10.5.1$ illustrates this relationship, along with some examples of various solutions. Because hydrogen ion concentrations are generally less than one (for example $1.3 \times 10^{-3}\ M$), the log of the number will be a negative number. To make pH even easier to work with, pH is defined as the *negative* log of $[H_3O^+]$, which will give a positive value for pH.

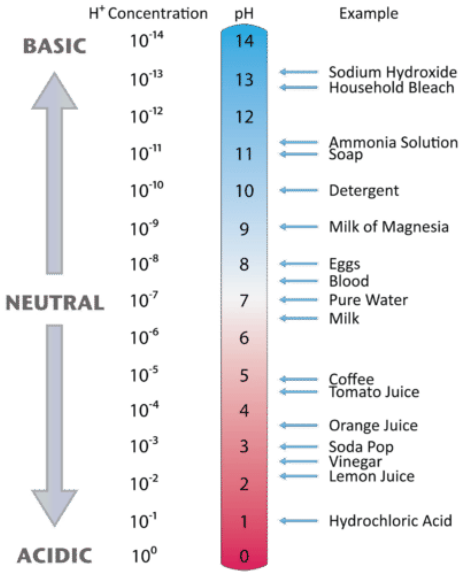


Figure $10.5.1$: The relationship between [H$^+$] and pH *values for several common materials.*

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 \({10{.}5{.}\eatSpaces{1}
\endSpaces}.

Table 10.5.1: Acidic, Basic and Neutral pH Values

Classification	Relative Ion Concentrations	pH at 25 °C
acidic	$[H^+] > [OH^-]$	pH < 7
neutral	$[H^+] = [OH^-]$	pH = 7
basic	$[H^+] < [OH^-]$	pH > 7

Example 10.5.1

Find the pH, given the $[H^+]$ of the following:

a. 1×10^{-3} M
b. 2.5×10^{-11} M
c. 4.7×10^{-9} M

Solution

$pH = - \log [H_3O^+]$

Substitute the known quantity into the equation and solve. Use a scientific calculator for b and c.

a. $pH = - \log [1 \times 10^{-3}] = 3.0$ (1 decimal place since 1 has 1 significant figure)
b. $pH = - \log [2.5 \times 10^{-11}] = 10.60$ (2 decimal places since 2.5 has 2 significant figures)
c. $pH = - \log [4.7 \times 10^{-9}] = 8.33$ (2 decimal places since 4.7 has 2 significant figures)

Note on significant figures:

Because the number(s) before the decimal point in the pH value relate to the power on 10, the number of digits *after* the decimal point (underlined) is what determines the number of significant figures in the final answer.

Exercise 10.5.1

Find the pH, given $[H^+]$ of the following:

a. 5.8×10^{-4} M
b. 1.0×10^{-7} M

Answer available at the end of this section.

Figure 10.5.2 lists the pH of several common solutions. The most *acid*ic among the listed solutions is 1 M HCl with the lowest pH value (0.0): battery acid is the next most acidic solution with a pH value of 0.3. The most *basic* is 1M NaOH solution with the highest pH value of 14.0. Notice that some biological fluids (stomach acid and urine) are nowhere near neutral. You may also notice that many food products are slightly acidic. They are acidic because they contain solutions of weak acids. If the acid components of these foods were strong acids, the food would likely be inedible.

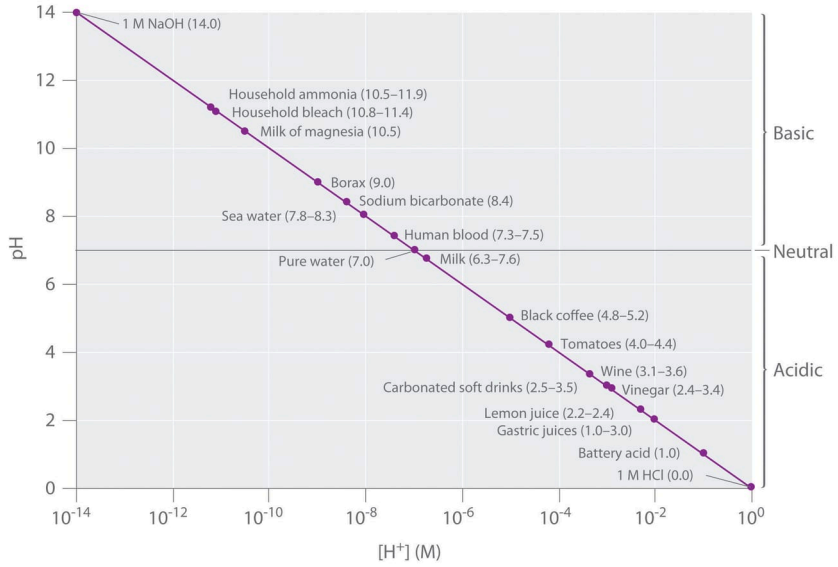


Figure 10.5.2: A Plot of pH versus [H^+] for Some Common Aqueous Solutions. Although many substances exist in a range of pH values (indicated in parentheses), they are plotted using typical values.

Example 10.5.2

Label each solution as acidic, basic, or neutral based only on the stated pH.

a. milk of magnesia, pH = 10.5
b. pure water, pH = 7
c. wine, pH = 3.0

Solution

a. With a pH greater than 7, milk of magnesia is basic. (Milk of magnesia is largely $Mg(OH)_2$.)
b. Pure water, with a pH of 7, is neutral.
c. With a pH of less than 7, wine is acidic.

Exercise 10.5.2

Identify each substance as acidic, basic, or neutral based only on the stated pH.

a. human blood with pH = 7.4
b. household ammonia with pH = 11.0
c. cherries with pH = 3.6

Answer available at the end of this section.

Measuring pH

Tools have been developed that make the measurement of pH simple and convenient. For example, pH paper (Figure 10.5.3)consists of strips of paper impregnated with one or more **acid-base indicators**, which are intensely colored organic molecules whose colors change dramatically depending on the pH of the solution. Placing a drop of a solution on a strip of pH paper and comparing its color with standards give the solution's approximate pH. A more accurate tool, the pH meter, uses a glass electrode, a device whose voltage depends on the H^+ ion concentration (Figure 10.5.3).

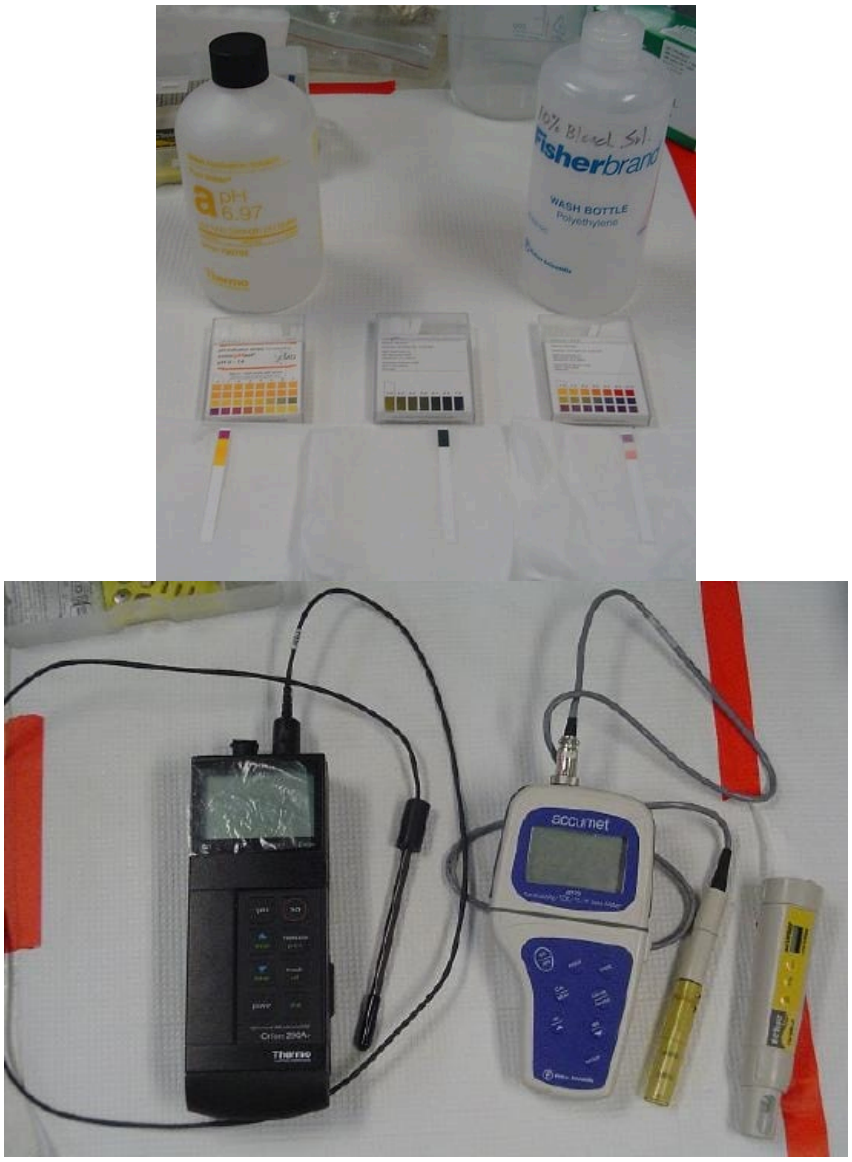


Figure 10.5.3: Ways to measure pH. (left) These pH strips can measure pH in a series of ranges by putting sample on a strip and comparing its color change with colors on the box that correspond to a certain pH. The strip on the left measures pH 0-7 and shows results of a strong acid sample; the center strip is pH range 5-10 and shows results of a 6.97 buffer solution sample; the strip on the right measures a broad range (pH 1-14) and shows results of a 10% bleach water solution sample. This image can be enlarged by clicking on it. (right) These three meters and probes can measure pH (left) and electrical conductivity (center and right). Photos by Monica Bruckner (courtesy of the Science Education Resource Center (SERC) at Carleton College).

Acid Rain

Normal rainwater has a pH between 5 and 6 due to the presence of dissolved CO_2 which forms carbonic acid:

$$\mathrm{H_2O\,(l) + CO_2\,(g) \longrightarrow H_2CO_3\,(aq)} \tag{10.5.1}$$

$$\mathrm{H_2CO_3\,(aq) \rightleftharpoons H^+\,(aq) + HCO_3{}^-\,(aq)} \tag{10.5.2}$$

Acid rain is rainwater that has a pH of less than 5, due to a variety of nonmetal oxides, including CO_2, SO_2, SO_3, NO, and NO_2 being dissolved in the water and reacting with it to form not only carbonic acid, but sulfuric acid and nitric acid. The formation and subsequent ionization of sulfuric acid are shown here:

$$\mathrm{H_2O\,(l) + SO_3\,(g) \longrightarrow H_2SO_4\,(aq)} \tag{10.5.3}$$

$$H_2SO_4\,(aq) \longrightarrow H^+\,(aq) + HSO_4{}^-\,(aq) \qquad (10.5.4)$$

Carbon dioxide is naturally present in the atmosphere because we and most other organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or when we burn wood or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also stems from burning fossil fuels, which have traces of sulfur, and from the process of "roasting" ores of metal sulfides in metal-refining processes. Oxides of nitrogen are formed in internal combustion engines where the high temperatures make it possible for the nitrogen and oxygen in air to chemically combine.

Acid rain is a particular problem in industrial areas where the products of combustion and smelting are released into the air without being stripped of sulfur and nitrogen oxides. In North America and Europe until the 1980s, it was responsible for the destruction of forests and freshwater lakes, when the acidity of the rain actually killed trees, damaged soil, and made lakes uninhabitable for all but the most acid-tolerant species. Acid rain also corrodes statuary and building facades that are made of marble and limestone (Figure 10.5.4). Regulations limiting the amount of sulfur and nitrogen oxides that can be released into the atmosphere by industry and automobiles have reduced the severity of acid damage to both natural and manmade environments in North America and Europe. It is now a growing problem in industrial areas of China and India.

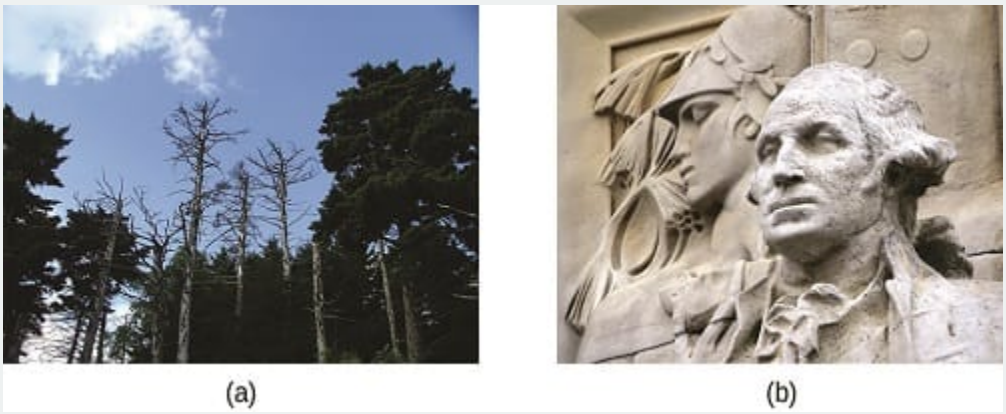


Figure 10.5.4: (a) Acid rain makes trees more susceptible to drought and insect infestation, and depletes nutrients in the soil. (b) It also is corrodes statues that are carved from marble or limestone. (credit a: modification of work by Chris M Morris; credit b: modification of work by "Eden, Janine and Jim"/Flickr)

Answers

Exercise 10.5.1

a. 3.24

b. 7.00

Exercise 10.5.2

a. slightly basic

b. basic

c. acidic

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10.6: Working with pH

Learning Objectives

- Calculate pH from $[H_3O^+]$ and $[H_3O^+]$ from pH.

Calculating pH from Hydronium Concentration

The pH of solutions can be determined by using logarithms as illustrated in the next example for stomach acid. Stomach acid is a solution of HCl with a hydronium ion concentration of $1.2 \times 10^{-3}\ M$, what is the pH of the solution?

$$\begin{aligned} \text{pH} &= -\log[\text{H}_3\text{O}^+] \\ &= -\log(1.2 \times 10^{-3}) \\ &= -(-2.92) = 2.92 \end{aligned}$$

Logarithms

To get the **log value** on your calculator, enter the number (in this case, the hydronium ion concentration) first, then press the LOG key.

If the number is 1.0 x 10^{-5} (for $[H_3O^+]$ = 1.0 x 10^{-5} M) you should get an answer of "-5".

If you get a different answer, or an error, try pressing the LOG key before you enter the number.

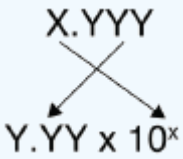
Example 10.6.2: Converting Ph to Hydronium Concentration

Find the pH, given the $[H_3O^+]$ of the following:

a. 1 ×10^{-3} M
b. 2.5 ×10^{-11} M
c. 4.7 ×10^{-9} M

Solution

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: a. $[H_3O^+]$ =1 × 10^{-3} M b. $[H_3O^+]$ =2.5 ×10^{-11} M c. $[H_3O^+]$ = 4.7 ×10^{-9} M Find: ? pH

Steps for Problem Solving	
Plan the problem.	Need to use the expression for pH (Equation ???). pH = - log $[H_3O^+]$
Calculate.	Now substitute the known quantity into the equation and solve. a. pH = - log [1 × 10^{-3}] = 3.0 (1 decimal places since 1 has 1 significant figure) b. pH = - log [2.5 ×10^{-11}] = 10.60 (2 decimal places since 2.5 has 2 significant figures) c. pH = - log [4.7 ×10^{-9}] = 8.30 (2 decimal places since 4.7 has 2 significant figures) The other issue that concerns us here is significant figures. Because the number(s) before the decimal point in a logarithm relate to the power on 10, the number of digits *after* the decimal point is what determines the number of significant figures in the final answer: 

Exercise 10.6.2

Find the pH, given $[H_3O^+]$ of the following:

a. 5.8 ×10^{-4} M
b. 1.0×10^{-7}

Answer a available at the end of this section.

Answer b available at the end of this section.

Calculating Hydronium Concentration from pH

Sometimes you need to work "backwards"—you know the pH of a solution and need to find $[H_3O^+]$, or even the concentration of the acid solution. How do you do that? To convert pH into $[H_3O^+]$ we solve Equation ??? for $[H_3O^+]$. This involves taking the antilog (or inverse log) of the negative value of pH .

$$[\mathrm{H_3O^+}] = \mathrm{antilog}(-pH) \tag{10.6.1}$$

or

$$[\mathrm{H_3O^+}] = 10^{-pH} \tag{10.6.2}$$

As mentioned above, different calculators work slightly differently—make sure you can do the following calculations using ***your***

calculator.

Calculator Skills

We have a solution with a pH = 8.3. What is $[H_3O^+]$?

With some calculators you will do things in the following order:

1. Enter 8.3 as a negative number (use the key with both the +/- signs, not the subtraction key).
2. Use your calculator's 2nd or Shift or INV (inverse) key to type in the symbol found above the LOG key. The shifted function should be 10^x.
3. You should get the answer $\mathbf{5.0 \times 10^{-9}}$.

Other calculators require you to enter keys in the order they appear in the equation.

1. Use the Shift or second function to key in the 10^x function.
2. Use the +/- key to type in a negative number, then type in 8.3.
3. You should get the answer $\mathbf{5.0 \times 10^{-9}}$.

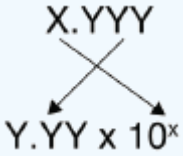
If neither of these methods work, try rearranging the order in which you type in the keys. Don't give up—you must master your calculator!

Example 10.6.3: Calculating Hydronium Concentration from pH

Find the hydronium ion concentration in a solution with a pH of 12.6. Is this solution an acid or a base? How do you know?

Solution

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: pH = 12.6 Find: $[H_3O^+]$ = ? M
Plan the problem.	Need to use the expression for $[H_3O^+]$ (Equation 10.6.2). $[H_3O^+]$ = antilog (-pH) or $[H_3O^+] = 10^{-pH}$

Steps for Problem Solving	
Calculate.	Now substitute the known quantity into the equation and solve. $[H_3O^+]$ = antilog (12.60) = 2.5 x 10^{-13} M (2 significant figures since 4.7 has 12.60 2 decimal places) or $[H_3O^+] = 10^{-12.60} = 2.5 \times 10^{-13}$ M (2 significant figures since 4.7 has 12.60 2 decimal places) The other issue that concerns us here is significant figures. Because the number(s) before the decimal point in a logarithm relate to the power on 10, the number of digits *after* the decimal point is what determines the number of significant figures in the final answer: 

Exercise 10.6.3

If moist soil has a pH of 7.84, what is $[H_3O^+]$ of the soil solution?

Answer available at the end of this section.

Answers

Exercise 10.6.2

3.22

Exercise 10.6.2

7.00

Exercise 10.6.3

1.5 x 10^{-8} M

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10.7: Acid and Base Equivalents



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10.8: Some Common Acid-Base Reactions



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10.9: Acidity and Basicity of Salt Solutions

Learning Objectives

- Identify a salt solution as acidic, basic, or neutral.

A salt is an ionic compound that is formed when an acid and a base neutralize each other. While it may seem that salt solutions are always neutral, they can frequently be either acidic or basic.

Consider the salt formed when the weak acid hydrofluoric acid is neutralized by the strong base sodium hydroxide. The molecular and net ionic equations are shown below.

$$\mathrm{HF}\,(aq) + \mathrm{NaOH}\,(aq) \rightarrow \mathrm{NaF}\,(aq) + \mathrm{H_2O}\,(l)$$
$$\mathrm{HF}\,(aq) + \mathrm{OH^-}\,(aq) \rightarrow \mathrm{F^-}\,(aq) + \mathrm{H_2O}\,(l)$$

Since sodium fluoride is soluble, the sodium ion is a spectator ion in the neutralization reaction. The fluoride ion is capable of reacting, to a small extent, with water, accepting a proton.

$$\mathrm{F^-}\,(aq) + \mathrm{H_2O}\,(l) \rightleftharpoons \mathrm{HF}\,(aq) + \mathrm{OH^-}\,(aq)$$

The fluoride ion is acting as a weak Brønsted-Lowry base. The hydroxide ion that is produced as a result of the above reaction makes the solution slightly basic. **Salt hydrolysis** is a reaction in which one of the ions from a salt reacts with water, forming either an acidic or basic solution.

Salts That Form Basic Solutions

When solid sodium fluoride is dissolved into water, it completely dissociates into sodium ions and fluoride ions. The sodium ions do not have any capability of hydrolyzing, but the fluoride ions hydrolyze to produce a small amount of hydrofluoric acid and hydroxide ion.

$$\mathrm{F^-}\,(aq) + \mathrm{H_2O}\,(l) \rightleftharpoons \mathrm{HF}\,(aq) + \mathrm{OH^-}\,(aq)$$

Salts that are derived from the neutralization of a weak acid (HF) by a strong base (NaOH) will always produce salt solutions that are basic.

Salts That Form Acidic Solutions

Ammonium chloride $(\mathrm{NH_4Cl})$ is a salt that is formed when the strong acid HCl is neutralized by the weak base $\mathrm{NH_3}$. Ammonium chloride is soluble in water. The chloride ion produced is incapable of hydrolyzing because it is the conjugate base of the strong acid HCl. In other words, the $\mathrm{Cl^-}$ ion cannot accept a proton from water to form HCl and $\mathrm{OH^-}$, as the fluoride ion did in the previous section. However, the ammonium ion is capable of reacting slightly with water, donating a proton and so acting as an acid.

$$\mathrm{NH_4{}^+}\,(aq) + \mathrm{H_2O}\,(l) \rightleftharpoons \mathrm{H_3O^+}\,(aq) + \mathrm{NH_3}\,(aq)$$

Salts That Form Neutral Solutions

A salt that is derived from the reaction of a strong acid with a strong base forms a solution that has a pH of 7. An example is sodium chloride, formed from the neutralization of HCl by NaOH. A solution of NaCl in water has no acidic or basic properties, since neither ion is capable of hydrolyzing. Other salts that form neutral solutions include potassium nitrate $(\mathrm{KNO_3})$ and lithium bromide (LiBr). The table below summarizes how to determine the acidity or basicity of a salt solution.

Table 10.9.1

Salt formed from:	Salt Solution
Strong acid + Strong base	Neutral
Strong acid + Weak base	Acidic
Weak acid + Strong base	Basic

Salts formed from the reaction of a weak acid and a weak base are more difficult to analyze due to competing hydrolysis reactions between the cation and the anion. These salts are not considered in this chapter's concept.

Summary

- Salt hydrolysis is a reaction in which one of the ions from a salt reacts with water, forming either an acidic or basic solution.
- Salts that are derived from the neutralization of a weak acid by a strong base will always produce salt solutions that are basic.
- Salts that are derived from the neutralization of a strong acid by a weak base will always produce salt solutions that are acidic.
- A salt that is derived from the reaction of a strong acid with a strong base forms a solution that has a pH of 7.

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10.10: Buffer Solutions

Learning Objectives

- Describe the composition and function of acid–base buffers
- Calculate the pH of a buffer before and after the addition of added acid or base

A mixture of a weak acid and its conjugate base (or a mixture of a weak base and its conjugate acid) is called a buffer solution, or a buffer. Buffer solutions resist a change in pH when small amounts of a strong acid or a strong base are added (Figure 10.10.1). A solution of acetic acid (CH_3COOH and sodium acetate CH_3COONa) is an example of a buffer that consists of a weak acid and its salt. An example of a buffer that consists of a weak base and its salt is a solution of ammonia ($NH_3\,(aq)$) and ammonium chloride ($NH_4Cl\,(aq)$).

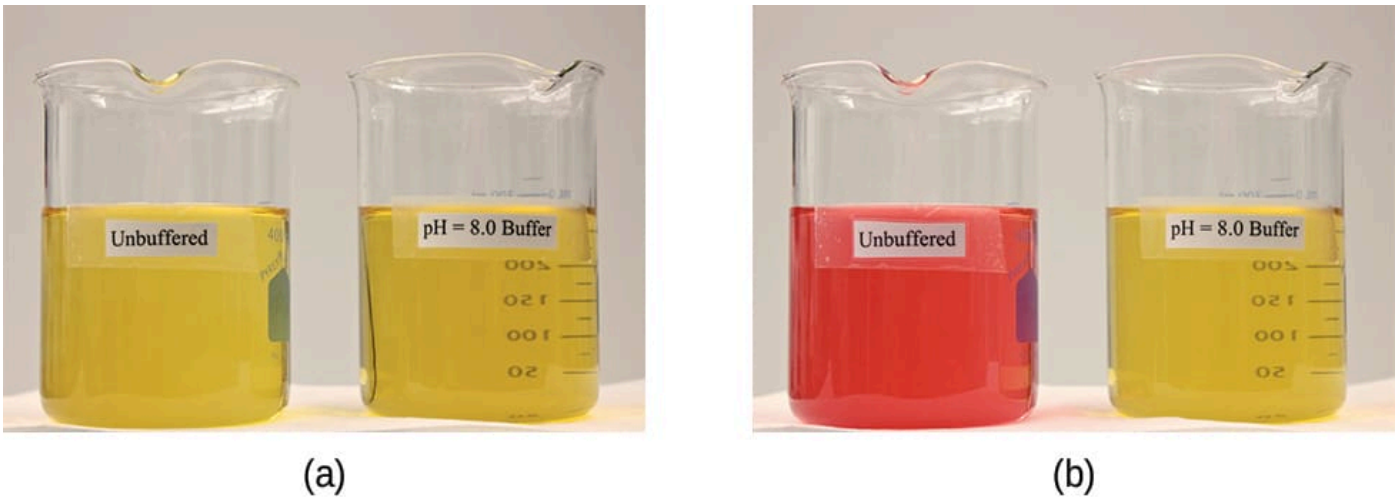


Figure 10.10.1: (a) The unbuffered solution on the left and the buffered solution on the right have the same pH (pH 8); they are basic, showing the yellow color of the indicator methyl orange at this pH. (b) After the addition of 1 mL of a 0.01-M HCl solution, the buffered solution has not detectably changed its pH but the unbuffered solution has become acidic, as indicated by the change in color of the methyl orange, which turns red at a pH of about 4. (credit: modification of work by Mark Ott)

How Buffers Work

A mixture of acetic acid and sodium acetate is acidic because the K_a of acetic acid is greater than the K_b of its conjugate base acetate. It is a buffer because it contains both the weak acid and its salt. Hence, it acts to keep the hydronium ion concentration (and the pH) almost constant by the addition of either a small amount of a strong acid or a strong base. If we add a base such as sodium hydroxide, the hydroxide ions react with the few hydronium ions present. Then more of the acetic acid reacts with water, restoring the hydronium ion concentration almost to its original value:

$$CH_3CO_2H(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + CH_3CO_2{}^-(aq)$$

The pH changes very little. If we add an acid such as hydrochloric acid, most of the hydronium ions from the hydrochloric acid combine with acetate ions, forming acetic acid molecules:

$$H_3O^+(aq) + CH_3CO_2{}^-(aq) \longrightarrow CH_3CO_2H(aq) + H_2O(l)$$

Thus, there is very little increase in the concentration of the hydronium ion, and the pH remains practically unchanged (Figure 10.10.2).

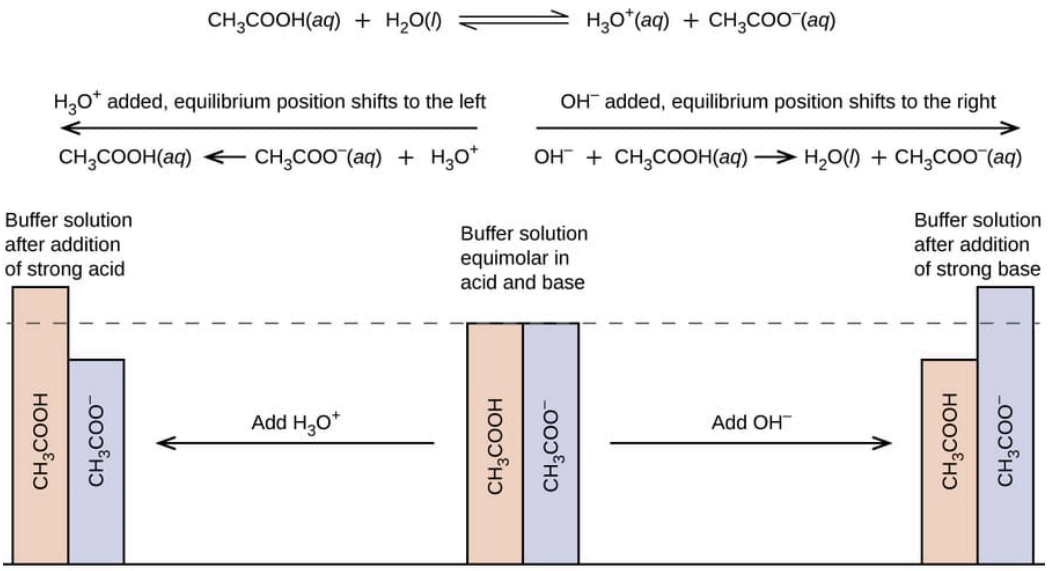


Figure 10.10.2: This diagram shows the buffer action of these reactions.

A mixture of ammonia and ammonium chloride is basic because the K_b for ammonia is greater than the K_a for the ammonium ion. It is a buffer because it also contains the salt of the weak base. If we add a base (hydroxide ions), ammonium ions in the buffer react with the hydroxide ions to form ammonia and water and reduce the hydroxide ion concentration almost to its original value:

$$\mathrm{NH_4^+}(aq)+\mathrm{OH^-}(aq) \longrightarrow \mathrm{NH_3}(aq) + \mathrm{H_2O}(l)$$

If we add an acid (hydronium ions), ammonia molecules in the buffer mixture react with the hydronium ions to form ammonium ions and reduce the hydronium ion concentration almost to its original value:

$$\mathrm{H_3O^+}(aq) + \mathrm{NH_3}(aq) \longrightarrow \mathrm{NH_4^+}(aq) + \mathrm{H_2O}(l)$$

The three parts of the following example illustrate the change in pH that accompanies the addition of base to a buffered solution of a weak acid and to an unbuffered solution of a strong acid.

Example 10.10.1: pH Changes in Buffered and Unbuffered Solutions

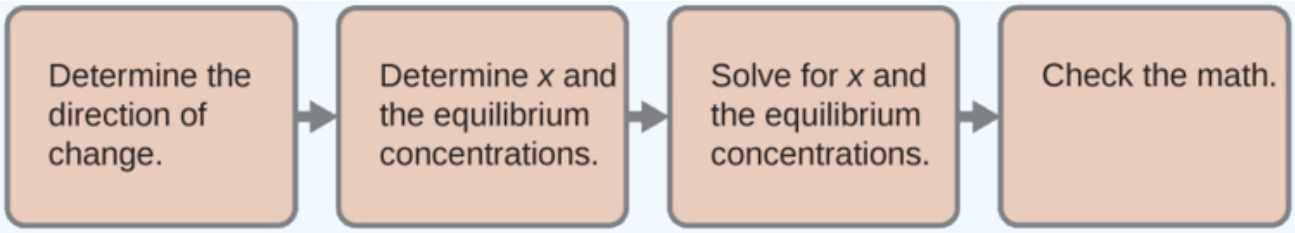
Acetate buffers are used in biochemical studies of enzymes and other chemical components of cells to prevent pH changes that might change the biochemical activity of these compounds.

a. Calculate the pH of an acetate buffer that is a mixture with 0.10 *M* acetic acid and 0.10 *M* sodium acetate.
b. Calculate the pH after 1.0 mL of 0.10 *M* NaOH is added to 100 mL of this buffer, giving a solution with a volume of 101 mL.

Solution

a. Calculate the pH of an acetate buffer that is a mixture with 0.10 *M* acetic acid and 0.10 *M* sodium acetate.

   To determine the pH of the buffer solution we use a typical equilibrium calculation (as illustrated in earlier Examples):



1. *Determine the direction of change*. The equilibrium in a mixture of H_3O^+, $CH_3CO_2^-$, and CH_3CO_2H is:

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$

The equilibrium constant for CH_3CO_2H is not given, so we look it up in Table E1: $K_a = 1.8 \times 10^{-5}$. With $[CH_3CO_2H] = [CH_3CO_2^-] = 0.10\ M$ and $[H_3O^+] = \sim 0\ M$, the reaction shifts to the right to form H_3O^+.

2. *Determine* x *and equilibrium concentrations*. A table of changes and concentrations follows:

	$[CH_3CO_2H]$ + $[H_2O]$ $\rightleftharpoons$	H_3O^+	+ $[CH_3CO_2^-]$
Initial concentration (*M*)	0.10	~0	0.10
Change (*M*)	$-x$	x	x
Equilibrium constant (*M*)	$0.10 - x$	x	$0.10 + x$

- *Solve for x and the equilibrium concentrations*. We find:

$$x = 1.8 \times 10^{-5}\ M$$

- and

$$[H_3O^+] = 0 + x = 1.8 \times 10^{-5}\ M$$

Thus:

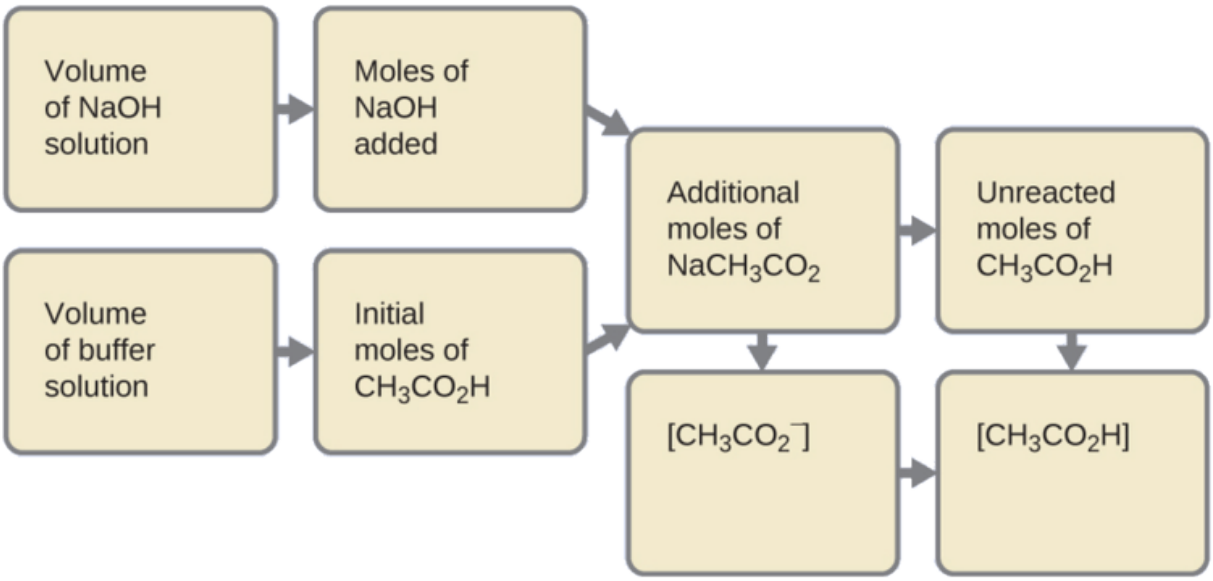
$$pH = -\log[H_3O^+] = -\log(1.8 \times 10^{-5})$$

$$= 4.74$$

4. *Check the work*. If we calculate all calculated equilibrium concentrations, we find that the equilibrium value of the reaction coefficient, $Q = K_a$.

(b) Calculate the pH after 1.0 mL of 0.10 *M* NaOH is added to 100 mL of this buffer, giving a solution with a volume of 101 mL.

First, we calculate the concentrations of an intermediate mixture resulting from the complete reaction between the acid in the buffer and the added base. Then we determine the concentrations of the mixture at the new equilibrium:



1. *Determine the moles of NaOH.* One milliliter (0.0010 L) of 0.10 *M* NaOH contains:

$$0.0010 \cancel{L} \times \left(\frac{0.10 \text{ mol NaOH}}{1 \cancel{L}} \right) = 1.0 \times 10^{-4} \text{ mol NaOH}$$

2. *Determine the moles of CH_2CO_2H.* Before reaction, 0.100 L of the buffer solution contains:

$$0.100 \cancel{L} \times \left(\frac{0.100 \text{ mol } CH_3CO_2H}{1 \cancel{L}} \right) = 1.00 \times 10^{-2} \text{ mol } CH_3CO_2H$$

3. *Solve for the amount of $NaCH_3CO_2$ produced.* The 1.0×10^{-4} mol of NaOH neutralizes 1.0×10^{-4} mol of CH_3CO_2H, leaving:

$$(1.0 \times 10^{-2}) - (0.01 \times 10^{-2}) = 0.99 \times 10^{-2} \text{ mol } CH_3CO_2H$$

and producing 1.0×10^{-4} mol of $NaCH_3CO_2$. This makes a total of:

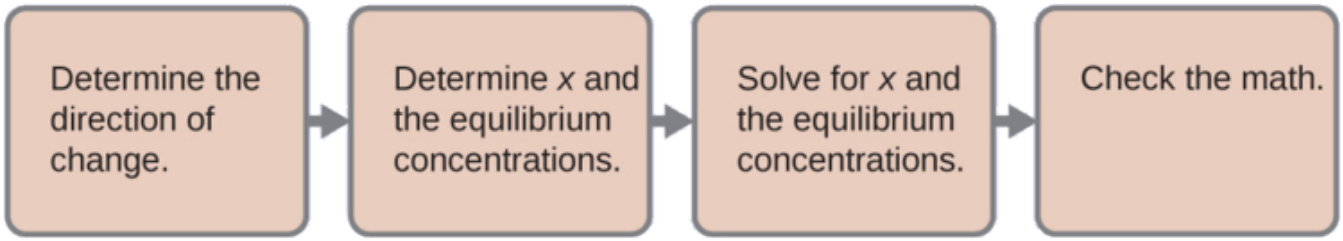
[\mathrm{(1.0×10^{−2})+(0.01×10^{−2})=1.01×10^{−2}\:mol\:NaCH_3CO_2} \nonumber \]

4. *Find the molarity of the products.* After reaction, CH_3CO_2H and $NaCH_3CO_2$ are contained in 101 mL of the intermediate solution, so:

$$[CH_3CO_2H] = \frac{9.9 \times 10^{-3} \text{ mol}}{0.101 \text{ L}} = 0.098 \, M$$

$$[NaCH_3CO_2] = \frac{1.01 \times 10^{-2} \text{ mol}}{0.101 \text{ L}} = 0.100 \, M$$

Now we calculate the pH after the intermediate solution, which is 0.098 *M* in CH_3CO_2H and 0.100 *M* in $NaCH_3CO_2$, comes to equilibrium. The calculation is very similar to that in part (a) of this example:



This series of calculations gives a pH = 4.75. Thus the addition of the base barely changes the pH of the solution.

(c) For comparison, calculate the pH after 1.0 mL of 0.10 *M* NaOH is added to 100 mL of a solution of an unbuffered solution with a pH of 4.74 (a 1.8×10^{-5}-*M* solution of HCl). The volume of the final solution is 101 mL.

Solution

This 1.8×10^{-5}-*M* solution of HCl has the same hydronium ion concentration as the 0.10-*M* solution of acetic acid-sodium acetate buffer described in part (a) of this example. The solution contains:

$$0.100\ \text{L} \times \left(\frac{1.8 \times 10^{-5}\ \text{mol HCl}}{1\ \text{L}}\right) = 1.8 \times 10^{-6}\ \text{mol HCl}$$

As shown in part (b), 1 mL of 0.10 *M* NaOH contains 1.0×10^{-4} mol of NaOH. When the NaOH and HCl solutions are mixed, the HCl is the limiting reagent in the reaction. All of the HCl reacts, and the amount of NaOH that remains is:

$$(1.0 \times 10^{-4}) - (1.8 \times 10^{-6}) = 9.8 \times 10^{-5}\ \ M$$

The concentration of NaOH is:

$$\frac{9.8 \times 10^{-5}\ M\ \text{NaOH}}{0.101\ \text{L}} = 9.7 \times 10^{-4}\ \ M$$

The pOH of this solution is:

$$\text{pOH} = -\log[\text{OH}^-] = -\log(9.7 \times 10^{-4}) = 3.01$$

The pH is:

$$\text{pH} = 14.00 - \text{pOH} = 10.99$$

The pH changes from 4.74 to 10.99 in this unbuffered solution. This compares to the change of 4.74 to 4.75 that occurred when the same amount of NaOH was added to the buffered solution described in part (b).

Exercise 10.10.1

Show that adding 1.0 mL of 0.10 *M* HCl changes the pH of 100 mL of a 1.8×10^{-5} *M* HCl solution from 4.74 to 3.00.

Answer available at the end of this section.

Buffer Capacity

Buffer solutions do not have an unlimited capacity to keep the pH relatively constant (Figure 10.10.3). If we add so much base to a buffer that the weak acid is exhausted, no more buffering action toward the base is possible. On the other hand, if we add an excess of acid, the weak base would be exhausted, and no more buffering action toward any additional acid would be possible. In fact, we do not even need to exhaust all of the acid or base in a buffer to overwhelm it; its buffering action will diminish rapidly as a given component nears depletion.



Figure 10.10.3: The indicator color (methyl orange) shows that a small amount of acid added to a buffered solution of pH 8 (beaker on the left) has little affect on the buffered system (middle beaker). However, a large amount of acid exhausts the buffering capacity of the solution and the pH changes dramatically (beaker on the right). (credit: modification of work by Mark Ott)

The buffer capacity is the amount of acid or base that can be added to a given volume of a buffer solution before the pH changes significantly, usually by one unit. Buffer capacity depends on the amounts of the weak acid and its conjugate base that are in a buffer mixture. For example, 1 L of a solution that is 1.0 *M* in acetic acid and 1.0 *M* in sodium acetate has a greater buffer capacity than 1 L of a solution that is 0.10 *M* in acetic acid and 0.10 *M* in sodium acetate even though both solutions have the same pH. The first solution has more buffer capacity because it contains more acetic acid and acetate ion.

Selection of Suitable Buffer Mixtures

There are two useful rules of thumb for selecting buffer mixtures:

1. A good buffer mixture should have about equal concentrations of both of its components. A buffer solution has generally lost its usefulness when one component of the buffer pair is less than about 10% of the other. Figure 10.10.4 shows an acetic acid-acetate ion buffer as base is added. The initial pH is 4.74. A change of 1 pH unit occurs when the acetic acid concentration is reduced to 11% of the acetate ion concentration.

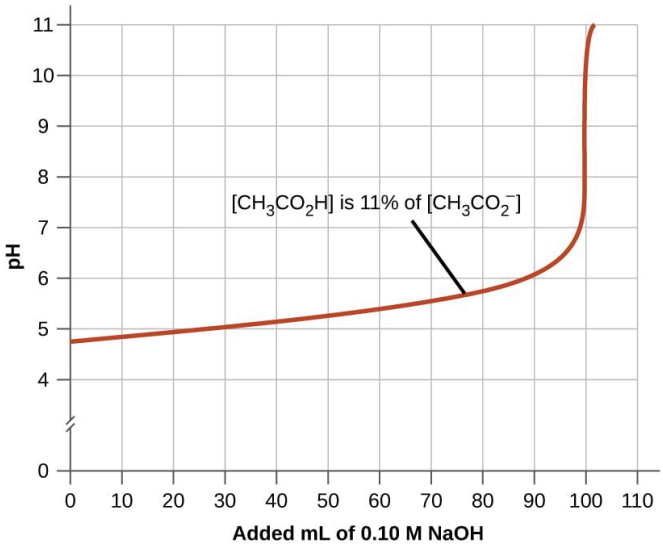


Figure 10.10.4: The graph, an illustration of buffering action, shows change of pH as an increasing amount of a 0.10-M NaOH solution is added to 100 mL of a buffer solution in which, initially, $[CH_3CO_2H] = 0.10\ M$ and $[CH_3CO_2{}^-] = 0.10\ M$.

2. Weak acids and their salts are better as buffers for pHs less than 7; weak bases and their salts are better as buffers for pHs greater than 7.

Blood is an important example of a buffered solution, with the principal acid and ion responsible for the buffering action being carbonic acid, H_2CO_3, and the bicarbonate ion, $HCO_3{}^-$. When an excess of hydrogen ion enters the blood stream, it is

removed primarily by the reaction:

$$H_3O^+(aq) + HCO_3^-(aq) \longrightarrow H_2CO_3(aq) + H_2O(l)$$

When an excess of the hydroxide ion is present, it is removed by the reaction:

$$OH^-(aq) + H_2CO_3(aq) \longrightarrow HCO_3^-(aq) + H_2O(l)$$

The pH of human blood thus remains very near 7.35, that is, slightly basic. Variations are usually less than 0.1 of a pH unit. A change of 0.4 of a pH unit is likely to be fatal.

The Henderson-Hasselbalch Approximation

The ionization-constant expression for a solution of a weak acid can be written as:

$$K_a = \frac{[H3O+][A-]}{[HA]}$$

Rearranging to solve for $[H_3O^+]$, we get:

$$[H_3O^+] = K_a \times \frac{[HA]}{[A-]}$$

Taking the negative logarithm of both sides of this equation, we arrive at:

$$-\log[H_3O^+] = -\log K_a - \log\frac{[HA]}{[A^-]}$$

which can be written as

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

where pK_a is the negative of the common logarithm of the ionization constant of the weak acid ($pK_a = -\log K_a$). This equation relates the pH, the ionization constant of a weak acid, and the concentrations of the weak acid and its salt in a buffered solution. Scientists often use this expression, called the Henderson-Hasselbalch approximation, to calculate the pH of buffer solutions. It is important to note that the "*x* is small" assumption must be valid to use this equation.

Lawrence Joseph Henderson and Karl Albert Hasselbalch

Lawrence Joseph Henderson (1878–1942) was an American physician, biochemist and physiologist, to name only a few of his many pursuits. He obtained a medical degree from Harvard and then spent 2 years studying in Strasbourg, then a part of Germany, before returning to take a lecturer position at Harvard. He eventually became a professor at Harvard and worked there his entire life. He discovered that the acid-base balance in human blood is regulated by a buffer system formed by the dissolved carbon dioxide in blood. He wrote an equation in 1908 to describe the carbonic acid-carbonate buffer system in blood. Henderson was broadly knowledgeable; in addition to his important research on the physiology of blood, he also wrote on the adaptations of organisms and their fit with their environments, on sociology and on university education. He also founded the Fatigue Laboratory, at the Harvard Business School, which examined human physiology with specific focus on work in industry, exercise, and nutrition.

In 1916, Karl Albert Hasselbalch (1874–1962), a Danish physician and chemist, shared authorship in a paper with Christian Bohr in 1904 that described the Bohr effect, which showed that the ability of hemoglobin in the blood to bind with oxygen was inversely related to the acidity of the blood and the concentration of carbon dioxide. The pH scale was introduced in 1909 by another Dane, Sørensen, and in 1912, Hasselbalch published measurements of the pH of blood. In 1916, Hasselbalch expressed Henderson's equation in logarithmic terms, consistent with the logarithmic scale of pH, and thus the Henderson-Hasselbalch equation was born.

Medicine: The Buffer System in Blood

The normal pH of human blood is about 7.4. The carbonate buffer system in the blood uses the following equilibrium reaction:

$$\mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2CO_3}(aq) \rightleftharpoons \mathrm{HCO_3}^-(aq) + \mathrm{H_3O}^+(aq)$$

The concentration of carbonic acid, H_2CO_3 is approximately 0.0012 *M*, and the concentration of the hydrogen carbonate ion, $\mathrm{HCO_3}^-$, is around 0.024 *M*. Using the Henderson-Hasselbalch equation and the pK_a of carbonic acid at body temperature, we can calculate the pH of blood:

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{base}]}{[\mathrm{acid}]} = 6.1 + \log\frac{0.024}{0.0012} = 7.4$$

The fact that the H_2CO_3 concentration is significantly lower than that of the $\mathrm{HCO_3}^-$ ion may seem unusual, but this imbalance is due to the fact that most of the by-products of our metabolism that enter our bloodstream are acidic. Therefore, there must be a larger proportion of base than acid, so that the capacity of the buffer will not be exceeded.

Lactic acid is produced in our muscles when we exercise. As the lactic acid enters the bloodstream, it is neutralized by the $\mathrm{HCO_3}^-$ ion, producing H_2CO_3. An enzyme then accelerates the breakdown of the excess carbonic acid to carbon dioxide and water, which can be eliminated by breathing. In fact, in addition to the regulating effects of the carbonate buffering system on the pH of blood, the body uses breathing to regulate blood pH. If the pH of the blood decreases too far, an increase in breathing removes CO_2 from the blood through the lungs driving the equilibrium reaction such that $[H_3O^+]$ is lowered. If the blood is too alkaline, a lower breath rate increases CO_2 concentration in the blood, driving the equilibrium reaction the other way, increasing $[H^+]$ and restoring an appropriate pH.

Summary

A solution containing a mixture of an acid and its conjugate base, or of a base and its conjugate acid, is called a buffer solution. Unlike in the case of an acid, base, or salt solution, the hydronium ion concentration of a buffer solution does not change greatly when a small amount of acid or base is added to the buffer solution. The base (or acid) in the buffer reacts with the added acid (or base).

Key Equations

- pK_a = –log K_a
- pK_b = –log K_b
- $\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}$

Glossary

buffer capacity
: amount of an acid or base that can be added to a volume of a buffer solution before its pH changes significantly (usually by one pH unit)

buffer
: mixture of a weak acid or a weak base and the salt of its conjugate; the pH of a buffer resists change when small amounts of acid or base are added

Henderson-Hasselbalch equation
: equation used to calculate the pH of buffer solutions

Answers

Exercise 10.10.1

Initial pH of 1.8×10^{-5} *M* HCl; pH = $-\log[H_3O^+] = -\log[1.8 \times 10^{-5}] = 4.74$

Moles of H_3O^+ added by addition of 1.0 mL of 0.10 *M* HCl: 0.10 moles/L × 0.0010 L = 1.0×10^{-4} moles; final pH after addition of 1.0 mL of 0.10 *M* HCl:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log\left(\frac{\text{total moles H}_3\text{O}^+}{\text{total volume}}\right) = -\log\left(\frac{1.0 \times 10^{-4}\ \text{mol} + 1.8 \times 10^{-6}\ \text{mol}}{101\ \text{mL}\left(\frac{1\ \text{L}}{1000\ \text{mL}}\right)}\right) = 3.00$$

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10.11: Titration

Learning Objectives

- Describe a titration experiment.
- Explain what an indicator does.
- Perform a titration calculation correctly.

The reaction of an acid with a base to make a salt and water is a common reaction in the laboratory, partly because many compounds can act as acids or bases. Another reason that acid-base reactions are so prevalent is because they are often used to determine quantitative amounts of one or the other. Performing chemical reactions quantitatively to determine the exact amount of a reagent is called a **titration**. A titration can be performed with almost any chemical reaction for which the balanced chemical equation is known. Here, we will consider titrations that involve acid-base reactions.

In a titration, one reagent has a known concentration or amount, while the other reagent has an unknown concentration or amount. Typically, the known reagent (the **titrant**) is added to the unknown quantity and is dissolved in solution. The unknown amount of substance (the **analyte**) may or may not be dissolved in solution (but usually is). The titrant is added to the analyte using a precisely calibrated volumetric delivery tube called a burette (also spelled buret; see Figure 10.11.1). The burette has markings to determine how much volume of solution has been added to the analyte. When the reaction is complete, it is said to be at the **equivalence point**; the number of moles of titrant can be calculated from the concentration and the volume, and the balanced chemical equation can be used to determine the number of moles (and then concentration or mass) of the unknown reactant.



Figure 10.11.1 Equipment for Titrations. A burette is a type of liquid dispensing system that can accurately indicate the volume of liquid dispensed.

For example, suppose 25.66 mL (or 0.02566 L) of 0.1078 M HCl was used to titrate an unknown sample of NaOH. What mass of NaOH was in the sample? We can calculate the number of moles of HCl reacted:

$$\text{\# mol HCl} = (0.02566\ \text{L})(0.1078\ \text{M}) = 0.002766\ \text{mol HCl}$$

We also have the balanced chemical reaction between HCl and NaOH:

$$\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$$

So we can construct a conversion factor to convert to number of moles of NaOH reacted:

$$0.002766\,\cancel{mol\ HCl} \times \frac{1\,mol\,NaOH}{1\,\cancel{mol\ HCl}} = 0.002766\,mol\,NaOH$$

Then we convert this amount to mass, using the molar mass of NaOH (40.00 g/mol):

$$0.002766\,\cancel{mol\ HCl} \times \frac{40.00\,g\,NaOH}{1\,\cancel{mol\ HCl}} = 0.1106\,g\,NaOH$$

This type of calculation is performed as part of a titration.

Example 10.11.1

What mass of Ca(OH)2 is present in a sample if it is titrated to its equivalence point with 44.02 mL of 0.0885 M HNO3? The balanced chemical equation is as follows:

$$2HNO_3 + Ca(OH)_2 \rightarrow Ca(NO_3)_2 + 2H_2O$$

Solution

In liters, the volume is 0.04402 L. We calculate the number of moles of titrant:

$$\#\text{ moles } HNO_3 = (0.04402\text{ L})(0.0885\text{ M}) = 0.00390\text{ mol } HNO_3$$

Using the balanced chemical equation, we can determine the number of moles of Ca(OH)2 present in the analyte:

$$0.00390\ \cancel{mol\ HNO_3} \times \frac{1\,mol\,Ca(OH)_2}{2\ \cancel{mol\ HNO_3}} = 0.00195\,mol\,Ca(OH)_2$$

Then we convert this to a mass using the molar mass of Ca(OH)2:

$$0.00195\ \cancel{mol\,Ca(OH)_2} \times \frac{74.1\,g\,Ca(OH)_2}{\cancel{mol\,Ca(OH)_2}} = 0.144\,g\,Ca(OH)_2$$

Exercise 10.11.1

What mass of H2C2O4 is present in a sample if it is titrated to its equivalence point with 18.09 mL of 0.2235 M NaOH? The balanced chemical reaction is as follows:

$$H_2C_2O_4 + 2\,NaOH \longrightarrow Na_2C_2O_4 + 2\,H_2O$$

Answer available at the end of this section.

How does one know if a reaction is at its equivalence point? Usually, the person performing the titration adds a small amount of an **indicator**, a substance that changes color depending on the acidity or basicity of the solution. Because different indicators change colors at different levels of acidity, choosing the correct one is important in performing an accurate titration.

Answers

Exercise 10.11.1

0.182 g

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11: NUCLEAR CHEMISTRY

Most chemists pay little attention to the nucleus of an atom except to consider the number of protons it contains because that determines an element's identity. However, in nuclear chemistry, the composition of the nucleus and the changes that occur there are very important. Applications of nuclear chemistry may be more widespread than you realize. Many people are aware of nuclear power plants and nuclear bombs, but nuclear chemistry also has applications ranging from smoke detectors to medicine, from the sterilization of food to the analysis of ancient artifacts. In this chapter, we will examine some of the basic concepts of nuclear chemistry and some of the nuclear reactions that are important in our everyday lives.

11.1: Nuclear Reactions

11.2: The Discovery and Nature of Radioactivity

11.3: Stable and Unstable Isotopes

11.4: Nuclear Decay

11.5: Radioactive Half-Life

11.6: Ionizing Radiation

11.7: Detecting and Measuring Radiation

11.8: Artificial Transmutation

11.9: Nuclear Fission and Nuclear Fusion

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11.1: Nuclear Reactions

Learning Objectives

- Describe nuclear structure in terms of protons, neutrons, and electrons
- Identify a nuclear reaction
- Identify the key characteristics separating nuclear and chemical reactions

Nuclear chemistry is the study of reactions that involve changes in nuclear structure. The chapter on atoms, molecules, and ions introduced the basic idea of nuclear structure, that the nucleus of an atom is composed of protons and, with the exception of $^{1}_{1}\mathrm{H}$, neutrons. Recall that the number of protons in the nucleus is called the atomic number (Z) of the element, and the sum of the number of protons and the number of neutrons is the mass number (A). Atoms with the same atomic number but different mass numbers are isotopes of the same element. When referring to a single type of nucleus, we often use the term **nuclide** and identify it by the notation:

$$^{\mathrm{A}}_{\mathrm{Z}}\mathrm{X} \tag{11.1.1}$$

where

- X is the symbol for the element,
- A is the mass number, and
- Z is the atomic number.

Often a nuclide is referenced by the name of the element followed by a hyphen and the mass number. For example, $^{14}_{6}\mathrm{C}$ is called "carbon-14." The element in this example, represented by the symbol *C*, is carbon. Its atomic number, 6, is the lower left subscript on the symbol and is the number of protons in the atom. The mass number, the superscript to the upper left of the symbol, is the sum of the number of protons and neutrons in the nucleus of this particular isotope. In this case, the mass number is 14, which means that the number of neutrons in the atom is 14 – 6 = 8 (that is, the mass number of the atom minus the number of protons in the nucleus equals the number of neutrons). Occasionally, the atomic number is omitted in this notation because the symbol of the element itself conveys its characteristic atomic number. The two isotopes of hydrogen, $^{2}\mathrm{H}$ and $^{3}\mathrm{H}$, are given their own names: deuterium (D) and tritium (T), respectively. Another way of expressing a particular isotope is to list the mass number after the element name, like carbon-12 or hydrogen-3.

Nuclear reactions are very different from chemical reactions. In chemical reactions, atoms become more stable by participating in a transfer of electrons or by sharing electrons with other atoms. In **nuclear reactions**, it is the nucleus of the atom that gains stability by undergoing a change of some kind. The energies that are released in nuclear reactions are many orders of magnitude greater than the energies involved in chemical reactions. Unlike chemical reactions, nuclear reactions are not noticeably affected by changes in environmental conditions, such as temperature or pressure.

As the following Sections will discuss, there are three main forms of radioactive emissions. The first is called an alpha particle,which is symbolized by the Greek letter α. An alpha particle is composed of two protons and two neutrons, and so it is the same as a helium nucleus. (We often use $^{4}_{2}\mathrm{He}$ to represent an alpha particle.) It has a 2+ charge. When a radioactive atom emits an alpha particle, the original atom's atomic number decreases by two (because of the loss of two protons), and its mass number decreases by four (because of the loss of four nuclear particles). We can represent the emission of an alpha particle with a **nuclear equation**—for example, the alpha-particle emission of uranium-235 is as follows:

$$^{235}_{92}\mathrm{U} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{231}_{90}\mathrm{Th} \tag{11.1.2}$$

Chemists often use the names **parent isotope** and **daughter isotope** to represent the original atom and the product other than the alpha particle. In the previous example, $^{235}_{92}\mathrm{U}$ is the parent isotope, and $^{231}_{90}\mathrm{Th}$ is the daughter isotope. When one element changes into another in this manner, it undergoes *radioactive decay*.

Major Differences between Nuclear and Chemical Reactions

1. Nuclear reactions involve a change in an atom's nucleus, usually producing a different element. Chemical reactions, on the other hand, involve only a rearrangement of electrons and do not involve changes in the nuclei.
2. Different isotopes of an element normally behave similarly in chemical reactions. The nuclear chemistry of different isotopes vary greatly from each other.
3. Rates of chemical reactions are influenced by temperature and catalysts. Rates of nuclear reactions are unaffected by such factors.
4. Nuclear reactions are independent of the chemical form of the element.
5. Energy changes accompanying nuclear reactions are much larger. This energy comes from destruction of mass.
6. In a nuclear reaction, mass is not strictly conserved. Some of the mass is converted into energy.

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11.2: The Discovery and Nature of Radioactivity

Learning Objectives

- To define and give examples of the major types of radioactivity.

Atomic theory in the 19th century presumed that nuclei had fixed compositions. But in 1896, the French scientist Henri Becquerel found that a uranium compound placed near a photographic plate made an image on the plate, even if the compound was wrapped in black cloth. He reasoned that the uranium compound was emitting some kind of radiation that passed through the cloth to expose the photographic plate. Further investigations showed that the radiation was a combination of particles and electromagnetic rays, with its ultimate source as the atomic nucleus. These emanations were ultimately called, collectively, **radioactivity**.

There are three main forms of radioactive emissions. The first is called an **alpha particle**,which is symbolized by the Greek letter α. An alpha particle is composed of two protons and two neutrons, and so it is the same as a helium nucleus. (We often use ${}^{4}_{2}\mathrm{He}$ to represent an alpha particle.) It has a 2+ charge. When a radioactive atom emits an alpha particle, the original atom's atomic number decreases by two (because of the loss of two protons), and its mass number decreases by four (because of the loss of four nuclear particles). We can represent the emission of an alpha particle with a nuclear equation—for example, the alpha-particle emission of uranium-235 is as follows:

$$ {}^{235}_{92}\mathrm{U} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{231}_{90}\mathrm{Th} \tag{11.2.1} $$

Ernest Rutherford's experiments involving the interaction of radiation with a magnetic or electric field (Figure 11.2.1) helped him determine that one type of radiation consisted of positively charged and relatively massive α particles; a second type was made up of negatively charged and much less massive β **particles**; and a third was uncharged electromagnetic waves, γ **rays**. We now know that α particles are high-energy helium nuclei, β particles are high-energy electrons, and γ radiation compose high-energy electromagnetic radiation. We classify different types of radioactive decay by the radiation produced.

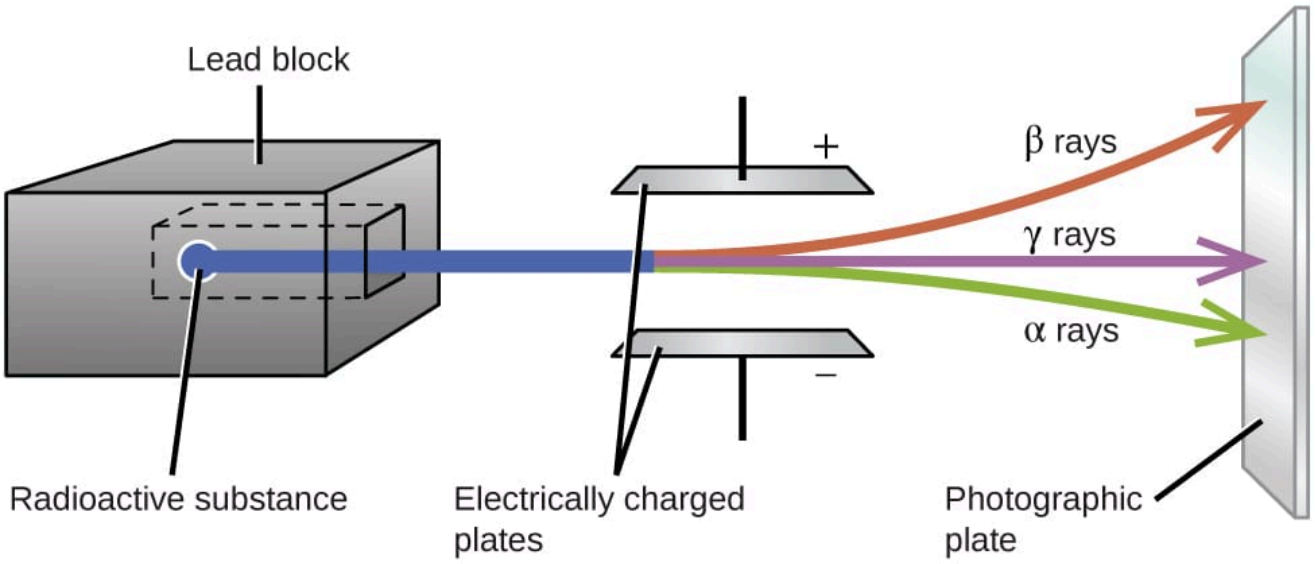


Figure 11.2.1: Alpha particles, which are attracted to the negative plate and deflected by a relatively small amount, must be positively charged and relatively massive. Beta particles, which are attracted to the positive plate and deflected a relatively large amount, must be negatively charged and relatively light. Gamma rays, which are unaffected by the electric field, must be uncharged. (CC BY 4.0; OpenStax)

Alpha, beta, and gamma emissions have different abilities to penetrate matter (Figure 11.2.2). The relatively large alpha particle is easily stopped by matter (although it may impart a significant amount of energy to the matter it contacts). Beta particles penetrate slightly into matter, perhaps a few centimeters at most. Gamma rays can penetrate deeply into matter and can impart a large amount of energy into the surrounding matter. Table 11.2.1 summarizes the properties of the three main types of radioactive

emissions.

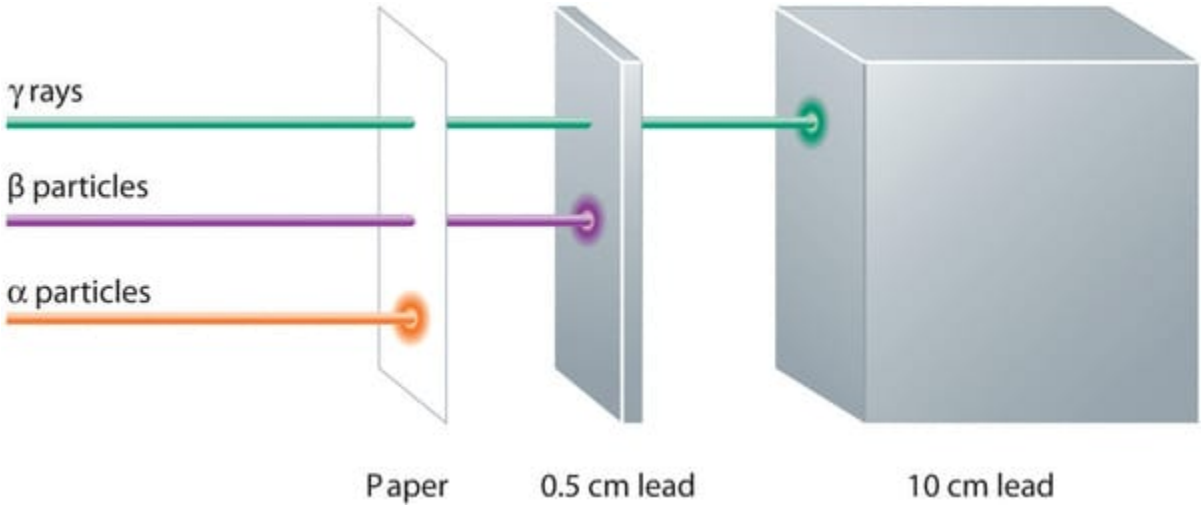


Figure 11.2.2: Different emissions exhibit different pentration powers. (CC BY-NC-SA 3.0; anonymous)

Table 11.2.1: The Three Main Forms of Radioactive Emissions

Characteristic	Alpha Particles	Beta Particles	Gamma Rays
symbols	α, ${}_{2}^{4}\mathrm{He}$	β, ${}_{-1}^{0}\mathrm{e}$	γ
identity	helium nucleus	electron	electromagnetic radiation
charge	2+	1–	none
mass number	4	0	0
penetrating power	minimal (will not penetrate skin)	short (will penetrate skin and some tissues slightly)	deep (will penetrate tissues deeply)

Key Takeaway

The major types of radioactivity include alpha particles, beta particles, and gamma rays.

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11.3: Stable and Unstable Isotopes

Learning Outcomes

- Recognize that radioactivity is a signature of unstable nuclide - radioisotopes.
- Describe a radioisotope.
- Explain how the stability of isotopes depends on the composition of its nucleus.
- Use the "band of stability" to identify stable isotopes.

The discovery of radioactivity and its effects on the nuclei of elements disproved Dalton's assumption that atoms are indivisible. A **nuclide** *is a term for an atom with a specific number of protons and neutrons in its nucleus*. When nuclides of one type emit radiation, they are changed into different nuclides. Radioactive decay is spontaneous and does not required an input of energy to occur. The stability of a particular nuclide depends on the composition of its nucleus, including the number of protons, the number of neutrons, and the proton-to-neutron ratio.

In nuclear reactions, it is the nucleus of the atom that gains stability by undergoing a change of some kind. Some elements have no stable isotopes, which means that any atom of that element is radioactive. For some other elements, only certain isotopes are radioactive. A **radioisotope** *is an isotope of an element that is unstable and undergoes radioactive decay*. The energies that are released in nuclear reactions are many orders of magnitude greater than the energies involved in chemical reactions. Unlike chemical reactions, nuclear reactions are not noticeably affected by changes in environmental conditions, such as temperature or pressure.

Carbon-12, with six protons and six neutrons, is a *stable* nucleus, meaning that it does not spontaneously emit radioactivity. Carbon-14, with six protons and eight neutrons, is *unstable* and naturally radioactive. Among atoms with lower atomic numbers, the ideal ratio of neutrons to protons is approximately 1:1. As the atomic number increases, the stable neutron-proton ratio gradually increases to about 1.5:1 for the heaviest known elements. For example, lead-206 is a stable nucleus that contains 124 neutrons and 82 protons, a ratio of 1.51 to 1.

This observation is shown in Figure 11.3.1. The **band of stability** *is the range of stable nuclei on a graph that plots the number of neutrons in a nuclide against the number of protons*. Known stable nuclides are shown with individual blue dots, while the 1:1 and 1.5:1 ratios are shown with a solid red line and a green line, respectively.

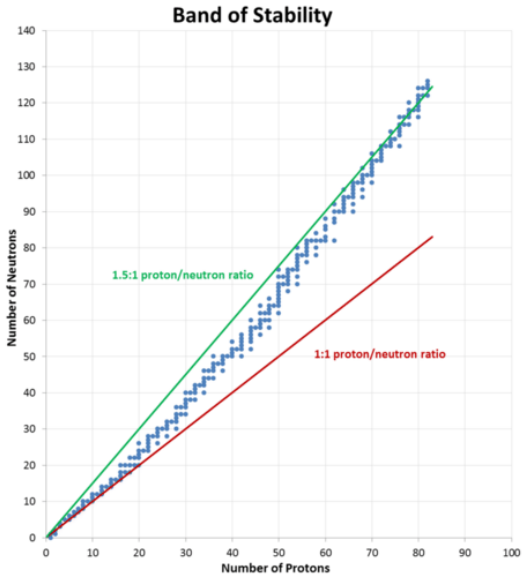


Figure 11.3.1: A graph of the number of neutrons in a nucleus as a function of the number of protons. Each known stable nucleus is represented by a blue dot. The ideal neutron to proton ratio changes from 1:1 for light nuclei to 1.5:1 for the heaviest nuclei.

It should be noted that just because a nucleus is "unstable" (able to undergo spontaneous radioactive decay) does not mean that

it will rapidly decompose. For example, uranium-238 is unstable because it spontaneously decays over time, but if a sample of uranium-238 is allowed to sit for 1000 years, only 0.0000155% of the sample will have decayed. However, other unstable nuclei, such as berkelium-243, will be almost completely gone (>99.9999% decayed) in less than a day.

Contributors and Attributions

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11.4: Nuclear Decay

Learning Objectives

- Write and balance nuclear equations.

Unstable nuclei spontaneously emit radiation in the form of particles and energy. This generally changes the number of protons and/or neutrons in the nucleus, resulting in a more stable nuclide. One type of a nuclear reaction is **radioactive decay**, *a reaction in which a nucleus spontaneously disintegrates into a slightly lighter nucleus, accompanied by the emission of particles, energy, or both*. An example is shown below, in which the nucleus of a polonium atom radioactively decays into a lead nucleus.

$$^{235}_{92}\mathrm{U} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{231}_{90}\mathrm{Th} \tag{11.4.1}$$

Note that in a balanced nuclear equation, the sum of the atomic numbers (subscripts) and the sum of the mass numbers (superscripts) must be equal on both sides of the equation. How do we know that a product of the reaction is $^{231}_{90}\mathrm{Th}$? We use a modified type of the **law of conservation of matter**, which says that we must have the same number of protons and neutrons on both sides of the chemical equation. If our uranium nucleus loses 2 protons from the alpha particle, then there are 90 protons remaining, identifying the element as thorium. Moreover, if we lose 4 nuclear particles of the original 235, there are 231 remaining. Thus, we use subtraction to identify the isotope of the thorium atom—in this case, $^{231}_{90}\mathrm{Th}$.

Because the number of protons changes as a result of this nuclear reaction, the identity of the element changes. **Transmutation** *is a change in the identity of a nucleus as a result of a change in the number of protons*. There are several different types of naturally occurring radioactive decay, and we will examine each separately.

Alpha Emission

An **alpha particle** (α) *is a helium nucleus with two protons and two neutrons*. Alpha particles are emitted during some types of radioactive decay. The net charge of an alpha particle is $2+$, and its mass is approximately $4\ \mathrm{amu}$. The symbol for an alpha particle in a nuclear equation is usually $^{4}_{2}\mathrm{He}$, though sometimes α is used. Alpha emission typically occurs for very heavy nuclei in which the nuclei are unstable due to large numbers of nucleons. For nuclei that undergo alpha decay, their stability is increased by the subtraction of two protons and two neutrons. For example, uranium-238 decays into thorium-234 by the emission of an alpha particle (see Figure 11.4.1).

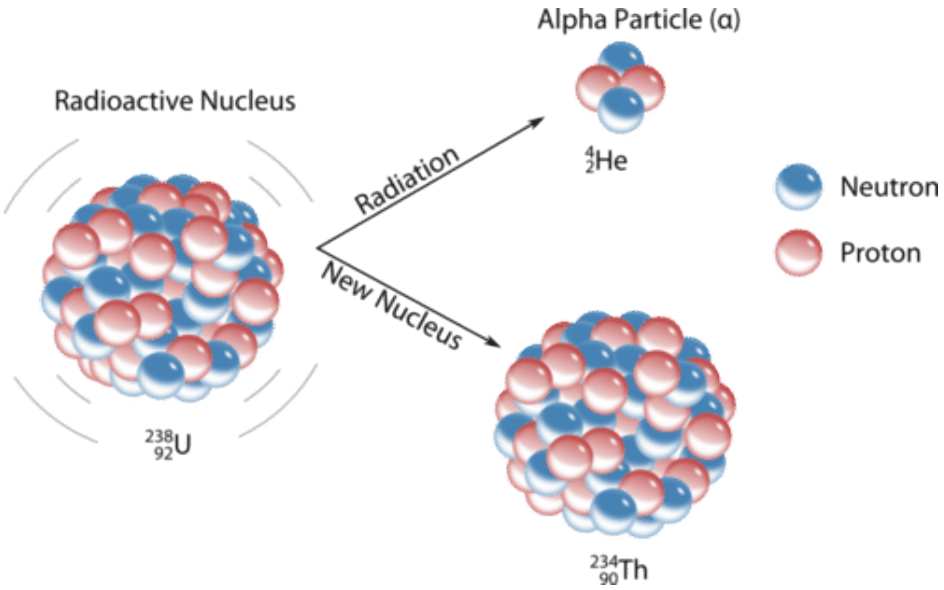


Figure 11.4.1: The unstable uranium-238 nucleus spontaneously decays into a thorium-234 nucleus by emitting an alpha particle.

Example 11.4.1: Radon-222

Write the nuclear equation that represents the radioactive decay of radon-222 by alpha particle emission and identify the daughter isotope.

Solution

Radon has an atomic number of 86, so the parent isotope is represented as $^{222}_{86}\mathrm{Rn}$. We represent the alpha particle as $^{4}_{2}\mathrm{He}$ and use subtraction (222 – 4 = 218 and 86 – 2 = 84) to identify the daughter isotope as an isotope of polonium, $^{218}_{84}\mathrm{Po}$:

$$^{222}_{86}\mathrm{Rn} \rightarrow \ ^{4}_{2}\mathrm{He} + \ ^{218}_{84}\mathrm{Po}$$

Exercise 11.4.1: Polonium-209

Write the nuclear equation that represents the radioactive decay of polonium-209 by alpha particle emission and identify the daughter isotope.

Answer available at the end of this section.

Beta Emission

Nuclei above the band of stability are unstable because their neutron to proton ratio is too high. To decrease that ratio, a neutron in the nucleus is capable of turning into a proton and an electron. The electron is immediately ejected at a high speed from the nucleus. A **beta particle** (β) *is a high-speed electron emitted from the nucleus of an atom during some kinds of radioactive decay* (see Figure 11.4.2). The symbol for a beta particle in an equation is either β or $^{0}_{-1}\mathrm{e}$. Carbon-14 undergoes beta decay, transmutating into a nitrogen-14 nucleus.

$$^{14}_{6}\mathrm{C} \rightarrow \ ^{14}_{7}\mathrm{N} + \ ^{0}_{-1}\mathrm{e} \tag{11.4.2}$$

Note that beta decay increases the atomic number by one, but the mass number remains the same.

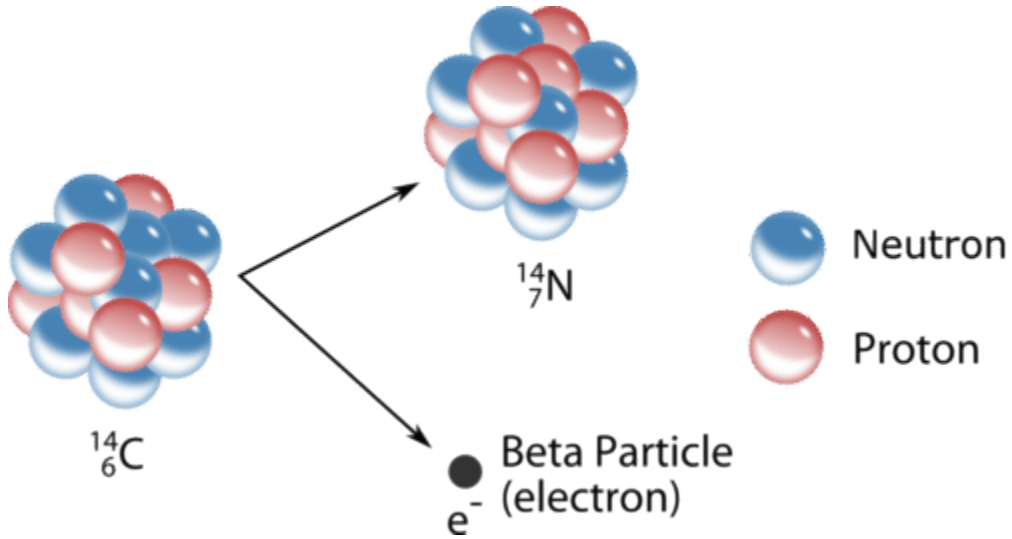


Figure 11.4.2: The beta emission of a carbon-14 nuclide involves the conversion of a neutron to a proton and an electron, with the electron being emitted from the nucleus.

Example 11.4.2: Boron-12

Write the nuclear equation that represents the radioactive decay of boron-12 by beta particle emission and identify the daughter isotope. A gamma ray is emitted simultaneously with the beta particle.

Solution

The parent isotope is ${}^{12}_{5}\mathrm{B}$ while one of the products is an electron, ${}^{0}_{-1}\mathrm{e}$. So that the mass and atomic numbers have the same value on both sides, the mass number of the daughter isotope must be 12, and its atomic number must be 6. The element having an atomic number of 6 is carbon. Thus, the complete nuclear equation is as follows:

$$ {}^{12}_{5}\mathrm{B} \rightarrow \ {}^{12}_{6}\mathrm{C} + \ {}^{0}_{-1}\mathrm{e} + \gamma $$

The daughter isotope is ${}^{12}_{6}\mathrm{C}$.

Exercise 11.4.2: Iodine-131

Write the nuclear equation that represents the radioactive decay of iodine-131 by beta particle emission and identify the daughter isotope. A gamma ray is emitted simultaneously with the beta particle.

Answer available at the end of this section.

Gamma Emission

Gamma rays (γ) *are very high energy electromagnetic waves emitted from a nucleus.* Gamma rays are emitted by a nucleus when nuclear particles undergo transitions between nuclear energy levels. This is analogous to the electromagnetic radiation emitted when excited electrons drop from higher to lower energy levels; the only difference is that nuclear transitions release much more energetic radiation. Gamma ray emission often accompanies the decay of a nuclide by other means.

$$ {}^{230}_{90}\mathrm{Th} \rightarrow {}^{226}_{88}\mathrm{Ra} + {}^{4}_{2}\mathrm{He} + \gamma \tag{11.4.3} $$

The emission of gamma radiation has no effect on the atomic number or mass number of the products, but it reduces their energy.

Positron Emission

Nuclei below the band of stability are unstable because their neutron to proton ratio is too low. One way to increase that ratio is for a proton in the nucleus to turn into a neutron and another particle called a positron. A **positron** *is a particle with the same mass as an electron, but with a positive charge*. Like the beta particle, a positron is immediately ejected from the nucleus upon its formation. The symbol for a positron in an equation is ${}^{0}_{+1}\mathrm{e}$. For example, potassium-38 emits a positron, becoming argon-38.

$$ {}^{38}_{19}\mathrm{K} \rightarrow {}^{38}_{18}\mathrm{Ar} + {}^{0}_{1}\mathrm{e} \tag{11.4.4} $$

Positron emission decreases the atomic number by one, but the mass number remains the same.

Electron Capture

An alternate way for a nuclide to increase its neutron to proton ratio is by a phenomenon called **electron capture**, sympolized E.C. In electron capture, an electron from an inner orbital is captured by the nucleus of the atom and combined with a proton to form a neutron. For example, silver-106 undergoes electron capture to become palladium-106.

$$ {}^{106}_{47}\mathrm{Ag} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{106}_{46}\mathrm{Pd} \tag{11.4.5} $$

Note that the overall result of electron capture is identical to positron emission. The atomic number decreases by one while the

mass number remains the same.

Summary of Nuclear Radiation

Table 11.4.1 lists the characteristics of the different types of radioactive decay.

Table 11.4.1 *Summary of types of radioactive decay.*

Type	Symbol	Change in Atomic Number	Change in Mass Number	Change in Number of Neutrons
Alpha emission	${}^{4}_{2}\mathrm{He}$ or α	–2	–4	–2
Beta emission	${}^{0}_{-1}\mathrm{e}$ or β	+1	0	–1
Gamma emission	γ or ${}^{0}_{0}\gamma$	0	0	0
Positron emission	${}^{0}_{1}\mathrm{e}$ or β^{+}	–1	0	+1
electron capture	E.C.	–1	0	+1

Example 11.4.3

Write a balanced nuclear equation to describe each reaction.

a. the beta decay of ${}^{35}_{16}\mathrm{S}$
b. the decay of ${}^{201}_{80}\mathrm{Hg}$ by electron capture
c. the decay of ${}^{30}_{15}\mathrm{P}$ by positron emission

Given: radioactive nuclide and mode of decay

Asked for: balanced nuclear equation

Strategy:

A Identify the reactants and the products from the information given.

B Use the values of *A* and *Z* to identify any missing components needed to balance the equation.

Solution

a.

A We know the identities of the reactant and one of the products (a β particle). We can therefore begin by writing an equation that shows the reactant and one of the products and indicates the unknown product as ${}^{A}_{Z}\mathrm{X}$:

$$ {}^{35}_{16}\mathrm{S} \rightarrow {}^{A}_{Z}\mathrm{X} + {}^{0}_{-1}\beta $$

B Because both protons and neutrons must be conserved in a nuclear reaction, the unknown product must have a mass number of $A = 35 - 0 = 35$ and an atomic number of $Z = 16 - (-1) = 17$. The element with $Z = 17$ is chlorine, so the balanced nuclear equation is as follows:

$$ {}^{35}_{16}\mathrm{S} \rightarrow {}^{35}_{17}\mathrm{Cl} + {}^{0}_{-1}\beta $$

b.

A We know the identities of both reactants: ${}^{201}_{80}\mathrm{Hg}$ and an inner electron, ${}^{0}_{-1}\mathrm{e}$. The reaction is as follows:

$$ {}^{201}_{80}\mathrm{Hg} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{A}_{Z}\mathrm{X} $$

B Both protons and neutrons are conserved, so the mass number of the product must be $A = 201 + 0 = 201$, and the atomic number of the product must be $Z = 80 + (-1) = 79$, which corresponds to the element gold. The balanced nuclear equation is thus

$$^{201}_{80}\mathrm{Hg} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{201}_{79}\mathrm{Au}$$

c.

A As in part (a), we are given the identities of the reactant and one of the products—in this case, a positron. The unbalanced nuclear equation is therefore

$$^{30}_{15}\mathrm{P} \rightarrow {}^{A}_{Z}\mathrm{X} + {}^{0}_{+1}\beta$$

B The mass number of the second product is $A = 30 - 0 = 30$, and its atomic number is $Z = 15 - 1 = 14$, which corresponds to silicon. The balanced nuclear equation for the reaction is as follows:

$$^{30}_{15}\mathrm{P} \rightarrow {}^{30}_{14}\mathrm{Si} + {}^{0}_{+1}\beta$$

Exercise 11.4.3

Write a balanced nuclear equation to describe each reaction.

a. $^{11}_{6}\mathrm{C}$ by positron emission
b. the beta decay of molybdenum-99
c. the emission of an α particle followed by gamma emission from $^{185}_{74}\mathrm{W}$

Answer a available at the end of this section.

Example 11.4.4

Predict the kind of nuclear change each unstable nuclide undergoes when it decays.

a. $^{45}_{22}\mathrm{Ti}$
b. $^{242}_{94}\mathrm{Pu}$
c. $^{12}_{5}\mathrm{B}$
d. $^{256}_{100}\mathrm{Fm}$

Given: nuclide

Asked for: type of nuclear decay

Strategy:

Based on the neutron-to-proton ratio and the value of Z, predict the type of nuclear decay reaction that will produce a more stable nuclide.

Solution

a. This nuclide has a neutron-to-proton ratio of only 1.05, which is much less than the requirement for stability for an element with an atomic number in this range. Nuclei that have low neutron-to-proton ratios decay by converting a proton to a neutron. The two possibilities are positron emission, which converts a proton to a neutron and a positron, and electron capture, which converts a proton and a core electron to a neutron. In this case, both are observed, with positron emission occurring about 86% of the time and electron capture about 14% of the time.
b. Nuclei with $Z > 83$ are too heavy to be stable and usually undergo alpha decay, which decreases both the mass number and the atomic number. Thus $^{242}_{94}\mathrm{Pu}$ is expected to decay by alpha emission.

c. This nuclide has a neutron-to-proton ratio of 1.4, which is very high for a light element. Nuclei with high neutron-to-proton ratios decay by converting a neutron to a proton and an electron. The electron is emitted as a β particle, and the proton remains in the nucleus, causing an increase in the atomic number with no change in the mass number. We therefore predict that $^{12}_{5}\mathrm{B}$ will undergo beta decay.
d. This is a massive nuclide, with an atomic number of 100 and a mass number much greater than 200. Nuclides with $A \geq 200$ tend to decay by alpha emission, and even heavier nuclei tend to undergo spontaneous fission. We therefore predict that $^{256}_{100}\mathrm{Fm}$ will decay by either or both of these two processes. In fact, it decays by both spontaneous fission and alpha emission, in a 97:3 ratio.

Exercise 11.4.4

Predict the kind of nuclear change each unstable nuclide undergoes when it decays.

a. $^{32}_{14}\mathrm{Si}$
b. $^{43}_{21}\mathrm{Sc}$
c. $^{231}_{91}\mathrm{Pa}$

Answer a available at the end of this section.

Contributors and Attributions

-

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Answers

Exercise 11.4.1: Polonium-209

$$^{209}_{84}\mathrm{Po} \rightarrow \ ^{4}_{2}\mathrm{He} + \ ^{205}_{82}\mathrm{Pb}$$

Exercise 11.4.2: Iodine-131

$$^{131}_{53}\mathrm{I} \rightarrow \ ^{131}_{54}\mathrm{Xe} + \ ^{0}_{-1}\mathrm{e} + \gamma$$

Exercise 11.4.3

$^{11}_{6}\mathrm{C} \rightarrow \ ^{11}_{5}\mathrm{B} + \ ^{0}_{+1}\beta$
$^{99}_{42}\mathrm{Mo} \rightarrow \ ^{99m}_{43}\mathrm{Tc} + \ ^{0}_{-1}\beta$
$^{185}_{74}\mathrm{W} \rightarrow \ ^{181}_{72}\mathrm{Hf} + \ ^{4}_{2}\alpha + \ ^{0}_{0}\gamma$

Exercise 11.4.4

beta decay
positron emission or electron capture
alpha decay

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11.5: Radioactive Half-Life

Learning Objectives

- Define *half-life*.
- Determine the amount of radioactive substance remaining after a given number of half-lives.
- Describe common radiometric carbon-14 dating technique.

Whether or not a given isotope is radioactive is a characteristic of that particular isotope. Some isotopes are stable indefinitely, while others are radioactive and decay through a characteristic form of emission. As time passes, less and less of the radioactive isotope will be present, and the level of radioactivity decreases. An interesting and useful aspect of radioactive decay is **half life** (**$t_{1/2}$**), which is the amount of time it takes for one-half of a radioactive isotope to decay. The half-life of a specific radioactive isotope is constant; it is unaffected by conditions and is independent of the initial amount of that isotope.

Each radioactive nuclide has a characteristic, constant half-life ($t_{1/2}$), the time required for half of the atoms in a sample to decay. An isotope's half-life allows us to determine how long a sample of a useful isotope will be available, and how long a sample of an undesirable or dangerous isotope must be stored before it decays to a low-enough radiation level that is no longer a problem.

For example, cobalt-60 source, since half of the $^{60}_{27}\mathrm{Co}$ nuclei decay every 5.27 years, both the amount of material and the intensity of the radiation emitted is cut in half every 5.27 years. (Note that for a given substance, the intensity of radiation that it produces is directly proportional to the rate of decay of the substance and the amount of the substance.) Thus, a cobalt-60 source that is used for cancer treatment must be replaced regularly to continue to be effective.

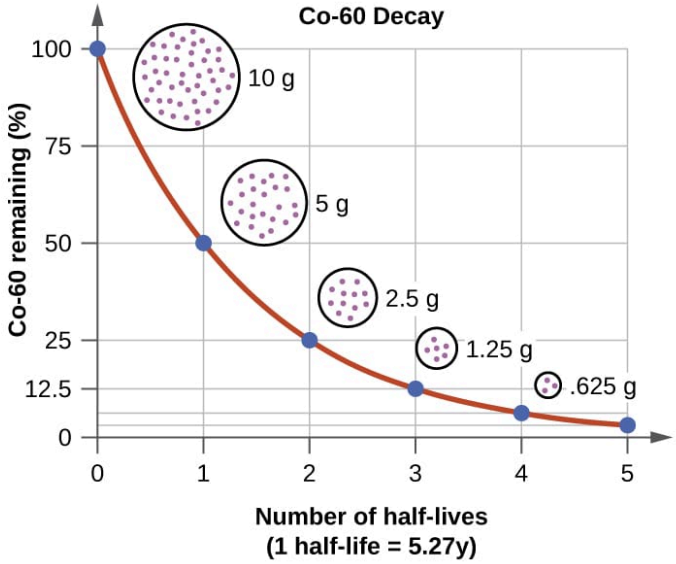


Figure 11.5.1: For cobalt-60, which has a half-life of 5.27 years, 50% remains after 5.27 years (one half-life), 25% remains after 10.54 years (two half-lives), 12.5% remains after 15.81 years (three half-lives), and so on. (CC BY 4.0; OpenStax)

We can determine the amount of a radioactive isotope remaining after a given number half-lives by using the following expression:

$$\text{amount remaining} = \text{initial amount} \times \left(\frac{1}{2}\right)^{n} \tag{11.5.1}$$

where n is the number of half-lives. This expression works even if the number of half-lives is not a whole number.

11.5.1 Example : Fluorine-20

The half-life of fluorine-20 is 11.0 s. If a sample initially contains 5.00 g of fluorine-20, how much remains after 44.0 s?

Solution

If we compare the time that has passed to the isotope's half-life, we note that 44.0 s is exactly 4 half-lives, so using the previous expression, *n* = 4. Substituting and solving results in the following:

$$\begin{aligned}\text{amount remaining} &= 5.00\,g \times \left(\frac{1}{2}\right)^4 \\ &= 5.00\,g \times \left(\frac{1}{16}\right) \\ &= 0.313\,g\end{aligned}$$

Less than one-third of a gram of fluorine-20 remains.

11.5.1 Exercise : Titanium-44

The half-life of titanium-44 is 60.0 y. A sample of titanium contains 0.600 g of titanium-44. How much remains after 240.0 y?

Answer available at the end of this section.

Half-lives of isotopes range from fractions of a microsecond to billions of years. Table 11.5.1 - Half-Lives of Various Isotopes, lists the half-lives of some isotopes.

Table 11.5.1 Half-Lives of Various Isotopes

Isotope	Half-Life
$^{3}_{H}$	12.3 y
$^{14}_{C}$	5730 y
$^{40}_{K}$	1.26×10^{9} y
$^{51}_{Cr}$	27.70 d
$^{90}_{Sr}$	29.1 y
$^{131}_{I}$	8.04 d
$^{222}_{Rn}$	3.823 d
$^{235}_{U}$	7.04×10^{8} y
$^{238}_{U}$	4.47×10^{9} y
$^{241}_{Am}$	432.7 y
$^{248}_{Bk}$	23.7 h

Isotope	Half-Life
$^{260}_{Sg}$	4 ms

Chemistry Is Everywhere: Radioactive Elements in the Body

You may not think of yourself as radioactive, but you are. A small portion of certain elements in the human body are radioactive and constantly undergo decay. Most of the radioactivity in the human body comes from potassium-40 and carbon-14. Potassium and carbon are two elements that we absolutely cannot live without, so unless we can remove all the radioactive isotopes of these elements, there is no way to escape at least some radioactivity. There is debate about which radioactive element is more problematic. There is more potassium-40 in the body than carbon-14, and it has a much longer half-life. Potassium-40 also decays with about 10 times more energy than carbon-14, making each decay potentially more problematic. However, carbon is the element that makes up the backbone of most living molecules, making carbon-14 more likely to be present around important molecules, such as proteins and DNA molecules. Most experts agree that while it is foolhardy to expect absolutely no exposure to radioactivity, we can and should minimize exposure to excess radioactivity.

Radiometric Dating

Several radioisotopes have half-lives and other properties that make them useful for purposes of "dating" the origin of objects such as archaeological artifacts, formerly living organisms, or geological formations. The radioactivity of carbon-14 provides a method for dating objects that were a part of a living organism. This method of radiometric dating, which is also called **radiocarbon dating** or **carbon-14 dating**, is accurate for dating carbon-containing substances that are up to about 30,000 years old, and can provide reasonably accurate dates up to a maximum of about 50,000 years old.

Naturally occurring carbon consists of three isotopes: $^{12}_{6}\mathrm{C}$, which constitutes about 99% of the carbon on earth; $^{13}_{6}\mathrm{C}$, about 1% of the total; and trace amounts of $^{14}_{6}\mathrm{C}$. Carbon-14 forms in the upper atmosphere by the reaction of nitrogen atoms with neutrons from cosmic rays in space:

$$^{14}_{7}\mathrm{N} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{14}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{H}$$

All isotopes of carbon react with oxygen to produce CO_2 molecules. The ratio of $^{14}_{6}\mathrm{CO}_2$ to $^{12}_{6}\mathrm{CO}_2$ depends on the ratio of $^{14}_{6}\mathrm{CO}$ to $^{12}_{6}\mathrm{CO}$ in the atmosphere. The natural abundance of $^{14}_{6}\mathrm{CO}$ in the atmosphere is approximately 1 part per trillion; until recently, this has generally been constant over time, as seen is gas samples found trapped in ice. The incorporation of $^{14}_{6}\mathrm{C}$ $^{14}_{6}\mathrm{CO}_2$ and $^{12}_{6}\mathrm{CO}_2$ into plants is a regular part of the photosynthesis process, which means that the $^{14}_{6}\mathrm{C}:\ {}^{12}_{6}\mathrm{C}$ ratio found in a living plant is the same as the $^{14}_{6}\mathrm{C}:\ {}^{12}_{6}\mathrm{C}$ ratio in the atmosphere. But when the plant dies, it no longer traps carbon through photosynthesis. Because $^{12}_{6}\mathrm{C}$ is a stable isotope and does not undergo radioactive decay, its concentration in the plant does not change. However, carbon-14 decays by β emission with a half-life of 5730 years:

$$^{14}_{6}\mathrm{C} \longrightarrow {}^{14}_{7}\mathrm{N} + {}^{0}_{-1}\mathrm{e}$$

Thus, the $^{14}_{6}\mathrm{C}:\ {}^{12}_{6}\mathrm{C}$ ratio gradually decreases after the plant dies. The decrease in the ratio with time provides a measure of the time that has elapsed since the death of the plant (or other organism that ate the plant). Figure $11.5.2$ visually depicts this process.

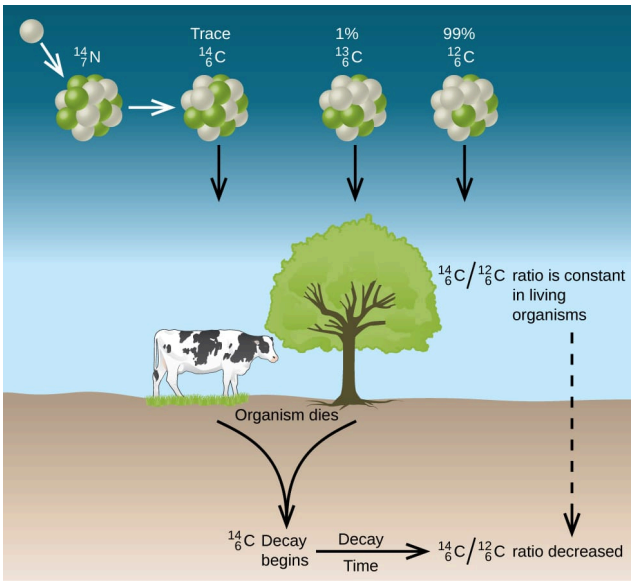


Figure 11.5.2: Along with stable carbon-12, radioactive carbon-14 is taken in by plants and animals, and remains at a constant level within them while they are alive. After death, the C-14 decays and the C-14:C-12 ratio in the remains decreases. Comparing this ratio to the C-14:C-12 ratio in living organisms allows us to determine how long ago the organism lived (and died). (CC BY 4.0; OpenStax)

For example, with the half-life of $^{14}_{6}\mathrm{C}$ being 5730 years, if the $^{14}_{6}\mathrm{C}:\ ^{12}_{6}\mathrm{C}$ ratio in a wooden object found in an archaeological dig is half what it is in a living tree, this indicates that the wooden object is 5730 years old. Highly accurate determinations of $^{14}_{6}\mathrm{C}:\ ^{12}_{6}\mathrm{C}$ ratios can be obtained from very small samples (as little as a milligram) by the use of a mass spectrometer.

Key Takeaways

- Natural radioactive processes are characterized by a half-life, the time it takes for half of the material to decay radioactively.
- The amount of material left over after a certain number of half-lives can be easily calculated.

Answers

0.0375 g

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11.6: Ionizing Radiation

Learning Objectives

- To know the differences between ionizing and nonionizing radiation and their effects on matter.
- To identify natural and artificial sources of radiation.

Because nuclear reactions do not typically affect the valence electrons of the atom (although electron capture draws an electron from an orbital of the lowest energy level), they do not directly cause chemical changes. Nonetheless, the particles and the photons emitted during nuclear decay are very energetic, and they can indirectly produce chemical changes in the matter surrounding the nucleus that has decayed. For instance, an α particle can act as a powerful oxidant.

Ionizing versus Nonionizing Radiation

The effects of radiation on matter are determined primarily by the energy of the radiation, which depends on the nuclear decay reaction that produced it. **Nonionizing radiation** is relatively low in energy; when it collides with an atom in a molecule or an ion, most or all of its energy can be absorbed without causing a structural or a chemical change. Instead, the kinetic energy of the radiation is transferred to the atom or molecule with which it collides, causing it to rotate, vibrate, or move more rapidly. Because this energy can be transferred to adjacent molecules or ions in the form of heat, many radioactive substances are warm to the touch. Highly radioactive elements such as polonium, for example, have been used as heat sources in the US space program. As long as the intensity of the nonionizing radiation is not great enough to cause overheating, it is relatively harmless, and its effects can be neutralized by cooling.

In contrast, **ionizing radiation** is higher in energy, and some of its energy can be transferred to one or more atoms with which it collides as it passes through matter. If enough energy is transferred, electrons can be excited to very high energy levels, resulting in the formation of positively charged ions:

$$\text{atom} + \text{ionizing radiation} \rightarrow \text{ion}^+ + \text{e}^- \tag{11.6.1}$$

Molecules that have been ionized in this way are often highly reactive, and they can decompose or undergo other chemical changes that create a cascade of reactive molecules that can damage biological tissues and other materials (Figure 11.6.1). Because the energy of ionizing radiation is very high, we often report its energy in units such as megaelectronvolts (MeV) per particle:

$$1 \text{ MeV/particle} = 96 \text{ billion J/mol.} \tag{11.6.2}$$



Figure 11.6.1: Radiation Damage. When high-energy particles emitted by radioactive decay interact with matter, they can break bonds or ionize molecules, resulting in changes in physical properties such as ductility or color. The glass electrical insulator on the left has not been exposed to radiation, but the insulator on the right has received intense radiation doses over a long period of time. Radiation damage changed the chemical structure of the glass, causing it to become bright blue.

The Effects of Ionizing Radiation on Matter

The effects of ionizing radiation depend on four factors:

1. The type of radiation, which dictates how far it can penetrate into matter
2. The energy of the individual particles or photons
3. The number of particles or photons that strike a given area per unit time
4. The chemical nature of the substance exposed to the radiation

Because of its high charge and mass, α radiation interacts strongly with matter. Consequently, it does not penetrate deeply into an object, and it can be stopped by a piece of paper, clothing, or skin. In contrast, γ rays, with no charge and essentially no mass, do not interact strongly with matter and penetrate deeply into most objects, including the human body. Several inches of lead or more than 12 inches of special concrete are needed to completely stop γ rays. Because β particles are intermediate in mass and charge between α particles and γ rays, their interaction with matter is also intermediate. Beta particles readily penetrate paper or skin, but they can be stopped by a piece of wood or a relatively thin sheet of metal.

Because of their great penetrating ability, γ rays are by far the most dangerous type of radiation when they come from a source *outside* the body. Alpha particles, however, are the most damaging if their source is *inside* the body because internal tissues absorb all of their energy. Thus danger from radiation depends strongly on the type of radiation emitted and the extent of exposure, which allows scientists to safely handle many radioactive materials if they take precautions to avoid, for example, inhaling fine particulate dust that contains alpha emitters. Some properties of ionizing radiation are summarized in Table 11.6.1.

Table 11.6.1: Some Properties of Ionizing Radiation

Type	Energy Range (MeV)	Penetration Distance in Water*	Penetration Distance in Air*
α particles	3–9	< 0.005 mm	< 10 cm
β particles	≤ 3	< 4 mm	1 m
X rays	$<10^{-2}$	< 1 cm	< 3 m
γ rays	10^{-2} –10^{1}	< 20 cm	> 3 m
***Distance at which half of the radiation has been absorbed.**			

There are many different ways to measure radiation exposure, or the dose. The **roentgen (R)**, which measures the amount of energy absorbed by dry air, can be used to describe quantitative exposure. Named after the German physicist Wilhelm Röntgen (1845–1923; Nobel Prize in Physics, 1901), who discovered X rays. The roentgen is actually defined as the amount of radiation needed to produce an electrical charge of 2.58×10^{-4} C in 1 kg of dry air. Damage to biological tissues, however, is proportional to the amount of energy absorbed by tissues, not air. The most common unit used to measure the effects of radiation on biological tissue is the **rad (radiation absorbed dose)**; the SI equivalent is the gray (Gy). The rad is defined as the amount of radiation that causes 0.01 J of energy to be absorbed by 1 kg of matter, and the gray is defined as the amount of radiation that causes 1 J of energy to be absorbed per kilogram:

$$1 \text{ rad} = 0.010 \text{ J/kg} \qquad 1 \text{ Gy} = 1 \text{ J/kg} \tag{11.6.3}$$

Thus a 70 kg human who receives a dose of 1.0 rad over his or her entire body absorbs 0.010 J/70 kg = 1.4×10^{-4} J, or 0.14 mJ. To put this in perspective, 0.14 mJ is the amount of energy transferred to your skin by a 3.8×10^{-5} g droplet of boiling water. Because the energy of the droplet of water is transferred to a relatively large area of tissue, it is harmless. A radioactive particle, however, transfers its energy to a single molecule, which makes it the atomic equivalent of a bullet fired from a high-powered rifle.

Because α particles have a much higher mass and charge than β particles or γ rays, the difference in mass between α and β particles is analogous to being hit by a bowling ball instead of a table tennis ball traveling at the same speed. Thus the amount of tissue damage caused by 1 rad of α particles is much greater than the damage caused by 1 rad of β particles or γ rays.

Wilhelm Röntgen

Born in the Lower Rhine Province of Germany, Röntgen was the only child of a cloth manufacturer and merchant. His family moved to the Netherlands where he showed no particular aptitude in school, but where he was fond of roaming the countryside. Röntgen was expelled from technical school in Utrecht after being unjustly accused of drawing a caricature of one of the teachers. He began studying mechanical engineering in Zurich, which he could enter without having the credentials of a regular student, and received a PhD at the University of Zurich in 1869. In 1876 he became professor of physics.

Summary

Nonionizing radiation is relatively low in energy and can be used as a heat source, whereas ionizing radiation, which is higher in energy, can penetrate biological tissues and is highly reactive. The effects of radiation on matter depend on the energy of the radiation. Nonionizing radiation is relatively low in energy, and the energy is transferred to matter in the form of heat. Ionizing radiation is relatively high in energy, and when it collides with an atom, it can completely remove an electron to form a positively charged ion that can damage biological tissues. Alpha particles do not penetrate very far into matter, whereas γ rays penetrate more deeply. Common units of radiation exposure, or dose, are the roentgen (R), the amount of energy absorbed by dry air, and the rad (radiation absorbed dose), the amount of radiation that produces 0.01 J of energy in 1 kg of matter. The rem (roentgen equivalent in man) measures the actual amount of tissue damage caused by a given amount of radiation.

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11.7: Detecting and Measuring Radiation

Learning Objectives

- Define units for measuring radiation exposure

Radioactivity is determined by measuring the number of decay processes per unit time. Perhaps the easiest way is simply to determine the number of counts/minute, with each count measuring a single decay process, such as the emission of an α -particle. A particular isotope may have an activity of 5,000 counts/minute (cpm) while another isotope might only have $250\ \mathrm{cpm}$. The amount of activity gives a rough indication of the amount of the radioisotope present - the higher the activity, the more radioactivity isotope in the sample.

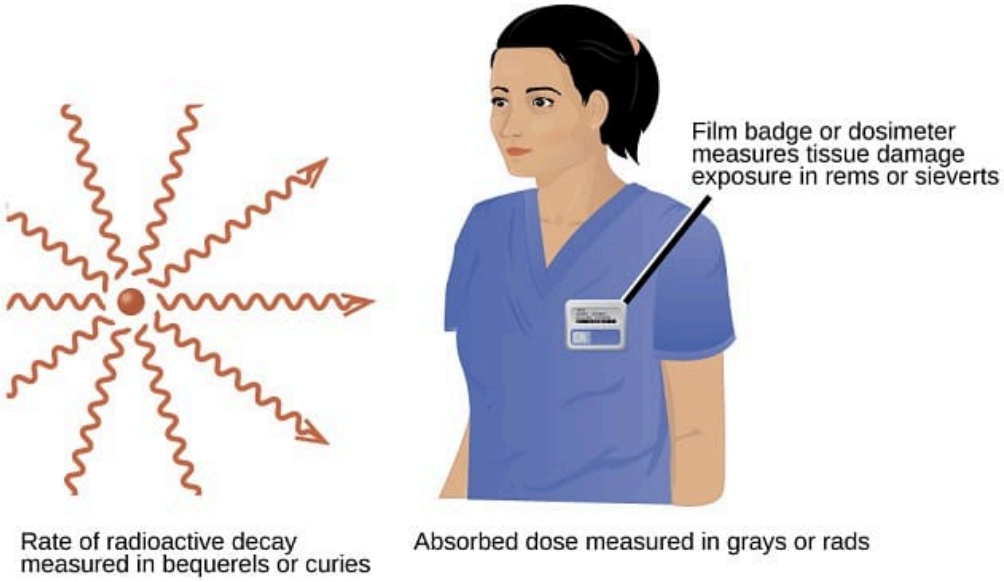


Figure 11.7.1: Different units are used to measure the rate of emission from a radioactive source, the energy that is absorbed from the source, and the amount of damage the absorbed radiation does. (CC BY 4.0; OpenStax)

Measurement of exposure to radioactivity is important for anyone who deals with radioactive materials on a regular basis. Perhaps the simplest device is a personal **dosimeter** - a film badge that will fog up when exposed to radiation (Figure 11.7.1). The amount of fogging is proportional to the amount of radiation present. These devices are not very sensitive to low levels of radiation. More sensitive systems use crystals that respond in some way to radioactivity by registering the number of emissions in a given time. These systems tend to be more sensitive and more reliable than film badges.

When alpha, beta or gamma particles collides with a target, some of the energy in the particle is transferred to the target, typically resulting in the promotion of an electron to an “excited state”. In many “targets”, especially gasses, this results in *ionization*. A **Geiger counter** (or Geiger-Müller counter) takes advantage of this to detect these particles (Figure 11.7.2). In a Geiger tube, the electron produced by ionization of a captive gas travels to the anode and the change in voltage is detected by the attached circuitry.



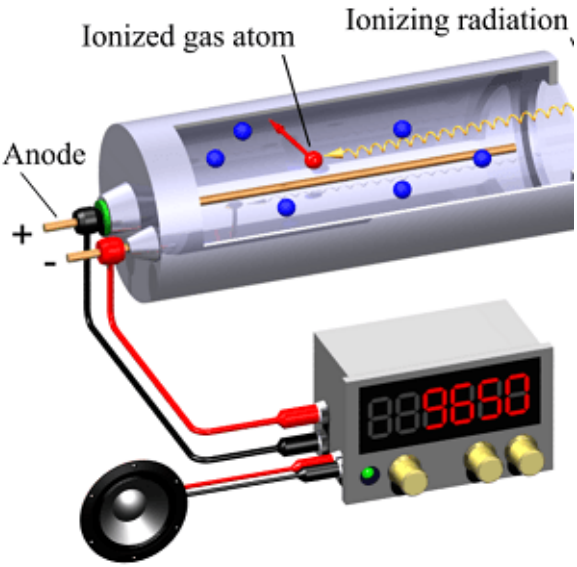


Figure 11.7.2: (left) Geiger counter with pancake type probe. Public Domain; TimVickers via Wikipedia). (right) Schematic of a Geiger-Müller counter using an "end window" tube for low penetration radiation. A loudspeaker is also used for indication. (CC-BY-SA-3.0 Svjo-2 vai Wikipedia).

Most counters of this type are designed to emit an audible “click” in response to the change in voltage, and to also show it on a digital or analog meter.

We previously used mass to indicate the amount of radioactive substance present. However, this is only one of several units used to express amounts of radiation. Some units describe the number of radioactive events occurring per unit time, while others express the amount of a person's exposure to radiation. A variety of units are used to measure various aspects of radiation (Table 11.7.1).

Table 11.7.1: Units Used for Measuring Radiation

Measurement Purpose	Unit	Quantity Measured	Description
activity of source	becquerel (Bq)	radioactive decays or emissions	amount of sample that undergoes 1 decay/second
	curie (Ci)		amount of sample that undergoes 3.7×10^{10} decays/second
absorbed dose	gray (Gy)	energy absorbed per kg of tissue	1 Gy = 1 J/kg tissue
	radiation absorbed dose (rad)		1 rad = 0.01 J/kg tissue
biologically effective dose	sievert (Sv)	tissue damage	Sv = RBE × Gy
	roentgen equivalent for humans (rem)		Rem = RBE × rad

The roentgen equivalent for humans (rem) is the unit for radiation damage that is used most frequently in medicine (1 rem = 1 Sv). Note that the tissue damage units (rem or Sv) includes the energy of the radiation dose (rad or Gy) along with a biological factor referred to as the RBE (for relative biological effectiveness) that is an approximate measure of the relative damage done by the radiation. These are related by:

$$\text{number of rems} = \text{RBE} \times \text{number of rads} \tag{11.7.1}$$

with RBE approximately 10 for α radiation, 2(+) for protons and neutrons, and 1 for β and γ radiation.

The Becquerel Unit

Perhaps the direct way of reporting radioactivity is the number of radioactive decays per second. One decay per second is called one **becquerel (Bq).** Even in a small mass of radioactive material, however, there are thousands upon thousands of decays or disintegrations per second. The becquerel is named after Henri Becquerel, who discovered radioactivity in 1896.

The Curie Unit

The **curie** (Ci) is one measure of the rate of decay (named after Pierre and Marie Curie). One curie is equivalent to 3.7×10^{10} disintegrations per second. Since this is obviously a large and unwieldy number, radiation is often expressed in millicuries or microcuries (still very large numbers). The curie is named after Polish scientist Marie Curie, who performed some of the initial investigations into radioactive phenomena in the early 1900s. The curie can be used in place of grams to describe quantities of radioactive material. As an example, the amount of americium in an average smoke detector has an activity of 0.9 μCi.

The Roentgen Unit

There are many different ways to measure radiation exposure, or the dose. The **roentgen (R)**, which measures the amount of energy absorbed by dry air, can be used to describe quantitative exposure.Named after the German physicist Wilhelm Röntgen (1845–1923; Nobel Prize in Physics, 1901), who discovered x-rays. The roentgen is actually defined as the amount of radiation needed to produce an electrical charge of 2.58×10^{-4} C in 1 kg of dry air. Damage to biological tissues, however, is proportional to the amount of energy absorbed by tissues, not air.

The Rad Unit

The most common unit used to measure the effects of radiation on biological tissue is the **rad (radiation absorbed dose)**; the SI equivalent is the gray (Gy). The rad is defined as the amount of radiation that causes 0.01 J of energy to be absorbed by 1 kg of matter, and the gray is defined as the amount of radiation that causes 1 J of energy to be absorbed per kilogram:

$$1\ rad = 0.010\ J/kg \quad 1\ Gy = 1\ J/kg \tag{11.7.2}$$

Thus a 70 kg human who receives a dose of 1.0 rad over his or her entire body absorbs 0.010 J/70 kg = 1.4×10^{-4} J, or 0.14 mJ. To put this in perspective, 0.14 mJ is the amount of energy transferred to your skin by a 3.8×10^{-5} g droplet of boiling water. Because the energy of the droplet of water is transferred to a relatively large area of tissue, it is harmless. A radioactive particle, however, transfers its energy to a single molecule, which makes it the atomic equivalent of a bullet fired from a high-powered rifle.

The Gray Unit

Another unit of radiation absorption is the **gray (Gy)**:

1 Gy = 100 rad

The rad is more common. To get an idea of the amount of energy this represents, consider that the absorption of 1 rad by 70,000 g of H_2O (approximately the same mass as a 150 lb person) would increase its temperature by only 0.002°C. This may not seem like a lot, but it is enough energy to break about 1×10^{21} molecular C–C bonds in a person's body. That amount of damage would not be desirable.

The Rem Unit

Because α particles have a much higher mass and charge than β particles or γ rays, the difference in mass between α and β particles is analogous to being hit by a bowling ball instead of a table tennis ball traveling at the same speed. Thus the amount of tissue damage caused by 1 rad of α particles is much greater than the damage caused by 1 rad of β particles or γ rays. Thus a unit called the **rem (roentgen equivalent in human)** was devised to describe the actual amount of tissue damage caused by a given

amount of radiation. The number of rems of radiation is equal to the number of rads multiplied by the RBE (relative biological effectiveness) factor:

$$em = rad \times RBE \tag{11.7.3}$$

where RBE is the *relative biological effectiveness factor* is a number greater than or equal to 1 that takes into account the type of radioactive emission and sometimes the type of tissue being exposed. For beta particles, RBE factor equals 1. For alpha particles striking most tissues, the factor is 10, but for eye tissue, the factor is 30. Most radioactive emissions that people are exposed to are on the order of a few dozen millirems (mrem) or less; a medical X ray is about 20 mrem.

The Sievert Unit

A sievert (Sv) is related to the rem unit and is defined as 100 rem. Because actual radiation doses tend to be very small, most measurements are reported in millirems (1 mrem = 10^{-3} rem).

Assessing the Impact of Radiation Exposure

One of the more controversial public policy issues debated today is whether the radiation exposure from artificial sources, when combined with exposure from natural sources, poses a significant risk to human health. The effects of single radiation doses of different magnitudes on humans are listed in Table 11.7.2. Because of the many factors involved in radiation exposure (length of exposure, intensity of the source, and energy and type of particle), it is difficult to quantify the specific dangers of one radioisotope versus another. Nonetheless, some general conclusions regarding the effects of radiation exposure are generally accepted as valid.

Table 11.7.2: The Effects of a Single Radiation Dose on a 70 kg Human

Dose (rem)	Symptoms/Effects
< 5	no observable effect
5–20	possible chromosomal damage
20–100	temporary reduction in white blood cell count
50–100	temporary sterility in men (up to a year)
100–200	mild radiation sickness, vomiting, diarrhea, fatigue; immune system suppressed; bone growth in children retarded
> 300	permanent sterility in women
> 500	fatal to 50% within 30 days; destruction of bone marrow and intestine
> 3000	fatal within hours

Radiation doses of 600 rem and higher are invariably fatal, while a dose of 500 rem kills half the exposed subjects within 30 days. Smaller doses (≤ 50 rem) appear to cause only limited health effects, even though they correspond to tens of years of natural radiation. This does not, however, mean that such doses have no ill effects; they may cause long-term health problems, such as cancer or genetic changes that affect offspring. The possible detrimental effects of the much smaller doses attributable to artificial sources (< 100 mrem/yr) are more difficult to assess.

The tissues most affected by large, whole-body exposures are bone marrow, intestinal tissue, hair follicles, and reproductive organs, all of which contain rapidly dividing cells. The susceptibility of rapidly dividing cells to radiation exposure explains why cancers are often treated by radiation. Because cancer cells divide faster than normal cells, they are destroyed preferentially by radiation. Long-term radiation-exposure studies on fruit flies show a linear relationship between the number of genetic defects and both the magnitude of the dose and the exposure time. In contrast, similar studies on mice show a much lower number of defects when a given dose of radiation is spread out over a long period of time rather than received all at once. Which of the two is applicable to humans?

According to one hypothesis, mice have very low risk from low doses because their bodies have ways of dealing with the damage caused by natural radiation. At much higher doses, however, their natural repair mechanisms are overwhelmed, leading to irreversible damage. Because mice are biochemically much more similar to humans than are fruit flies, many scientists believe that this model also applies to humans. In contrast, the linear model assumes that all exposure to radiation is intrinsically damaging and suggests that stringent regulation of low-level radiation exposure is necessary. Which view is more accurate? The answer—while yet unknown—has extremely important consequences for regulating radiation exposure.

Summary

The SI unit for rate of radioactive decay is the becquerel (Bq), with 1 Bq = 1 disintegration per second. The curie (Ci) and millicurie (mCi) are much larger units and are frequently used in medicine (1 curie = 1 Ci = 3.7×10^{10} disintegrations per second). The SI unit for measuring radiation dose is the gray (Gy), with 1 Gy = 1 J of energy absorbed per kilogram of tissue. In medical applications, the radiation absorbed dose (rad) is more often used (1 rad = 0.01 Gy; 1 rad results in the absorption of 0.01 J/kg of tissue). The SI unit measuring tissue damage caused by radiation is the sievert (Sv). This takes into account both the energy and the biological effects of the type of radiation involved in the radiation dose.

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11.8: Artificial Transmutation

Learning Objectives

- Describe transmutation.
- Write and balance transmutation equations.

Although the conversion of one element to another is the basis of natural radioactive decay, it is also possible to convert one element to another artificially. The conversion of one element to another is the process of **transmutation**. Between 1921 and 1924, Patrick Blackett conducted experiments in which he converted a stable isotope of nitrogen to a stable isotope of oxygen. By bombarding $^{14}\mathrm{N}$ with α particles he created $^{17}\mathrm{O}$. Transmutation may also be accomplished by bombardment with neutrons.

$$^{14}_{7}\mathrm{N} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{H}$$

The $^{17}_{8}\mathrm{O}$ and $^{1}_{1}\mathrm{H}$ nuclei that are produced are stable, so no further (nuclear) changes occur.

To reach the kinetic energies necessary to produce transmutation reactions, devices called **particle accelerators** are used. These devices use magnetic and electric fields to increase the speeds of nuclear particles. In all accelerators, the particles move in a vacuum to avoid collisions with gas molecules. When neutrons are required for transmutation reactions, they are usually obtained from radioactive decay reactions or from various nuclear reactions occurring in nuclear reactors.

CERN Particle Accelerator

Located near Geneva, the CERN ("Conseil Européen pour la Recherche Nucléaire," or European Council for Nuclear Research) Laboratory is the world's premier center for the investigations of the fundamental particles that make up matter. It contains the 27-kilometer (17 mile) long, circular Large Hadron Collider (LHC), the largest particle accelerator in the world (Figure 11.8.1). In the LHC, particles are boosted to high energies and are then made to collide with each other or with stationary targets at nearly the speed of light. Superconducting electromagnets are used to produce a strong magnetic field that guides the particles around the ring. Specialized, purpose-built detectors observe and record the results of these collisions, which are then analyzed by CERN scientists using powerful computers.



Figure 11.8.1: A small section of the LHC is shown with workers traveling along it. (credit: Christophe Delaere)

In 2012, CERN announced that experiments at the LHC showed the first observations of the Higgs boson, an elementary particle that helps explain the origin of mass in fundamental particles. This long-anticipated discovery made worldwide news and resulted in the awarding of the 2103 Nobel Prize in Physics to François Englert and Peter Higgs, who had predicted the existence of this particle almost 50 years previously.

Prior to 1940, the heaviest-known element was uranium, whose atomic number is 92. Now, many artificial elements have been synthesized and isolated, including several on such a large scale that they have had a profound effect on society. One of these—element 93, neptunium (Np)—was first made in 1940 by McMillan and Abelson by bombarding uranium-238 with neutrons. The reaction creates unstable uranium-239, with a half-life of 23.5 minutes, which then decays into neptunium-239. Neptunium-239 is also radioactive, with a half-life of 2.36 days, and it decays into plutonium-239. The nuclear reactions are:

$$\begin{aligned} {}^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} &\longrightarrow {}^{239}_{92}\mathrm{U} \\ {}^{239}_{92}\mathrm{U} &\longrightarrow {}^{239}_{93}\mathrm{Np} + {}^{0}_{-1}\mathrm{e} \qquad \text{half-life} = 23.5\ \text{min} \\ {}^{239}_{93}\mathrm{Np} &\longrightarrow {}^{239}_{94}\mathrm{Pu} + {}^{0}_{-1}\mathrm{e} \qquad \text{half-life} = 2.36\ \text{days} \end{aligned}$$

Plutonium is now mostly formed in nuclear reactors as a byproduct during the decay of uranium. Some of the neutrons that are released during U-235 decay combine with U-238 nuclei to form uranium-239; this undergoes β decay to form neptunium-239, which in turn undergoes β decay to form plutonium-239 as illustrated in the preceding three equations. It is possible to summarize these equations as:

$${}^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{239}_{92}\mathrm{U} \xrightarrow{\beta^-} {}^{239}_{93}\mathrm{Np} \xrightarrow{\beta^-} {}^{239}_{94}\mathrm{Pu} \tag{11.8.1}$$

Heavier isotopes of plutonium—Pu-240, Pu-241, and Pu-242—are also produced when lighter plutonium nuclei capture neutrons. Some of this highly radioactive plutonium is used to produce military weapons, and the rest presents a serious storage problem because they have half-lives from thousands to hundreds of thousands of years.

Although they have not been prepared in the same quantity as plutonium, many other synthetic nuclei have been produced. Nuclear medicine has developed from the ability to convert atoms of one type into other types of atoms. Radioactive isotopes of several dozen elements are currently used for medical applications. The radiation produced by their decay is used to image or treat various organs or portions of the body, among other uses.

The elements beyond element 92 (uranium) are called transuranium elements. As of this writing, 22 transuranium elements have been produced and officially recognized by IUPAC; several other elements have formation claims that are waiting for approval. Some of these elements are shown in Table 11.8.1.

Table 11.8.1: Preparation of Some of the Transuranium Elements

Name	Symbol	Atomic Number	Reaction
americium	Am	95	${}^{239}_{94}\mathrm{Pu} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{240}_{95}\mathrm{Am} + {}^{0}_{-1}\mathrm{e}$
curium	Cm	96	${}^{239}_{94}\mathrm{Pu} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{242}_{96}\mathrm{Cm} + {}^{1}_{0}\mathrm{n}$
californium	Cf	98	${}^{242}_{96}\mathrm{Cm} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{243}_{97}\mathrm{Bk} + 2{}^{1}_{0}\mathrm{n}$
einsteinium	Es	99	${}^{238}_{92}\mathrm{U} + 15{}^{1}_{0}\mathrm{n} \longrightarrow {}^{253}_{99}\mathrm{Es} + 7{}^{0}_{-1}\mathrm{e}$
mendelevium	Md	101	${}^{253}_{99}\mathrm{Es} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{256}_{101}\mathrm{Md} + {}^{1}_{0}\mathrm{n}$
nobelium	No	102	${}^{246}_{96}\mathrm{Cm} + {}^{12}_{6}\mathrm{C} \longrightarrow {}^{254}_{102}\mathrm{No} + 4\,{}^{1}_{0}\mathrm{n}$
rutherfordium	Rf	104	${}^{249}_{98}\mathrm{Cf} + {}^{12}_{6}\mathrm{C} \longrightarrow {}^{257}_{104}\mathrm{Rf} + 4\,{}^{1}_{0}\mathrm{n}$
seaborgium	Sg	106	${}^{206}_{82}\mathrm{Pb} + {}^{54}_{24}\mathrm{Cr} \longrightarrow {}^{257}_{106}\mathrm{Sg} + 3\,{}^{1}_{0}\mathrm{n}$ ${}^{249}_{98}\mathrm{Cf} + {}^{18}_{8}\mathrm{O} \longrightarrow {}^{263}_{106}\mathrm{Sg} + 4\,{}^{1}_{0}\mathrm{n}$

Name	Symbol	Atomic Number	Reaction
meitnerium	Mt	107	$^{209}_{83}\mathrm{Bi} + {}^{58}_{26}\mathrm{Fe} \longrightarrow {}^{266}_{109}\mathrm{Mt} + {}^{1}_{0}\mathrm{n}$

Example 11.8.1

Write the balanced nuclear equation for the production of the following transuranium elements:

a. berkelium-244, made by the reaction of Am-241 and He-4
b. fermium-254, made by the reaction of Pu-239 with a large number of neutrons
c. lawrencium-257, made by the reaction of Cf-250 and B-11
d. dubnium-260, made by the reaction of Cf-249 and N-15

Solution

a

From the given information we can write the nuclear equation

$$^{241}_{95}\mathrm{Am} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{244}_{97}\mathrm{Bk}$$

On the left side the total mass number is

$$241 + 4 = 245$$

and the total atomic number is

$$95 + 2 = 97$$

On the right side the total mass number is 244 and the total atomic number is 97. This shows that one neutron needs to be added which would increase the total mass number needs to by one while keeping the total atomic number the same. The balanced nuclear equation would be

$$^{241}_{95}\mathrm{Am} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{244}_{97}\mathrm{Bk} + {}^{1}_{0}\mathrm{n}$$

b

From the given information we can write the nuclear equation

$$^{239}_{94}\mathrm{Pu} + \mathrm{x}\ {}^{1}_{0}\mathrm{n} \rightarrow {}^{254}_{100}\mathrm{Fm}$$

On the left side we see that the total mass number is the sum of $239 + (1)\mathrm{x}$. on the right side we see that the total mass number is 254. since the total mass number of the reactants must equal that of the products we can write

$$239 + \mathrm{x} = 254$$

showing 15 neutrons need to be added to balance the mass number.

$$^{239}_{94}\mathrm{Pu} + 15\ {}^{1}_{0}\mathrm{n} \rightarrow {}^{254}_{100}\mathrm{Fm}$$

To balance the total atomic number of the equation, 6 electrons need to be added to the right side. Therefore the balanced equation reads:

$$^{239}_{94}\mathrm{Pu} + 15\ {}^{1}_{0}\mathrm{n} \rightarrow {}^{254}_{100}\mathrm{Fm} + 6\ {}^{0}_{-1}\mathrm{e}$$

c

From the given information we can write the nuclear equation

$$^{250}_{98}\mathrm{Cf} + {}^{11}_{5}\mathrm{B} \rightarrow {}^{257}_{103}\mathrm{Lr}$$

On the left side the total mass number is

$$250 + 11 = 261$$

and the total atomic number is

$$98 + 5 = 103$$

On the right side the total mass number is 257 and the total atomic number is 103. This means that 4 neutrons need to be added to the right side to balance the equation. The balanced nuclear equation is

$$^{250}_{98}\mathrm{Cf} + ^{11}_{5}\mathrm{B} \rightarrow ^{257}_{103}\mathrm{Lr} + 4\ ^{1}_{0}\mathrm{n}$$

d

From the given information we can write the nuclear equation

$$^{249}_{98}\mathrm{Cf} + ^{15}_{7}\mathrm{N} \rightarrow ^{260}_{105}\mathrm{Db}$$

On the left side the total mass number is

$$249 + 15 = 264$$

and the total atomic number is

$$98 + 7 = 105$$

On the right side the total mass number is 260 and the total atomic number is 105. This means that 4 neutrons need to be added to the right side t obalance the equation. The balanced nuclear equation is

$$^{249}_{98}\mathrm{Cf} + ^{15}_{7}\mathrm{N} \rightarrow ^{260}_{105}\mathrm{Lr} + 4\ ^{1}_{0}\mathrm{n}$$

Contributors and Attributions

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11.9: Nuclear Fission and Nuclear Fusion

Learning Objectives

- Explain nuclear fission and fusion processes.
- Write and balance nuclear fission and fusion equations.
- Relate the concepts of critical mass and nuclear chain reactions.

Nuclear fusion and **nuclear fission** are two different types of energy-releasing reactions in which energy is released from high-powered atomic bonds between the particles within the nucleus. The main difference between these two processes is that fission is the splitting of an atom into two or more smaller ones while fusion is the fusing of two or more smaller atoms into a larger one.

Protons and neutrons make up a nucleus, which is the foundation of nuclear science. Fission and fusion involves the dispersal and combination of elemental nucleus and isotopes, and part of nuclear science is to understand the process behind this phenomenon. Adding up the individual masses of each of these subatomic particles of any given element will always give you a greater mass than the mass of the nucleus as a whole. The missing idea in this observation is the concept called nuclear binding energy. Nuclear binding energy is the energy required to keep the protons and neutrons of a nucleus intact, and the energy that is released during a nuclear fission or fusion is nuclear power. There are some things to consider however. The mass of an element's nucleus as a whole is less than the total mass of its individual protons and neutrons.

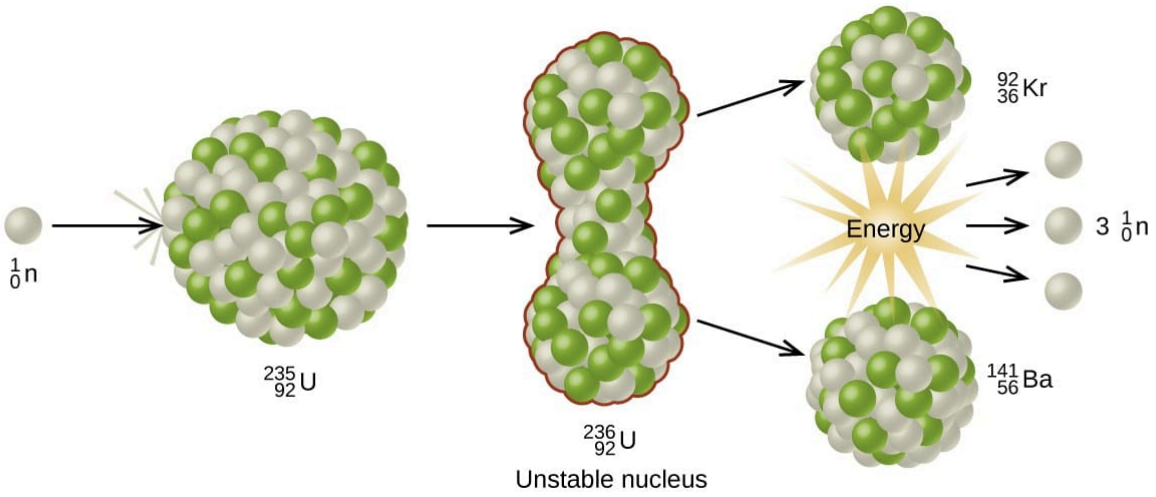
To calculate the energy released during mass destruction in both nuclear fission and fusion, we use Einstein's equation that equates energy and mass:

$$E = mc^2 \tag{11.9.1}$$

with m is mass (kilograms), c is speed of light (meters/sec) and E is energy (Joules).

Nuclear Fission

Many heavier elements with smaller binding energies per nucleon can decompose into more stable elements that have intermediate mass numbers and larger binding energies per nucleon—that is, mass numbers and binding energies per nucleon that are closer to the "peak" of the binding energy graph near 56. Sometimes neutrons are also produced. This decomposition is called fission, the breaking of a large nucleus into smaller pieces. The breaking is rather random with the formation of a large number of different products. Fission usually does not occur naturally, but is induced by bombardment with neutrons. The first reported nuclear fission occurred in 1939 when three German scientists, Lise Meitner, Otto Hahn, and Fritz Strassman, bombarded uranium-235 atoms with slow-moving neutrons that split the U-238 nuclei into smaller fragments that consisted of several neutrons and elements near the middle of the periodic table. Since then, fission has been observed in many other isotopes, including most actinide isotopes that have an odd number of neutrons. A typical nuclear fission reaction is shown in Figure 11.9.1.



$$^{235}_{92}U + {}^{0}_{1}n \longrightarrow {}^{236}_{92}U \longrightarrow {}^{141}_{56}Ba + {}^{92}_{36}Kr + 3\ {}^{1}_{0}n$$

Figure 11.9.1: When a slow neutron hits a fissionable U-235 nucleus, it is absorbed and forms an unstable U-236 nucleus. The U-236 nucleus then rapidly breaks apart into two smaller nuclei (in this case, Ba-141 and Kr-92) along with several neutrons (usually two or three), and releases a very large amount of energy.

Among the products of Meitner, Hahn, and Strassman's fission reaction were barium, krypton, lanthanum, and cerium, all of which have nuclei that are more stable than uranium-235. Since then, hundreds of different isotopes have been observed among the products of fissionable substances. A few of the many reactions that occur for U-235, and a graph showing the distribution of its fission products and their yields, are shown in Figure 11.9.2. Similar fission reactions have been observed with other uranium isotopes, as well as with a variety of other isotopes such as those of plutonium.

$$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{236}_{92}U \longrightarrow {}^{90}_{38}Sr + {}^{144}_{54}Xe + 2\ {}^{1}_{0}n$$

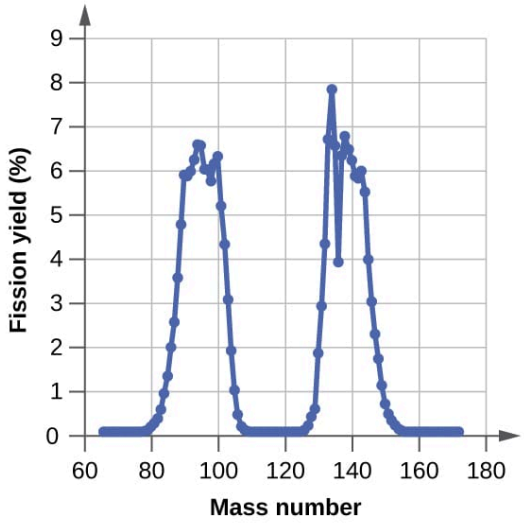
$$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{236}_{92}U \longrightarrow {}^{87}_{35}Br + {}^{146}_{57}La + 3\ {}^{1}_{0}n$$

$$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{236}_{92}U \longrightarrow {}^{96}_{37}Rb + {}^{137}_{55}Cs + 3\ {}^{1}_{0}n$$

$$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{236}_{92}U \longrightarrow {}^{137}_{52}Te + {}^{97}_{40}Zr + 2\ {}^{1}_{0}n$$

$$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{236}_{92}U \longrightarrow {}^{141}_{56}Ba + {}^{92}_{36}Kr + 3\ {}^{1}_{0}n$$

(a)



(b)

Figure 11.9.2: (a) Nuclear fission of U-235 produces a range of fission products. (b) The larger fission products of U-235 are typically one isotope with a mass number around 85–105, and another isotope with a mass number that is about 50% larger, that is, about 130–150.

A tremendous amount of energy is produced by the fission of heavy elements. For instance, when one mole of U-235 undergoes fission, the products weigh about 0.2 grams less than the reactants; this "lost" mass is converted into a very large amount of energy, about 1.8×10^{10} kJ per mole of U-235. Nuclear fission reactions produce incredibly large amounts of energy compared to chemical reactions. The fission of 1 kilogram of uranium-235, for example, produces about 2.5 million times as much energy as is produced by burning 1 kilogram of coal.

When undergoing fission U-235 produces two "medium-sized" nuclei, and two or three neutrons. These neutrons may then cause the fission of other uranium-235 atoms, which in turn provide more neutrons that can cause fission of even more nuclei, and

so on. If this occurs, we have a nuclear chain reaction (Figure 11.9.3). On the other hand, if too many neutrons escape the bulk material without interacting with a nucleus, then no chain reaction will occur.

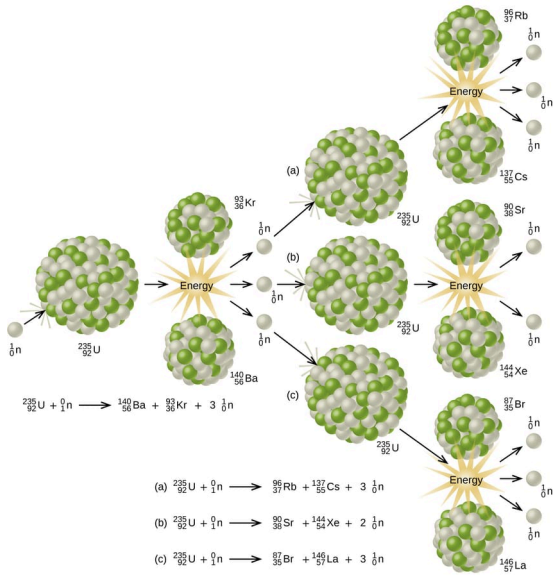


Figure 11.9.3: The fission of a large nucleus, such as U-235, produces two or three neutrons, each of which is capable of causing fission of another nucleus by the reactions shown. If this process continues, a nuclear chain reaction occurs.

Material that can sustain a nuclear fission chain reaction is said to be fissile or fissionable. (Technically, fissile material can undergo fission with neutrons of any energy, whereas fissionable material requires high-energy neutrons.) Nuclear fission becomes self-sustaining when the number of neutrons produced by fission equals or exceeds the number of neutrons absorbed by splitting nuclei plus the number that escape into the surroundings. The amount of a fissionable material that will support a self-sustaining chain reaction is a **critical mass**. An amount of fissionable material that cannot sustain a chain reaction is a subcritical mass. An amount of material in which there is an increasing rate of fission is known as a supercritical mass.

Nuclear power plants are designed in such a way that they cannot form a supercritical mass of fissionable material and therefore cannot create a nuclear explosion. But as history has shown, failures of systems and safeguards can cause catastrophic accidents, including chemical explosions and nuclear meltdowns (damage to the reactor core from overheating). The following Chemistry in Everyday Life feature explores three infamous meltdown incidents.

Nuclear Accidents

The importance of cooling and containment are amply illustrated by three major accidents that occurred with the nuclear reactors at nuclear power generating stations in the United States (Three Mile Island), the former Soviet Union (Chernobyl), and Japan (Fukushima).

In March 1979, the cooling system of the Unit 2 reactor at Three Mile Island Nuclear Generating Station in Pennsylvania failed, and the cooling water spilled from the reactor onto the floor of the containment building. After the pumps stopped, the reactors overheated due to the high radioactive decay heat produced in the first few days after the nuclear reactor shut down. The temperature of the core climbed to at least 2200 °C, and the upper portion of the core began to melt. In addition, the zirconium alloy cladding of the fuel rods began to react with steam and produced hydrogen:

$$\mathrm{Zr}(s) + 2\,\mathrm{H_2O}(g) \longrightarrow \mathrm{ZrO_2}(s) + 2\,\mathrm{H_2}(g)$$

The hydrogen accumulated in the confinement building, and it was feared that there was danger of an explosion of the mixture of hydrogen and air in the building. Consequently, hydrogen gas and radioactive gases (primarily krypton and xenon) were vented from the building. Within a week, cooling water circulation was restored and the core began to cool. The plant was closed for nearly 10 years during the cleanup process.

Although zero discharge of radioactive material is desirable, the discharge of radioactive krypton and xenon, such as occurred at the Three Mile Island plant, is among the most tolerable. These gases readily disperse in the atmosphere and thus do not produce highly radioactive areas. Moreover, they are noble gases and are not incorporated into plant and animal matter in the food chain. Effectively none of the heavy elements of the core of the reactor were released into the environment, and no cleanup of the area outside of the containment building was necessary (Figure 11.9.4).

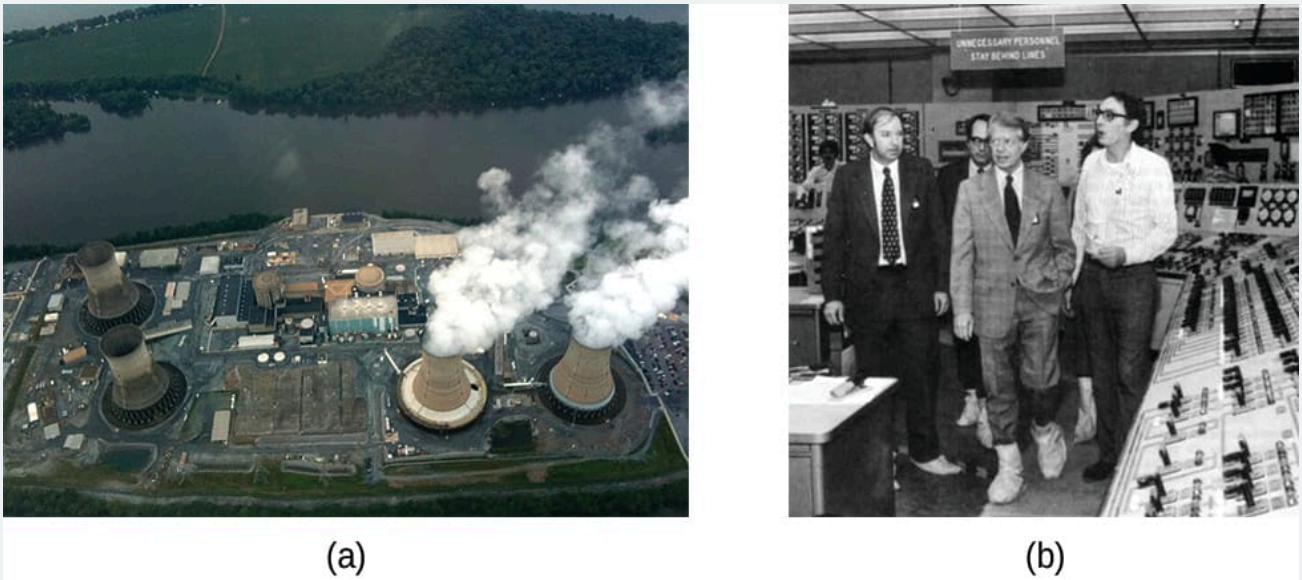


Figure 11.9.4: (a) In this 2010 photo of Three Mile Island, the remaining structures from the damaged Unit 2 reactor are seen on the left, whereas the separate Unit 1 reactor, unaffected by the accident, continues generating power to this day (right). (b) President Jimmy Carter visited the Unit 2 control room a few days after the accident in 1979.

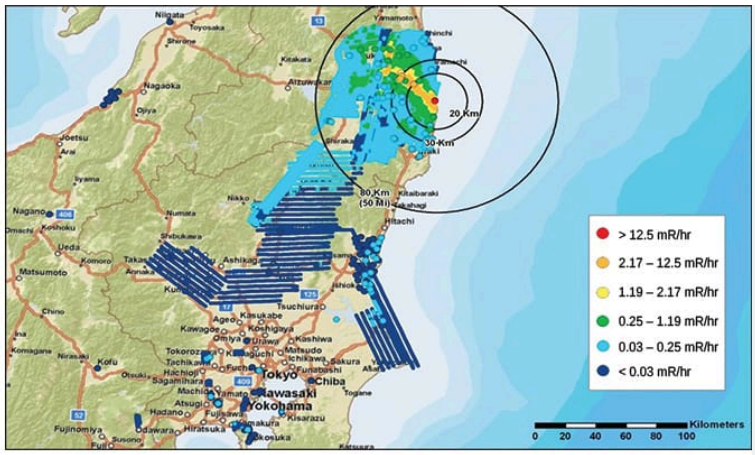
Another major nuclear accident involving a reactor occurred in April 1986, at the Chernobyl Nuclear Power Plant in Ukraine, which was still a part of the former Soviet Union. While operating at low power during an unauthorized experiment with some of its safety devices shut off, one of the reactors at the plant became unstable. Its chain reaction became uncontrollable and increased to a level far beyond what the reactor was designed for. The steam pressure in the reactor rose to between 100 and 500 times the full power pressure and ruptured the reactor. Because the reactor was not enclosed in a containment building, a large amount of radioactive material spewed out, and additional fission products were released, as the graphite (carbon) moderator of the core ignited and burned. The fire was controlled, but over 200 plant workers and firefighters developed acute radiation sickness and at least 32 soon died from the effects of the radiation. It is predicted that about 4000 more deaths will occur among emergency workers and former Chernobyl residents from radiation-induced cancer and leukemia. The reactor has since been encapsulated in steel and concrete, a now-decaying structure known as the sarcophagus. Almost 30 years later, significant radiation problems still persist in the area, and Chernobyl largely remains a wasteland.

In 2011, the Fukushima Daiichi Nuclear Power Plant in Japan was badly damaged by a 9.0-magnitude earthquake and resulting tsunami. Three reactors up and running at the time were shut down automatically, and emergency generators came online to power electronics and coolant systems. However, the tsunami quickly flooded the emergency generators and cut power to the pumps that circulated coolant water through the reactors. High-temperature steam in the reactors reacted with zirconium alloy to produce hydrogen gas. The gas escaped into the containment building, and the mixture of hydrogen and air exploded. Radioactive material was released from the containment vessels as the result of deliberate venting to reduce the hydrogen pressure, deliberate discharge of coolant water into the sea, and accidental or uncontrolled events.

An evacuation zone around the damaged plant extended over 12.4 miles away, and an estimated 200,000 people were evacuated from the area. All 48 of Japan's nuclear power plants were subsequently shut down, remaining shuttered as of December 2014. Since the disaster, public opinion has shifted from largely favoring to largely opposing increasing the use of nuclear power plants, and a restart of Japan's atomic energy program is still stalled (Figure 11.9.5).



(a)



(b)

Figure 11.9.5: (a) After the accident, contaminated waste had to be removed, and (b) an evacuation zone was set up around the plant in areas that received heavy doses of radioactive fallout. (credit a: modification of work by “Live Action Hero”/Flickr)

The energy produced by a reactor fueled with enriched uranium results from the fission of uranium as well as from the fission of plutonium produced as the reactor operates. As discussed previously, the plutonium forms from the combination of neutrons and the uranium in the fuel. In any nuclear reactor, only about 0.1% of the mass of the fuel is converted into energy. The other 99.9% remains in the fuel rods as fission products and unused fuel. All of the fission products absorb neutrons, and after a period of several months to a few years, depending on the reactor, the fission products must be removed by changing the fuel rods. Otherwise, the concentration of these fission products would increase and absorb more neutrons until the reactor could no longer operate.

Spent fuel rods contain a variety of products, consisting of unstable nuclei ranging in atomic number from 25 to 60, some transuranium elements, including plutonium and americium, and unreacted uranium isotopes. The unstable nuclei and the transuranium isotopes give the spent fuel a dangerously high level of radioactivity. The long-lived isotopes require thousands of years to decay to a safe level. The ultimate fate of the nuclear reactor as a significant source of energy in the United States probably rests on whether or not a politically and scientifically satisfactory technique for processing and storing the components of spent fuel rods can be developed.

Nuclear Fusion

The process of converting very light nuclei into heavier nuclei is also accompanied by the conversion of mass into large amounts of energy, a process called fusion. The principal source of energy in the sun is a net fusion reaction in which four hydrogen nuclei fuse and produce one helium nucleus and two positrons. This is a net reaction of a more complicated series of events:

$$4\,{}^{1}_{1}\mathrm{H} \longrightarrow {}^{4}_{2}\mathrm{He} + 2\,{}^{0}_{+1} \tag{11.9.2}$$

A helium nucleus has a mass that is 0.7% less than that of four hydrogen nuclei; this lost mass is converted into energy during the fusion. This reaction produces about 3.6×10^{11} kJ of energy per mole of ${}^{4}_{2}\mathrm{He}$ produced. This is somewhat larger than the energy produced by the nuclear fission of one mole of U-235 (1.8×10^{10} kJ), and over 3 million times larger than the energy produced by the (chemical) combustion of one mole of octane (5471 kJ).

It has been determined that the nuclei of the heavy isotopes of hydrogen, a deuteron, ${}^{2}_{1}$ and a triton, ${}^{3}_{1}$, undergo fusion at extremely high temperatures (thermonuclear fusion). They form a helium nucleus and a neutron:

$${}^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \longrightarrow {}^{4}_{2}\mathrm{He} + 2\,{}^{1}_{0}\mathrm{n} \tag{11.9.3}$$

This change proceeds with a mass loss of 0.0188 amu, corresponding to the release of 1.69×10^{9} kilojoules per mole of ${}^{4}_{2}\mathrm{He}$ formed. The very high temperature is necessary to give the nuclei enough kinetic energy to overcome the very strong repulsive forces resulting from the positive charges on their nuclei so they can collide.

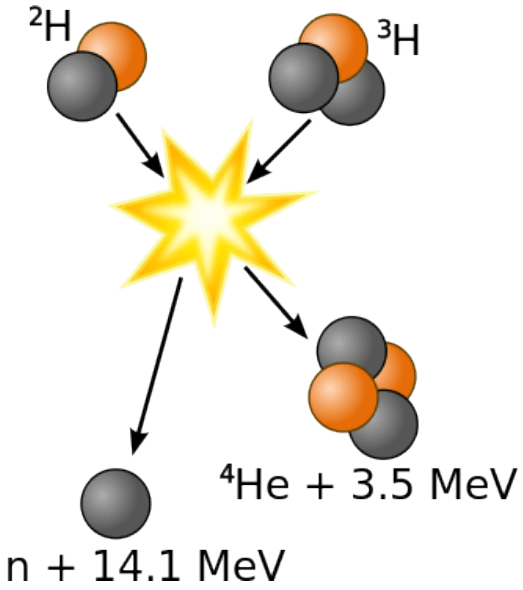


Figure 11.9.6: Fusion of deuterium with tritium creating helium-4, freeing a neutron, and releasing 17.59 MeV of energy, as an appropriate amount of mass changing forms to appear as the kinetic energy of the products, in agreement with kinetic $E = \Delta mc^2$, where Δm is the change in rest mass of particles.[Image use with permission via Wikipedia (Wykis)

The most important fusion process in nature is the one that powers stars. In the 20th century, it was realized that the energy released from nuclear fusion reactions accounted for the longevity of the Sun and other stars as a source of heat and light. The fusion of nuclei in a star, starting from its initial hydrogen and helium abundance, provides that energy and synthesizes new nuclei as a byproduct of that fusion process. The prime energy producer in the Sun is the fusion of hydrogen to form helium, which occurs at a solar-core temperature of 14 million kelvin. The net result is the fusion of four protons into one alpha particle, with the release of two positrons, two neutrinos (which changes two of the protons into neutrons), and energy (Figure 11.9.7).

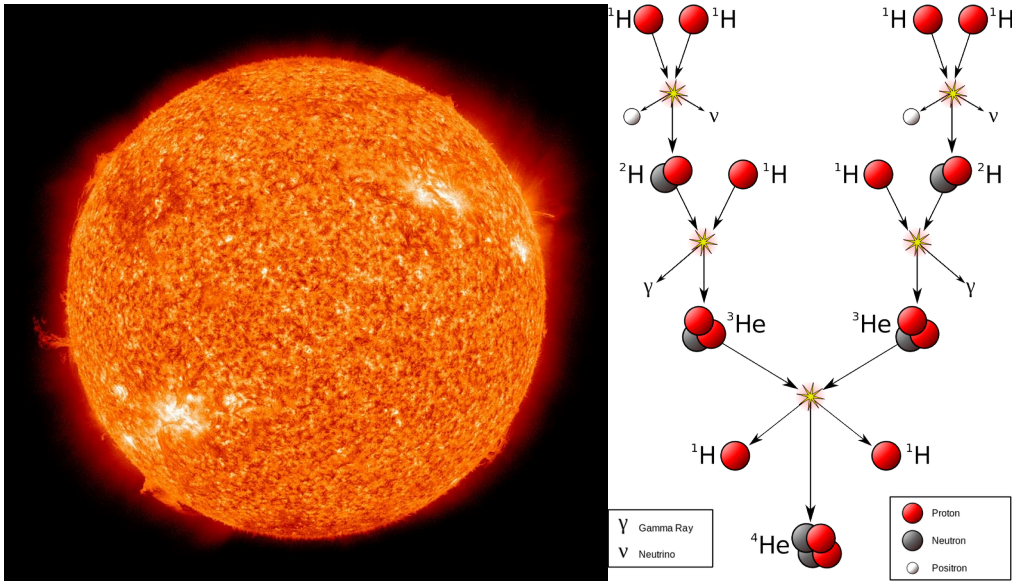


Figure 11.9.7: (left) The Sun is a main-sequence star, and thus generates its energy by nuclear fusion of hydrogen nuclei into helium. In its core, the Sun fuses 620 million metric tons of hydrogen each second. (right) The proton-proton chain dominates in stars the size of the Sun or smaller.

Example 11.9.1

Calculate the energy released in each of the following hypothetical processes.

a. $3\,{}^{4}_{2}\mathrm{He} \rightarrow {}^{12}_{6}\mathrm{C}$
b. $6\,{}^{1}_{1}\mathrm{H} + 6\,{}^{1}_{0}\mathrm{n} \rightarrow {}^{12}_{6}\mathrm{C}$
c. $6\,{}^{2}_{1}\mathrm{D} \rightarrow {}^{12}_{6}\mathrm{C}$

Solution

a. $Q_a = 3 \times 4.0026 - 12.000)\ amu \times (1.4924 \times 10^{-10}\ J/amu) = 1.17 \times 10^{-12}\ J$
b. $Q_b = (6 \times (1.007825 + 1.008665) - 12.00000)\ amu \times (1.4924 \times 10^{1-0} J/amu) = 1.476 \times 10^{-11}\ J$
c. $Q_c = 6 \times 2.014102 - 12.00000\ amu \times (1.4924 \times 10^{-10}\ J/amu) = 1.263 \times 10^{-11}\ J$

Fusion of He to give C releases the least amount of energy, because the fusion to produce He has released a large amount. The difference between the second and the third is the binding energy of deuterium. The conservation of mass-and-energy is well illustrated in these calculations. On the other hand, the calculation is based on the conservation of mass-and-energy.

Nuclear Reactors

Useful fusion reactions require very high temperatures for their initiation—about 15,000,000 K or more. At these temperatures, all molecules dissociate into atoms, and the atoms ionize, forming plasma. These conditions occur in an extremely large number of locations throughout the universe—stars are powered by fusion. Humans have already figured out how to create temperatures high enough to achieve fusion on a large scale in thermonuclear weapons. A thermonuclear weapon such as a hydrogen bomb contains a nuclear fission bomb that, when exploded, gives off enough energy to produce the extremely high temperatures necessary for fusion to occur.

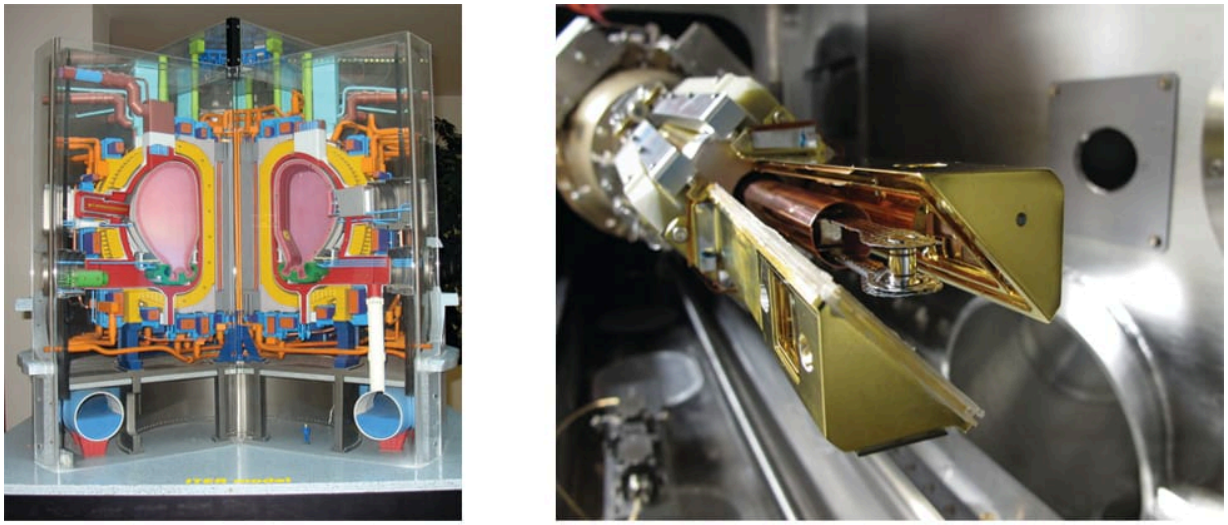


Figure 11.9.8: (a) This model is of the International Thermonuclear Experimental Reactor (ITER) reactor. Currently under construction in the south of France with an expected completion date of 2027, the ITER will be the world's largest experimental Tokamak nuclear fusion reactor with a goal of achieving larg\times 10^{scale sustained energy production. (b) In 2012, the National Ignition Facility at Lawrence Livermore National Laboratory briefly produced over 500,000,000,000 watts (500 terawatts, or 500 TW) of peak power and delivered 1,850,000 joules (1.85 MJ) of energy, the largest laser energy ever produced and 1000 times the power usage of the entire United States in any given moment. Although lasting only a few billionths of a second, the 192 lasers attained the conditions needed for nuclear fusion ignition. This image shows the target prior to the laser shot. (credit a: modification of work by Stephan Mosel)

Another much more beneficial way to create fusion reactions is in a fusion reactor, a nuclear reactor in which fusion reactions of light nuclei are controlled. Because no solid materials are stable at such high temperatures, mechanical devices cannot contain the plasma in which fusion reactions occur. Two techniques to contain plasma at the density and temperature necessary for a fusion reaction are currently the focus of intensive research efforts: containment by a magnetic field and by the use of focused laser beams (Figure 11.9.8). A number of large projects are working to attain one of the biggest goals in science: getting hydrogen fuel to ignite and produce more energy than the amount supplied to achieve the extremely high temperatures and pressures that are required for fusion. At the time of this writing, there are no self-sustaining fusion reactors operating in the world, although small-scale controlled fusion reactions have been run for very brief periods.

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12: INTRODUCTION TO ORGANIC CHEMISTRY - ALKANES

12.1: The Nature of Organic Molecules
12.2: Families of Organic Molecules - Functional Groups
12.3: The Structure of Organic Molecules - Alkanes and Their Isomers
12.4: Drawing Organic Structures
12.5: The Shapes of Organic Molecules
12.6: Naming Alkanes
12.7: Properties of Alkanes
12.8: Reactions of Alkanes
12.9: Cycloalkanes
12.10: Drawing and Naming Cycloalkanes

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12.1: The Nature of Organic Molecules

Learning Objectives

- Describe the basic structural properties of simple organic molecules.

Organic chemistry is the study of the chemistry of carbon-containing 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.

Structural Properties of Carbon Compounds

A carbon atom has four valence electrons, it is **tetravalent**. Carbon can form four *covalent* bonds, or *share electrons with* up to four atoms in order to gain a complete octet. The simplest carbon compounds contain only carbon and hydrogen and are called **hydrocarbons**. Methane, the simplest hydrocarbon, contains a single carbon with four covalently bonded hydrogen atoms. Recalling what you have learned about molecular structures and VSEPR, we know that methane is **tetrahedral** (four electron groups and no lone pairs).

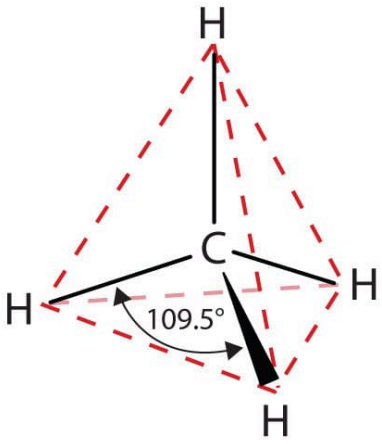
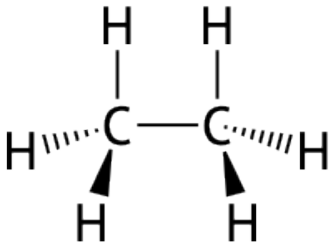
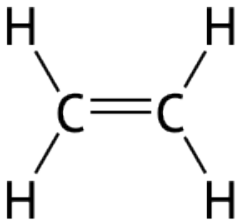


Figure 12.1.1: The Tetrahedral Methane Molecule

Carbon can also form **double bonds** by sharing *four electrons* with a neighboring carbon atom or **triple bonds** by sharing *six electrons* with a neighboring carbon atom. As shown in Figure 12.1.2 below, carbon with three electron groups attached will be **trigonal planar**, and carbon with two electron groups attached will be **linear**.



ethane
C_2H_6



ethene
C_2H_4



ethyne
C_2H_2

Figure 12.1.2: Two carbons can be attached together in single bond, a double bond, or a triple bond. Notice, in each example carbon makes four total bonds. The number of hydrogen atoms in each molecule decreases as the number of carbon–carbon bonds increase.

Simple hydrocarbon compounds are *nonpolar* due to the shape and the small electronegativity difference between carbon and hydrogen atoms. When carbon is bonded to a halogen or oxygen atom, the resulting bond is *polar*. It may be useful to review the section on electronegativity and polarity of bonds and molecules to be able to describe the properties of different organic compounds, specifically how they react and interact with other molecules.

Comparing Organic and Inorganic Compounds

Organic compounds, like inorganic compounds, obey all the natural laws. Often there is no clear distinction in the chemical or physical properties among organic and inorganic molecules. Nevertheless, it is useful to compare typical members of each class, as in Table 12.1.1. Keep in mind, however, that there are exceptions to every category in this table.

Table 12.1.1: Contrasting Properties and Examples of Organic and Inorganic Compounds

Organic Properties	Example: Hexane	Inorganic Properties	Example: NaCl
low melting points	−95°C	high melting points	801°C
low boiling points	69°C	high boiling points	1,413°C
low solubility in water; high solubility in nonpolar solvents	insoluble in water; soluble in gasoline	greater solubility in water; low solubility in nonpolar solvents	soluble in water; insoluble in gasoline
flammable	highly flammable	nonflammable	nonflammable
aqueous solutions do not conduct electricity	nonconductive	aqueous solutions conduct electricity	conductive in aqueous solution
exhibit covalent bonding	covalent bonds	exhibit ionic bonding	ionic bonds

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12.2: Families of Organic Molecules - Functional Groups

Learning Objectives

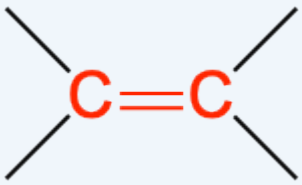
- Identify and describe functional groups in organic molecules.

Organic molecules can be classified into *families* based on structural similarities. Within a family, molecules have similar physical behavior and often have predictable chemical reactivity. The structural components differentiating different organic families involve specific arrangements of atoms or bonds, called **functional groups**. If you understand the behavior of a particular functional group, you can describe the general properties of that class of compounds.

The simplest organic compounds are in the **alkane** family and contain only carbon–carbon and carbon–hydrogen *single* bonds but do not have any specific functional group. Hydrocarbons containing at least one carbon–carbon double bond, (denoted C=C), are in the **alkene** family. **Alkynes** have at least one carbon–carbon triple bond (C≡C). Both carbon–carbon double bonds and triple bonds chemically react in specific ways that differ from reactions of alkanes and each other, making these specific functional groups.

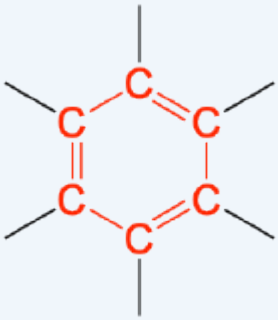
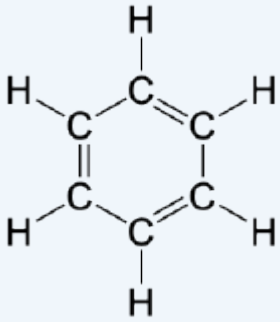
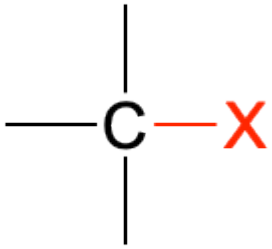
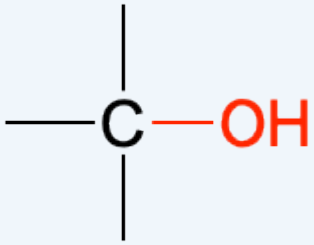
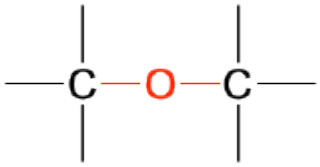
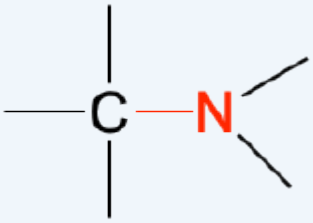
In the next few chapters, we will learn more about additional functional groups that are made up of atoms or groups of atoms attached to hydrocarbons. Being able to recognize different functional groups will help to understand and describe common medications and biomolecules such as amino acids, carbohydrates, and fats. Table 12.2.1 and Figure 12.2.1 below list several of the functional groups to become familiar with as you learn about organic chemistry.

Table 12.2.1: Organic Families and Functional Groups

Family Name	Functional Group Structure	Simple Example Structure	Simple Example Name
alkane	none	$CH_3CH_2CH_3$	propane
alkene		$H_2C{=}CH_2$	ethene (ethylene)
alkyne		HC≡CH	ethyne (acetylene)

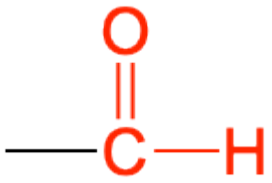
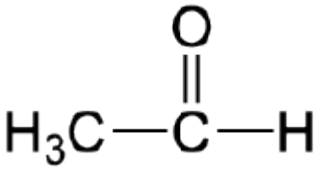
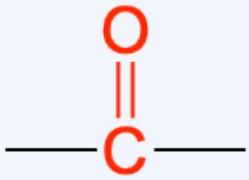
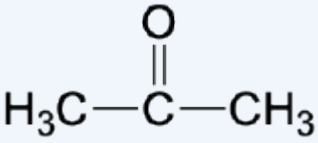
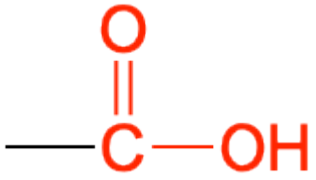
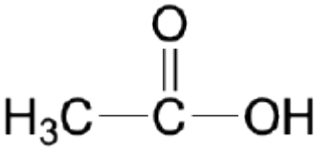
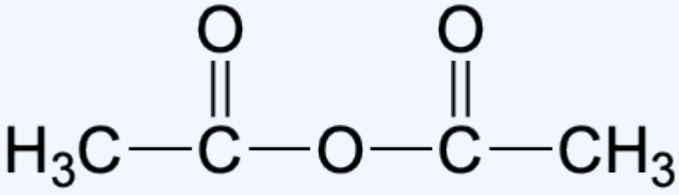
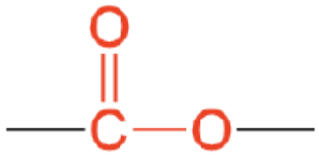
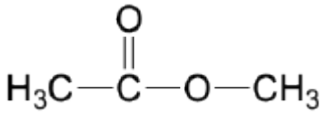
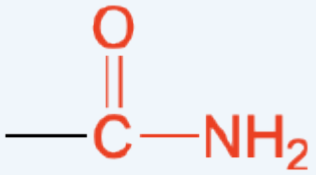
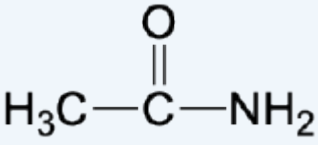
Atoms and bonds in red indicate the functional group. Bonds not specified are attached to R groups (carbons and hyd

***Ethers do not have a suffix in their common name; all ethers end with the word *ether*.**

Family Name	Functional Group Structure	Simple Example Structure	Simple Example Name
aromatic			benzene
alkyl halide	 (X = F, Cl, Br, I)	CH_3CH_2Cl	chloroetha
alcohol		CH_3CH_2OH	ethanol
ether		$CH_3CH_2–O–CH_2CH_3$	diethyl eth
amine		$CH_3CH_2NH_2$	ethylamine

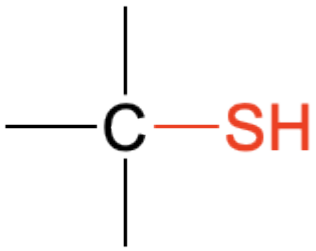
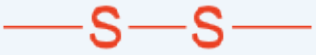
Atoms and bonds in red indicate the functional group. Bonds not specified are attached to R groups (carbons and hyd

***Ethers do not have a suffix in their common name; all ethers end with the word *ether*.**

Family Name	Functional Group Structure	Simple Example Structure	Simple Example Name
aldehyde			ethanal
ketone			propanone (acetone)
carboxylic acid			ethanoic acid (aceti acid)
anhydride			acetic anhydride
ester			methyl ethanoate (methyl acetate)
amide			acetamide

Atoms and bonds in red indicate the functional group. Bonds not specified are attached to R groups (carbons and hyd

***Ethers do not have a suffix in their common name; all ethers end with the word *ether*.**

Family Name	Functional Group Structure	Simple Example Structure	Simple Example Name
thiol		CH_3CH_2SH	ethanethio
disulfide		$CH_3S–SCH_3$	dimethyl disulfide
sulfide		$CH_3CH_2SCH_3$	ethyl meth sulfide

Atoms and bonds in red indicate the functional group. Bonds not specified are attached to R groups (carbons and hyd

***Ethers do not have a suffix in their common name; all ethers end with the word *ether*.**

Organic-Functional-Groups-2016_24ee.pdfOrganic-Functional-Groups-2016.pdf

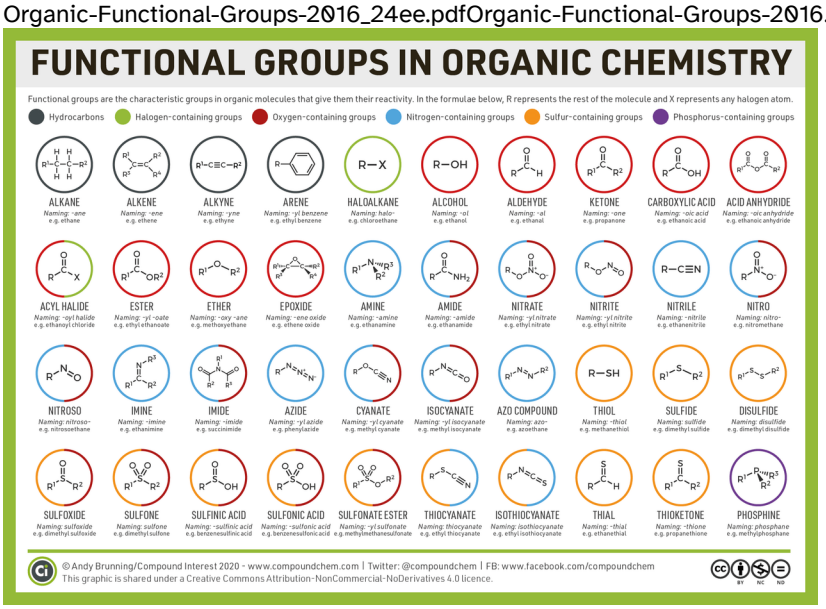


Figure 12.2.1: Functional groups in organic chemistry. (CC BY-NC-ND, CompoundChem.com).

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12.3: The Structure of Organic Molecules - Alkanes and Their Isomers

Learning Objectives

- To identify simple alkanes as straight-chain or branched-chain.
- Describe and recognize structural and functional group isomers.

As you just learned, there is a wide variety of organic compounds containing different functional groups. However, all organic compounds are hydrocarbons, they contain hydrogen and carbon. The general rule for hydrocarbons is that any carbon must be bonded to at least one other carbon atom, except in the case of methane which only contains one carbon. The bonded carbons form the *backbone* of the molecule to which the hydrogen atoms (or other functional groups) are attached.

Hydrocarbons with only carbon-to-carbon single bonds (C–C) are called **alkanes** (or saturated hydrocarbons). *Saturated*, in this case, means that each carbon atom is bonded to four other atoms (hydrogen or carbon)—the most possible; there are no double or triple bonds in these molecules.

> Saturated fats and oils are organic molecules that do not have carbon-to-carbon double bonds (C=C).

The three simplest alkanes—methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) shown in Figure 12.3.1, are the beginning of a series of compounds in which any two members in a sequence differ by one carbon atom and two hydrogen atoms—namely, a CH_2 unit (called methylene). Alkanes follow the general formula: C_nH_{2n+2}. Using this formula, we can write a molecular formula for any alkane with a given number of carbon atoms. For example, an alkane with eight carbon atoms has the molecular formula $C_8H_{(2 \times 8) + 2} = C_8H_{18}$.

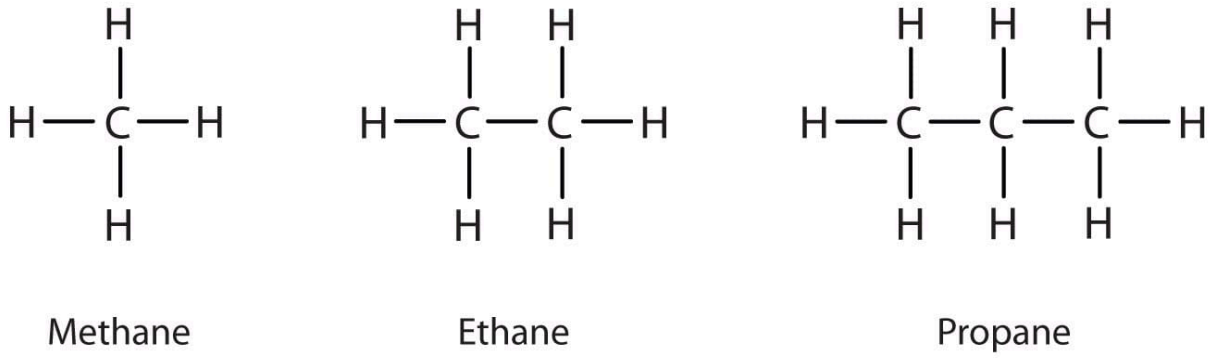


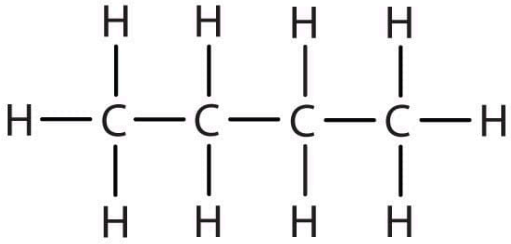
Figure 12.3.1: The Three Simplest Alkanes

Isomers

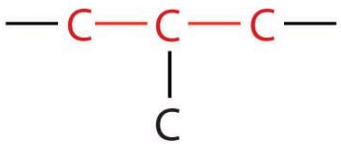
Alkanes that contain one continuous chain of linked carbons are called **straight-chain** alkanes. As the number of carbons in a chain increases beyond three, the arrangement of atoms can expand to include **branched-chain** alkanes. In a branched chain, one or more hydrogen atoms along the chain is replaced by a carbon atom (or a separate chain of carbon atoms). It is important to note that while the structural arrangement of these chains are different, continuous versus branched, they both still follow the same general formula for alkanes as introduced above, C_nH_{2n+2}. In fact, alkane chains that have the same molecular formula (same number of carbon and hydrogen), but a different arrangement of atoms, are called **isomers**. Let's look at an example below:

The structure of butane (C_4H_{10}) is written by stringing four carbon atoms in a row, and then adding enough hydrogen atoms to

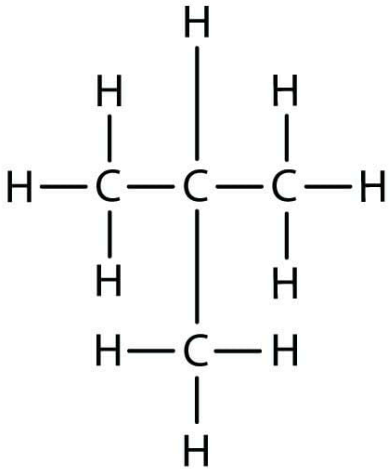
give each carbon atom four bonds:



Butane is a straight-chain alkane, 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 carbon off the middle carbon atom:



Now we add enough hydrogen atoms to give each carbon four bonds:



The result is the isomer 2-methylpropane (also called isobutane), which is a branched-chain alkane with the same formula as butane, (C_4H_{10}). However, it is a *different* molecule with a *different* name and *different* chemical properties. A side-by-side comparison of these two molecules is shown in the below figure.

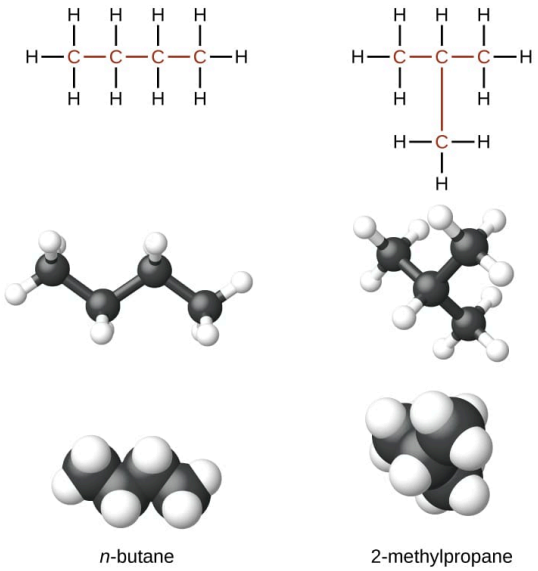


Figure 12.3.1: n-butane and 2-methylpropane. The compounds *n*-butane and 2-methylpropane are structural isomers, meaning they have the same molecular formula, C_4H_{10}, but different spatial arrangements of the atoms in their molecules. We use the term *normal*, or the prefix *n*, to refer to a chain of carbon atoms without branching.

The four-carbon straight chain butane may be drawn with different bends or kinks in the backbone (Figure 12.3.2) because the groups can rotate freely about the C–C bonds. This rotation or bending of the carbon chain does *not* change the identity of the compound; all of the following structures represent the *same* compound, butane, with different bends in the chain:

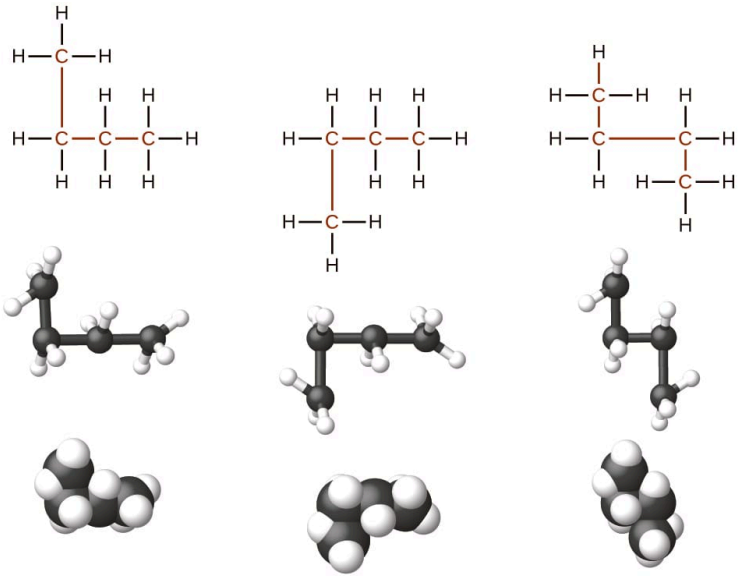
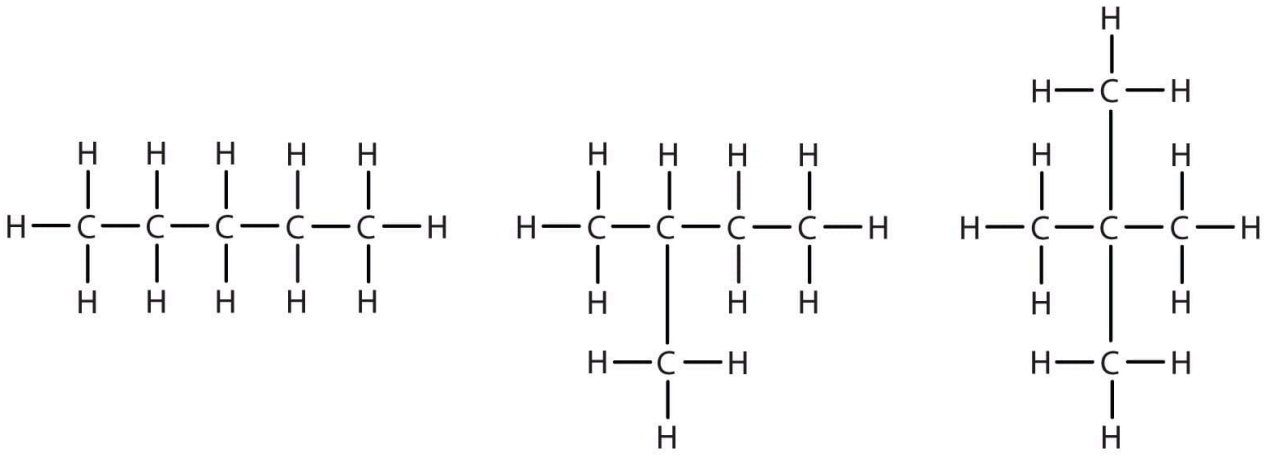


Figure 12.3.2: These three representations of the structure of n-butane are not isomers because they all contain the same arrangement of atoms and bonds.

When identifying isomers, it is useful to trace the carbon backbone with your finger or a pencil and count carbons until you need to lift your hand or pencil to get the another carbon. Try this with each of the above arrangements of four carbons, then do the same with 2-methylpropane. Butane has a continuous chain of four carbons no matter how the bonds are rotated – you can connect the carbons in a line without lifting your finger from the page. How many continuous carbons are in the 2-methylpropane backbone? You should be able to count a continuous chain of three carbon atoms only, with the fourth carbon attached as a branch, (compare the two structures in Figure 12.3.1). In a later chapter, you will learn how to systematically name compounds by counting the number of carbons in the longest continuous chain and identifying any functional groups present.

Adding one more carbon to the butane chain gives pentane, which has the formula, C_5H_{12}. Pentane and its two branched-chain isomers are shown below. The compound at the far left is pentane because it has all five carbon atoms in a continuous

chain. The compound in the middle is isopentane; like isobutane, it has a one CH_3 branch off the second carbon atom of the continuous chain. The compound at the far right, discovered after the other two, was named neopentane (from the Greek *neos*, meaning "new"). Although all three have the same molecular formula, they have different properties, including boiling points: pentane, 36.1°C; isopentane, 27.7°C; and neopentane, 9.5°C. The names isopentane and neopentane are common names for these molecules. As mentioned above, we will learn the systematic rules for naming compounds in later chapters.



Pentane Isopentane Neopentane

A continuous (unbranched) chain of carbon atoms is often called a *straight chain* even though the tetrahedral arrangement about each carbon gives it a zigzag shape. Straight-chain alkanes are sometimes called *normal alkanes*, and their names are given the prefix *n*-. For example, butane is called *n*-butane. We will not use that prefix here because it is not a part of the system established by the International Union of Pure and Applied Chemistry.

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12.4: Drawing Organic Structures

Learning Objectives

- Draw condensed structures and line structures for simple compounds from the given molecular formulas.
- Convert between expanded, condensed and line structures.

We use several kinds of formulas to describe organic compounds. A *molecular formula* shows only the number and type 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 2-methylpropane. A structural formula shows all the carbon and hydrogen atoms and the bonds attaching them (**expanded structure**). This type of structure allows for easy identification of specific isomers by showing the order of attachment of the various atoms.

Unfortunately, structural formulas that show the bonds between *all* atoms are sometimes difficult to type/write and take up a lot of space, especially when the number of atoms greatly increases. Chemists often use **condensed structures**, that show hydrogen atoms right next to the carbon atoms to which they are attached, to alleviate these problems. The ultimate condensed formula is a **line (or line-angle) structure**, in which carbon atoms are implied at the corners and ends of lines rather than written out, and each carbon atom is understood to be attached to the appropriate amount of hydrogen atoms to give each carbon atom four bonds. Parentheses in condensed structural formulas indicate that the enclosed grouping of atoms is attached to the adjacent carbon atom. All three of these structure types are illustrated for butane and its isomer, 2-methylpropane in Figure 12.4.1 below.

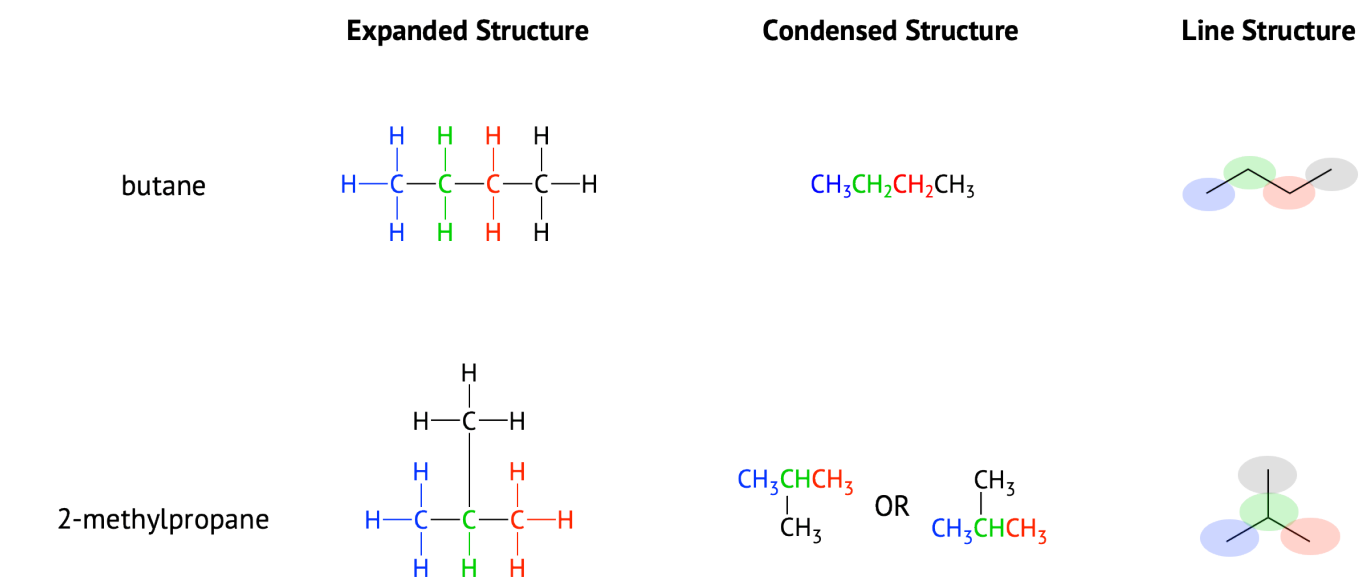


Figure 12.4.1: Structural representations for butane and its isomer, 2-methylpropane. (The colors are used to help identify carbons and do not represent any special properties.)

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12.5: The Shapes of Organic Molecules



Maps take some time to build because we have to find or write matching materials. LibreTexts POV is that it is best to make available pages that we have finished rather than wait till the entire project is complete .This map is not completely finished, some pages are missing but we are workin' on it. . . (Public Domain ; Public Domain Pictures)

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12.6: Naming Alkanes

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, etc. It would be difficult to assign each compound unique individual names that we could remember easily. 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 mentioned earlier, such as isobutane, isopentane, and neopentane, do not follow these rules and are called *common names*.)

In the IUPAC system, a compound is named according to the number of carbons in the longest continuous chain (LCC) or parent chain and the family it belongs to. Atoms or groups attached to this carbon chain, called *substituents*, are then named, with their positions indicated by a numerical prefix at the beginning of the name:

Prefix (substituent) – Parent (# carbons) – Suffix (family name)

2-methylpropane

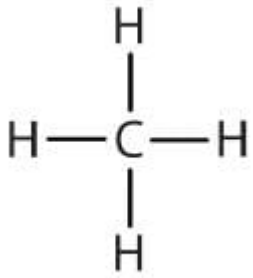
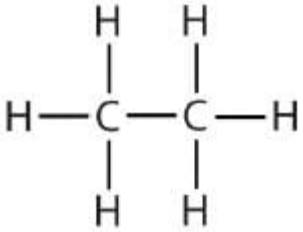
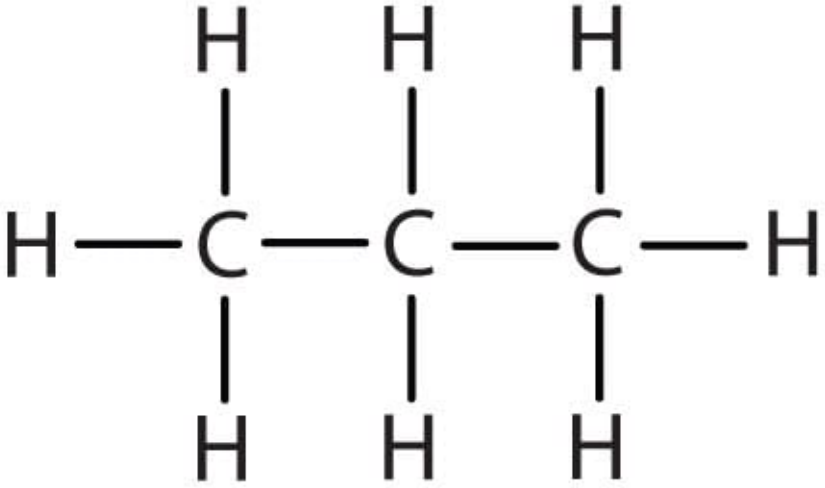
(Table 12.6.1) below lists the IUPAC parent names that are used for charbon chains containing 1 to 10 carbons, along with straight-chain alkane examples for each. Notice that the suffix for each example in this table is *-ane*, which indicates these are members of the alk*ane* family.

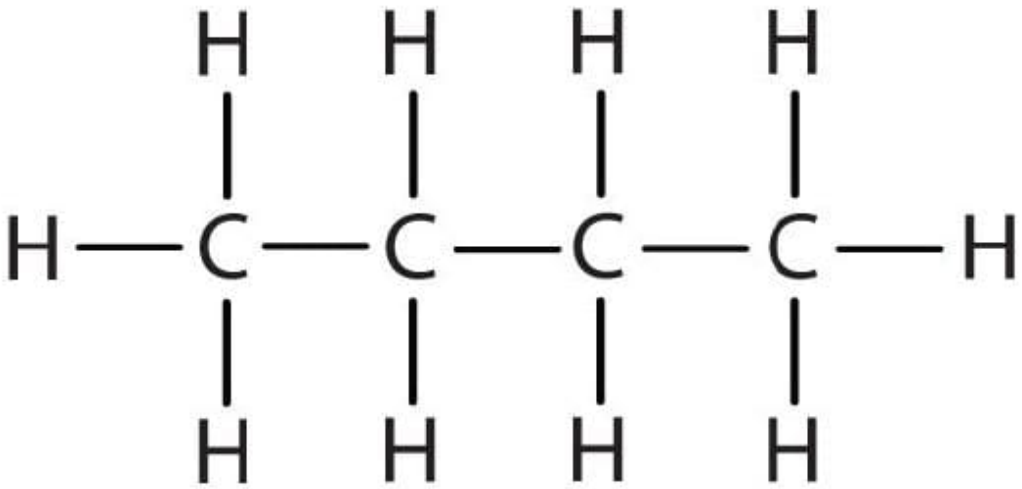
Table 12.6.1: Parent name for 1-10 carbons and Example Alkanes

Number of Carbons	Parent Chain (LCC) Name	Example Alkane Name	Example Condensed Structural Formula
1	*meth-*	methane	CH_4
2	*eth-*	ethane	CH_3CH_3
3	*prop-*	propane	$CH_3CH_2CH_3$
4	*but-*	butane	$CH_3CH_2CH_2CH_3$
5	*pent-*	pentane	$CH_3CH_2CH_2CH_2CH_3$
6	*hex-*	hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$
7	*hept-*	heptane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$
8	*oct-*	octane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
9	*non-*	nonane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
10	*dec-*	decane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

Atoms or groups of atoms that branch off the parent chain are called **substituents**. When the substituent is a carbon or group of carbons, such as $-CH_3$ or $-CH_2CH_3$, it is called an **alkyl group**. Alkyl groups are alkanes that have had one hydrogen removed to allow for binding to a main chain carbon and are 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**. Removing a hydrogen from ethane, CH_3CH_3, gives $-CH_2CH_3$, or the **ethyl group**. The alkyl groups we will use most frequently are listed in Table 12.6.2. Alkyl groups are not independent molecules; they are parts of molecules that we consider as a unit to name compounds systematically.

Table 12.6.2*: Common Alkyl Groups*

Parent Alkane			
methane		methyl	
ethane		ethyl	
propane		propyl	

Parent Alkane			
		isopropyl	
butane		butyl	
		sec-butyl	
		isobutyl	
		tert-butyl (tBu)	

Simplified IUPAC rules for naming alkanes are as follows (demonstrated in Example 12.6.1).

Step 1: **Name the parent chain.** Find the longest continuous chain, (it may not always be the most obvious chain written in one line), and name according to the number of carbon atoms it contains. Add the suffix *-ane* to indicate that the molecule is an alkane. Use Table 12.6.1 as a reference to start, but it is a good idea to commit these to memory.

Step 2: **Number the carbon atoms in the parent chain,** giving carbons with any substituents attached the lowest number possible. These numbers are used to locate where substituents are attached to a main chain.

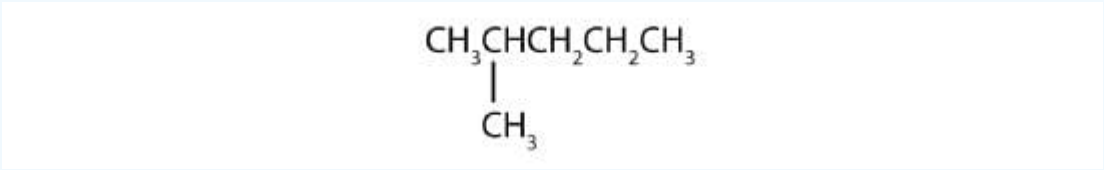
Step 3: **Name any substituents (including the location number).** If the same alkyl group appears more than once, the numbers of all the carbon atoms to which it is attached are expressed. If the same group appears more than once on the same carbon atom, the number of that carbon atom is repeated as 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.

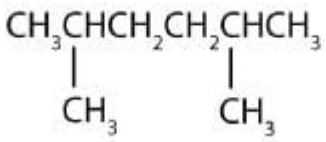
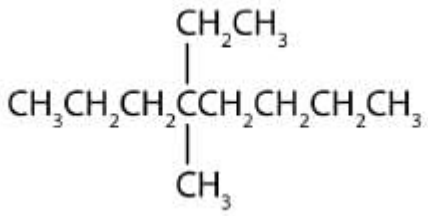
Step 4: **Write the name of the compound as a single word placing the substituent groups first (in alphabetical order), then the parent name, then the family name.** Hyphens are used to separate numbers from the names of substituents; commas separate numbers from each other.

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 practice it, not just memorize the rules. It's easier than it looks.

Example 12.6.1

Name each compound.

1. 

- 
- 

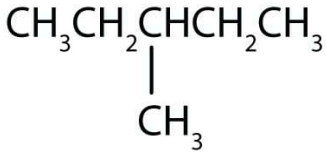
Solution

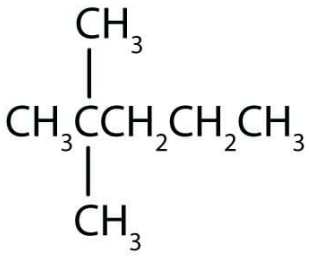
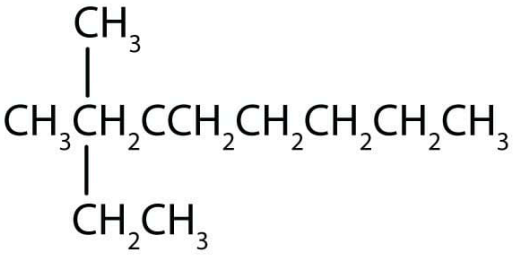
1. Step 1: The LCC has five carbon atoms, and so the parent compound name is pentane. Step 2: Number the carbons in the LCC from left to right. Step 3: There is a methyl group attached to carbon #2 of the pentane chain. Step 4: The name is 2-methylpentane.
2. Step 1: The LCC has six carbon atoms, so the parent compound is hexane. Step 2: Number the carbons in the LCC from left to right (or right to left, either way will be identical numbering). Step 3: There are two methyl groups attached to the second and fifth carbon atoms. Step 4: The name is 2,5-dimethylhexane.
3. Step 1: The LCC has eight carbon atoms, so the parent compound is octane. Step 2: Number the carbons in the LCC from left to right to give the *lower* number. Step 3: There are methyl and ethyl groups, both attached to the fourth carbon atom. Step

4: The correct name is thus 4-ethyl-4-methyloctane.

Exercise 12.6.1

Name each compound.

1. 

- 
- 

Example 12.6.2

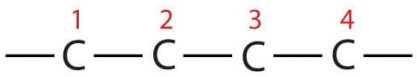
Draw the structure for each compound.

a. 2,3-dimethylbutane
b. 4-ethyl-2-methylheptane

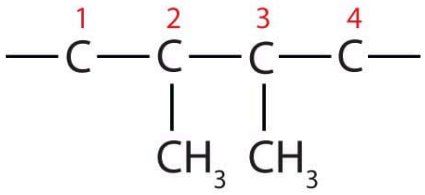
Solution

In drawing structures, always start with the parent chain.

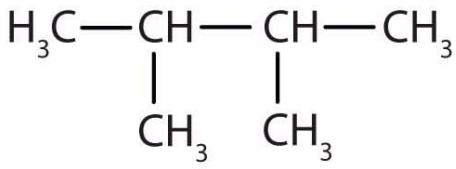
a. The parent chain is butane, indicating four carbon atoms in the LCC.



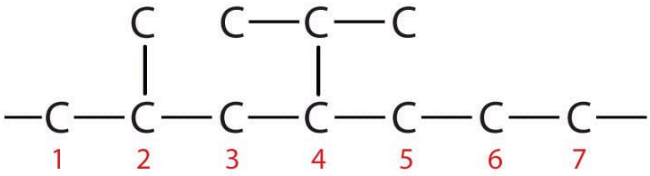
Then add the substituents at their proper positions. You can number the parent chain from either direction as long as you are consistent; just don't change directions before the structure is done. The name indicates two methyl ($-CH_3$) groups, one on the second carbon atom and one on the third.



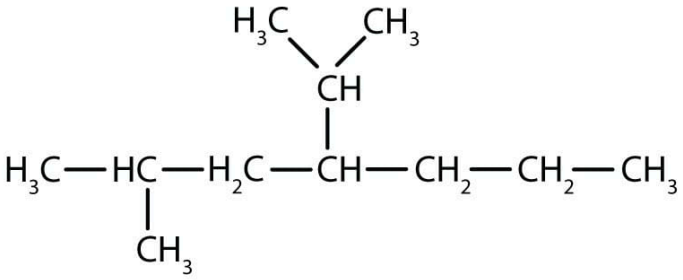
Finally, fill in all the hydrogen atoms, keeping in mind that each carbon atom must have four bonds total.



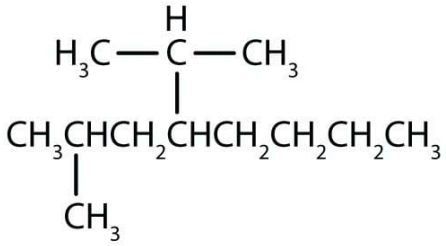
- Adding the substituents at their proper positions gives



Filling in all the hydrogen atoms gives the following condensed structural formulas (both are correct):



or



Note that the bonds (dashes) can be shown or not; sometimes they are needed for spacing.

Exercise 12.6.2

Draw the structure for each compound.

a. 4-ethyloctane
b. 3-ethyl-2-methylpentane
c. 3,3,5-trimethylheptane

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12.7: Properties of Alkanes

Learning Objectives

- To identify the physical properties of alkanes and describe trends in these properties.

Because alkanes have relatively predictable physical properties and undergo relatively few chemical reactions other than combustion, they serve as a basis of comparison for the properties of many other organic compound families. Let's consider their physical properties first.

Table 12.7.1 describes some of the properties of some of the first 10 straight-chain alkanes. Because alkane molecules are nonpolar, they are insoluble in water, which is a polar solvent, but are soluble in nonpolar and slightly polar solvents. Consequently, alkanes themselves are commonly used as solvents for organic substances of low polarity, such as fats, oils, and waxes. Nearly all alkanes have densities less than 1.0 g/mL and are therefore less dense than water (the density of H_2O is 1.00 g/mL at 20°C). These properties explain why oil and grease do not mix with water but rather float on its surface.

Table 12.7.1: Physical Properties of Some Alkanes

Molecular Name	Formula	Melting Point (°C)	Boiling Point (°C)	Density (20°C)*	Physical State (at 20°C)
methane	CH_4	–182	–164	0.668 g/L	gas
ethane	C_2H_6	–183	–89	1.265 g/L	gas
propane	C_3H_8	–190	–42	1.867 g/L	gas
butane	C_4H_{10}	–138	–1	2.493 g/L	gas
pentane	C_5H_{12}	–130	36	0.626 g/mL	liquid
hexane	C_6H_{14}	–95	69	0.659 g/mL	liquid
octane	C_8H_{18}	–57	125	0.703 g/mL	liquid
decane	$C_{10}H_{22}$	–30	174	0.730 g/mL	liquid
***Note the change in units going from gases (grams per liter) to liquids (grams per milliliter). Gas densities are at 1 atm pressure.**					

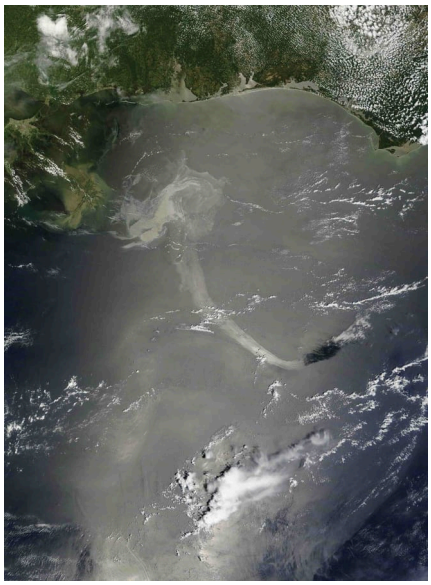


Figure 12.7.1: Oil Spills. Crude oil coats the water's surface in the Gulf of Mexico after the *Deepwater Horizon* oil rig sank following an explosion. The leak was a mile below the surface, making it difficult to estimate the size of the spill. One liter of oil can create a slick 2.5 hectares (6.3 acres) in size. This and similar spills provide a reminder that hydrocarbons and water don't mix. Source: Photo courtesy of NASA Goddard / MODIS Rapid Response Team, NASA.gov, Topics, Earth Features, Oil Spill(opens in new window) [www.nasa.gov].

Looking Closer: Gas Densities and Fire Hazards

Table 12.7.1 indicates that the first four members of the alkane series are gases at ordinary temperatures. Natural gas is composed chiefly of methane, which has a density of about 0.67 g/L. The density of air is about 1.29 g/L. Because natural gas is less dense than air, it rises. When a natural-gas leak is detected and shut off in a room, the gas can be removed by opening an upper window. On the other hand, bottled gas can be either propane (density 1.88 g/L) or butanes (a mixture of butane and isobutane; density about 2.5 g/L). Both are much heavier than air (density 1.2 g/L). If bottled gas escapes into a building, it collects near the floor. This presents a much more serious fire hazard than a natural-gas leak because it is more difficult to rid the room of the heavier gas.

Also shown in Table 12.7.1 are the boiling points of the straight-chain alkanes increase with increasing molar mass. This general rule holds true for the straight-chain homologs of all organic compound families. Larger molecules have greater surface areas and consequently interact more strongly; more energy is therefore required to separate them. For a given molar mass, the boiling points of alkanes are relatively low because these nonpolar molecules have only weak dispersion forces to hold them together in the liquid state.

Looking Closer: An Alkane Basis for Properties of Other Compounds

An understanding of the physical properties of the alkanes is important in that petroleum and natural gas and the many products derived from them—gasoline, bottled gas, solvents, plastics, and more—are composed primarily of alkanes. This understanding is also vital because it is the basis for describing the properties of other organic and biological compound families. For example, large portions of the structures of lipids consist of nonpolar alkyl groups. Lipids include the dietary fats and fatlike compounds called phospholipids and sphingolipids that serve as structural components of living tissues. These compounds have both polar and nonpolar groups, enabling them to bridge the gap between water-soluble and water-insoluble phases. This characteristic is essential for the selective permeability of cell membranes.

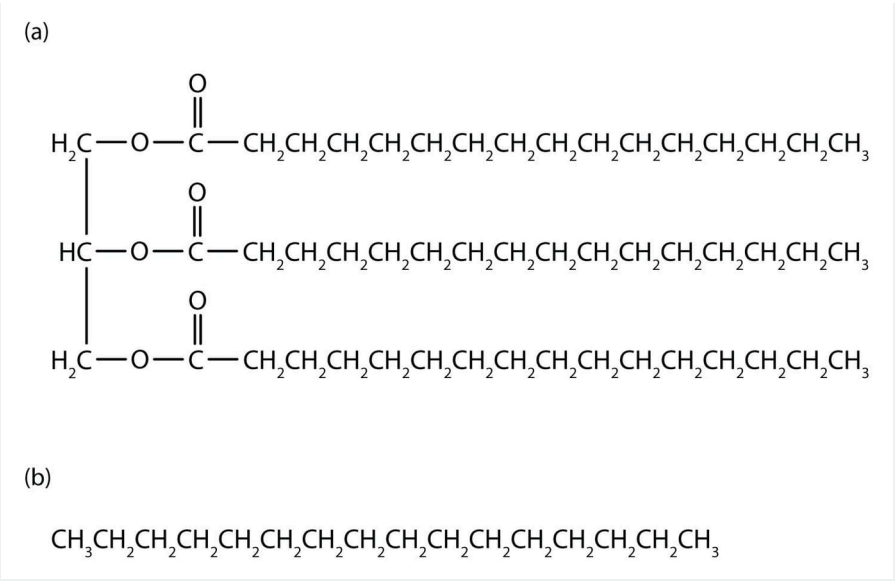


Figure 12.7.2: Tripalmitin (a), a typical fat molecule, has long hydrocarbon chains typical of most lipids. Compare these chains to hexadecane (b), an alkane with 16 carbon atoms

Key Takeaway

- Alkanes are nonpolar compounds that are low boiling and insoluble in water.

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12.8: Reactions of Alkanes

Learning Objectives

- Understand the reactions of alkanes: combustion and halogenation.

Alkanes are relatively stable, nonpolar molecules, that will not react with acids, bases, or oxidizing or reducing reagents. Alkanes undergo so few reactions that they are sometimes called *paraffins*, from the Latin *parum affinis*, meaning “little affinity.”

However, heat or light can initiate the breaking of C–H or C–C single bonds in reactions called **combustion** and **halogenation**.

Combustion

Nothing happens when alkanes are merely mixed with oxygen (O_2) at room temperature, but when a flame or spark provides the activation energy, a highly exothermic combustion reaction proceeds vigorously. For methane (CH_4), the **combustion** reaction is as follows:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + \text{heat} \tag{12.8.1}$$

As a consequence, alkanes are excellent fuels. For example, methane, CH_4, is the principal component of natural gas. Butane, C_4H_{10}, used in camping stoves and lighters is an alkane. Gasoline is a liquid mixture of straight- and branched-chain alkanes, each containing from five to nine carbon atoms, plus various additives to improve its performance as a fuel. Kerosene, diesel oil, and fuel oil are primarily mixtures of alkanes with higher molecular masses. The main source of these liquid alkane fuels is crude oil, a complex mixture that is separated by fractional distillation. Fractional distillation takes advantage of differences in the boiling points of the components of the mixture (Figure 12.8.1). You may recall that boiling point is a function of intermolecular interactions, which was discussed in an earlier chapter.

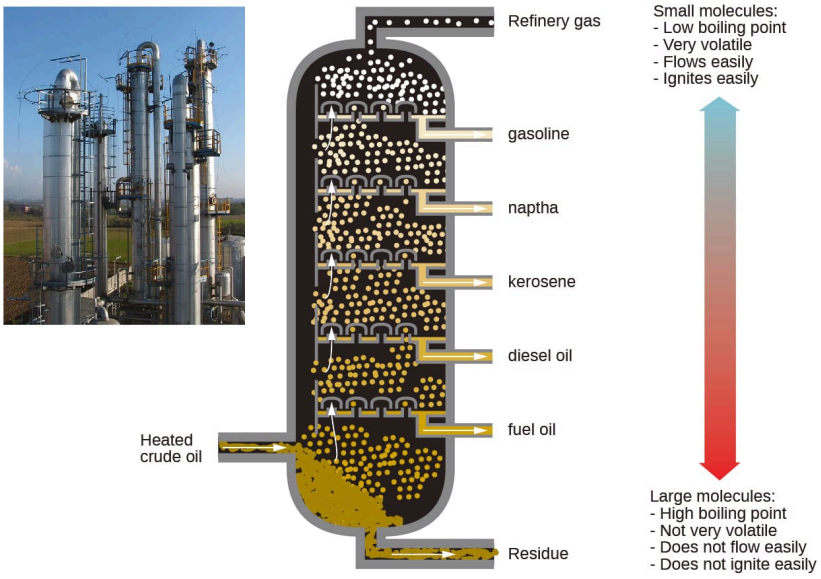


Figure 12.8.1:In a column for the fractional distillation of crude oil, oil heated to about 425 °C in the furnace vaporizes when it enters the base of the tower. The vapors rise through bubble caps in a series of trays in the tower. As the vapors gradually cool, fractions of higher, then of lower, boiling points condense to liquids and are drawn off. (credit left: modification of work by Luigi Chiesa)

If the reactants of combustion reactions are adequately mixed, and there is sufficient oxygen, the only products are carbon dioxide (CO_2), water (H_2O), and energy—heat for cooking foods, heating homes, and drying clothes. Because conditions are rarely ideal, other unwanted by-products are frequently formed. When the oxygen supply is limited, carbon monoxide (CO) is a by-product:

$$2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O \tag{12.8.2}$$

This reaction is responsible for dozens of deaths each year from unventilated or improperly adjusted gas heaters. (Similar reactions with similar results occur with kerosene heaters.)

Halogenation

In **halogenation** reactions, alkanes react with the halogens chlorine (Cl_2) and bromine (Br_2) in the presence of ultraviolet light or at high temperatures to yield chlorinated and brominated alkanes. For example, chlorine reacts with excess methane (CH_4) to give methyl chloride (CH_3Cl).

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl \tag{12.8.3}$$

With more chlorine, a mixture of products is obtained: CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4. Fluorine (F_2), the lightest halogen, combines explosively with most hydrocarbons. Iodine (I_2) is relatively unreactive. Fluorinated and iodinated alkanes are produced by indirect methods.

A wide variety of interesting and often useful compounds have one or more halogen atoms per molecule. For example, methane (CH_4) can react with chlorine (Cl_2), replacing one, two, three, or all four hydrogen atoms with Cl atoms. Several halogenated products derived from methane and ethane (CH_3CH_3) are listed in Table 12.8.1, along with some of their uses.

Table 12.8.1: Some Halogenated Hydrocarbons

Formula	Common Name	IUPAC Name	Some Important Uses
Derived from CH_4			
CH_3Cl	methyl chloride	chloromethane	refrigerant; the manufacture of silicones, methyl cellulose, and synthetic rubber
CH_2Cl_2	methylene chloride	dichloromethane	laboratory and industrial solvent
$CHCl_3$	chloroform	trichloromethane	industrial solvent
CCl_4	carbon tetrachloride	tetrachloromethane	dry-cleaning solvent and fire extinguishers (but no longer recommended for use)
$CBrF_3$	halon-1301	bromotrifluoromethane	fire extinguisher systems
CCl_3F	chlorofluorocarbon-11 (CFC-11)	trichlorofluoromethane	foaming plastics
CCl_2F_2	chlorofluorocarbon-12 (CFC-12)	dichlorodifluoromethane	refrigerant
Derived from CH_3CH_3			
CH_3CH_2Cl	ethyl chloride	chloroethane	local anesthetic
$ClCH_2CH_2Cl$	ethylene dichloride	1,2-dichloroethane	solvent for rubber
CCl_3CH_3	methylchloroform	1,1,1-trichloroethane	solvent for cleaning computer chips and molds for shaping plastics

Note To Your Health: Halogenated Hydrocarbons

Once widely used in consumer products, many chlorinated hydrocarbons are suspected carcinogens (cancer-causing substances) and also are known to cause severe liver damage. An example is carbon tetrachloride (CCl_4), once used as a dry-cleaning solvent and in fire extinguishers but no longer recommended for either use. Even in small amounts, its vapor can cause serious illness if exposure is prolonged. Moreover, it reacts with water at high temperatures to form deadly phosgene ($COCl_2$) gas, which makes the use of CCl_4 in fire extinguishers particularly dangerous.

Ethyl chloride, in contrast, is used as an external local anesthetic. When sprayed on the skin, it evaporates quickly, cooling the area enough to make it insensitive to pain. It can also be used as an emergency general anesthetic.

Bromine-containing compounds are widely used in fire extinguishers and as fire retardants on clothing and other materials. Because they too are toxic and have adverse effects on the environment, scientists are engaged in designing safer substitutes for them, as for many other halogenated compounds.

Note To Your Health: Chlorofluorocarbons and The Ozone Layer

Alkanes substituted with both fluorine (F) and chlorine (Cl) atoms have been used as the dispersing gases in aerosol cans, as foaming agents for plastics, and as refrigerants. Two of the best known of these chlorofluorocarbons (CFCs) are listed in Table 12.8.2.

Chlorofluorocarbons contribute to the greenhouse effect in the lower atmosphere. They also diffuse into the stratosphere, where they are broken down by ultraviolet (UV) radiation to release Cl atoms. These in turn break down the ozone (O_3) molecules that protect Earth from harmful UV radiation. Worldwide action has reduced the use of CFCs and related compounds. The CFCs and other Cl- or bromine (Br)-containing ozone-destroying compounds are being replaced with more benign substances. Hydrofluorocarbons (HFCs), such as CH_2FCF_3, which have no Cl or Br to form radicals, are one alternative. Another is hydrochlorofluorocarbons (HCFCs), such as $CHCl_2CF_3$. HCFC molecules break down more readily in the troposphere, and fewer ozone-destroying molecules reach the stratosphere.

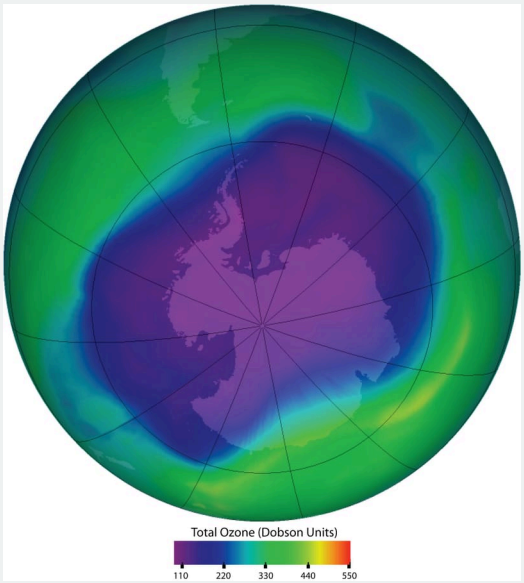


Figure 12.8.2: Ozone in the upper atmosphere shields Earth's surface from UV radiation from the sun, which can cause skin cancer in humans and is also harmful to other animals and to some plants. Ozone "holes" in the upper atmosphere (the gray, pink, and purple areas at the center) are large areas of substantial ozone depletion. They occur mainly over Antarctica from late August through early October and fill in about mid-November. Ozone depletion has also been noted over the Arctic regions. The largest ozone hole ever observed occurred on 24 September 2006. Source: Image courtesy of NASA, http://ozonewatch.gsfc.nasa.gov/daily.php?date=2006-09-24.

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12.9: Cycloalkanes

Learning Objectives

- Identify the structures of cycloalkanes.

A **cyclic hydrocarbon** is a hydrocarbon in which the carbon chain joins to itself in a ring. A **cycloalkane** is a cyclic hydrocarbon in which all of the carbon-carbon bonds are single bonds and each carbon is bonded to two hydrogen atoms, they are saturated compounds. Cycloalkanes have the general formula $\mathrm{C}_n\mathrm{H}_{2n}$. The simplest of these cyclic hydrocarbons, cyclopropane, has the formula C_3H_6, which makes a three-carbon ring.

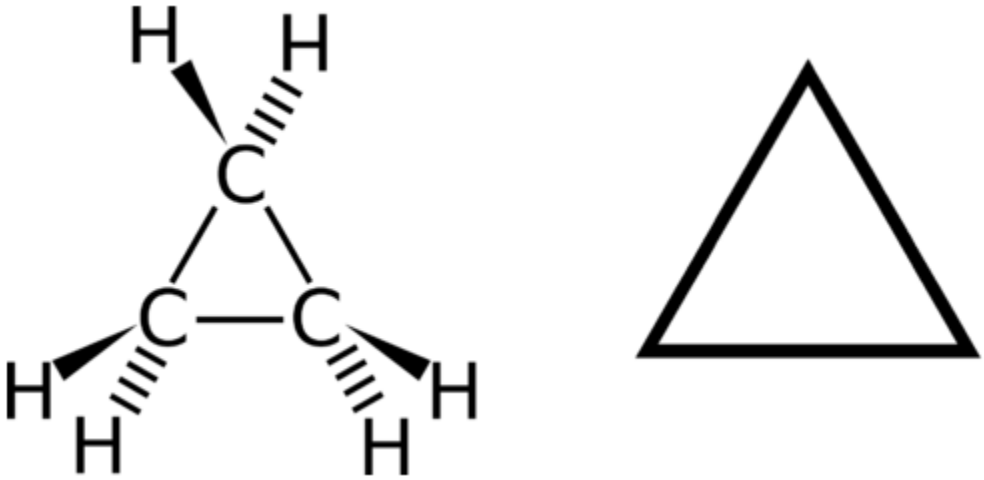
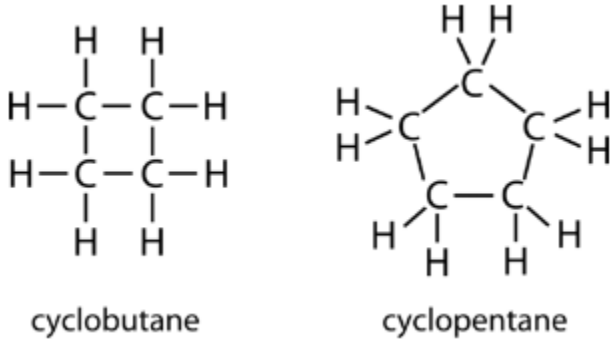


Figure $12.9.1$: Cyclopropane is the simplest cycloalkane. Its highly strained geometry makes it rather unstable and highly reactive.

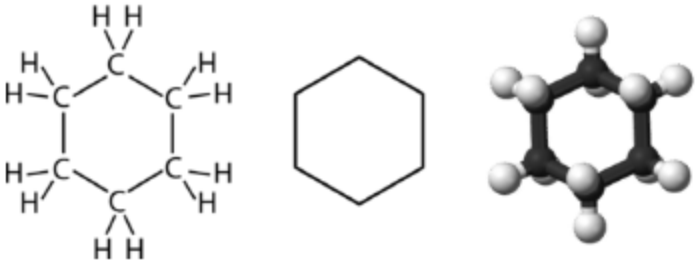
The structural formulas of cyclic hydrocarbons can be represented in multiple ways, two of which are shown above. Each atom can be shown as in the structure on the left from the figure above. A convenient shorthand is to omit the element symbols and only show the shape, as in the triangle on the right. Carbon atoms are understood to be the vertices of the triangle.

The carbon atoms in cycloalkanes have a bond angle of 109.5°. However, an examination of the cyclopropane structure shows that the triangular structure results in a $\mathrm{C{-}C{-}C}$ bond angle of 60°. This deviation from the ideal angle is called ring strain and makes cyclopropane a fairly unstable and reactive molecule. Ring strain is decreased for cyclobutane, with a bond angle of 90°, but is still significant. Cyclopentane has a bond angle of about 108°. This minimal ring strain for cyclopentane makes it a more stable compound.



cyclobutane cyclopentane

Cyclohexane is a six-carbon cycloalkane, shown below.



All three of the depictions of cyclohexane above are somewhat misleading, because the molecule is not planar. In order to reduce the ring strain and attain a bond angle of approximately 109.5°, the molecule is actually puckered.

The ring structure in cycloalkanes also prevents rotation around the carbon–carbon bonds without breaking open the ring, thus they are more rigid and less flexible than acyclic alkanes. This property is called **restricted rotation**.

Note 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.

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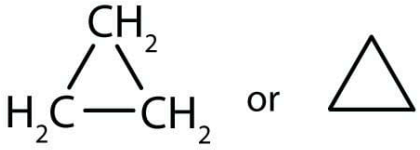
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12.10: Drawing and Naming Cycloalkanes

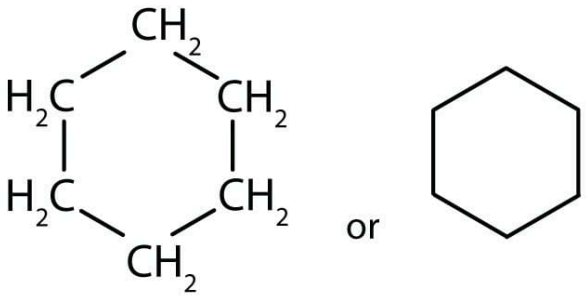
Learning Objectives

- To name cycloalkanes given their formulas and write formulas for these compounds given their names.

The cycloalkanes—cyclic hydrocarbons with only single bonds—are named by adding the prefix *cyclo-* to the name of the open-chain compound having the same number of carbon atoms as there are in the ring. Thus the name for the cyclic compound C_4H_8 is cyclobutane. The carbon atoms in cyclic compounds can be represented by *line-angle formulas* that result in regular geometric figures. Keep in mind, however, that each corner of the geometric figure represents a carbon atom plus as many hydrogen atoms as needed to give each carbon atom four bonds.



cyclopropane



cyclohexane

Some cyclic compounds have substituent groups attached. Example 12.10.1 interprets the name of a cycloalkane with a single substituent group.

Example 12.10.1

Draw the structure for each compound.

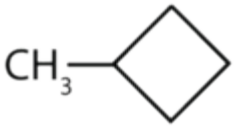
a. cyclopentane
b. methylcyclobutane

Solution

a. The name *cyclopentane* indicates a cyclic (cyclo) alkane with five (pent-) carbon atoms. It can be represented as a pentagon.



- The name *methylcyclobutane* indicates a cyclic alkane with four (but-) carbon atoms in the cyclic part. It can be represented as a square with a CH_3 group attached.



Exercise 12.10.1

Draw the structure for each compound.

a. cycloheptane
b. ethylcyclohexane

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13: ALKENES, ALKYNES, AND AROMATIC COMPOUNDS

13.1: Alkenes and Alkynes
13.2: Naming Alkenes and Alkynes
13.3: The Structure of Alkenes- Cis-Trans Isomerism
13.4: Properties of Alkenes and Alkynes
13.5: Types of Organic Reactions
13.6: Addition Reactions of Alkenes
13.7: Alkene Polymers
13.8: Aromatic Compounds and the Structure of Benzene
13.9: Naming Aromatic Compounds
13.10: Reactions of Aromatic Compounds

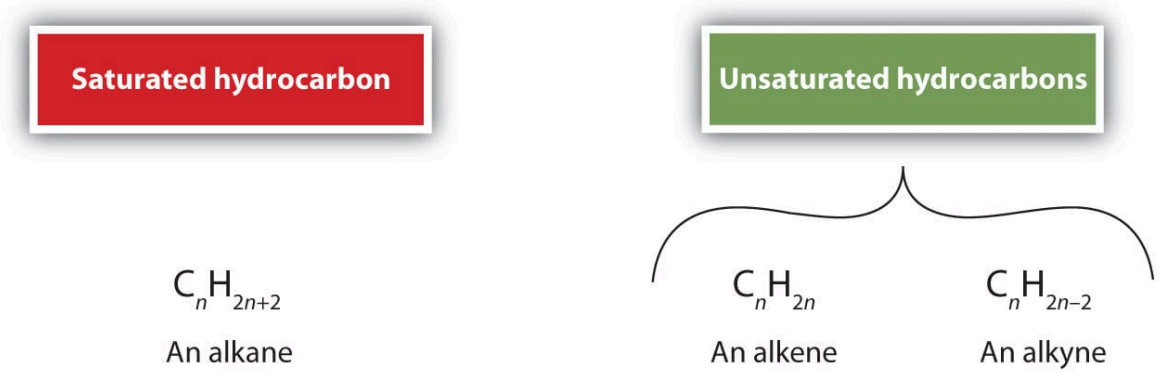
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13.1: Alkenes and Alkynes

Learning Objectives

- Identify the difference between saturated and unsaturated hydrocarbons.
- Describe the functional groups, alkenes and alkynes.

As noted before, **alkenes** are hydrocarbons with carbon-to-carbon double bonds ($R_2C{=}CR_2$) and **alkynes** are hydrocarbons with carbon-to-carbon triple bonds (R–C≡C–R). Collectively, they are called **unsaturated** hydrocarbons because they have fewer hydrogen atoms than does an alkane with the same number of carbon atoms, as is indicated in the following general formulas:



You have likely heard of *unsaturated fats*. These are complex organic molecules with long chains of carbon atoms, which contain at least one double bond between carbon atoms. Double and triple bonds give rise to a different geometry around the carbon atom that participates in them, leading to important differences in molecular shape and properties. The differing geometries are responsible for the different properties of unsaturated versus saturated fats.

Alkenes

Ethene, C_2H_4, is the simplest alkene. Each carbon atom in ethene, commonly called ethylene, has a trigonal planar structure. The second member of the series is propene (propylene) (Figure 13.1.1); the butene isomers follow in the series. Four carbon atoms in the chain of butene allows for the formation of isomers based on the position of the double bond, as well as a new form of isomerism.

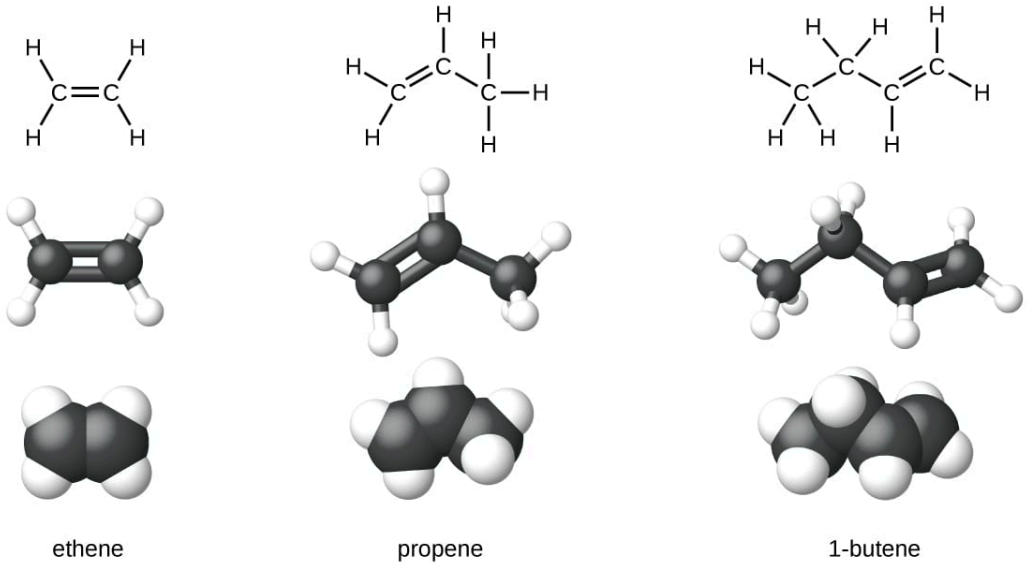


Figure 13.1.6: Expanded structures, ball-and-stick structures, and space-filling models for the alkenes ethene, propene, and 1-butene are shown.

Ethylene (the common industrial name for ethene) is a basic raw material in the production of polyethylene and other important compounds. Over 135 million tons of ethylene were produced worldwide in 2010 for use in the polymer, petrochemical, and plastic industries. Ethylene is produced industrially in a process called cracking, in which the long hydrocarbon chains in a petroleum mixture are broken into smaller molecules.

Alkynes

Hydrocarbon molecules with one or more triple bonds are called **alkynes**; they make up another series of unsaturated hydrocarbons. Two carbon atoms joined by a triple bond have bond angles of 180°, giving these types of bonds a linear shape.

The simplest member of the alkyne series is ethyne, C_2H_2, commonly called acetylene. The Lewis structure for ethyne, a linear molecule, is:



> 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*.

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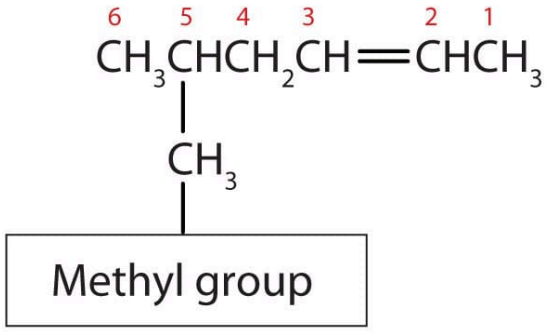
13.2: Naming Alkenes and Alkynes

Learning Objectives

- Objective 1
- Objective 2

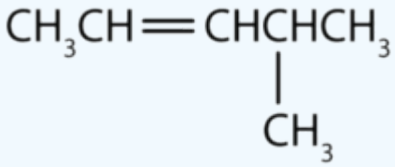
Here are some basic rules for naming alkenes from the International Union of Pure and Applied Chemistry (IUPAC):

1. The longest chain of carbon atoms *containing the double bond* is considered the parent chain. It is named using the same stem as the alkane having the same number of carbon atoms but ends in *-ene* to identify it as an alkene. Thus the compound CH_2=$CHCH_3$ is *propene*.
2. If there are four or more carbon atoms in a chain, we must indicate the position of the double bond. The carbons atoms are numbered so that the first of the two that are doubly bonded is given the lower of the two possible numbers.The compound CH_3CH=$CHCH_2CH_3$, for example, has the double bond between the second and third carbon atoms. Its name is 2-pentene (not 3-pentene).
3. Substituent groups are named as with alkanes, and their position is indicated by a number. Thus, the structure below is 5-methyl-2-hexene. Note that the numbering of the parent chain is always done in such a way as to give the double bond the lowest number, even if that causes a substituent to have a higher number. *The double bond always has priority in numbering.*

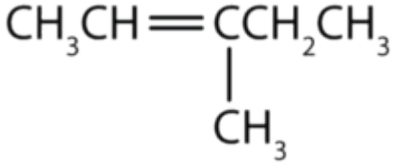


Example 13.2.1

Name each compound.



a.



b.

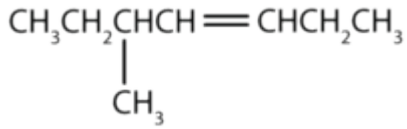
Solution

a. The longest chain containing the double bond has five carbon atoms, so the compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the fourth carbon atom (rule 3), so the compound's name is 4-methyl-2-pentene.
b. The longest chain containing the double bond has five carbon atoms, so the parent compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the third carbon atom (rule 3), so the compound's name is 3-methyl-2-pentene.

Exercise 13.2.1

Name each compound.

1. $CH_3CH_2CH_2CH_2CH_2CH{=}CHCH_3$



Just as there are cycloalkanes, there are *cycloalkenes*. These compounds are named like alkenes, but with the prefix *cyclo-* attached to the beginning of the parent alkene name.

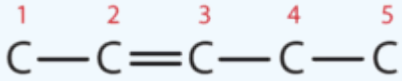
Example 13.2.2

Draw the structure for each compound.

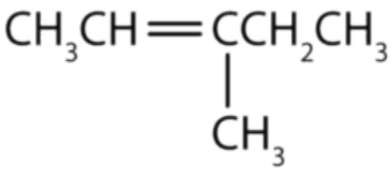
1. 3-methyl-2-pentene
2. cyclohexene

Solution

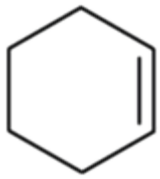
1. First write the parent chain of five carbon atoms: C–C–C–C–C. Then add the double bond between the second and third carbon atoms:



Now place the methyl group on the third carbon atom and add enough hydrogen atoms to give each carbon atom a total of four bonds.



- First, consider what each of the three parts of the name means. *Cyclo* means a ring compound, *hex* means 6 carbon atoms, and *-ene* means a double bond.



Exercise 13.2.2

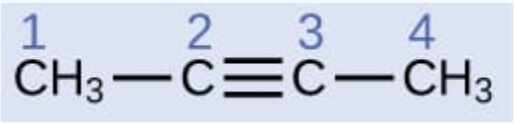
Draw the structure for each compound.

a. 2-ethyl-1-hexene
b. cyclopentene

The IUPAC nomenclature for alkynes is similar to that for alkenes except that the suffix *-yne* is used to indicate a triple bond in the chain. For example, $\mathrm{CH_3CH_2C \equiv CH}$ is called 1-butyne.

Example 13.2.6: Structure of Alkynes

Describe the geometry and hybridization of the carbon atoms in the following molecule:

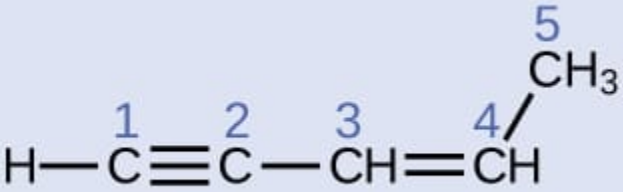


Solution

Carbon atoms 1 and 4 have four single bonds and are thus tetrahedral with sp^3 hybridization. Carbon atoms 2 and 3 are involved in the triple bond, so they have linear geometries and would be classified as *sp* hybrids.

Exercise 13.2.6

Identify the hybridization and bond angles at the carbon atoms in the molecule shown:



Answer available at the end of this section.

Answers

Exercise 13.2.6

carbon 1: *sp*, 180°; carbon 2: *sp*, 180°; carbon 3: sp^2, 120°; carbon 4: sp^2, 120°; carbon 5: sp^3, 109.5°

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13.3: The Structure of Alkenes- Cis-Trans Isomerism

Learning Objectives

- Recognize that alkenes that can exist as cis-trans isomers.
- Classify isomers as cis or trans.
- Draw structures for cis-trans isomers given their names.

There is free rotation about the carbon-to-carbon single bonds (C–C) in alkanes. In contrast, the structure of alkenes requires that the carbon atoms of a double bond and the two atoms bonded to each carbon atom all lie in a single plane, and that each doubly bonded carbon atom lies in the center of a triangle. This part of the molecule's structure is rigid; rotation about doubly bonded carbon atoms is *not* possible without rupturing the bond. Look at the two chlorinated hydrocarbons in Figure 13.3.1.

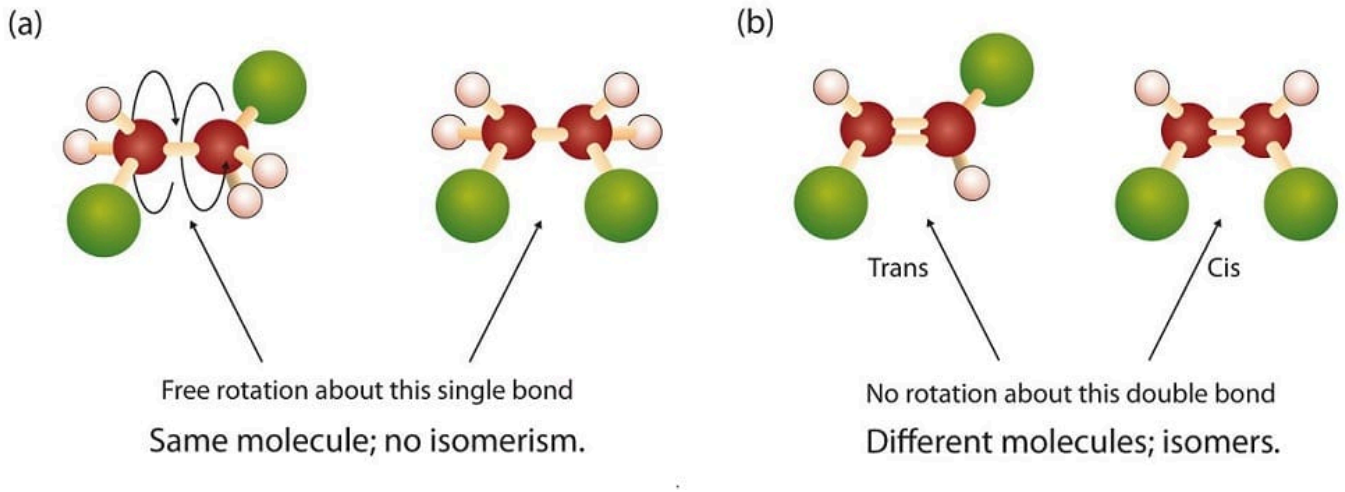


Figure 13.3.1*: Rotation about Bonds. In 1,2-dichloroethane (a), free rotation about the C–C bond allows the two structures to be interconverted by a twist of one end relative to the other. In 1,2-dichloroethene (b), restricted rotation about the double bond means that the relative positions of substituent groups above or below the double bond are significant.*

In 1,2-dichloroethane (part (a) of Figure 13.3.1), 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 13.3.1*b*), however, restricted rotation about the double bond means that the relative positions of substituent groups above or below the double bond become significant. This leads to a special kind of isomerism. The isomer in which the two chlorine (Cl) atoms lie on the same side of the molecule is called the cis isomer (Latin *cis*, meaning "on this side") and is named cis-1,2-dichloroethene. The isomer with the two Cl atoms on opposite sides of the molecule is the trans isomer (Latin *trans*, meaning "across") and is named *trans*-1,2-dichloroethene. These two compounds are cis-trans isomers (or geometric isomers), compounds that have different configurations (groups permanently in different places in space) because of

the presence of a rigid structure in their molecule.

Consider the alkene with the condensed structural formula $CH_3CH=CHCH_3$. We could name it 2-butene, but there are actually two such compounds; the double bond results in cis-trans isomerism (Figure 13.3.2).

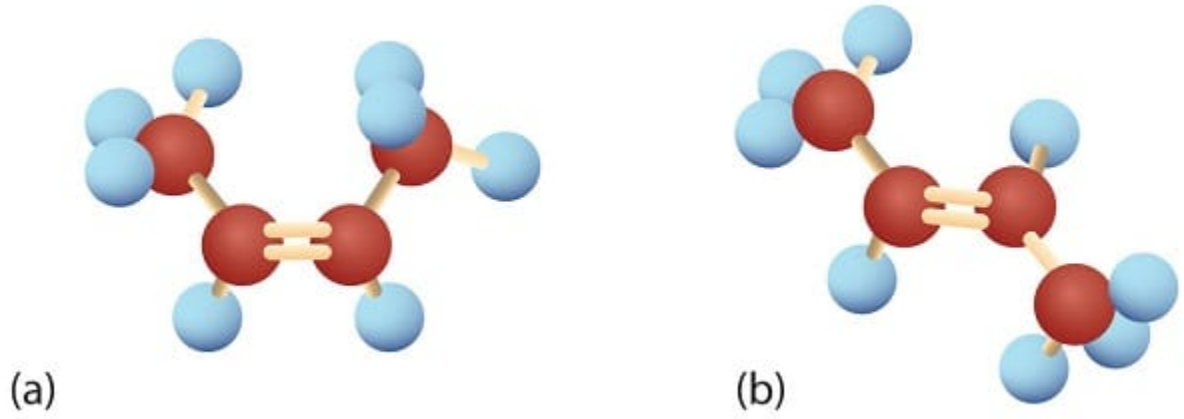


Figure 13.3.2: Ball-and-Spring Models of (a) Cis-2-Butene and (b) Trans-2-Butene. Cis-trans isomers have different physical, chemical, and physiological properties.

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 13.3.3*: Models of (left) Cis-2-Butene and (right) Trans-2-Butene.*

Note, however, that the presence of a double bond does **not** necessarily lead to cis-trans isomerism (Figure 13.3.4). We can draw two *seemingly* different propenes:



Figure 13.3.4*: Different views of the propene molecule (flip vertically). These are not isomers.*

However, these two structures are not really different from each other. If you could pick up either molecule from the page and flip it over top to bottom, you would see that the two formulas are identical. Thus there are two requirements for cis-trans isomerism:

1. Rotation must be restricted in the molecule.
2. There must be **two nonidentical groups** on **each** doubly bonded carbon atom.

In these propene structures, the second requirement for cis-trans isomerism is not fulfilled. One of the doubly bonded carbon

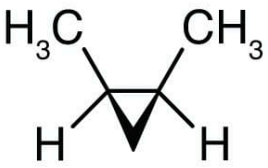
atoms does have two different groups attached, but the rules require that *both* carbon atoms have two different groups. In general, the following statements hold true in cis-trans isomerism:

- Alkenes with a $C=CH_2$ unit do not exist as cis-trans isomers.
- Alkenes with a $C=CR_2$ unit, where the two R groups are the same, do not exist as cis-trans isomers.
- Alkenes of the type R–CH=CH–R can exist as cis and trans isomers; cis if the two R groups are on the same side of the carbon-to-carbon double bond, and trans if the two R groups are on opposite sides of the carbon-to-carbon double bond.

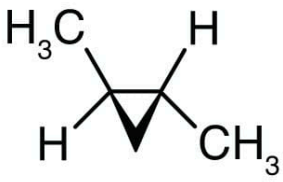
Advanced Note: E/Z Isomerization

If a molecule has a C=C bond with one non-hydrogen group attached to each of the carbons, cis/trans nomenclature descried above is enough to describe it. However, if you have three different groups (or four), then the cis/trans approach is insufficient to describe the different isomers, since we do not know which two of the three groups are being described. For example, if you have a C=C bond, with a methyl group and a bromine on one carbon , and an ethyl group on the other, it is neither trans nor cis, since it is not clear whether the ethyl group is trans to the bromine or the methyl. This is addressed with a more advanced E/Z nomenclature discussed elsewhere.

Cis-trans isomerism also occurs in cyclic compounds. In ring structures, groups are unable to rotate about any of the ring carbon–carbon bonds. Therefore, groups can be either on the same side of the ring (cis) or on opposite sides of the ring (trans). For our purposes here, we represent all cycloalkanes as planar structures, and we indicate the positions of the groups, either above or below the plane of the ring.



Cis-1,2-dimethylcyclopropane



Trans-1,2-dimethylcyclopropane

Example 13.3.1

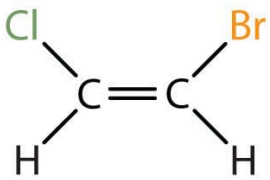
Which compounds can exist as cis-trans (geometric) isomers? Draw them.

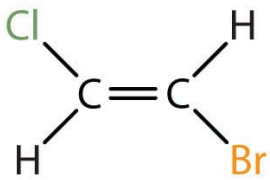
1. $CHCl=CHBr$
2. $CH_2=CBrCH_3$
3. $(CH_3)_2C=CHCH_2CH_3$
4. $CH_3CH=CHCH_2CH_3$

Solution

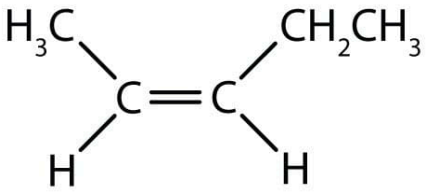
All four structures have a double bond and thus meet rule 1 for cis-trans isomerism.

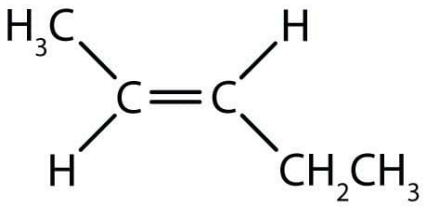
1. This compound meets rule 2; it has two nonidentical groups on *each* carbon atom (H and Cl on one and H and Br on the other). It exists as both cis and trans isomers:





- 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.
- 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.
- This compound meets rule 2; it has two nonidentical groups on *each* carbon atom and exists as both cis and trans isomers:

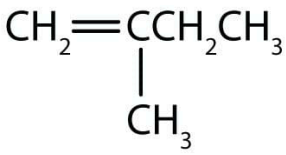




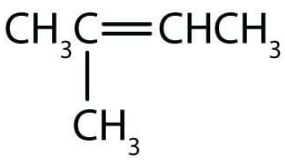
Exercise 13.3.1

Which compounds can exist as cis-trans isomers? Draw them.

a. $CH_2=CHCH_2CH_2CH_3$
b. $CH_3CH=CHCH_2CH_3$
c. $CH_3CH_2CH=CHCH_2CH_3$
d.



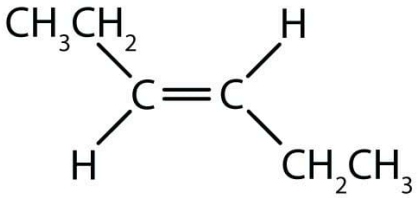
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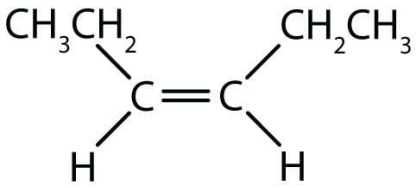
Concept Review Exercises

1. What are cis-trans (geometric) isomers? What two types of compounds can exhibit cis-trans isomerism?
2. Classify each compound as a cis isomer, a trans isomer, or neither.

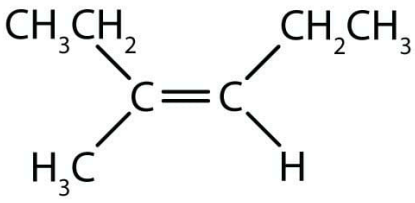
a.



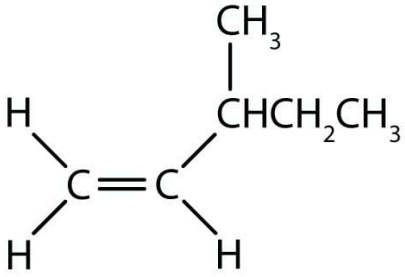
b.



c.



d.



Answers

1. Cis-trans isomers are compounds that have different configurations (groups permanently in different places in space) because of the presence of a rigid structure in their molecule. Alkenes and cyclic compounds can exhibit cis-trans isomerism.

2. a. trans (the two hydrogen atoms are on opposite sides)
   b. cis (the two hydrogen atoms are on the same side, as are the two ethyl groups)
   c. cis (the two ethyl groups are on the same side)
   d. neither (fliping the bond does not change the molecule. There are no isomers for this molecule)

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13.4: Properties of Alkenes and Alkynes

Learning Objectives

- To identify the physical properties of alkenes and describe trends in these properties.

The physical properties of alkenes are similar to those of the alkanes. The table at the start of the chapter shows that the boiling points of straight-chain alkenes increase with increasing molar mass, just as with alkanes. For molecules with the same number of carbon atoms and the same general shape, the boiling points usually differ only slightly, just as we would expect for substances whose molar mass differs by only 2 u (equivalent to two hydrogen atoms). Like other hydrocarbons, the alkenes are insoluble in water but soluble in organic solvents.

Looking Closer: Environmental Note

Alkenes occur widely in nature. Ripening fruits and vegetables give off ethylene, which triggers further ripening. Fruit processors artificially introduce ethylene to hasten the ripening process; exposure to as little as 0.1 mg of ethylene for 24 h can ripen 1 kg of tomatoes. Unfortunately, this process does not exactly duplicate the ripening process, and tomatoes picked green and treated this way don't taste much like vine-ripened tomatoes fresh from the garden.



The bright red color of tomatoes is due to lycopene—a polyene.

Other alkenes that occur in nature include 1-octene, a constituent of lemon oil, and octadecene ($C_{18}H_{36}$) found in fish liver. Dienes (two double bonds) and polyenes (three or more double bonds) are also common. Butadiene ($CH_2{=}CHCH{=}CH_2$) is found in coffee. Lycopene and the carotenes are isomeric polyenes ($C_{40}H_{56}$) that give the attractive red, orange, and yellow colors to watermelons, tomatoes, carrots, and other fruits and vegetables. Vitamin A, essential to good vision, is derived from a carotene. The world would be a much less colorful place without alkenes.

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13.5: Types of Organic Reactions



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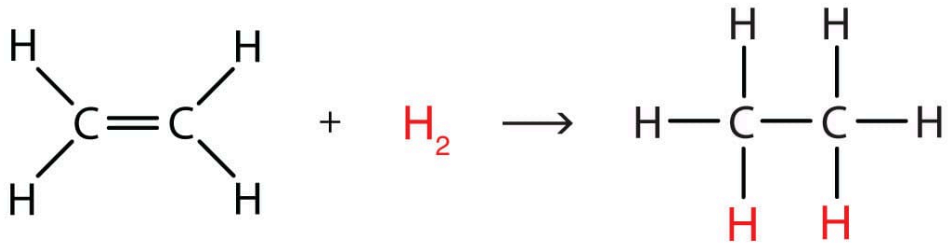
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13.6: Addition Reactions of Alkenes

Learning Objectives

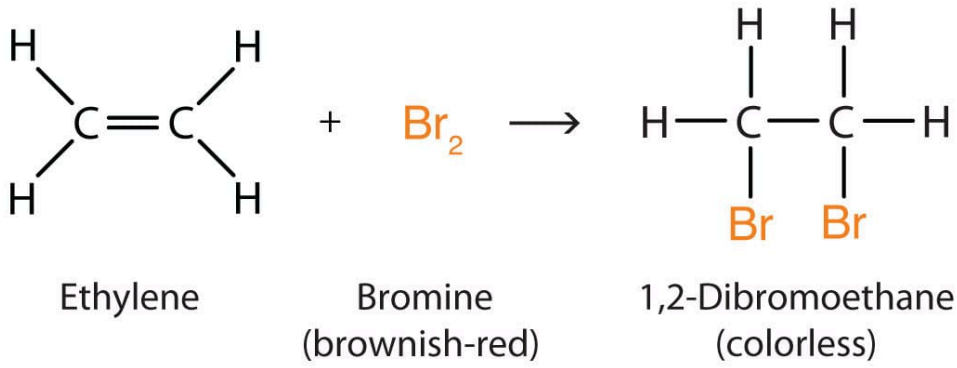
- To write equations for the addition reactions of alkenes with hydrogen, halogens, and water

Alkenes are valued mainly for addition reactions, in which one of the bonds in the double bond is broken. Each of the carbon atoms in the bond can then attach another atom or group while remaining joined to each other by a single bond. Perhaps the simplest addition reaction is hydrogenation—a reaction with hydrogen (H_2) in the presence of a catalyst such as nickel (Ni) or platinum (Pt).

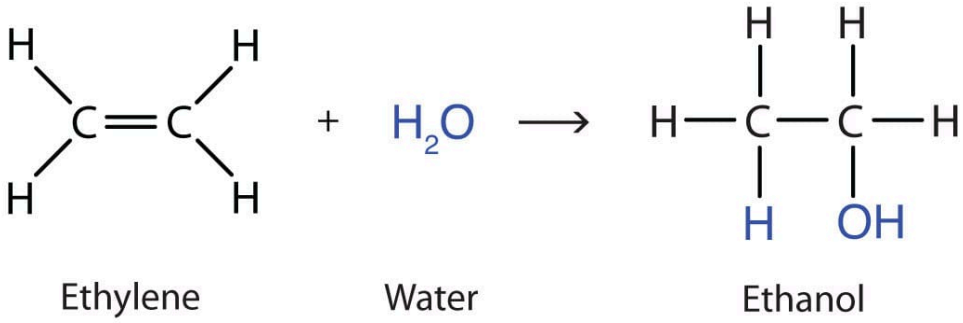


The product is an alkane having the same carbon skeleton as the alkene.

Alkenes also readily undergo halogenation—the addition of halogens. Indeed, the reaction with bromine (Br_2) can be used to test for alkenes. Bromine solutions are brownish red. When we add a Br_2 solution to an alkene, the color of the solution disappears because the alkene reacts with the bromine:



Another important addition reaction is that between an alkene and water to form an alcohol. This reaction, called hydration, requires a catalyst—usually a strong acid, such as sulfuric acid (H_2SO_4):



The hydration reaction is discussed later, where we deal with this reaction in the synthesis of alcohols.

Example 13.6.1

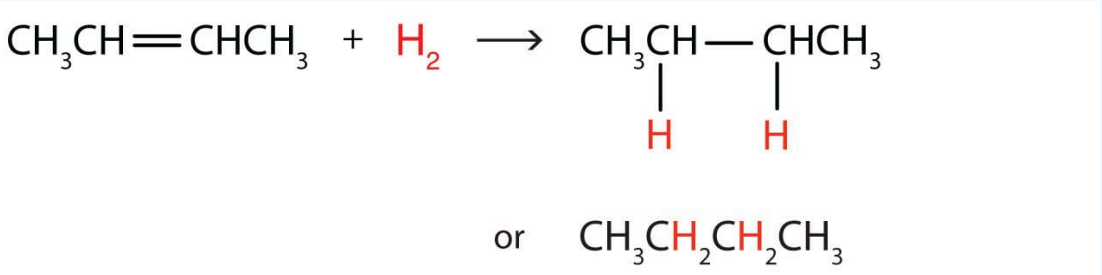
Write the equation for the reaction between $CH_3CH{=}CHCH_3$ and each substance.

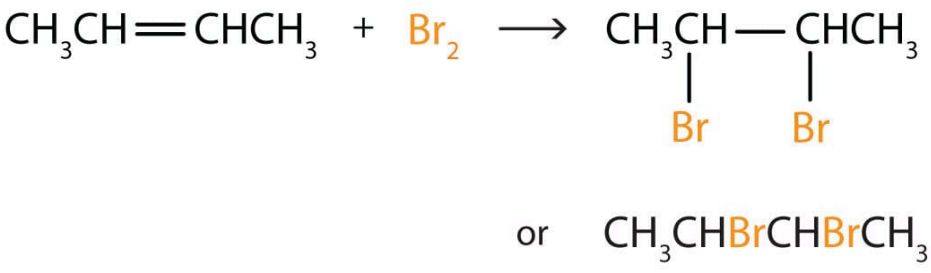
a. H_2 (Ni catalyst)
b. Br_2
c. H_2O (H_2SO_4 catalyst)

Solution

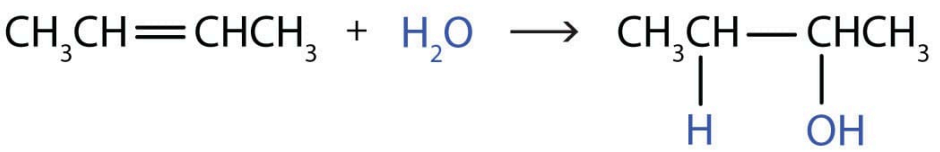
In each reaction, the reagent adds across the double bond.

a.





•



or $CH_3CH_2CHOHCH_3$

-

Exercise 13.6.1

Write the equation for each reaction.

a. $CH_3CH_2CH{=}CH_2$ with H_2 (Ni catalyst)
b. $CH_3CH{=}CH_2$ with Cl_2
c. $CH_3CH_2CH{=}CHCH_2CH_3$ with H_2O (H_2SO_4 catalyst)

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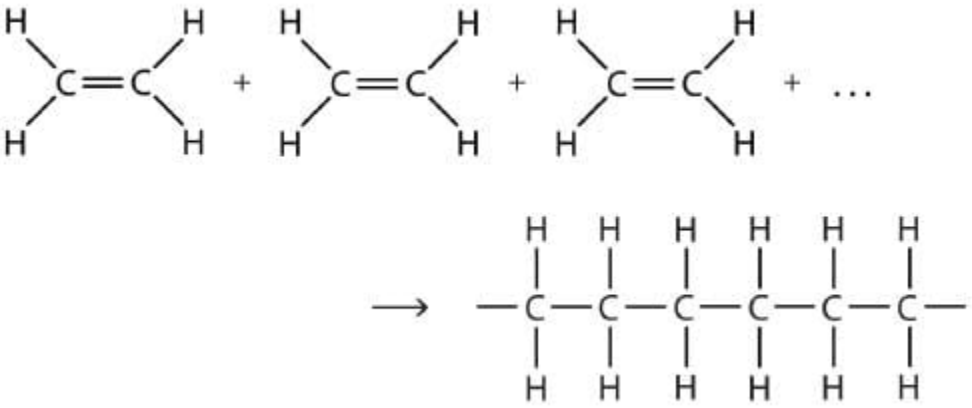
13.7: Alkene Polymers

Learning Objectives

- To draw structures for monomers that can undergo addition polymerization and for four-monomer-unit sections of an addition polymer.

The most important commercial reactions of alkenes are *polymerizations*, reactions in which small molecules, referred to in general as monomers (from the Greek *monos*, meaning "one," and *meros*, meaning "parts"), are assembled into giant molecules referred to as polymers (from the Greek *poly*, meaning "many," and *meros*, meaning "parts"). A polymer is as different from its monomer as a long strand of spaghetti is from a tiny speck of flour. For example, polyethylene, the familiar waxy material used to make plastic bags, is made from the monomer ethylene—a gas.

There are two general types of polymerization reactions: addition polymerization and condensation polymerization. In addition polymerization, the monomers add to one another in such a way that the polymer contains all the atoms of the starting monomers. Ethylene molecules are joined together in long chains. The polymerization can be represented by the reaction of a few monomer units:



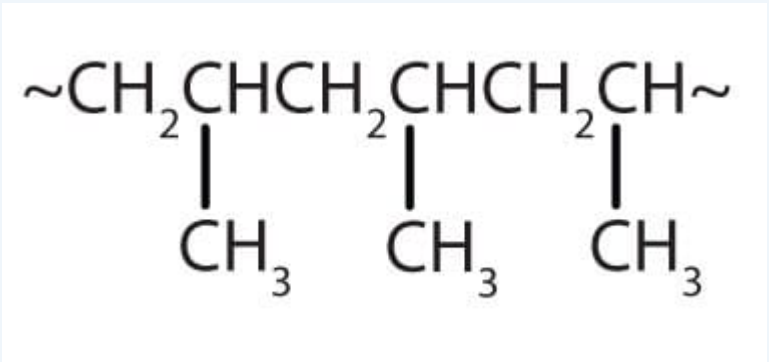
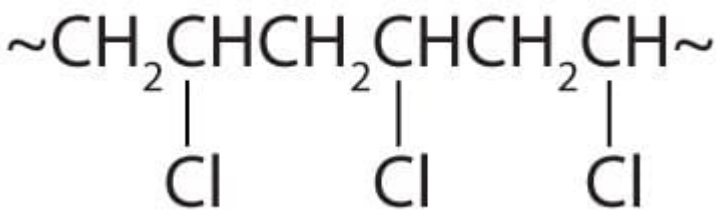
The bond lines extending at the ends in the formula of the product indicate that the structure extends for many units in each direction. Notice that all the atoms—two carbon atoms and four hydrogen atoms—of each monomer molecule are incorporated into the polymer structure. Because displays such as the one above are cumbersome, the polymerization is often abbreviated as follows:

$$n\mathrm{CH_2{=}CH_2} \rightarrow \left[\mathrm{CH_2CH_2}\right]_n$$

> Many natural materials—such as proteins, cellulose and starch, and complex silicate minerals—are polymers. Artificial fibers, films, plastics, semisolid resins, and rubbers are also polymers. More than half the compounds produced by the chemical industry are synthetic polymers.

Some common addition polymers are listed in Table 13.7.1. Note that all the monomers have carbon-to-carbon double bonds. Many polymers are mundane (e.g., plastic bags, food wrap, toys, and tableware), but there are also polymers that conduct electricity, have amazing adhesive properties, or are stronger than steel but much lighter in weight.

Table 13.7.1*: Some Addition Polymers*

Monomer	Polymer	Polymer Name	Some Uses
$CH_2=CH_2$	$\sim CH_2CH_2CH_2CH_2CH_2CH_2\sim$	polyethylene	plastic bags, bottles, toys, electrical insulation
$CH_2=CHCH_3$		polypropylene	carpeting, bottles, luggage, exercise clothing
$CH_2=CHCl$		polyvinyl chloride	bags for intravenous solutions, pipes, tubing, floor coverings
$CF_2=CF_2$	$\sim CF_2CF_2CF_2CF_2CF_2CF_2\sim$	polytetrafluoroethylene	nonstick coatings, electrical insulation

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13.8: Aromatic Compounds and the Structure of Benzene

Learning Objectives

- To describe the bonding in benzene and the way typical reactions of benzene differ from those of the alkenes.

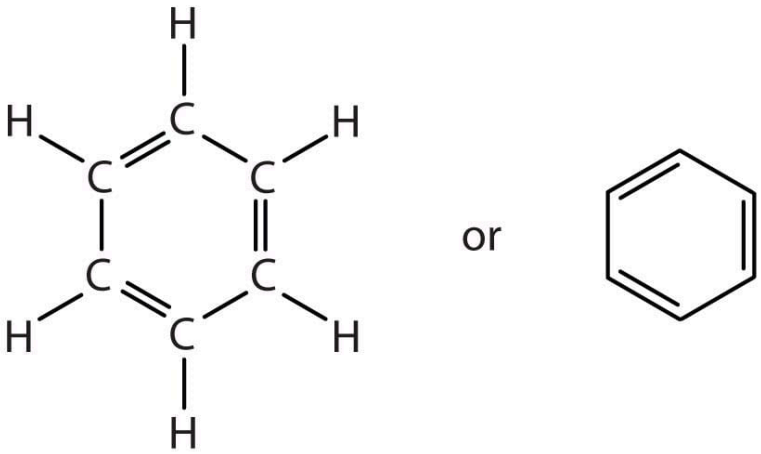
Next we consider a class of hydrocarbons with molecular formulas like those of unsaturated hydrocarbons, but which, unlike the alkenes, do not readily undergo addition reactions. These compounds comprise a distinct class, called aromatic hydrocarbons, with unique structures and properties. We start with the simplest of these compounds. Benzene (C_6H_6) is of great commercial importance, but it also has noteworthy health effects.

The formula C_6H_6 seems to indicate that benzene has a high degree of unsaturation. (Hexane, the saturated hydrocarbon with six carbon atoms has the formula C_6H_{14}—eight more hydrogen atoms than benzene.) However, despite the seeming low level of saturation, benzene is rather unreactive. It does not, for example, react readily with bromine, which, is a test for unsaturation.

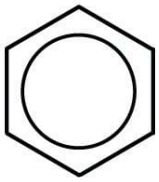
Note

Benzene is a liquid that smells like gasoline, boils at 80°C, and freezes at 5.5°C. It is the aromatic hydrocarbon produced in the largest volume. It was formerly used to decaffeinate coffee and was a significant component of many consumer products, such as paint strippers, rubber cements, and home dry-cleaning spot removers. It was removed from many product formulations in the 1950s, but others continued to use benzene in products until the 1970s when it was associated with leukemia deaths. Benzene is still important in industry as a precursor in the production of plastics (such as Styrofoam and nylon), drugs, detergents, synthetic rubber, pesticides, and dyes. It is used as a solvent for such things as cleaning and maintaining printing equipment and for adhesives such as those used to attach soles to shoes. Benzene is a natural constituent of petroleum products, but because it is a known carcinogen, its use as an additive in gasoline is now limited.

To explain the surprising properties of benzene, chemists suppose the molecule has a cyclic, hexagonal, planar structure of six carbon atoms with one hydrogen atom bonded to each. We can write a structure with alternate single and double bonds, either as a full structural formula or as a line-angle formula:



However, these structures do not explain the unique properties of benzene. Furthermore, experimental evidence indicates that all the carbon-to-carbon bonds in benzene are equivalent, and the molecule is unusually stable. Chemists often represent benzene as a hexagon with an inscribed circle:



The inner circle indicates that the valence electrons are shared equally by all six carbon atoms (that is, the electrons are *delocalized*, or spread out, over all the carbon atoms). It is understood that each corner of the hexagon is occupied by one carbon atom, and each carbon atom has one hydrogen atom attached to it. Any other atom or groups of atoms substituted for a hydrogen atom must be shown bonded to a particular corner of the hexagon. We use this modern symbolism, but many scientists still use the earlier structure with alternate double and single bonds.

To Your Health: Benzene and Us

Most of the benzene used commercially comes from petroleum. It is employed as a starting material for the production of detergents, drugs, dyes, insecticides, and plastics. Once widely used as an organic solvent, benzene is now known to have both short- and long-term toxic effects. The inhalation of large concentrations can cause nausea and even death due to respiratory or heart failure, while repeated exposure leads to a progressive disease in which the ability of the bone marrow to make new blood cells is eventually destroyed. This results in a condition called *aplastic anemia*, in which there is a decrease in the numbers of both the red and white blood cells.

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13.9: Naming Aromatic Compounds

Learning Objectives

- Recognize aromatic compounds from structural formulas.
- Name aromatic compounds given formulas.
- Write formulas for aromatic compounds given their names.

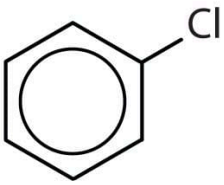
Historically, benzene-like substances were called aromatic hydrocarbons because they had distinctive aromas. Today, an aromatic compound is any compound that contains a benzene ring or has certain benzene-like properties (but not necessarily a strong aroma). You can recognize the aromatic compounds in this text by the presence of one or more benzene rings in their structure. Some representative aromatic compounds and their uses are listed in Table 13.9.1, where the benzene ring is represented as C_6H_5.

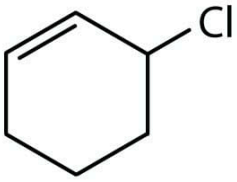
Table 13.9.1: Some Representative Aromatic Compounds

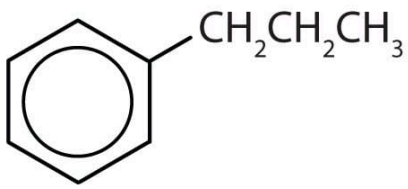
Name	Structure	Typical Uses
aniline	C_6H_5–NH_2	starting material for the synthesis of dyes, drugs, resins, varnishes, perfumes; solvent; vulcanizing rubber
benzoic acid	C_6H_5–COOH	food preservative; starting material for the synthesis of dyes and other organic compounds; curing of tobacco
bromobenzene	C_6H_5–Br	starting material for the synthesis of many other aromatic compounds; solvent; motor oil additive
nitrobenzene	C_6H_5–NO_2	starting material for the synthesis of aniline; solvent for cellulose nitrate; in soaps and shoe polish
phenol	C_6H_5–OH	disinfectant; starting material for the synthesis of resins, drugs, and other organic compounds
toluene	C_6H_5–CH_3	solvent; gasoline octane booster; starting material for the synthesis of benzoic acid, benzaldehyde, and many other organic compounds

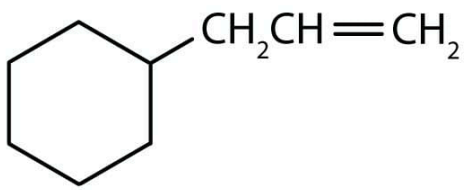
Example 13.9.1

Which compounds are aromatic?

1. 

- 

- 

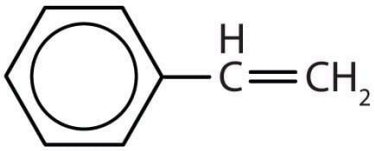
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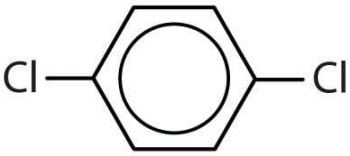
Solution

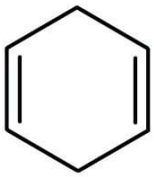
1. The compound has a benzene ring (with a chlorine atom substituted for one of the hydrogen atoms); it is aromatic.
2. The compound is cyclic, but it does not have a benzene ring; it is not aromatic.
3. The compound has a benzene ring (with a propyl group substituted for one of the hydrogen atoms); it is aromatic.
4. The compound is cyclic, but it does not have a benzene ring; it is not aromatic.

Exercise 13.9.1

Which compounds are aromatic?

1. 

- 

- 

In the International Union of Pure and Applied Chemistry (IUPAC) system, aromatic hydrocarbons are named as derivatives of benzene. Figure 13.9.1 shows four examples. In these structures, it is immaterial whether the single substituent is written at the top, side, or bottom of the ring: a hexagon is symmetrical, and therefore all positions are equivalent.

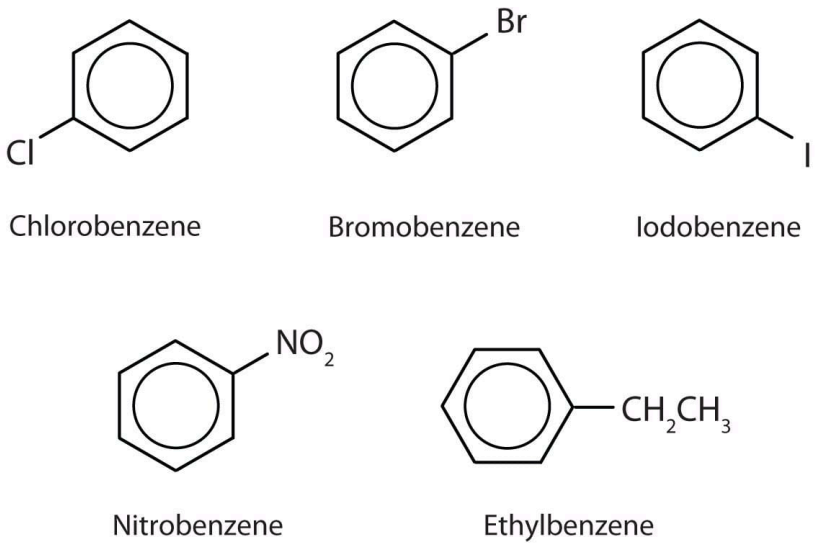
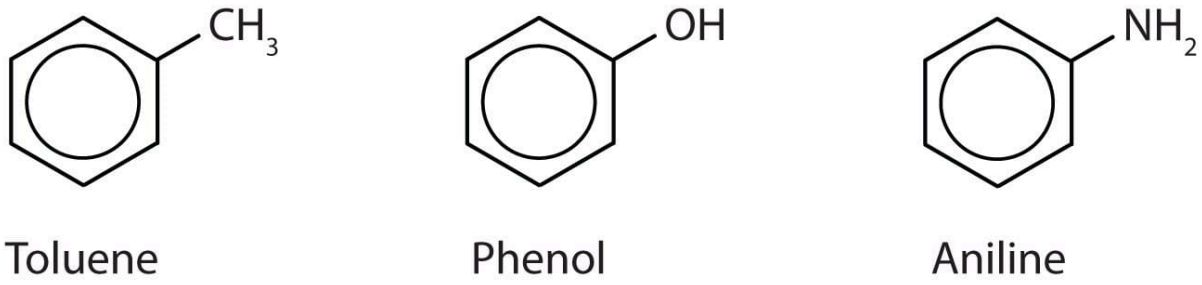


Figure 13.9.1: Some Benzene Derivatives. These compounds are named in the usual way with the group that replaces a hydrogen atom named as a substituent group: Cl as chloro, Br as bromo, I as iodo, NO_2 as nitro, and CH_3CH_2 as ethyl.

Although some compounds are referred to exclusively by IUPAC names, some are more frequently denoted by common names, as is indicated in Table 13.9.1.



When there is more than one substituent, the corners of the hexagon are no longer equivalent, so we must designate the relative positions. There are three possible disubstituted benzenes, and we can use numbers to distinguish them (Figure 13.9.2). 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.

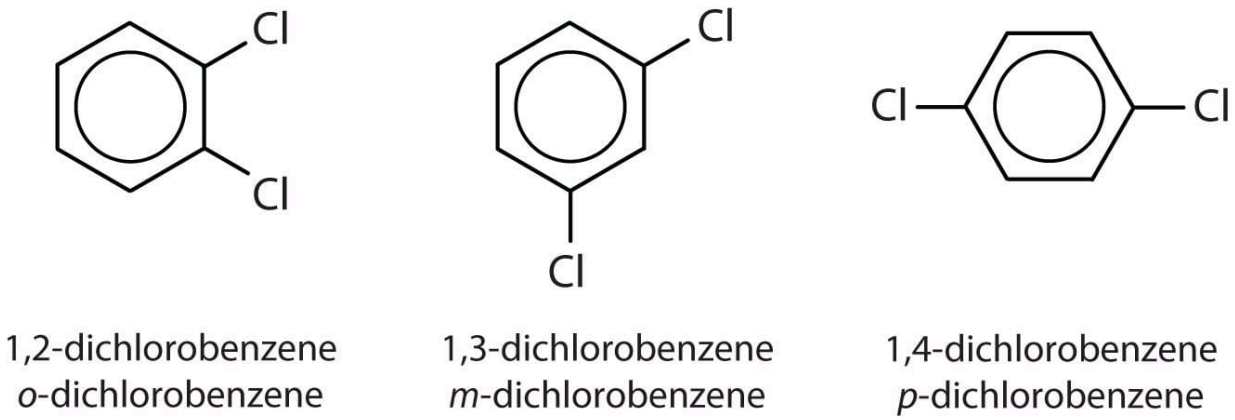
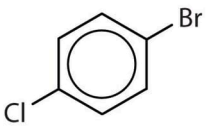
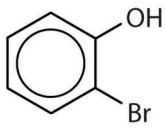


Figure 13.9.2: The Three Isomeric Dichlorobenzenes

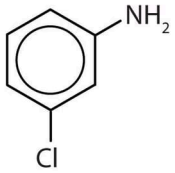
In Figure 13.9.2, common names are also used: the prefix *ortho* (*o*-) for 1,2-disubstitution, *meta* (*m*-) for 1,3-disubstitution, and *para* (*p*-) for 1,4-disubstitution. The substituent names are listed in alphabetical order. The first substituent is given the lowest number. When a common name is used, the carbon atom that bears the group responsible for the name is given the number 1:



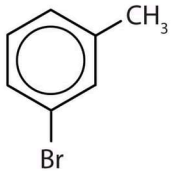
1-Bromo-4-chlorobenzene
p-Bromochlorobenzene



2-Bromophenol
o-Bromophenol



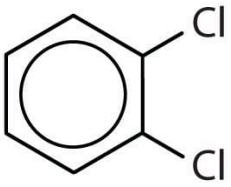
3-Chloroaniline
m-Chloroaniline

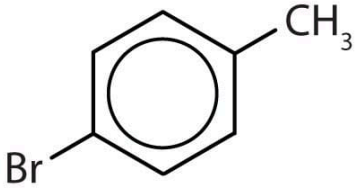


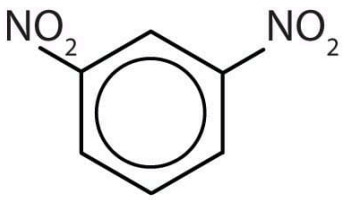
3-Bromotoluene
m-Bromotoluene

Example 13.9.2

Name each compound using both the common name and the IUPAC name.

1. 

- 

- 

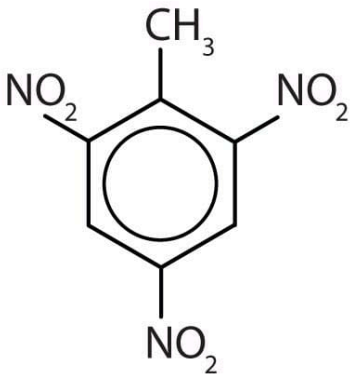
Solution

1. The benzene ring has two chlorine atoms (dichloro) in the first and second positions. The compound is *o*-dichlorobenzene

or 1,2-dichlorobenzene.

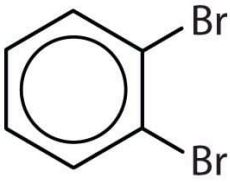
2. The benzene ring has a methyl (CH_3) group. The compound is therefore named as a derivative of toluene. The bromine atom is on the fourth carbon atom, counting from the methyl group. The compound is *p*-bromotoluene or 4-bromotoluene.
3. The benzene ring has two nitro (NO_2) groups in the first and third positions. It is *m*-dinitrobenzene or 1,3-dinitrobenzene.

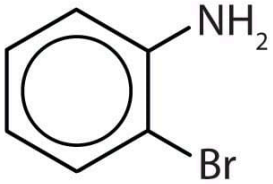
Note: The nitro (NO_2) group is a common substituent in aromatic compounds. Many nitro compounds are explosive, most notably 2,4,6-trinitrotoluene (TNT).

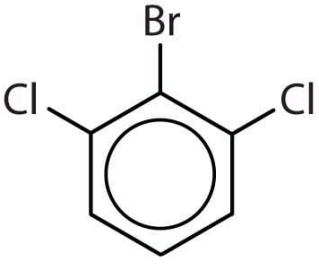


Exercise 13.9.2

Name each compound using both the common name and the IUPAC name.

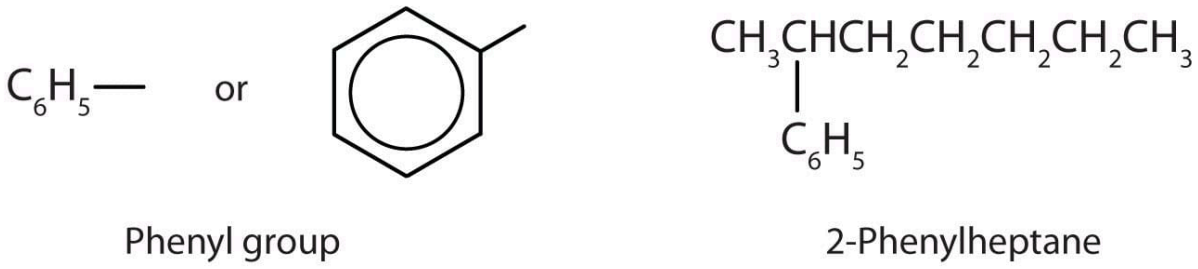
1. 

- 

- 

Sometimes an aromatic group is found as a substituent bonded to a nonaromatic entity or to another aromatic ring. The group of atoms remaining when a hydrogen atom is removed from an aromatic compound is called an aryl group. The most common aryl group is derived from benzene (C_6H_6) by removing one hydrogen atom (C_6H_5) and is called a *phenyl* group, from *pheno*, an old

name for benzene.

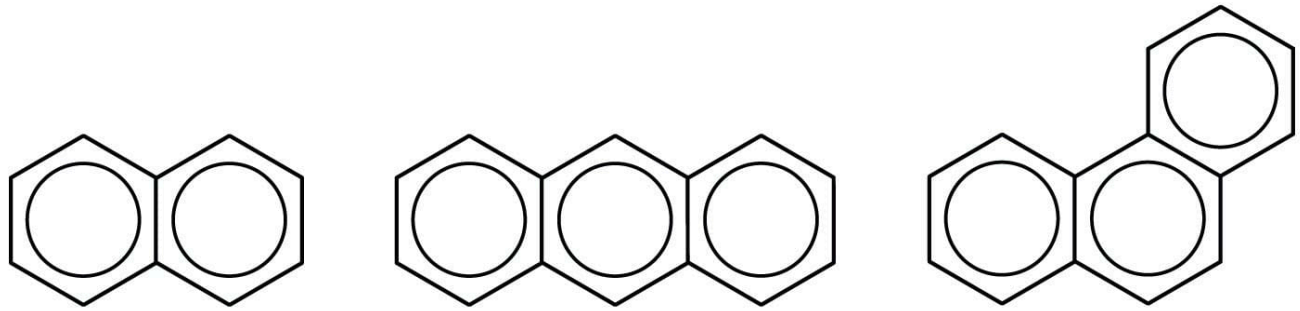


Phenyl group

2-Phenylheptane

Polycyclic Aromatic Hydrocarbons

Some common aromatic hydrocarbons consist of fused benzene rings—rings that share a common side. These compounds are called polycyclic aromatic hydrocarbons (PAHs).



Naphthalene

Anthracene

Phenanthrene

The three examples shown here are colorless, crystalline solids generally obtained from coal tar. Naphthalene has a pungent odor and is used in mothballs. Anthracene is used in the manufacture of certain dyes. Steroids, a large group of naturally occurring substances, contain the phenanthrene structure.

To Your Health: Polycyclic Aromatic Hydrocarbons and Cancer

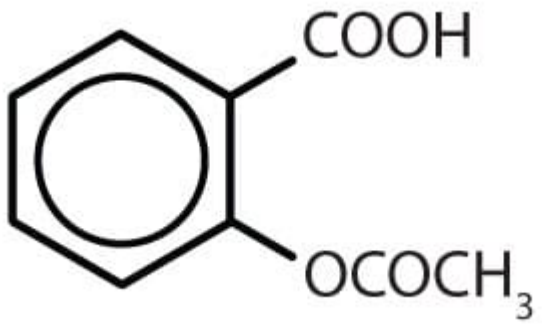
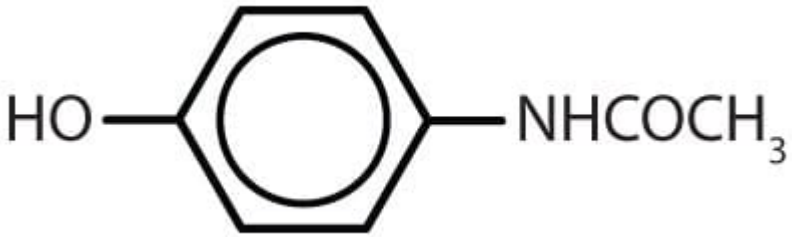
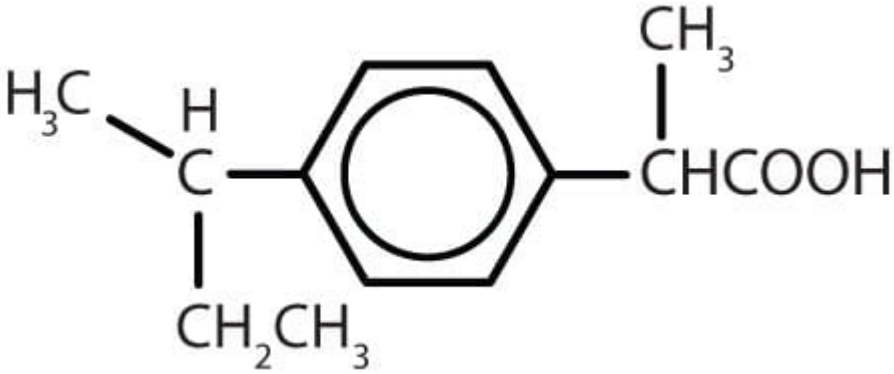
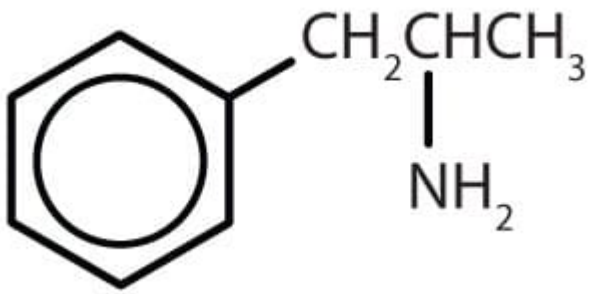
The intense heating required for distilling coal tar results in the formation of PAHs. For many years, it has been known that workers in coal-tar refineries are susceptible to a type of skin cancer known as tar cancer. Investigations have shown that a number of PAHs are carcinogens. One of the most active carcinogenic compounds, benzopyrene, occurs in coal tar and has also been isolated from cigarette smoke, automobile exhaust gases, and charcoal-broiled steaks. It is estimated that more than 1,000 t of benzopyrene are emitted into the air over the United States each year. Only a few milligrams of benzopyrene per kilogram of body weight are required to induce cancer in experimental animals.

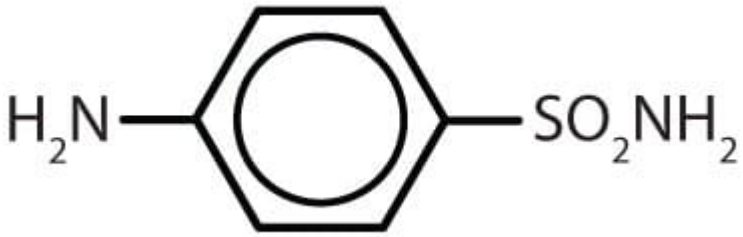
Biologically Important Compounds with Benzene Rings

Substances containing the benzene ring are common in both animals and plants, although they are more abundant in the latter. Plants can synthesize the benzene ring from carbon dioxide, water, and inorganic materials. Animals cannot synthesize it, but they are dependent on certain aromatic compounds for survival and therefore must obtain them from food. Phenylalanine, tyrosine, and tryptophan (essential amino acids) and vitamins K, B_2 (riboflavin), and B_9 (folic acid) all contain the benzene ring. Many important drugs, a few of which are shown in Table 13.9.2, also feature a benzene ring.

So far we have studied only aromatic compounds with carbon-containing rings. However, many cyclic compounds have an element other than carbon atoms in the ring. These compounds, called *heterocyclic compounds*, are discussed later. Some of these are heterocyclic aromatic compounds.

Table 13.9.2: Some Drugs That Contain a Benzene Ring

Name	Structure
aspirin	
acetaminophen	
ibuprofen	
amphetamine	

Name	Structure
sulfanilamide	

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13.10: Reactions of Aromatic Compounds



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14: SOME COMPOUNDS WITH OXYGEN, SULFUR, OR A HALOGEN

14.1: Alcohols, Phenols, and Ethers

14.2: Naming Alcohols

14.3: Properties of Alcohols

14.4: Reactions of Alcohols

14.5: Phenols

14.6: Acidity of Alcohols and Phenols

14.7: Ethers

14.8: Thiols and Disulfides

14.9: Halogen-Containing Compounds

14.10: Stereochemistry and Chirality

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14.1: Alcohols, Phenols, and Ethers



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14.2: Naming Alcohols



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14.3: Properties of Alcohols



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14.4: 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 14.4.1 , two—dehydration and oxidation—are considered here. The third reaction type—esterification—is covered elsewhere.

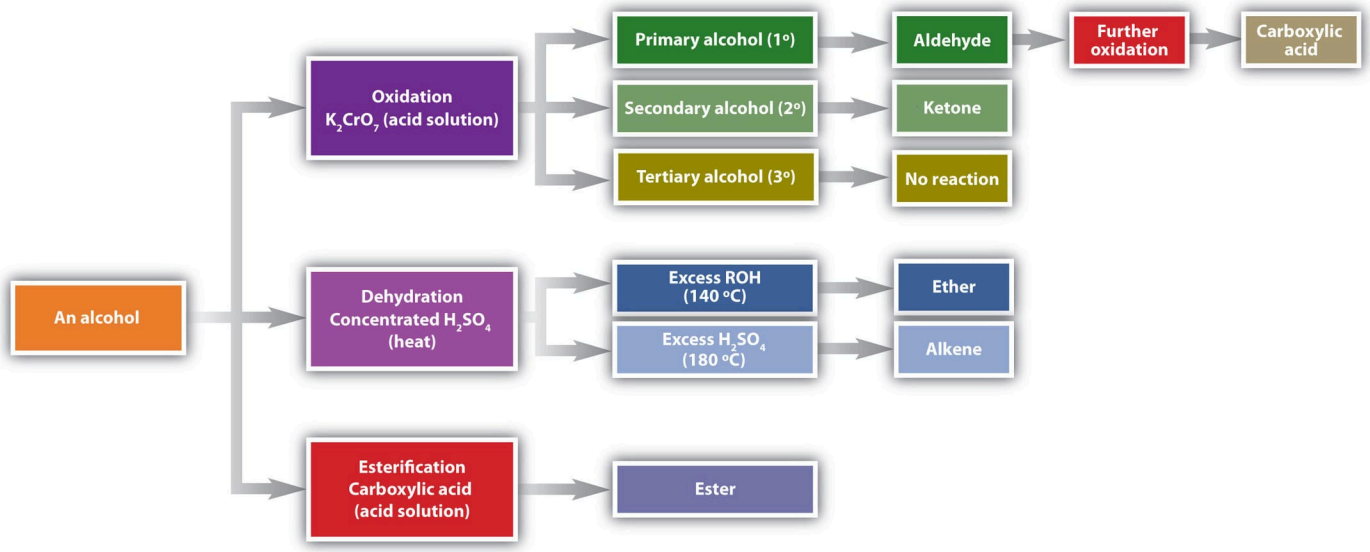


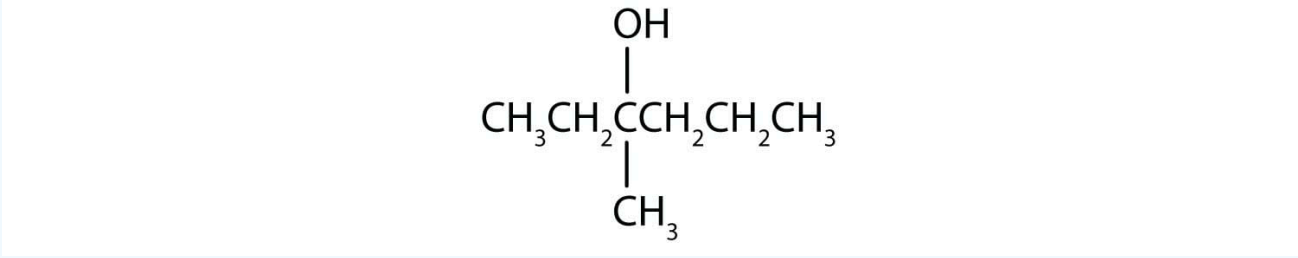
Figure 14.4.1: Reactions of Alcohols. Oxidation and dehydration of alcohols are considered here.

Solution

The first step is to recognize the class of each alcohol as primary, secondary, or tertiary.

Exercise 14.4.1

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.

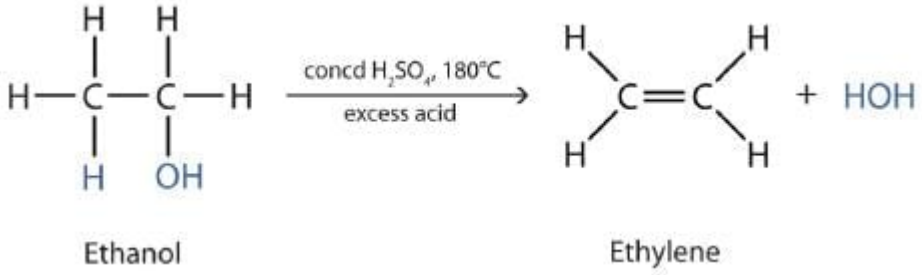
1. 

Summary

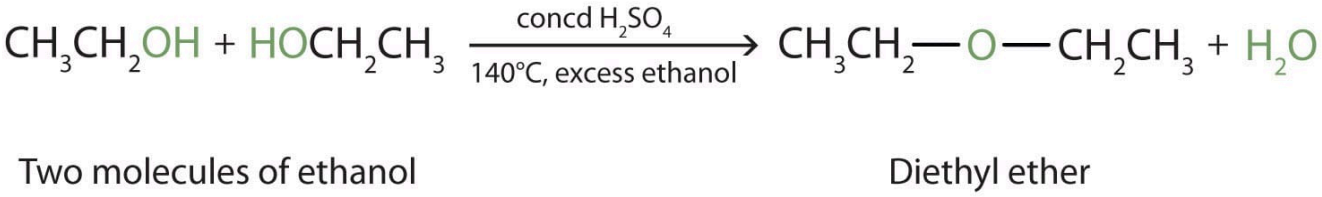
Alcohols can be dehydrated to form either alkenes (higher temperature, excess acid) or ethers (lower temperature, excess alcohol). Primary alcohols are oxidized to form aldehydes. Secondary alcohols are oxidized to form ketones. Tertiary alcohols are not readily oxidized.

- ## Dehydration

  As noted in Figure 14.4.1, 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:

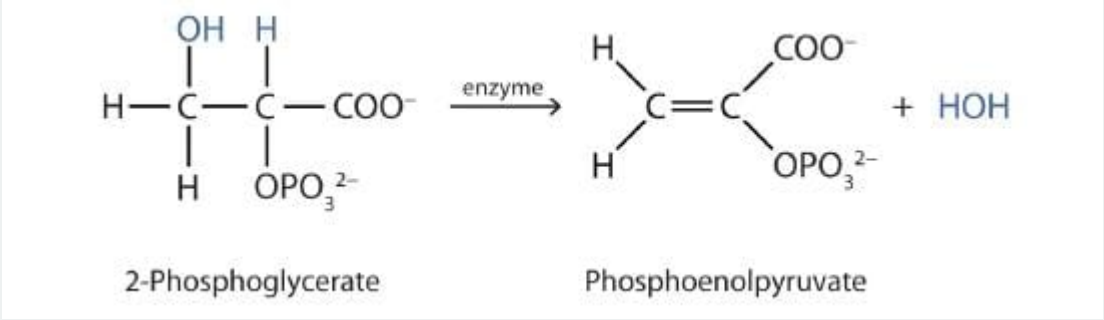


  Under the proper conditions, it is possible for the dehydration to occur between *two* alcohol molecules. The entire OH group of one molecule and only the hydrogen atom of the OH group of the second molecule are removed. The two ethyl groups attached to an oxygen atom form an ether molecule.



  (Ethers are discussed in elsewhere) Thus, depending on conditions, one can prepare either alkenes or ethers by the dehydration of alcohols.

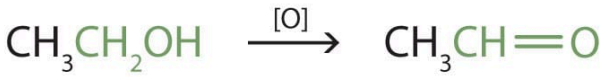
  Both dehydration and hydration reactions occur continuously in cellular metabolism, with enzymes serving as catalysts and at a temperature of about 37°C. The following reaction occurs in the "Embden–Meyerhof" pathway



  Although the participating compounds are complex, the reaction is the same: elimination of water from the starting material. The idea is that if you know the chemistry of a particular functional group, you know the chemistry of hundreds of different compounds.

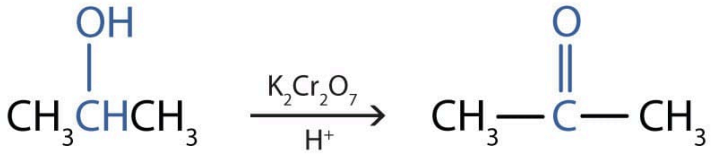
Oxidation

Primary and secondary alcohols are readily oxidized. We saw earlier how methanol and ethanol are oxidized by liver enzymes to form aldehydes. Because a variety of oxidizing agents can bring about oxidation, we can indicate an oxidizing agent without specifying a particular one by writing an equation with the symbol [O] above the arrow. For example, we write the oxidation of ethanol—a primary alcohol—to form acetaldehyde—an aldehyde—as follows:



Ethanol (a primary alcohol) — Acetaldehyde (an aldehyde)

We shall see that aldehydes are even more easily oxidized than alcohols and yield carboxylic acids. Secondary alcohols are oxidized to *ketone*s. The oxidation of isopropyl alcohol by potassium dichromate ($K_2Cr_2O_7$) gives acetone, the simplest ketone:



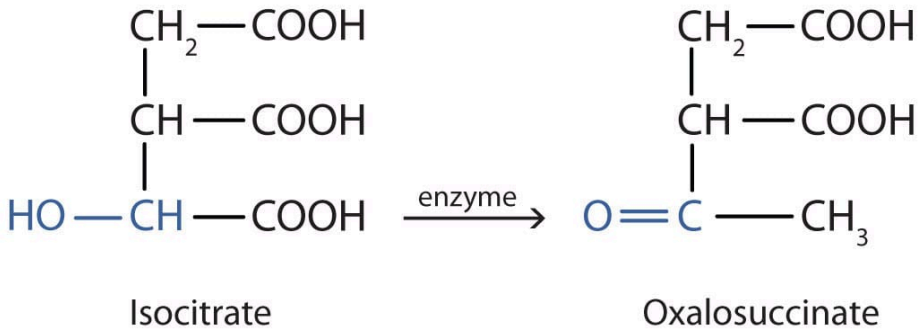
Isopropyl alcohol (a secondary alcohol) — Acetone (a ketone)

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.

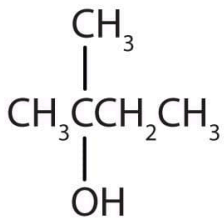
Tertiary alcohols (R_3COH) are resistant to oxidation because the carbon atom that carries the OH group does not have a hydrogen atom attached but is instead bonded to other carbon atoms. The oxidation reactions we have described involve the formation of a carbon-to-oxygen double bond. Thus, the carbon 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.

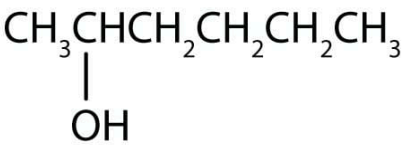
Example 14.4.1

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.

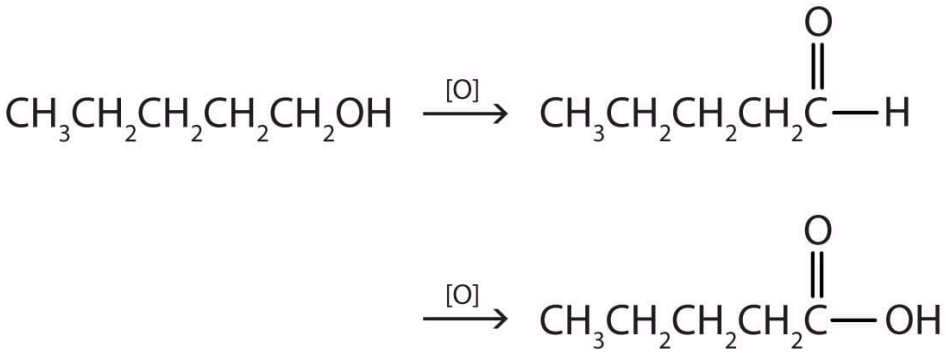
a. $CH_3CH_2CH_2CH_2CH_2OH$

b.

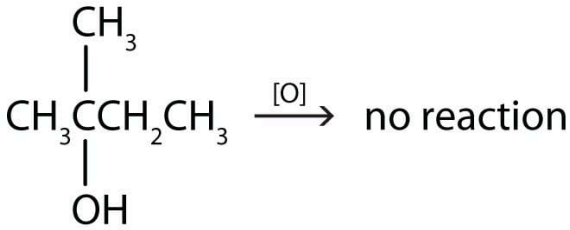




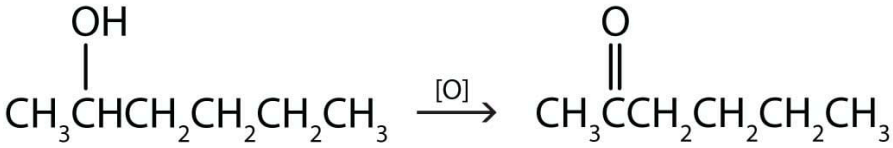
- a. This alcohol has the OH group on a carbon atom that is attached to only *one* other carbon atom, so it is a primary alcohol. Oxidation forms first an aldehyde and further oxidation forms a carboxylic acid.

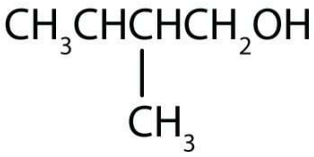


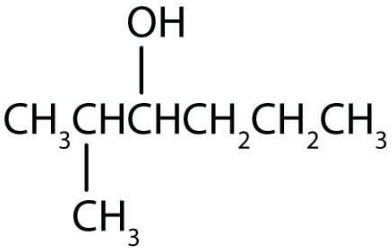
- b. This alcohol has the OH group on a carbon atom that is attached to three other carbon atoms, so it is a tertiary alcohol. No reaction occurs.



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.



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14.5: 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.

$$\mathrm{ArOH\,(aq) + NaOH\,(aq)\ \rightarrow ArONa\,(aq) + H_2O}$$

The parent compound, C_6H_5OH, is itself called phenol. (An old name, emphasizing its slight acidity, was *carbolic acid*.) Phenol is a white crystalline compound that has a distinctive ("hospital smell") odor.

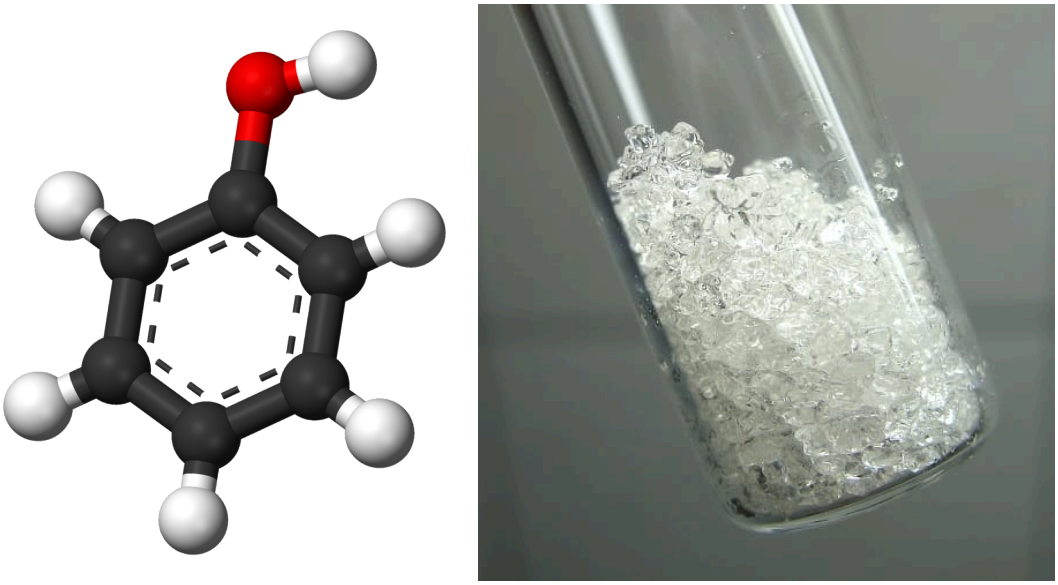


Figure 14.5.1***:*** *(Left) Structure of Phenol (right) Approximately two grams of phenol in glass vial. Image used with permisison from Wikipedia*

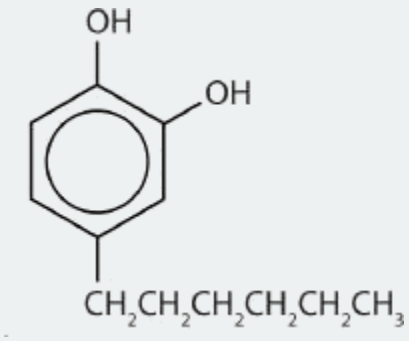
To Your Health: Phenols and Us

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.

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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14.6: Acidity of Alcohols and Phenols



Maps take some time to build because we have to find or write matching materials. LibreTexts POV is that it is best to make available pages that we have finished rather than wait till the entire project is complete .This map is not completely finished, some pages are missing but we are workin' on it. . . (Public Domain ; Public Domain Pictures)

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14.7: 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:

$$\mathrm{HOH} \xrightarrow[\text{H atoms}]{\text{replace both}} \mathrm{ROR'} \xleftarrow[\text{of OH group}]{\text{replace H atom}} \mathrm{ROH}$$

Simple ethers have simple common names, formed from the names of the groups attached to oxygen atom, followed by the generic name *ether*. For example, CH_3–O–$CH_2CH_2CH_3$ is methyl propyl ether. If both groups are the same, the group name should be preceded by the prefix *di-*, as in dimethyl ether (CH_3–O–CH_3) and diethyl ether CH_3CH_2–O–CH_2CH_3.

Ether molecules have no hydrogen atom on the oxygen atom (that is, no OH group). Therefore there is no intermolecular hydrogen bonding between ether molecules, and ethers therefore have quite low boiling points for a given molar mass. Indeed, ethers have boiling points about the same as those of alkanes of comparable molar mass and much lower than those of the corresponding alcohols (Table 14.7.1).

Table 14.7.1: Comparison of Boiling Points of Alkanes, Alcohols, and Ethers

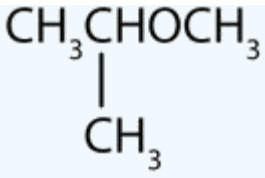
Condensed Structural Formula	Name	Molar Mass	Boiling Point (°C)	Intermolecular Hydrogen Bonding in Pure Liquid?
$CH_3CH_2CH_3$	propane	44	–42	no
CH_3OCH_3	dimethyl ether	46	–25	no
CH_3CH_2OH	ethyl alcohol	46	78	yes
$CH_3CH_2CH_2CH_2CH_3$	pentane	72	36	no
$CH_3CH_2OCH_2CH_3$	diethyl ether	74	35	no
$CH_3CH_2CH_2CH_2OH$	butyl alcohol	74	117	yes

Ether molecules do have an oxygen atom, however, and engage in hydrogen bonding with water molecules. Consequently, an ether has about the same solubility in water as the alcohol that is isomeric with it. For example, dimethyl ether and ethanol (both having the molecular formula C_2H_6O) are completely soluble in water, whereas diethyl ether and 1-butanol (both $C_4H_{10}O$) are barely soluble in water (8 g/100 mL of water).

Example 14.7.1

What is the common name for each ether?

a. $CH_3CH_2CH_2OCH_2CH_2CH_3$

b. 

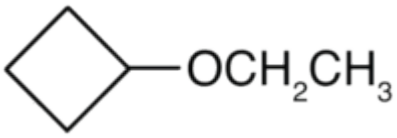
Solution

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 14.7.1

What is the common name for each ether?

a. $CH_3CH_2CH_2CH_2OCH_2CH_2CH_2CH_3$

- 

To Your Health: Ethers as General Anesthetics

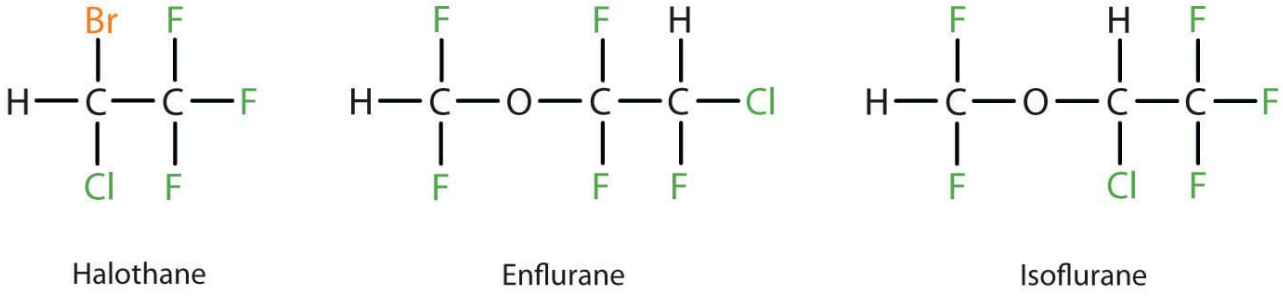
A *general anesthetic* acts on the brain to produce unconsciousness and a general insensitivity to feeling or pain. Diethyl ether ($CH_3CH_2OCH_2CH_3$) was the first general anesthetic to be used.



William Morton, a Boston dentist, introduced diethyl ether into surgical practice in 1846. This painting shows an operation in Boston in 1846 in which diethyl ether was used as an anesthetic. Inhalation of ether vapor produces unconsciousness by depressing the activity of the central nervous system. Source: Painting of William Morton by Ernest Board.

Diethyl ether is relatively safe because there is a fairly wide gap between the dose that produces an effective level of anesthesia

and the lethal dose. However, because it is highly flammable and has the added disadvantage of causing nausea, it has been replaced by newer inhalant anesthetics, including the fluorine-containing compounds halothane, enflurane, and isoflurane. Unfortunately, the safety of these compounds for operating room personnel has been questioned. For example, female operating room workers exposed to halothane suffer a higher rate of miscarriages than women in the general population.



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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14.8: Thiols and Disulfides

Learning Objectives

- Identify thiols (mercaptans) by the presence of an SH group.
- The mild oxidation of thiols gives disulfides.

Because sulfur is in the same group (6A) of the periodic table as oxygen, the two elements have some similar properties. We might expect sulfur to form organic compounds related to those of oxygen, and indeed it does. Thiols (also called mercaptans), which are sulfur analogs of alcohols, have the general formula RSH. Methanethiol (also called methyl mercaptan), has the formula CH_3SH. Ethanethiol (ethyl mercaptan) is the most common odorant for liquid propane (LP) gas.

The mild oxidation of thiols gives compounds called disulfides.

$$2\mathrm{RSH} \xrightarrow{[O]} \mathrm{RSSR}$$

The amino acids cysteine [$HSCH_2CH(NH_2)COOH$] and methionine [$CH_3SCH_2CH_2CH(NH_2)COOH$] contain sulfur atoms, as do all proteins that contain these amino acids. Disulfide linkages (–S–S–) between protein chains are extremely important in protein structure.

Thioethers, which are sulfur analogs of ethers, have the form general formula RSR′. An example is dimethylsulfide (CH_3SCH_3), which is responsible for the sometimes unpleasant odor of cooking cabbage and related vegetables. Note that methionine has a thioether functional group.

Career Focus: Paramedic

Paramedics are highly trained experts at providing emergency medical treatment. Their critical duties often include rescue work and emergency medical procedures in a wide variety of settings, sometimes under extremely harsh and difficult conditions. Like other science-based professions, their work requires knowledge, ingenuity, and complex thinking, as well as a great deal of technical skill. The recommended courses for preparation in this field include anatomy, physiology, medical terminology, and—not surprisingly—chemistry. An understanding of basic principles of organic chemistry, for example, is useful when paramedics have to deal with such traumas as burns from fuel (hydrocarbons) or solvent (alcohols, ethers, esters, and so on) fires and alcohol and drug overdoses.

To become a paramedic requires 2–4 y of training and usually includes a stint as an emergency medical technician (EMT). An EMT provides basic care, can administer certain medications and treatments, such as oxygen for respiratory problems and epinephrine (adrenalin) for allergic reactions, and has some knowledge of common medical conditions. A paramedic, in contrast, must have extensive knowledge of common medical problems and be trained to administer a wide variety of emergency drugs.

Paramedics usually work under the direction of a medical doctor with a title such as “medical director.” Some paramedics are employed by fire departments and may work from a fire engine that carries medical equipment as well as fire-fighting gear. Some work from hospital-sponsored ambulances and continue to care for their patients after reaching the hospital emergency room. Still other paramedics work for a government department responsible for emergency health care in a specific geographical area. Finally, some work for private companies that contract to provide service for a government body.

An experienced paramedic has a broad range of employment options, including training for mountain or ocean rescue, working with police department special weapons and tactics (SWAT) teams, or working in isolated settings such as on oil rigs. With their expertise at treating and stabilizing patients before quickly moving them to a hospital, paramedics often provide the first critical steps in saving an endangered life. The following quotation, inscribed on the Arlington National Cemetery headstone of Army Lieutenant R. Adams Cowley, who is often called the “father” of shock trauma medicine, serves as the motto for many paramedic units: “Next to creating a life the finest thing a man can do is save one.” —Abraham Lincoln

Summary

Thiols, thioethers, and disulfides are common in biological compounds.

Concept Review Exercises

1. What is the functional group of a thiol? Write the condensed structural formula for ethanethiol (ethyl mercaptan).
2. What is the functional group of a disulfide? Write the condensed structural formula for dipropyl disulfide.

Answers

1. SH; CH_3CH_2SH
2. –S–S–; $CH_3CH_2CH_2SSCH_2CH_2CH_3$

Exercises

1. A common natural gas odorant is *tert*-butyl mercaptan. What is its condensed structural formula?
2. Write the equation for the oxidation of ethanethiol to diethyl disulfide.

Answer

1. $(CH_3)_3CSH$

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14.9: Halogen-Containing Compounds

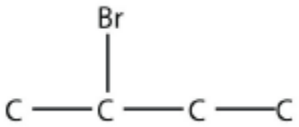
Learning Objectives

- Identify and name a simple alkyl halide.

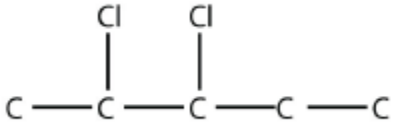
The presence of a halogen atom (F, Cl, Br, or I; also, X is used to represent any halogen atom) is one of the simplest functional groups. Organic compounds that contain a halogen atom are called **alkyl halides.** We have already seen some examples of alkyl halides when the addition of halogens across double and triple bonds was introduced in Section 16.3 - "Branched Hydrocarbons;" the products of these reactions were alkyl halides.

A simple alkyl halide can be named like an ionic salt, first by stating the name of the parent alkane as a substituent group (with the *-yl* suffix) and then the name of the halogen as if it were the anion. So CH_3Cl has the common name of methyl chloride, while CH_3CH_2Br is ethyl bromide and $CH_3CH_2CH_2I$ is propyl iodide. However, this system is not ideal for more complicated alkyl halides.

The systematic way of naming alkyl halides is to name the halogen as a substituent, just like an alkyl group, and use numbers to indicate the position of the halogen atom on the main chain. The name of the halogen as a substituent comes from the stem of the element's name plus the ending *-o*, so the substituent names are *fluoro-*, *chloro-*, *bromo-* and *iodo-*. If there is more than one of a certain halogen, we use numerical prefixes to indicate the number of each kind, just as with alkyl groups. For example, this molecule



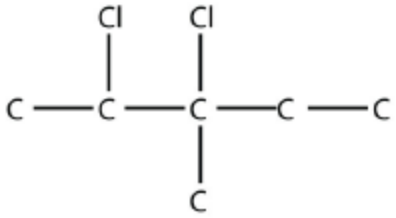
is 2-bromobutane, while this molecule



is 2,3-dichloropentane. If alkyl groups are present, the substituents are listed alphabetically. Numerical prefixes are ignored when determining the alphabetical ordering of substituent groups.

Example 14.9.1

Name this molecule.

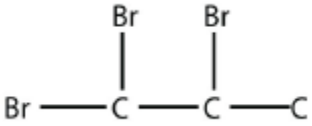


Solution

The longest carbon chain has five C atoms, so the molecule is a pentane. There are two chlorine substituents located on the second and third C atoms, with a one-carbon methyl group on the third C atom as well. The correct name for this molecule is 2,3-dichloro-3-methylpentane.

Exercise 14.9.1

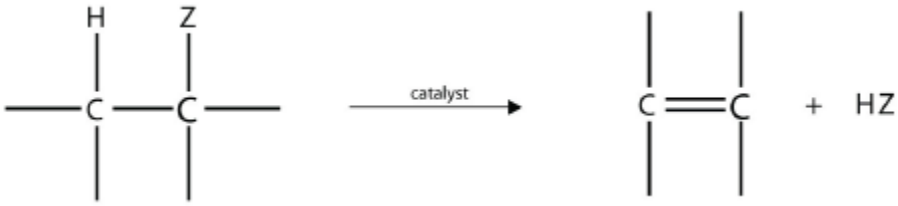
Name this molecule.



Answer available at the end of this section.

Most alkyl halides are insoluble in H_2O. Smaller alcohols, however, are very soluble in H_2O because these molecules can engage in hydrogen bonding with H_2O molecules. For larger molecules, however, the polar OH group is overwhelmed by the nonpolar alkyl part of the molecule. While methanol is soluble in H_2O in all proportions, only about 2.6 g of pentanol will dissolve in 100 g of H_2O. Larger alcohols have an even lower solubility in H_2O.

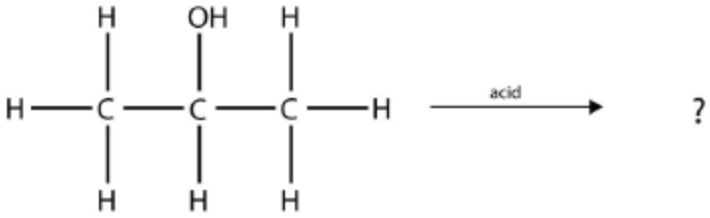
One reaction common to alcohols and alkyl halides is **elimination**, the removal of the functional group (either X or OH) and an H atom from an adjacent carbon. The general reaction can be written as follows:



where Z represents either the X or the OH group. The biggest difference between elimination in alkyl halides and elimination in alcohols is the identity of the catalyst: for alkyl halides, the catalyst is a strong base; for alcohols, the catalyst is a strong acid. For compounds in which there are H atoms on more than one adjacent carbon, a mixture of products results.

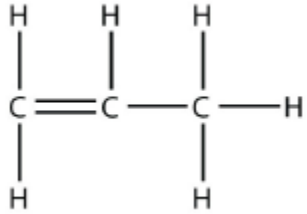
Example 14.9.3

Predict the organic product(s) of this reaction.



Solution

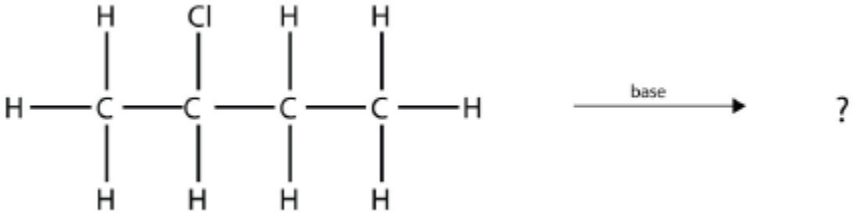
Under these conditions, an HOH (otherwise known as H_2O) molecule will be eliminated, and an alkene will be formed. It does not matter which adjacent carbon loses the H atom; in either case the product will be



which is propene.

Exercise 14.9.3

Predict the organic product(s) of this reaction.



Answer available at the end of this section.

Key Takeaways

- Alkyl halides have a halogen atom as a functional group.
- Alcohols have an OH group as a functional group.
- Nomenclature rules allow us to name alkyl halides and alcohols.
- In an elimination reaction, a double bond is formed as an HX or an HOH molecule is removed.

Answers

Exercise 14.9.1

1,1,2-tribromopropane

Exercise 14.9.3

1-butene and 2-butene

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14.10: Stereochemistry and Chirality



Maps take some time to build because we have to find or write matching materials. LibreTexts POV is that it is best to make available pages that we have finished rather than wait till the entire project is complete .This map is not completely finished, some pages are missing but we are workin' on it. . . (Public Domain ; Public Domain Pictures)

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15: ALDEHYDES AND KETONES

15.1: The Carbonyl Group
15.2: Naming Aldehydes and Ketones
15.3: Properties of Aldehydes and Ketones
15.4: Some Common Aldehydes and Ketones
15.5: Oxidation of Aldehydes
15.6: Reduction of Aldehydes and Ketones
15.7: Addition of Alcohols - Hemiacetals and Acetals

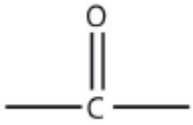
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15.1: The Carbonyl Group

Learning Objective

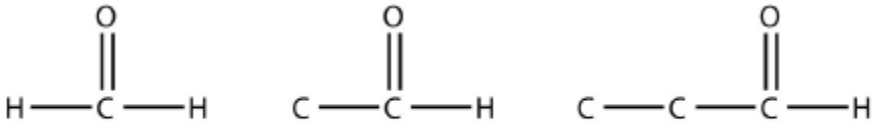
- Identify the aldehyde and ketone functional groups.

There are other functional groups that contain O atoms. Before we introduce them, we define the **carbonyl group**, which is formed when an O atom and a C atom are joined by a double bond:



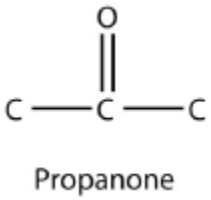
The other two bonds on the C atom are attached to other atoms. It is the identities of these other atoms that define what specific type of compound an organic molecule is.

If one bond of the carbonyl group is made to an H atom, then the molecule is classified as an **aldehyde** (If there are two H atoms, there is only 1 C atom). When naming aldehydes, the main chain of C atoms must include the carbon in the carbonyl group, which is numbered as position 1 in the carbon chain. The parent name of the hydrocarbon is used, but the suffix *-al* is appended. (Do not confuse *-al* with *-ol*, which is the suffix used for alcohols.) So we have

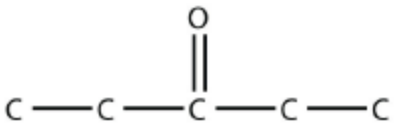


Methanal has a common name with which you may be familiar: formaldehyde. The main thing to note about aldehydes is that the carbonyl group is at the *end* of a carbon chain.

A carbonyl group in the middle of a carbon chain implies that both remaining bonds of the carbonyl group are made to C atoms. This type of molecule is called a **ketone.** Despite the fact that aldehydes and ketones have the same carbonyl group, they have different chemical and physical properties and are properly grouped as two different types of compounds. The smallest ketone has three C atoms in it. When naming a ketone, we take the name of the parent hydrocarbon and change the suffix to *-one*:



The common name for propanone is acetone. With larger ketones, we must use a number to indicate the position of the carbonyl group, much like a number is used with alkenes and alkynes:



3-Pentanone

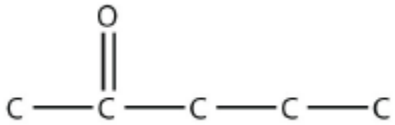
There is another way to name ketones: name the alkyl groups that are attached to the carbonyl group and add the word *ketone* to the name. So propanone can also be called dimethyl ketone, while 2-butanone is called methyl ethyl ketone.

Example 15.1.1

Draw the structure of 2-pentanone.

Solution

This molecule has five C atoms in a chain, with the carbonyl group on the second C atom. Its structure is as follows:



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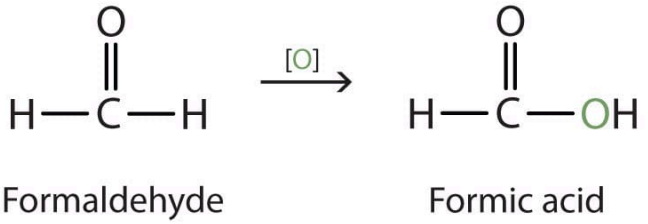
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15.2: Naming Aldehydes and Ketones

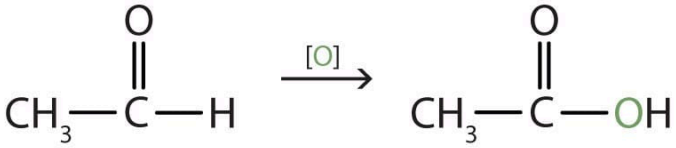
Learning Objectives

- Use the IUPAC system to name and draw 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*.



Formaldehyde Formic acid

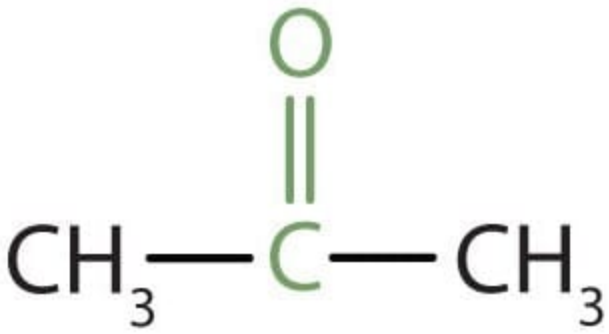


Acetaldehyde Acetic acid

The stems for the common names of the first four aldehydes are as follows:

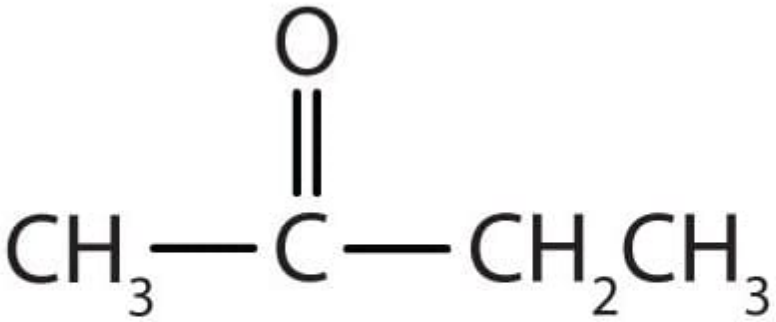
- 1 carbon atom: *form-*
- 2 carbon atoms: *acet-*
- 3 carbon atoms: *propion-*
- 4 carbon atoms: *butyr-*

Because the carbonyl group in a ketone must be attached to two carbon groups, the simplest ketone has three carbon atoms. It is widely known as *acetone*, a unique name unrelated to other common names for ketones.



Acetone

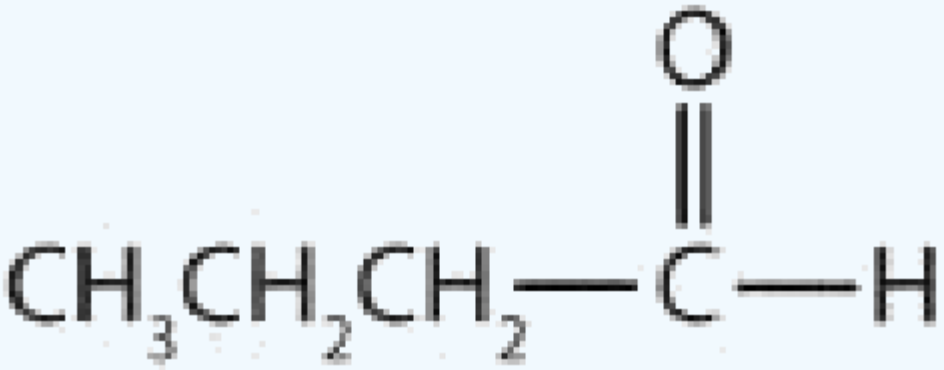
Generally, the common names of ketones consist of the names of the groups attached to the carbonyl group, followed by the word *ketone*. (Note the similarity to the naming of ethers.) Another name for acetone, then, is *dimethyl ketone*. The ketone with four carbon atoms is ethyl methyl ketone.

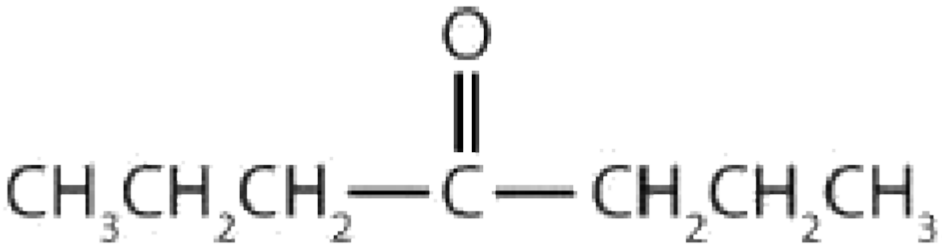
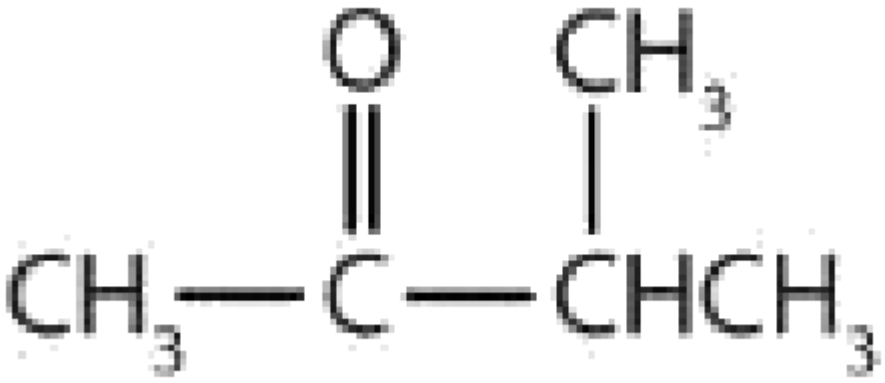


Ethyl methyl ketone

Example 15.2.1

Classify each compound as an aldehyde or a ketone. Give the common name for each ketone.

1. 

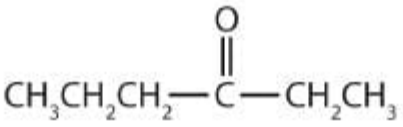
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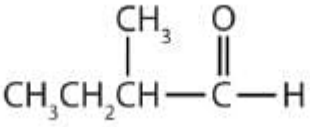
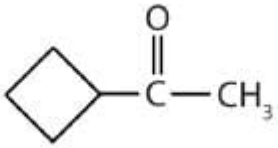
Solution

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 15.2.1

Classify each compound as an aldehyde or a ketone. Give the common name for each ketone.

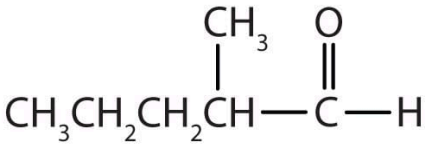
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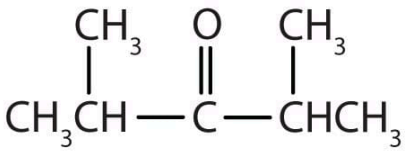
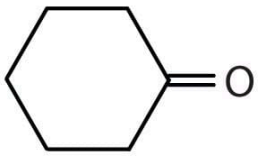
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Here are some simple IUPAC rules for naming aldehydes and ketones:

Example 15.2.2

Give the IUPAC name for each compound.

a. 

- 
- 

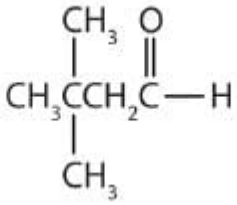
Solution

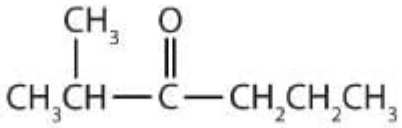
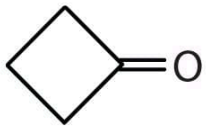
a. There are five carbon atoms in the LCC. The methyl group (CH_3) is a substituent on the second carbon atom of the chain; the aldehyde carbon atom is always C1. The name is derived from pentane. Dropping the *-e* and adding the ending *-al* gives pentanal. The methyl group on the second carbon atom makes the name 2-methylpentanal.
b. There are five carbon atoms in the LCC. The carbonyl carbon atom is C3, and there are methyl groups on C2 and C4. The IUPAC name is 2,4-dimethyl-3-pentanone.
c. There are six carbon atoms in the ring. The compound is cyclohexanone. No number is needed to indicate the position of the

carbonyl group because all six carbon atoms are equivalent.

Exercise

Give the IUPAC name for each compound.

a. 

- 
- 

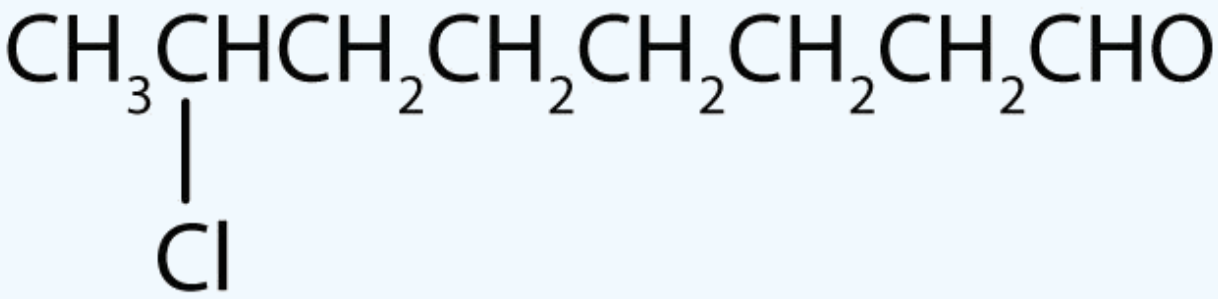
Example 15.2.3

Draw the structure for each compound.

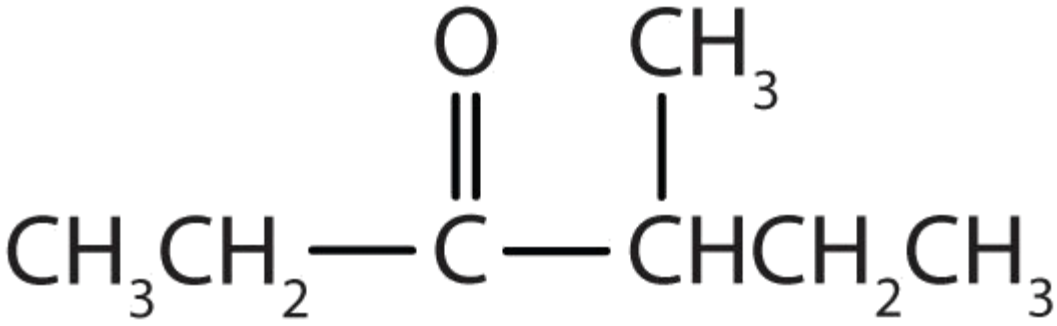
a. 7-chlorooctanal
b. 4-methyl–3-hexanone

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.



- 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

Draw the structure for each compound.

a. 5-bromo-3-iodoheptanal
b. 5-bromo-4-ethyl-2-heptanone

Concept Review Exercises

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.

1. The stem names of aldehydes and ketones are derived from those of the parent alkanes, defined by the longest continuous chain (LCC) of carbon atoms that contains the functional group.
2. For an aldehyde, drop the *-e* from the alkane name and add the ending *-al*. Methanal is the IUPAC name for formaldehyde, and ethanal is the name for acetaldehyde.
3. For a ketone, drop the *-e* from the alkane name and add the ending *-one*. Propanone is the IUPAC name for acetone, and butanone is the name for ethyl methyl ketone.
4. To indicate the position of a substituent on an aldehyde, the carbonyl carbon atom is always considered to be C1; it is unnecessary to designate this group by number.
5. To indicate the position of a substituent on a ketone, number the chain in the manner that gives the carbonyl carbon atom the lowest possible number. In cyclic ketones, it is understood that the carbonyl carbon atom is C1.

6. Give the structure and IUPAC name for the compound that has the common name *m*-bromobenzaldehyde.

7. Give the IUPAC name for glyceraldehyde, ($HOCH_2CHOHCHO$). (Hint: as a substituent, the OH group is named *hydroxy*.)

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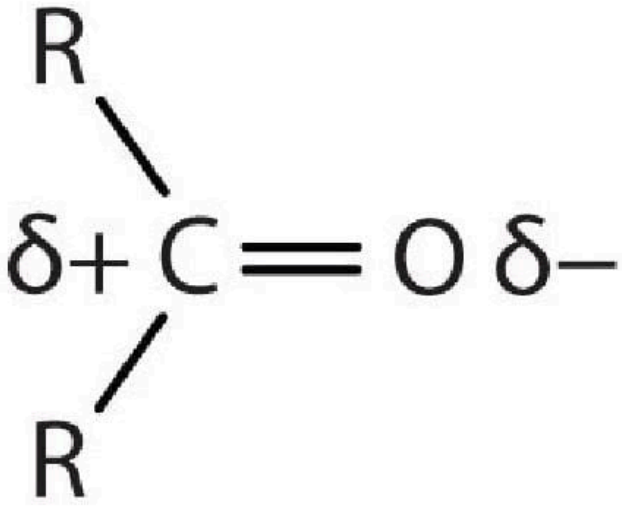
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15.3: Properties of Aldehydes and Ketones

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 15.3.1 shows that the polar single bonds in ethers have little such effect, whereas hydrogen bonding between alcohol molecules is even stronger.

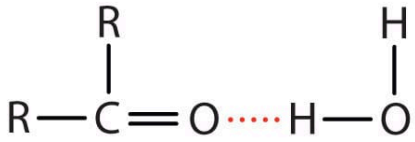
Table 15.3.1: Boiling Points of Compounds Having Similar Molar Masses but Different Types of Intermolecular Forces

Compound	Family	Molar Mass	Type of Intermolecular Forces	Boiling Point (°C)
$CH_3CH_2CH_2CH_3$	alkane	58	dispersion only	–1
$CH_3OCH_2CH_3$	ether	60	weak dipole	6
CH_3CH_2CHO	aldehyde	58	strong dipole	49
$CH_3CH_2CH_2OH$	alcohol	60	hydrogen bonding	97

Formaldehyde is a gas at room temperature. Acetaldehyde boils at 20°C; in an open vessel, it boils away in a warm room. Most other common aldehydes are liquids at room temperature.

Although the lower members of the homologous series have pungent odors, many higher aldehydes have pleasant odors and are used in perfumes and artificial flavorings. As for the ketones, acetone has a pleasant odor, but most of the higher homologs have rather bland odors.

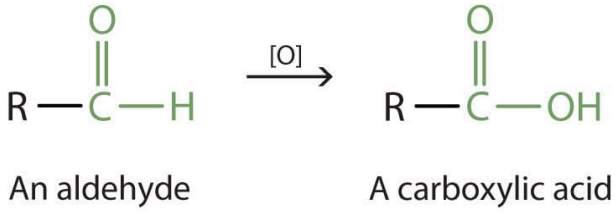
The oxygen atom of the carbonyl group engages in hydrogen bonding with a water molecule.

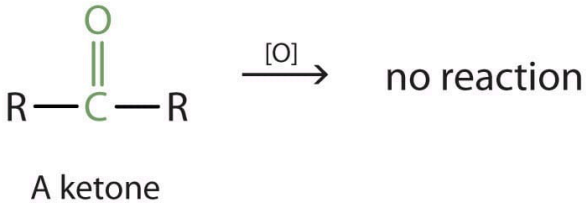


The solubility of aldehydes is therefore about the same as that of alcohols and ethers. Formaldehyde, acetaldehyde, and acetone are soluble in water. As the carbon chain increases in length, solubility in water decreases. The borderline of solubility occurs at about four carbon atoms per oxygen atom. All aldehydes and ketones are soluble in organic solvents and, in general, are less dense than water.

Oxidation of Aldehydes and Ketones

Aldehydes and ketones are much alike in many of their reactions, owing to the presence of the carbonyl functional group in both. They differ greatly, however, in one most important type of reaction: oxidation. Aldehydes are readily oxidized to carboxylic acids, whereas ketones resist oxidation.





The aldehydes are, in fact, among the most easily oxidized of organic compounds. They are oxidized by oxygen (O_2) in air to carboxylic acids.

$$2RCHO + O_2 \rightarrow 2RCOOH \tag{15.3.1}$$

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.

$$H_3N—Ag^+—NH_3 \tag{15.3.2}$$

When Tollens' reagent oxidizes an aldehyde, the Ag^+ ion is reduced to free silver (Ag).

$$RCHO(aq) + 2Ag(NH_3)_2^+(aq) + 3OH^-(aq) \longrightarrow$$

An aldehyde

$$RCOO^-(aq) + 2Ag(s) + 4\,NH_3(aq) + 2H_2O$$

Free silver

Deposited on a clean glass surface, the silver produces a mirror (Figure 15.3.1). Ordinary ketones do not react with Tollens' reagent.



Figure 15.3.1: 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.

Although ketones resist oxidation by ordinary laboratory oxidizing agents, they undergo combustion, as do aldehydes.

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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15.4: Some Common Aldehydes and Ketones

Learning Objectives

- Objective 1
- Objective 2

Formaldehyde has an irritating odor. Because of its reactivity, it is difficult to handle in the gaseous state. For many uses, it is therefore dissolved in water and sold as a 37% to 40% aqueous solution called *formalin*. Formaldehyde denatures proteins, rendering them insoluble in water and resistant to bacterial decay. For this reason, formalin is used in embalming solutions and in preserving biological specimens.

Aldehydes are the active components in many other familiar substances. Large quantities of formaldehyde are used to make phenol-formaldehyde resins for gluing the wood sheets in plywood and as adhesives in other building materials. Sometimes the formaldehyde escapes from the materials and causes health problems in some people. While some people seem unaffected, others experience coughing, wheezing, eye irritation, and other symptoms.

> The odor of green leaves is due in part to a carbonyl compound, cis-3-hexenal, which with related compounds is used to impart a “green” herbal odor to shampoos and other products.

Acetaldehyde is an extremely volatile, colorless liquid. It is a starting material for the preparation of many other organic compounds. Acetaldehyde is formed as a metabolite in the fermentation of sugars and in the detoxification of alcohol in the liver. Aldehydes are the active components of many other familiar materials (Figure 15.4.2).

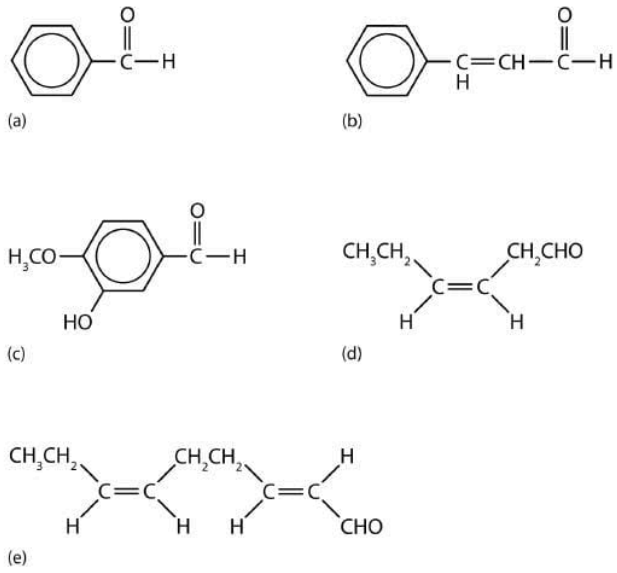


Figure 15.4.2 Some Interesting Aldehydes. (a) Benzaldehyde is an oil found in almonds; (b) cinnamaldehyde is oil of cinnamon; (c) vanillin gives vanilla its flavor; (d) *cis*-3-hexenal provides an herbal odor; and (e) *trans*-2-*cis*-6-nonadienal gives a cucumber odor.

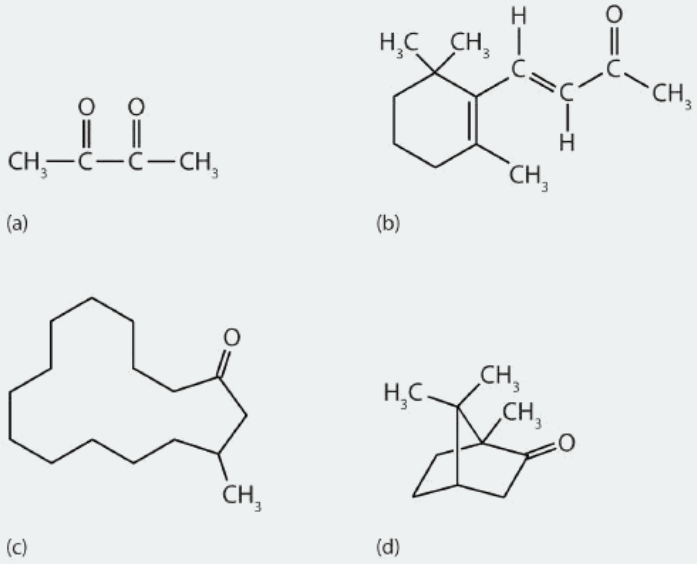
Acetone is the simplest and most important ketone. Because it is miscible with water as well as with most organic solvents, its chief use is as an industrial solvent (for example, for paints and lacquers). It is also the chief ingredient in some brands of nail

polish remover.

To Your Health: Acetone in Blood, Urine, and Breath

Acetone is formed in the human body as a by-product of lipid metabolism. Normally, acetone does not accumulate to an appreciable extent because it is oxidized to carbon dioxide and water. The normal concentration of acetone in the human body is less than 1 mg/100 mL of blood. In certain disease states, such as uncontrolled diabetes mellitus, the acetone concentration rises to higher levels. It is then excreted in the urine, where it is easily detected. In severe cases, its odor can be noted on the breath.

Ketones are also the active components of other familiar substances, some of which are noted in the accompanying figure.



Some ketones have interesting properties: (a) Butter flavoring comes from 2,3-butanedione; (b) β-ionone is responsible for the odor of violets; (c) muscone is musk oil, an ingredient in perfumes; and (d) camphor is used in some insect repellents.

Certain steroid hormones have the ketone functional group as a part of their structure. Two examples are progesterone, a hormone secreted by the ovaries that stimulates the growth of cells in the uterine wall and prepares it for attachment of a fertilized egg, and testosterone, the main male sex hormone. These and other sex hormones affect our development and our lives in fundamental ways.

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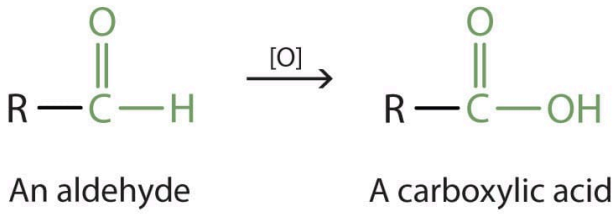
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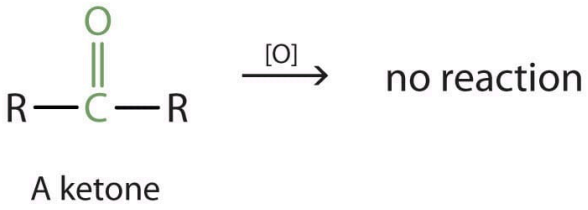
15.5: Oxidation of Aldehydes

Learning Objectives

- Objective 1
- Objective 2
-

ldehydes 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.

$$2RCHO + O_2 \rightarrow 2RCOOH \tag{15.5.1}$$

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.

$$H_3N—Ag^+—NH_3 \tag{15.5.2}$$

When Tollens' reagent oxidizes an aldehyde, the Ag^+ ion is reduced to free silver (Ag).

$$RCHO(aq) + 2Ag(NH_3)_2^+(aq) + 3OH^-(aq) \longrightarrow$$

An aldehyde

$$RCOO^-(aq) + 2Ag(s) + 4\,NH_3(aq) + 2H_2O$$

Free silver

Deposited on a clean glass surface, the silver produces a mirror (Figure 15.5.1). Ordinary ketones do not react with Tollens' reagent.



Figure 15.5.1: 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.

Although ketones resist oxidation by ordinary laboratory oxidizing agents, they undergo combustion, as do aldehydes.

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15.6: Reduction of Aldehydes and Ketones



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15.7: Addition of Alcohols - Hemiacetals and Acetals



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16: AMINES

16.1: Classifying Amines
16.2: Naming and Drawing Amines
16.3: Properties of Amines
16.4: Heterocyclic Nitrogen Compounds
16.5: Basicity of Amines
16.6: Amine Salts
16.7: Amines in Plants- Alkaloids

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16.1: Classifying Amines

Learning Objectives

- Determine the structural feature that classifies amines as primary, secondary, or tertiary.

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 16.1.1).

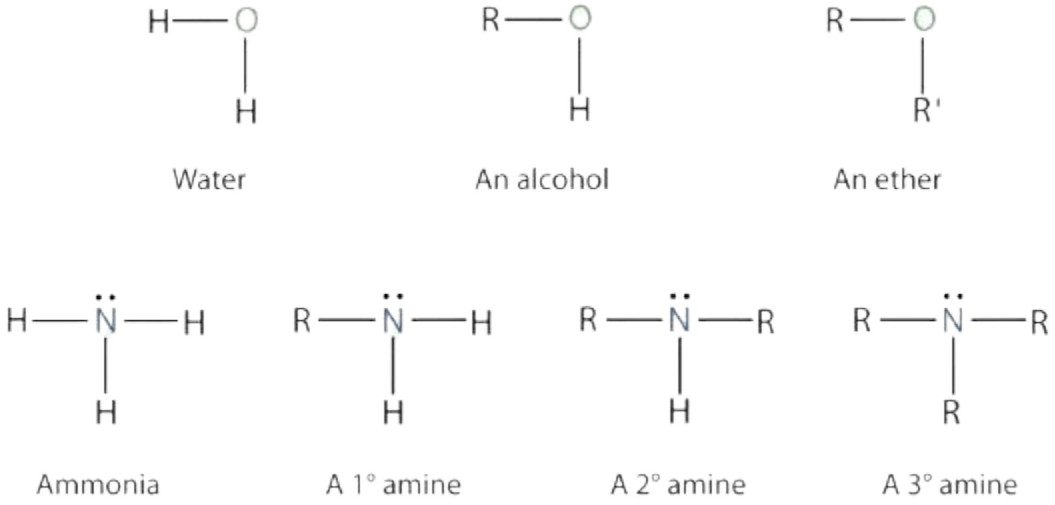


Figure 16.1.1: The Structure of Amines Compared to Water, an Alcohol, and an Ether

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.



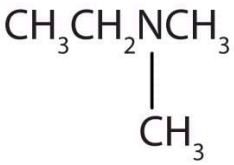
The common names for simple aliphatic amines consist of an alphabetic list of alkyl groups attached to the nitrogen atom, followed by the suffix *-amine*. (Systematic names are often used by some chemists.) The amino group (NH_2) is named as a substituent in more complicated amines, such as those that incorporate other functional groups or in which the alkyl groups

cannot be simply named.

Example 16.1.1

Name and classify each compound.

a. $CH_3CH_2CH_2NH_2$

b. 

- $CH_3CH_2NHCH_2CH_3$
- $CH_3CH_2CH_2NHCH_3$

Solution

a. There is only one alkyl group attached to the nitrogen atom, so the amine is primary. A group of three carbon atoms (a propyl group) is attached to the NH_2 group through an end carbon atom, so the name is propylamine.
b. There are two methyl groups and one ethyl group on the nitrogen atom. The compound is ethyldimethylamine, a tertiary amine.
c. There are two ethyl groups attached to the nitrogen atom; the amine is secondary, so the compound is diethylamine.
d. The nitrogen atom has a methyl group and a propyl group, so the compound is methylpropylamine, a secondary amine.

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16.2: Naming and Drawing Amines

Learning Objectives

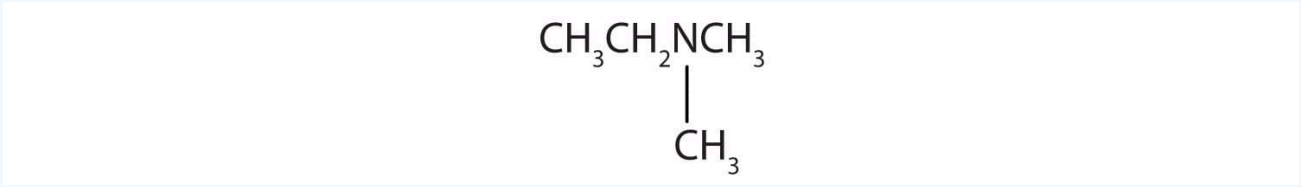
- Objective 1
- Objective 2

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 16.2.1

Name and classify each compound.

a. $CH_3CH_2CH_2NH_2$

b. 

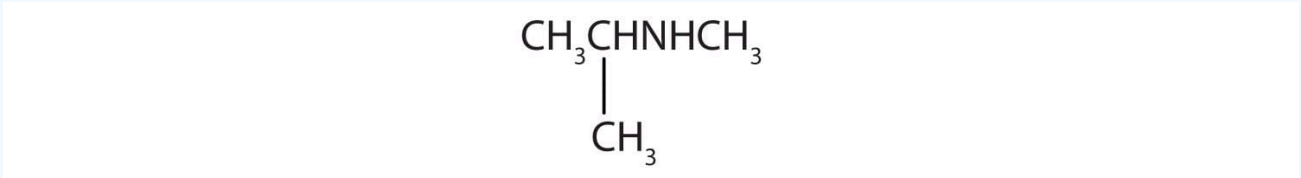
- $CH_3CH_2NHCH_2CH_3$
- $CH_3CH_2CH_2NHCH_3$

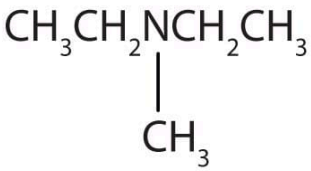
Solution

a. There is only one alkyl group attached to the nitrogen atom, so the amine is primary. A group of three carbon atoms (a propyl group) is attached to the NH_2 group through an end carbon atom, so the name is propylamine.
b. There are two methyl groups and one ethyl group on the nitrogen atom. The compound is ethyldimethylamine, a tertiary amine.
c. There are two ethyl groups attached to the nitrogen atom; the amine is secondary, so the compound is diethylamine.
d. The nitrogen atom has a methyl group and a propyl group, so the compound is methylpropylamine, a secondary amine.

Exercise 16.2.1

Name and classify each compound.

a. 



-
- $CH_3CH_2CH_2CH_2NH_2$
- $CH_3CH_2CH_2NHCH_2CH_2\ CH_3$

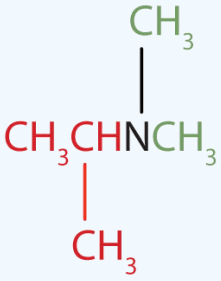
Example 16.2.2

Draw the structure for each compound and classify.

a. isopropyldimethylamine
b. dipropylamine

Solution

a. The name indicates that there are an isopropyl group (in red) and two methyl groups (in green) attached to the nitrogen atom; the amine is tertiary.



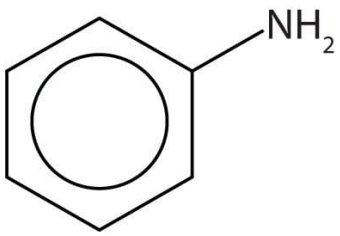
- The name indicates that there are two propyl groups attached to the nitrogen atom; the amine is secondary. (The third bond on the nitrogen atom goes to a hydrogen atom.) $CH_3CH_2CH_2NHCH_2CH_2CH_3$

Exercise 16.2.2

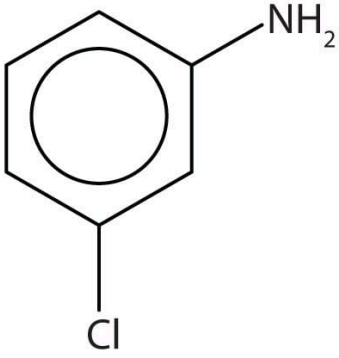
Draw the structure for each compound and classify.

a. ethylisopropylamine
b. diethylpropylamine

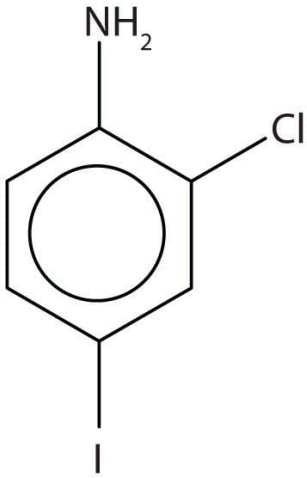
The primary amine in which the nitrogen atom is attached directly to a benzene ring has a special name—aniline. Aryl amines are named as derivatives of aniline.



Aniline



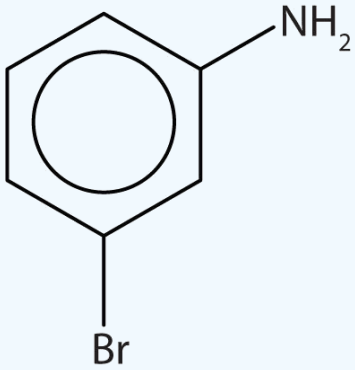
M-chloroaniline



2-Chloro-4-iodoaniline

Example 16.2.3

Name this compound.

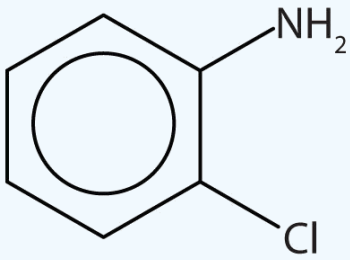


Solution

The benzene ring with an amino (NH_2) group is aniline. The compound is named as a derivative of aniline: 3-bromoaniline or *m*-bromoaniline.

Exercise 16.2.3

Name this compound.

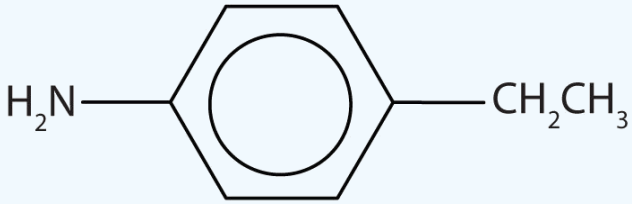


Example 16.2.4

Draw the structure for *p*-ethylaniline and classify.

Solution

The compound is a derivative of aniline. It is a primary amine having an ethyl group located *para* to the amino (NH_2) group.



Exercise 16.2.4

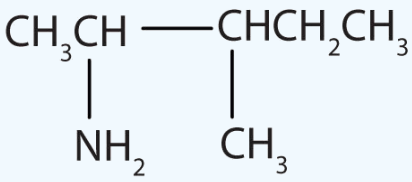
Draw the structure for *p*-isopropylaniline and classify.

Example 16.2.5

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 16.2.5

Draw the structure for 2-amino-3-ethyl-1-chloroheptane.

Ammonium (NH_4^+) ions, in which one or more hydrogen atoms are replaced with alkyl groups, are named in a manner analogous to that used for simple amines. The alkyl groups are named as substituents, and the parent species is regarded as the NH_4^+ ion.

For example, $CH_3NH_3^+$ is the methylammonium ion. The ion formed from aniline ($C_6H_5NH_3^+$) is called the anilinium ion.

Example 16.2.6

Name each ion.

a. $CH_3NH_3^+$
b. $(CH_3)_2NH_2^+$
c. $(CH_3)_3NH^+$
d. $(CH_3)_4N^+$

Solution

The ions have one, two, three, and four methyl (CH_3) groups attached to a nitrogen atom. Their names are as follows:

a. methylammonium ion
b. dimethylammonium ion
c. trimethylammonium ion
d. tetramethylammonium ion

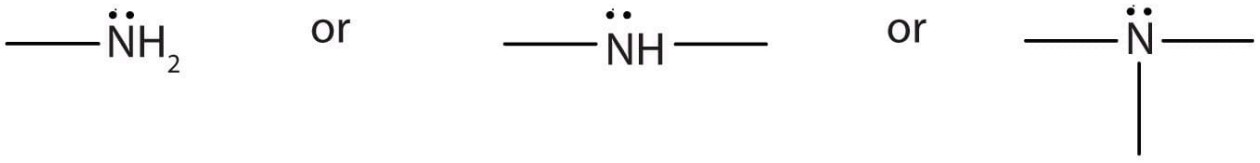
Exercise 16.2.6

Name each ion.

a. $CH_3CH_2NH_3^+$
b. $(CH_3CH_2)_3NH^+$
c. $(CH_3CH_2CH_2)_2NH_2^+$
d. $(CH_3CH_2CH_2CH_2)_4N^+$

Summary

An amine is a derivative of ammonia in which one, two, or all three hydrogen atoms are replaced by hydrocarbon groups. The amine functional group is as follows:



Amines are classified as primary, secondary, or tertiary by the number of hydrocarbon groups attached to the nitrogen atom. Amines are named by naming the alkyl groups attached to the nitrogen atom, followed by the suffix *-amine*.

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16.3: Properties of Amines

Learning Objectives

- Explain why the boiling points of primary and secondary amines are higher than those of alkanes or ethers of similar molar mass but are lower than those of alcohols.
- Compare the boiling points of tertiary amines with alcohols, alkanes, and ethers of similar molar mass.
- Compare the solubilities in water of amines of five or fewer carbon atoms with the solubilities of comparable alkanes and alcohols in water.

Primary and secondary amines have hydrogen atoms bonded to an nitrogen atom and are therefore capable of hydrogen bonding (part (a) of Figure 16.3.1), 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 16.3.1).

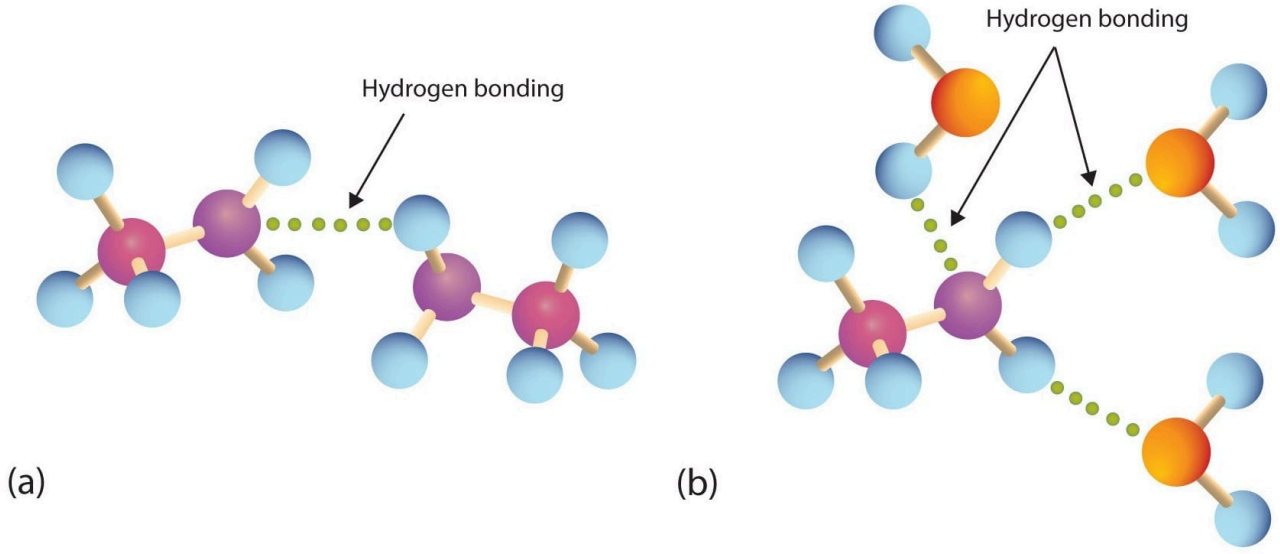


Figure 16.3.1: Hydrogen Bonding. (a) Amine molecules are associated through hydrogen bonding. (b) An amine molecule can form a hydrogen bond with water molecules.

Table 16.3.1: Physical Properties of Some Amines and Comparable Oxygen-Containing Compounds

Name	Condensed Structural Formula	Class	Molar Mass	Boiling Point (°C)	Solubility at 25°C (g/100 g Water)
butylamine	$CH_3CH_2CH_2CH_2NH_2$	1°	73	78	miscible
diethylamine	$(CH_3CH_2)_2NH$	2°	73	55	miscible
butyl alcohol	$CH_3CH_2CH_2CH_2OH$	—	74	118	8
dipropylamine	$(CH_3CH_2CH_2)_2NH$	2°	101	111	4
triethylamine	$(CH_3CH_2)_3N$	3°	101	90	14
dipropyl ether	$(CH_3CH_2CH_2)_2O$	—	102	91	0.25

All three classes of amines can engage in hydrogen bonding with water (Figure 16.3.1*b*). Amines of low molar mass are quite

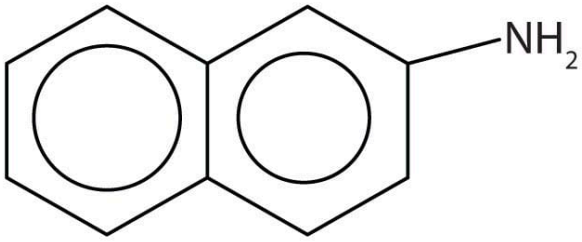
soluble in water; the borderline of solubility in water is at five or six carbon atoms.

To Your Health: Amines in Death and Life

Amines have “interesting” odors. The simple ones smell very much like ammonia. Higher aliphatic amines smell like decaying fish. Or perhaps we should put it the other way around: Decaying fish give off odorous amines. The stench of rotting fish is due in part to two diamines: putrescine and cadaverine. They arise from the decarboxylation of ornithine and lysine, respectively, amino acids that are found in animal cells.

$$HOCH_2CH_2OH$$

Aromatic amines generally are quite toxic. They are readily absorbed through the skin, and workers must exercise caution when handling these compounds. Several aromatic amines, including β-naphthylamine, are potent carcinogens.



Key Takeaways

- Primary and secondary amines have higher boiling points than those of alkanes or ethers of similar molar mass because they can engage in intermolecular hydrogen bonding. Their boiling points are lower than those of alcohols because alcohol molecules have hydrogen atoms bonded to an oxygen atom, which is more electronegative.
- The boiling points of tertiary amines, which cannot engage in hydrogen bonding because they have no hydrogen atom on the nitrogen atom, are comparable to those of alkanes and ethers of similar molar mass.
- Because all three classes of amines can engage in hydrogen bonding with water, amines of low molar mass are quite soluble in water.

Concept Review Exercises

1. Which compound has the higher boiling point, $CH_3CH_2CH_2CH_2CH_2NH_2$ or $CH_3CH_2CH_2CH_2CH_2CH_3$? Explain.

2. Which compound is more soluble in water, $CH_3CH_2CH_2CH_2CH_3$ or $CH_3CH_2NHCH_2CH_3$? Explain.

Answers

1. $CH_3CH_2CH_2CH_2CH_2NH_2$ because the nitrogen-to-hydrogen (N–H) bonds can engage in hydrogen bonding; $CH_3CH_2CH_2CH_2CH_2CH_3$ cannot engage in hydrogen bonding

2. $CH_3CH_2NHCH_2CH_3$ because amines can engage in hydrogen bonding with water; alkanes cannot engage in hydrogen bonding

Exercises

1. Which compound of each pair has the higher boiling point? Explain.

   a. butylamine or pentane
   b. CH_3NH_2 or $CH_3CH_2CH_2CH_2CH_2NH_2$

2. Which compound of each pair has the higher boiling point? Explain.

   a. butylamine or butyl alcohol
   b. trimethylamine or propylamine

3. Which compound is more soluble in water—$CH_3CH_2CH_3$ or $CH_3CH_2NH_2$? Explain.

4. Which compound is more soluble in water—$CH_3CH_2CH_2NH_2$ or $CH_3CH_2CH_2CH_2CH_2CH_2NH_2$? Explain.

Answers

1. a. butylamine because the N–H bonds can engage in hydrogen bonding; pentane cannot engage in hydrogen bonding
   b. $CH_3CH_2CH_2CH_2CH_2NH_2$ because it has a greater molar mass than CH_3NH_2

3. $CH_3CH_2NH_2$ because amines can engage in hydrogen bonding with water; alkanes cannot engage in hydrogen bonding

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16.4: Heterocyclic Nitrogen Compounds

Learning Objectives

- Objective 1
- Objective 2

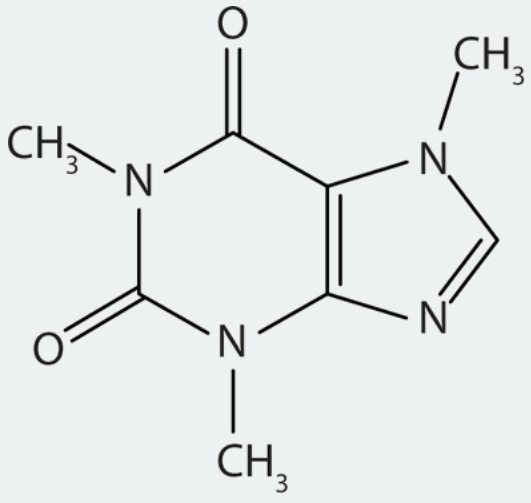
Heterocyclic Amines

Looking back at the various cyclic hydrocarbons discussed previously, we see that all the atoms in the rings of these compounds are carbon atoms. In other cyclic compounds, called **heterocyclic compounds** (Greek *heteros*, meaning "other"), nitrogen, oxygen, sulfur, or some other atom is incorporated in the ring. Many heterocyclic compounds are important in medicine and biochemistry. Some compose part of the structure of the nucleic acids, which in turn compose the genetic material of cells and direct protein synthesis.

Many heterocyclic amines occur naturally in plants. Like other amines, these compounds are basic. Such a compound is an **alkaloid**, a name that means "like alkalis." Many alkaloids are physiologically active, including the familiar drugs caffeine, nicotine, and cocaine.

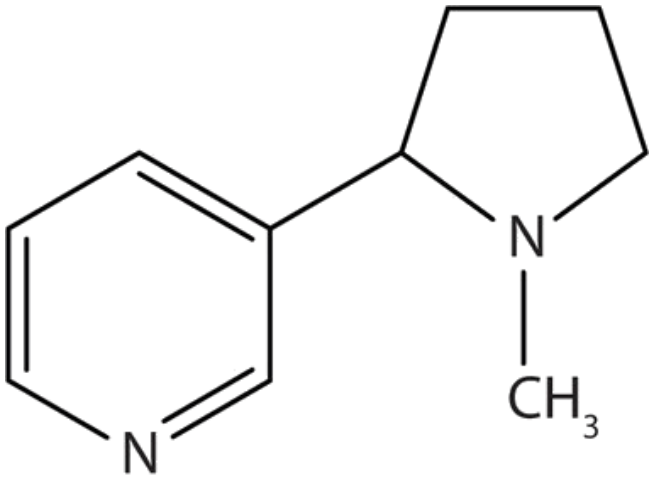
To Your Health: Three Well-Known Alkaloids

Caffeine is a stimulant found in coffee, tea, and some soft drinks. Its mechanism of action is not well understood, but it is thought to block the activity of adenosine, a heterocyclic base that acts as a neurotransmitter, a substance that carries messages across a tiny gap (synapse) from one nerve cell (neuron) to another cell. The effective dose of caffeine is about 200 mg, corresponding to about two cups of strong coffee or tea.



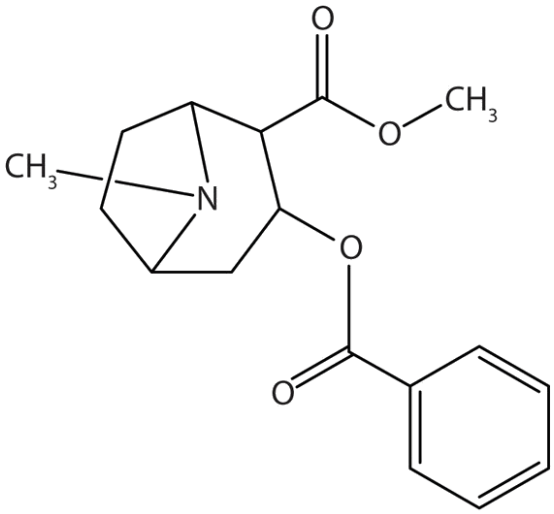
Caffeine

Nicotine acts as a stimulant by a different mechanism; it probably mimics the action of the neurotransmitter acetylcholine. People ingest this drug by smoking or chewing tobacco. Its stimulant effect seems transient, as this initial response is followed by depression. Nicotine is highly toxic to animals. It is especially deadly when injected; the lethal dose for a human is estimated to be about 50 mg. Nicotine has also been used in agriculture as a contact insecticide.



Nicotine

Cocaine acts as a stimulant by preventing nerve cells from taking up dopamine, another neurotransmitter, from the synapse. High levels of dopamine are therefore available to stimulate the pleasure centers of the brain. The enhancement of dopamine action is thought to be responsible for cocaine's "high" and its addictive properties. After the binge, dopamine is depleted in less than an hour. This leaves the user in a pleasureless state and (often) craving more cocaine.



Cocaine

Cocaine is used as the salt cocaine hydrochloride and in the form of broken lumps of the free (unneutralized) base, which is called *crack cocaine*.



Cocaine (freebase)

Cocaine hydrochloride

Because it is soluble in water, cocaine hydrochloride is readily absorbed through the watery mucous membranes of the nose when it is snorted. Crack cocaine is more volatile than cocaine hydrochloride. It vaporizes at the temperature of a burning cigarette. When smoked, cocaine reaches the brain in 15 s.

Summary

Amines are bases; they react with acids to form salts. Salts of aniline are properly named as *anilinium* compounds, but an older system is used to name drugs: the salts of amine drugs and hydrochloric acid are called “hydrochlorides.” Heterocyclic amines are cyclic compounds with one or more nitrogen atoms in the ring.

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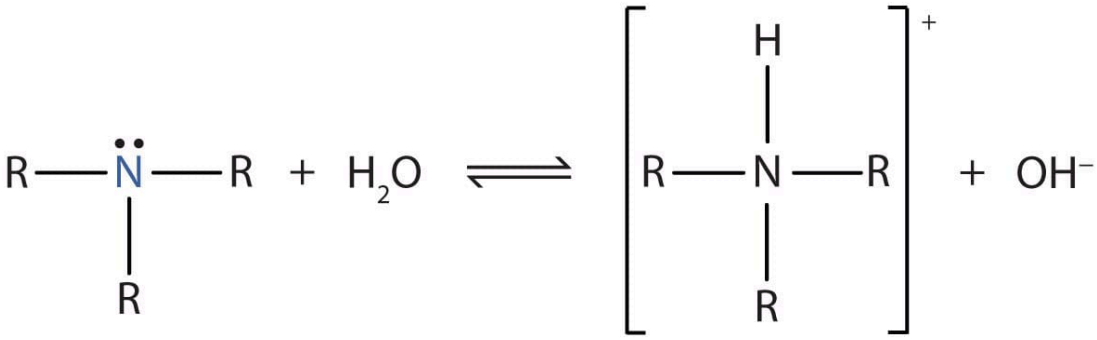
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16.5: Basicity of Amines

Learning Objectives

- Name the typical reactions that take place with amines.
- Describe heterocyclic amines.

Recall that ammonia (NH_3) acts as a base because the nitrogen atom has a lone pair of electrons that can accept a proton. Amines also have a lone electron pair on their nitrogen atoms and can accept a proton from water to form substituted ammonium (NH_4^+) ions and hydroxide (OH^-) ions:



As a specific example, methylamine reacts with water to form the methylammonium ion and the OH^- ion.

$$CH_3NH_2(aq) + H_2O \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$$

Methylamine — Methylammonium ion

Nearly all amines, including those that are not very soluble in water, will react with strong acids to form salts soluble in water.

$$CH_3(CH_2)_6NH_2(l) + HNO_3(aq) \longrightarrow CH_3(CH_2)_6NH_3^+NO_3^-(aq)$$

Octylamine (insoluble) — Octylammonium nitrate (soluble)

Amine salts are named like other salts: the name of the cation is followed by the name of the anion.

Example 16.5.1

What are the formulas of the acid and base that react to form $[CH_3NH_2CH_2CH_3]^+CH_3COO^-$?

Solution

The cation has two groups—methyl and ethyl—attached to the nitrogen atom. It comes from ethylmethylamine ($CH_3NHCH_2CH_3$). The anion is the acetate ion. It comes from acetic acid (CH_3COOH).

Exercise 16.5.1

What are the formulas of the acid and base that react to form $(CH_3CH_2CH_2)_3NH^+I^-$?

To Your Health: Amine Salts as Drugs

Salts of aniline are properly named as *anilinium* compounds, but an older system, still in use for naming drugs, identifies the salt of aniline and hydrochloric acid as "aniline hydrochloride." These compounds are ionic—they are salts—and the properties of the compounds (solubility, for example) are those characteristic of salts. Many drugs that are amines are converted to hydrochloride salts to increase their solubility in aqueous solution.

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16.6: Amine Salts



Maps take some time to build because we have to find or write matching materials. LibreTexts POV is that it is best to make available pages that we have finished rather than wait till the entire project is complete .This map is not completely finished, some pages are missing but we are workin' on it. . . (Public Domain ; Public Domain Pictures)

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16.7: Amines in Plants- Alkaloids

Learning Objectives

- Objective 1
- Objective 2

Addictive Alkaloids

Since ancient times, plants have been used for medicinal purposes. One class of substances, called *alkaloids*, found in many of these plants has been isolated and found to contain cyclic molecules with an amine functional group. These amines are bases. They can react with H_3O^+ in a dilute acid to form an ammonium salt, and this property is used to extract them from the plant:

$$R_3N + H_3O^+ + Cl^- \xrightarrow{R_3NH^+} Cl^- + H_2O$$

The name alkaloid means “like an alkali.” Thus, an alkaloid reacts with acid. The free compound can be recovered after extraction by reaction with a base:

$$[R_3NH^+]Cl^- + OH^- \longrightarrow R_3N + H_2O + Cl^-$$

The structures of many naturally occurring alkaloids have profound physiological and psychotropic effects in humans. Examples of these drugs include nicotine, morphine, codeine, and heroin. The plant produces these substances, collectively called secondary plant compounds, as chemical defenses against the numerous pests that attempt to feed on the plant:

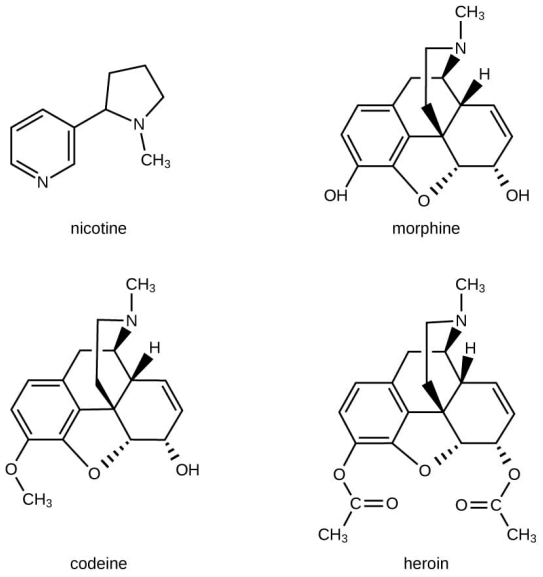


Figure 16.7.3).



Figure 16.7.3: Poppies can be used in the production of opium, a plant latex that contains morphine from which other opiates, such as heroin, can be synthesized. (credit: Karen Roe)

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17: CARBOXYLIC ACIDS AND THEIR DERIVATIVES

17.1: Carboxylic Acids and Their Derivatives- Properties and Names
17.2: Acidity of Carboxylic Acids
17.3: Reactions of Carboxylic Acids - Ester and Amide Formation
17.4: Hydrolysis of Esters and Amides
17.5: Polyamides and Polyesters
17.6: Phosphoric Acid Derivatives

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17.1: Carboxylic Acids and Their Derivatives- Properties and Names

Learning Objectives

- Objective 1
- Objective 2

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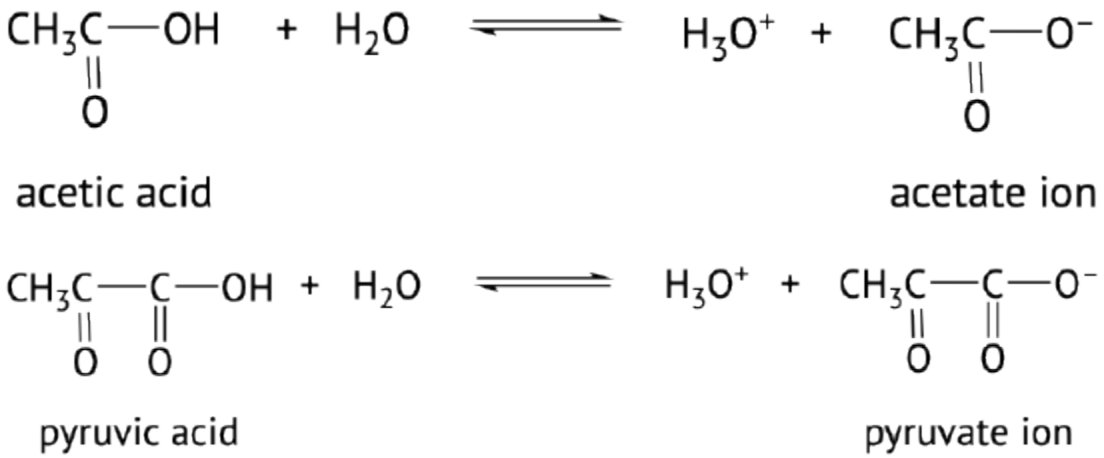
17.2: Acidity of Carboxylic Acids

Learning Objectives

- Define pK_a and use it to determine acidity of different carboxylic acids.
- Describe the reactions between carboxylic acids and strong bases.

Ionization of Carboxylic Acids

Carboxylic acids are named such because they tend to be more acidic than other functional groups in organic chemistry. In dilute aqueous solutions, they act as *weak acids* that partially dissociate to produce the corresponding **carboxylate anion** and hydronium cation (H_3O^+). Carboxylate anions are named by replacing the *-ic acid* ending from the carboxylic acid with *-ate*, see examples below.



The extent of dissociation of these weak acids in water is described by K_a values. Remember that a compound with a smaller K_a value will be a weaker acid.

$$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+ \; K_a = \frac{[\mathrm{RCOO^-}][\mathrm{H_3O^+}]}{[\mathrm{RCOOH}]}$$

When comparing the acidity of organic and biomolecules, it is useful (and more preferable) to use pK_a values instead of K_a values, which are calculated by taking the negative log of K_a: $pK_a = -\log K_a$. When using the pK_a scale, it is important to know that *weaker acids* have *larger* and more positive pK_a values, this is opposite of K_a values. The pK_a values of some typical carboxylic acids are listed in Table 17.2.1. (Remember that pK_a is a log expression, which means that every 1 pK_a unit represents a 10-fold change in acidity.)

Table 17.2.1: Comparisons of Carboxylic Acid K_a and pK_a Values

Name	Compound	K_a	pK_a
formic acid	HCOOH	1.8×10^{-4}	3.74
acetic acid	CH_3COOH	1.8×10^{-5}	4.74
propanoic acid	CH_3CH_2COOH	1.3×10^{-5}	4.89
butanoic acid	$CH_3CH_2CH_2COOH$	1.5×10^{-5}	4.82

Name	Compound	K_a	pK_a
chloroacetic acid	$ClCH_2COOH$	1.4×10^{-3}	2.85
trichloroacetic acid	Cl_3CCOOH	2.3×10^{-1}	0.64
hexanoic acid	$CH_3(CH_2)_4COOH$	1.3×10^{-5}	4.89
benzoic acid	C_6H_5COOH	6.5×10^{-5}	4.19
oxalic acid	$HOOCCOOH$	5.4×10^{-2}	1.27
	$^-OOCCOOH$	5.2×10^{-5}	4.28
glutaric acid	$HOOC(CH_2)_3COOH$	4.5×10^{-5}	4.35
	$^-OOC(CH_2)_3COOH$	3.8×10^{-6}	5.42

Neutralization of Carboxylic Acids

Carboxylic acids will react with bases such as sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), and sodium bicarbonate ($NaHCO_3$) to form water and a **carboxylic acid salt**:

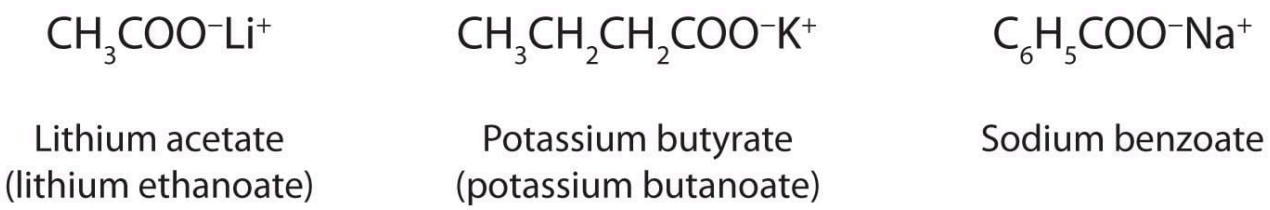
$$RCOOH + NaOH(aq) \rightarrow RCOO^-Na^+(aq) + H_2O$$

$$2RCOOH + Na_2CO_3(aq) \rightarrow 2RCOO^-Na^+(aq) + H_2O + CO_2(g)$$

$$RCOOH + NaHCO_3(aq) \rightarrow RCOO^-Na^+(aq) + H_2O + CO_2(g)$$

In these reactions, the carboxylic acids act like inorganic acids: they neutralize basic compounds. With solutions of carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions, they also form carbon dioxide gas.

Carboxylic acid salts are named in the same manner as inorganic salts: the name of the cation is followed by the name of the organic anion. The name of the anion is obtained by dropping the *-ic* ending of the acid name and replacing it with the suffix *-ate*. This rule applies whether we are using common names or International Union of Pure and Applied Chemistry (IUPAC) names:



Note

The salts of long-chain carboxylic acids are called soaps.

$$CH_3(CH_2)_{13}CH_2COO^-Na^+$$

Sodium palmitate (a soap)

Example 17.2.1

Write an equation for each reaction.

1. the ionization of propionic acid in water (H_2O)
2. the neutralization of propionic acid with aqueous sodium hydroxide (NaOH)

Solution

Propionic acid has three carbon atoms, so its formula is CH_2CH_2COOH.

1. Propionic acid ionizes in water to form a propionate ion and a hydronium (H_3O^+) ion. $CH_3CH_2COOH(aq) + H_2O(\ell) \rightarrow CH_3CH_2COO^-(aq) + H_3O^+(aq)$
2. Propionic acid reacts with NaOH(aq) to form sodium propionate and water. $CH_3CH_2COOH(aq) + NaOH(aq) \rightarrow CH_3CH_2COO^-Na^+(aq) + H_2O(\ell)$

Exercise 17.2.1

Write an equation for each reaction.

a. the ionization of formic acid in water
b. the ionization of *p*-chlorobenzoic acid in water

Example 17.2.2

Write an equation for the reaction of decanoic acid with each compound.

a. aqueous sodium hydoxide (NaOH)
b. aqueous sodium bicarbonate ($NaHCO_3$)

Solution

a. Decanoic acid has 10 carbon atoms. It reacts with NaOH to form a salt and water (H_2O). $CH_3(CH_2)_8COOH + NaOH(aq) \rightarrow CH_3(CH_2)_8COO^-Na^+(aq) + H_2O(\ell)$
b. With $NaHCO_3$, the products are a salt, H_2O, and carbon dioxide (CO_2). $CH_3(CH_2)_8COOH + NaHCO_3(aq) \rightarrow CH_3(CH_2)_8COO^-Na^+(aq) + H_2O(\ell) + CO_2(g)$

Exercise 17.2.3

Write an equation for the reaction of benzoic acid with each compound.

a. aqueous sodium hydroxide (NaOH)

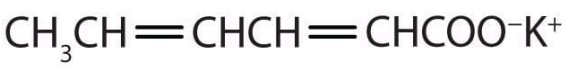
b. aqueous sodium bicarbonate ($NaHCO_3$)

Note 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

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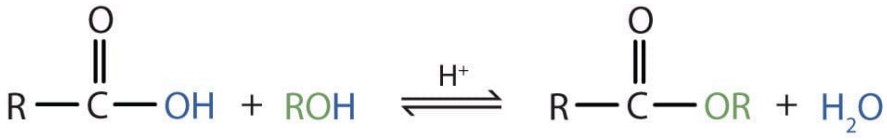
17.3: Reactions of Carboxylic Acids - Ester and Amide Formation

Learning Objectives

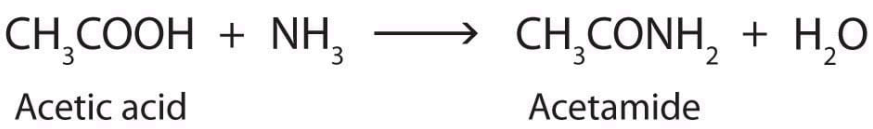
- To identify and describe the substances from which most esters are prepared.
- To identify and describe the substances from which most amides are prepared.

Carboxylic acids will react with alcohols and amines following a similar pattern. In both cases, the –OH group of the carboxylic acid will be replaced by a different group to form either an ester or an amide, with water formed as a by-product. When the reaction involves an alcohol, the –OH of the acid is replaced by the –OR' of the alcohol. When the reaction involves an amine, the –OH of the acid is replaced by the $-NH_2$, or –NHR', or $-NR'_2$ of the amine.

Ester formation

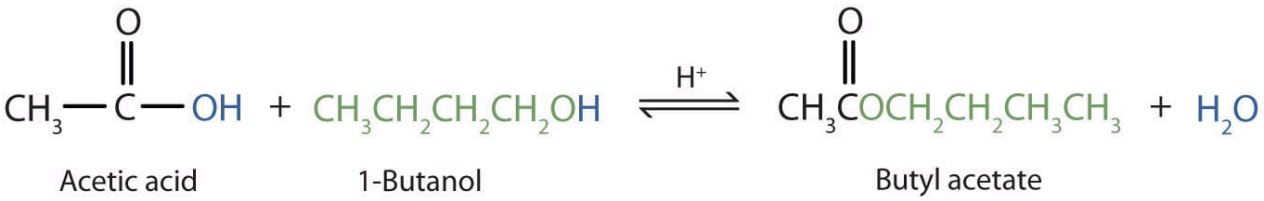


Amide formation



Esterification

Esters are prepared by **esterification**, a reaction in which a carboxylic acid and an alcohol are heated in the presence of an acid catalyst:



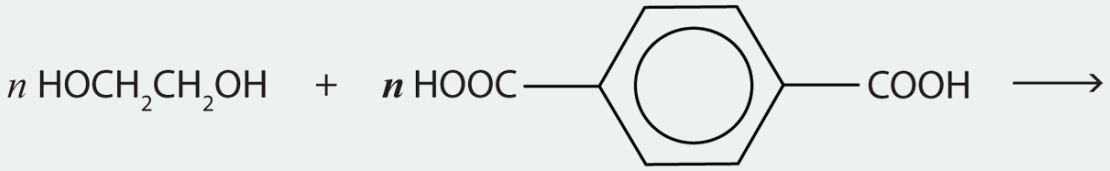
The reaction is reversible and will reach equilibrium with approximately equivalent amounts of reactants and products. Using excess amounts of alcohol and continuously removing a product, can drive the reaction towards the product side as per

LeChatelier's principle.

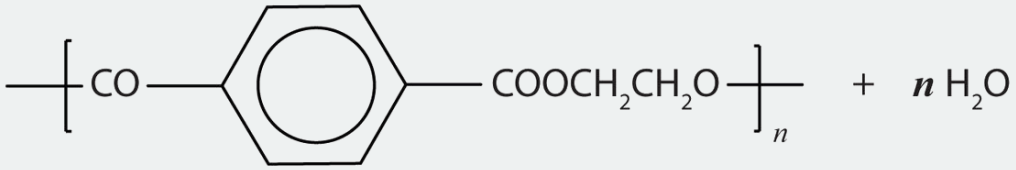
A Closer Look: Condensation Polymers

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:



Ethylene glycol — Terephthalic acid



Polyethylene terephthalate

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.

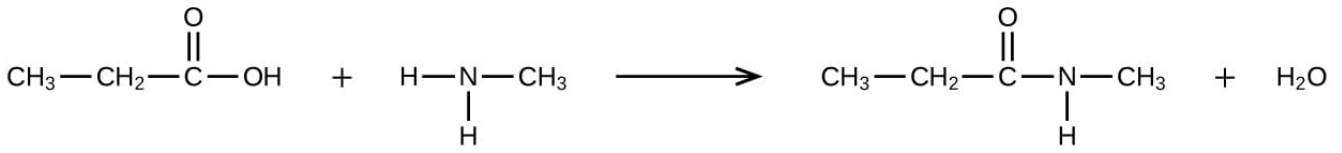
Amide Formation

When a carboxylic acid reacts with ammonia (NH_3) a *primary amide* is formed:



Acetic acid — Acetamide

When a carboxylic acid reacts with primary or secondary amines, secondary or tertiary amides are produced, respectively.



carboxylic acid — amine — amide — water

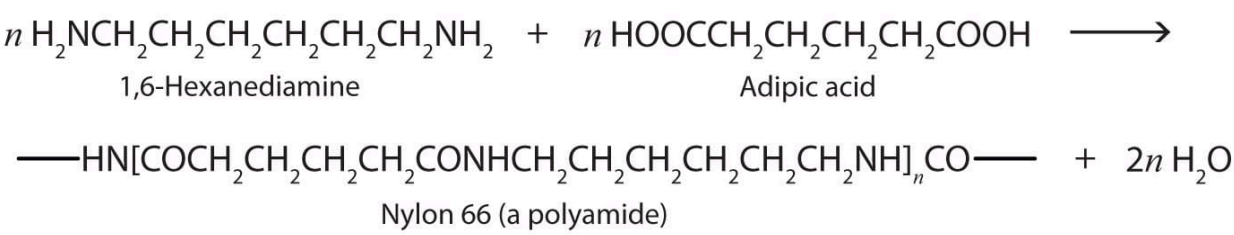
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Tertiary amines do not have a hydrogen attached to the nitrogen and therefore do not form amides when mixed with carboxylic acids. However, an acid-base reaction does occur with the amine accepting a proton (acts as a base) and the carboxylic acid donating a proton. In this case the ammonium and carboxylate salts are formed:

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Note 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.

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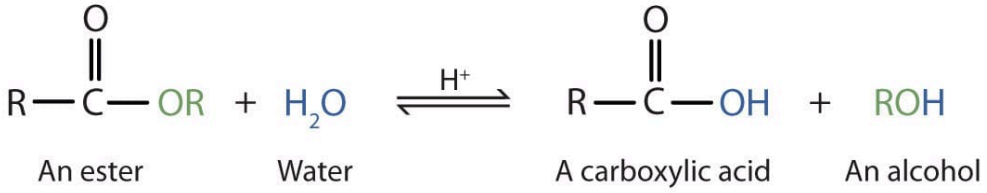
17.4: Hydrolysis of Esters and Amides

Learning Objectives

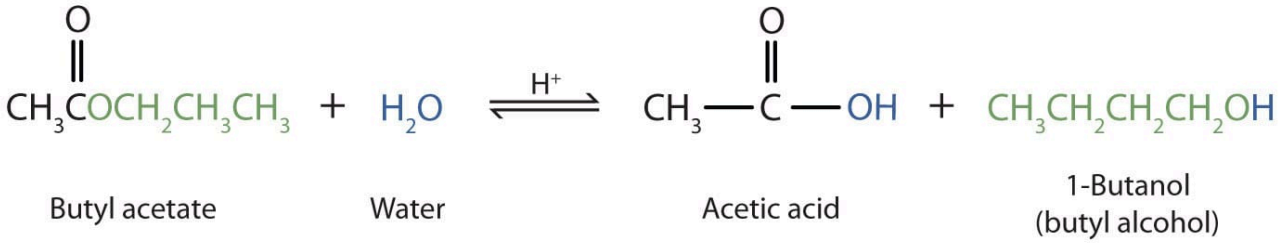
- Describe the typical reaction that takes place with esters.
- Identify the products of an acidic hydrolysis of an ester.
- Identify the products of a basic hydrolysis of an ester.

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.

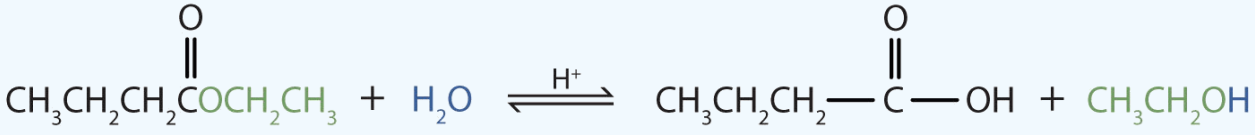


Example 17.4.1

Write an equation for the acidic hydrolysis of ethyl butyrate ($CH_3CH_2CH_2COOCH_2CH_3$) and name the products.

Solution

Remember that in acidic hydrolysis, water (HOH) splits the ester bond. The H of HOH joins to the oxygen atom in the OR part of the original ester, and the OH of HOH joins to the carbonyl carbon atom:

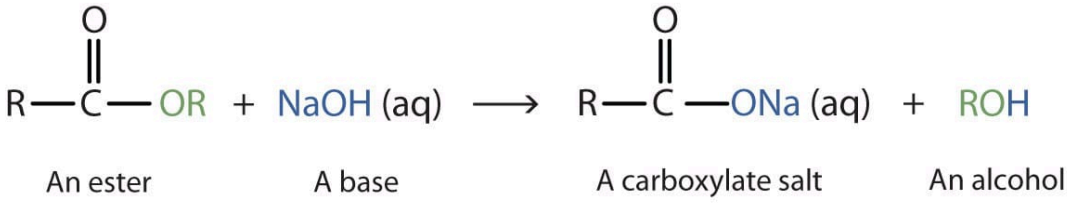


The products are butyric acid (butanoic acid) and ethanol.

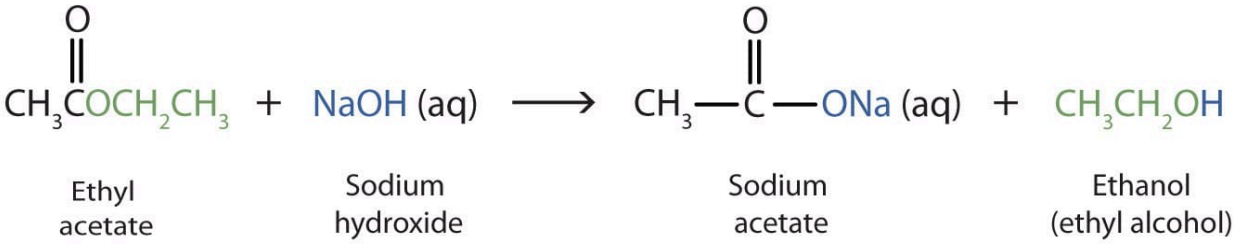
Exercise 17.4.1

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:

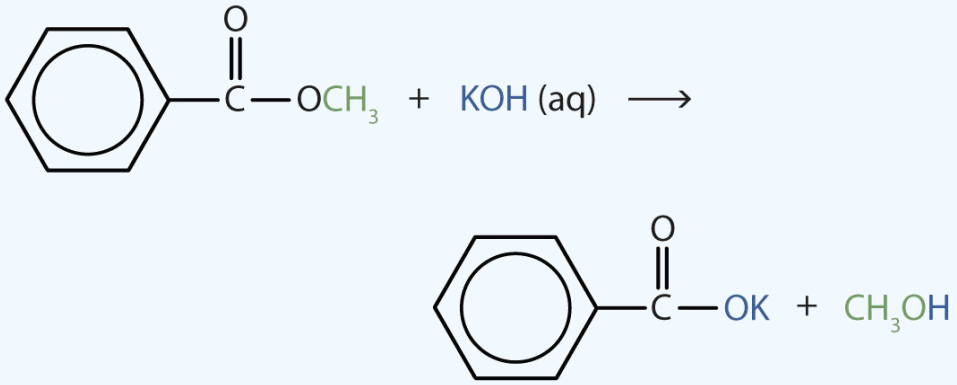


Example 17.4.2

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 s*alt* of the acid (in this case, the potassium salt). The alcohol portion of the ester ends up as the free alcohol.

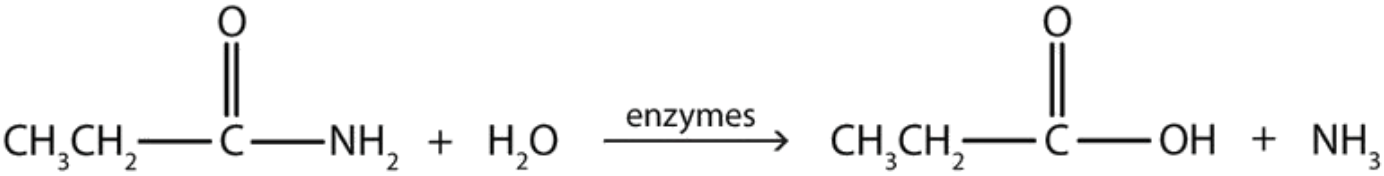


Exercise 17.4.2

Write the equation for the hydrolysis of ethyl propanoate in a sodium hydroxide solution.

Hydrolysis of Amides

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.

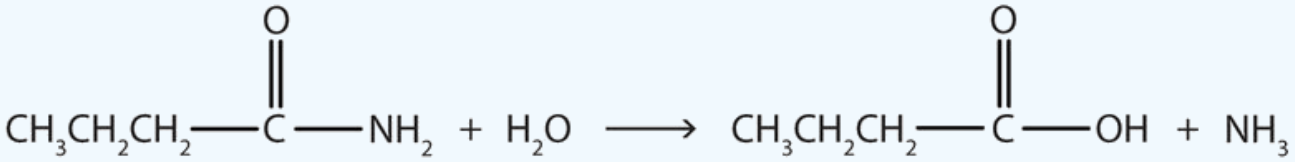
Example 17.4.1

Write the equation for the hydrolysis of each compound.

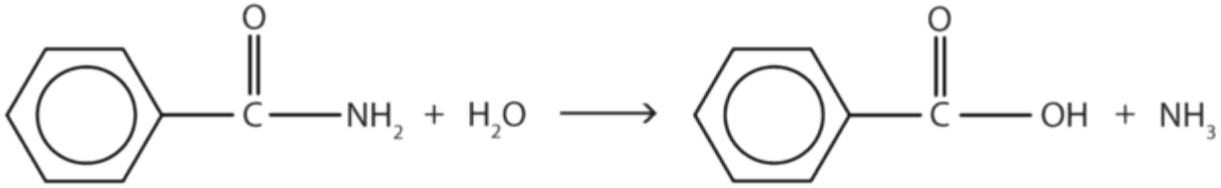
a. butyramide
b. benzamide

Solution

a. The hydrolysis of a simple amide produces an organic acid and ammonia. Butyramide thus yields butyric acid and ammonia.



- The hydrolysis of an amide produces an organic acid and ammonia. Benzamide thus yields benzoic acid and ammonia.



Exercise 17.4.1

Write the equation for the hydrolysis of each compound.

a. propionamide (propanamide)
b. hexanamide

Career Focus: Athletic Trainer

Athletic training is an allied health-care profession recognized by the American Medical Association. The athletic trainer's role is to recognize, evaluate, and provide immediate care for athletic injuries; prevent athletic injuries by taping, bandaging, and bracing vulnerable body parts; make referrals to medical doctors when necessary; and rehabilitate injured athletes. Athletic trainers work in high schools, colleges, and other organizations where athletics programs are found. Athletic trainers usually have a degree from an accredited athletic training program whose curriculum includes such basic science courses as biology, chemistry, and physics. These studies provide the necessary background for more applied courses, such as anatomy and physiology, exercise physiology, kinesiology, and nutrition. Knowledge of chemistry is necessary for understanding pharmacological and medical terminology. For example, athletic trainers must understand the action of numerous drugs, many of which are esters, amines, or amides like those mentioned in this chapter.

Athletic trainers may have administrative duties, such as the responsibility for ordering supplies. They also need to be able to evaluate nutritional supplements because providing the wrong one can get an athlete banned from competition and may bring sanctions against a school. In short, the athletic trainer is responsible for the overall health and well-being of the athletes in his or her charge.

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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17.5: Polyamides and Polyesters

Learning Objectives

- Describe how polyamides and polyesters are formed.

Animal intestines and silk were used for all guitar strings for centuries, until modern technology and changes in musical taste brought about significant changes. There are two major types of guitar strings in use today. Steel strings (first developed around 1900) are found on acoustic and electric guitars. They have a bright, crisp sound that lends itself well to diverse music such as jazz, rock 'n' roll, and bluegrass. Nylon strings are a more recent development. During World War II, the silk and animal products needed to manufacture steel guitar strings were not available. Nylon quickly proved to be a more-than-adequate substitute. Now nylon strings are found on all classical guitars. Their sound is somewhat softer than the steel strings, making the tone quality well-suited for the classical genre of music.

Polymerization - Condensation Polymers

A condensation polymer is a polymer formed by condensation reactions. Monomers of condensation polymers must contain two functional groups so that each monomer can link up with two other monomers. One type of condensation polymer is called a polyamide.

One pair of monomers that can form a *polyamide* is that of adipic acid and hexanediamine. Adipic acid is a carboxylic acid with two carboxyl groups on either end of the molecule. Hexanediamine has amino groups on either end of a six-carbon chain. When these molecules react with each other, a molecule of water is eliminated, classifying it as a condensation reaction (see figure below).

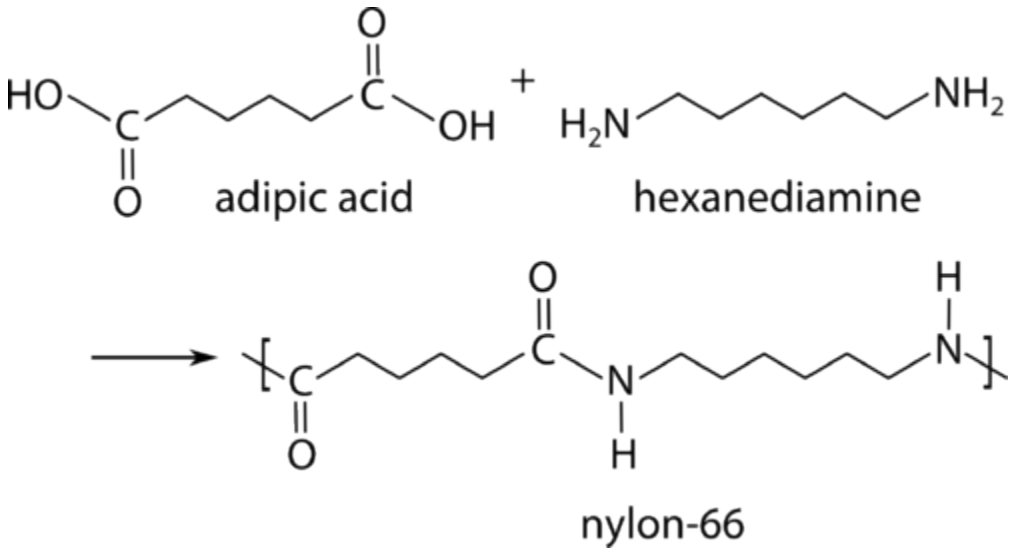


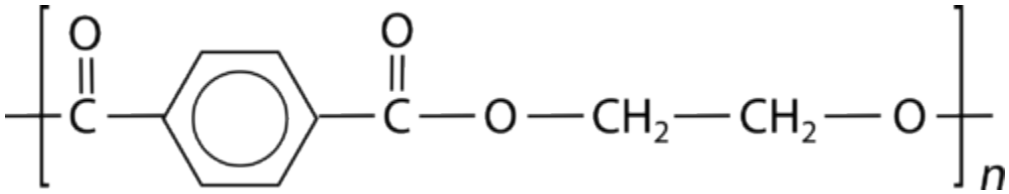
Figure 17.5.2: Nylon synthesis.

The polymer that results from the repetition of the condensation reaction is a polyamide called nylon-66. Nylon-66 was first invented in 1935 and has been used in all sorts of products. Polyamides, including Nylon-66, are commonly found in fibers and clothing, cooking utensils, fishing line, and carpeting—among many other applications.



Figure 17.5.3: Nylon spatula.

Polyester is another common type of condensation polymer. Recall that esters are formed from the reaction of an alcohol with a carboxylic acid. When both the acid and alcohol have two functional groups, the ester is capable of being polymerized. One such polyester is called polyethylene terephthalate (PET) and is formed from the reaction of ethylene glycol with terephthalic acid. The structure of PET is shown below.



PET is used in tires, photographic film, food packaging, and clothing. Polyester fabric is used in permanent-press clothing. Its resistance to wrinkling comes from the cross-linking of the polymer strands.

Summary

- A condensation polymer is a polymer formed by condensation reactions.
- Polyamides and polyesters are common types of condensation polymers.

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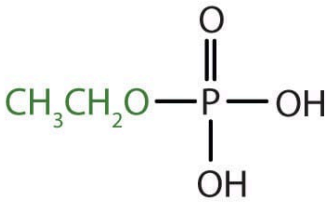
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17.6: Phosphoric Acid Derivatives

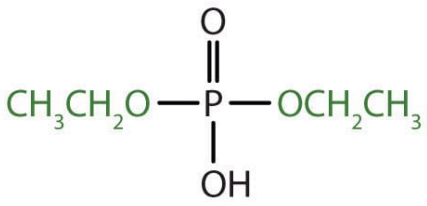
Learning Objectives

- Objective 1
- Objective 2

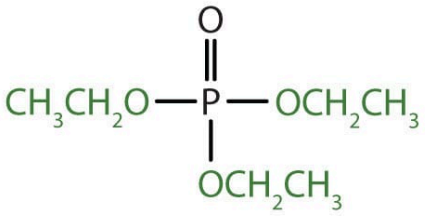
Just as carboxylic acids do, inorganic acids such as nitric acid (HNO_3), sulfuric acid (H_2SO_4), and phosphoric acid (H_3PO_4) also form esters. The esters of phosphoric acid are especially important in biochemistry. A phosphoric acid molecule can form a monoalkyl, a dialkyl, or a trialkyl ester by reaction with one, two, or three molecules of an alcohol.



Ethyl dihydrogen phosphate

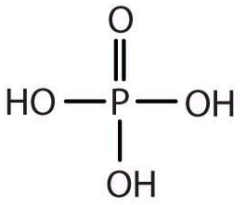


Diethyl hydrogen phosphate

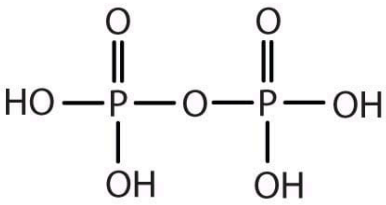


Triethyl phosphate

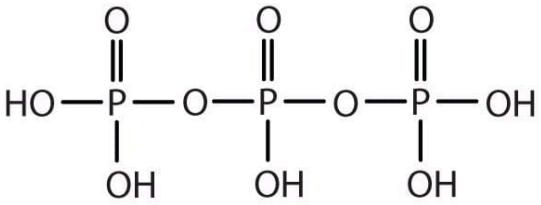
Esters of pyrophosphoric acid and triphosphoric acid are also important in biochemistry.



Phosphoric acid



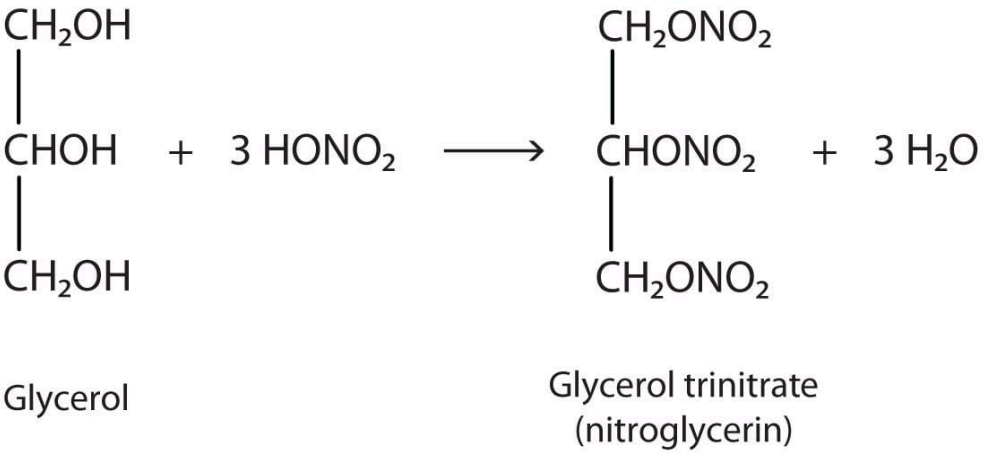
Pyrophosphoric acid



Triphosphoric acid

Esters of these acids are present in every plant and animal cell. They are biochemical intermediates in the transformation of food into usable energy. The bonds between phosphate units in adenosine triphosphate (ATP) are called *phosphoanhydride* bonds. These are high-energy bonds that store energy from the metabolism of foods. Hydrolysis of ATP releases energy as it is needed for biochemical processes (for instance, for muscle contraction). Phosphate esters are also important structural constituents of phospholipids and nucleic acids.

The explosive nitroglycerin (glyceryl trinitrate) is an ester formed from glycerol and nitric acid. It is used in medicine to relieve chest pain in heart disease.



Summary

Inorganic acids such as H_3PO_4 form esters. The esters of phosphoric acid are especially important in biochemistry.

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18: AMINO ACIDS AND PROTEINS

18.1: An Introduction to Biochemistry
18.2: Proteins and Their Functions- An Overview
18.3: Amino Acids
18.4: Acid-Base Properties of Amino Acids
18.5: Peptides
18.6: Protein Structure- An Overview and Primary Protein Structure
18.7: Secondary Protein Structure
18.8: Tertiary Protein Structure
18.9: Quaternary Protein Structure
18.10: Chemical Properties of Proteins

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18.1: An Introduction to Biochemistry

Learning Objectives

- Explain what a biomolecule is and list the four main types.

Biochemistry is the study of the molecules of life, (**biomolecules**); those that structurally make up living organisms and function to keep them alive. Although the complexity of biomolecules ranges from individual small molecules, such as glycine, to very large complexes made up of multiple molecules linked together, like ATP synthase, most biomolecules can be categorized into for main groups based on their structural similarities: *carbohydrates*, *proteins*, *lipids*, or *nucleic acids*. There are also many other small molecules and ions that play a wide variety of roles in the cell, ranging chemical messengers (or signals), to toxins produced as a means of defense against invaders, to coordination complexes that play important rolls in protein function.

Now that you have learned the basics of general and organic chemistry, you are ready to apply your knowledge to understanding the chemistry of these biomolecules. You will recognize some of the organic functional groups in these biomolecules, which will help you predict the physical and chemical properties of these new molecules. Living cells are very complex, however, the same principles that govern chemistry apply to all of biochemistry.

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18.2: Proteins and Their Functions- An Overview

Learning Objectives

- Describe the different structural classes of proteins.
- Understand the different functional roles of proteins.

The ability to serve a variety of functions is characteristic of most biomolecules. Nowhere is this versatility better exemplified than by the proteins. Perhaps because of their many functions, proteins are the most abundant organic molecules in living cells, constituting more than 50 percent of the mass once water is removed. It is estimated that the human body contains well over a million different kinds of protein, and even a single-cell organism contains thousands. Each of these is a polymer of amino acids which has a highly specific composition, a unique molecular weight (usually in the range from 6000 to 1 000 000) and its own sequence of different amino acids along the polymer chain.

Proteins may be subdivided on the basis of their *molecular shape* or *conformation*. In the **fibrous proteins**, long polymer chains are arranged parallel or nearly parallel to one another to give long fibers or sheets. This arrangement results in physically tough materials which do not dissolve in water. The fibrous proteins are fundamental components of structural tissues such as tendons, bone, hair, horn, leather, claws, and feathers.

By contrast, polymer chains of the **globular proteins** fold back on themselves to produce compact, nearly spherical shapes. Most globular proteins are water soluble and hence are relatively mobile within a cell. Some examples are enzymes, antibodies, hormones, toxins, and substances such as hemoglobin whose function is to transport simple molecules or even electrons from one place to another. The enzyme trypsin, is a typical globular protein.

Another class of proteins are the **membrane proteins**, which, as the name would suggest, reside in a cell's lipid bilayer membrane. Such proteins can act as channels for ions or other molecules unable to pass through the lipid bilayer; as signal transducers, able to respond to signal molecules on one side of a membrane to begin a molecular response on the other side of the membrane; or as anchors of other molecules to the cell membrane, to name a few exemplars of membrane protein function. Because these proteins interface with non-polar portions of the lipid bilayer, they do no maintain function and structure in an aqueous solution, making them far more difficult to study than globular proteins or fibrous proteins.

Proteins are also classified based on their function as listed in Table 18.2.1 below. As you will see in the following chapters, the structure and function of a protein are directly related, meaning that if a protein adopts a certain structure, the general function of that protein can be predicted with a good amount of certainty.

Table

:
Classes
of
Proteins
by
Function

Type	Function	Example
Enzymes	Catalyze biochemical reactions	*Amylase* – helps digest carbohydrates
Hormone proteins	Regulate and coordinate cell functions	*Insulin* – controls the amount of sugar (glucose) in the blood
Storage proteins	Storage and release of essential substances	*Myoglobin* – stores oxygen in muscle tissue
Transport proteins	Carries substances through the body	*Hemoglobin* – transports oxygen between the lungs and other tissues

Type	Function	Example
Structural proteins	Provides structural shape and support	*Keratin* – main structural component of hair, nails, feathers, hooves, etc.
Defense proteins	Protects the body against foreign invaders	*Immunoglobulin* – recognizes and binds to foreign matter, aiding in destruction
Contractile proteins	Mediate contractile processes, i.e., movement	*Actin* and *Myosin* – control the movement of muscles

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18.3: Amino Acids

Learning Objectives

- To recognize amino acids and classify them based on the characteristics of their side chains.
- Identify which amino acids are chiral.

The **proteins** in all living species, from bacteria to humans, are *polymers* constructed from the same set of 20 **amino acids**. 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.

Amino Acid Structure

Every amino acid contains an amino group, ($-NH_2$), a carboxyl group, (–COOH), and a **side chain** or R group, which are all attached to the alpha (α-) carbon (the one directly bonded to the carboxyl functional group). Therefore, amino acids are commonly called alpha-amino (α-amino) acids. Figure 18.3.1 below shows the structure of a generic α-amino acid.

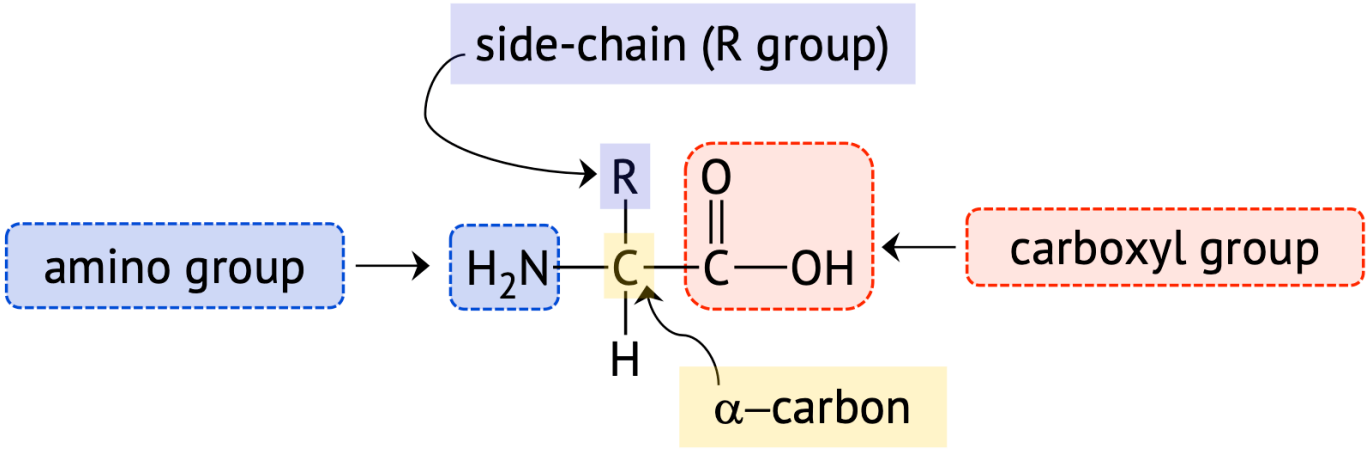


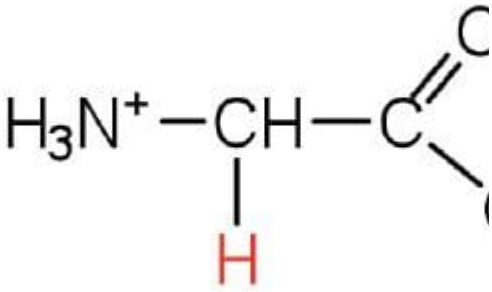
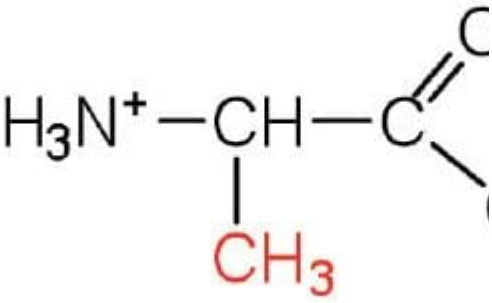
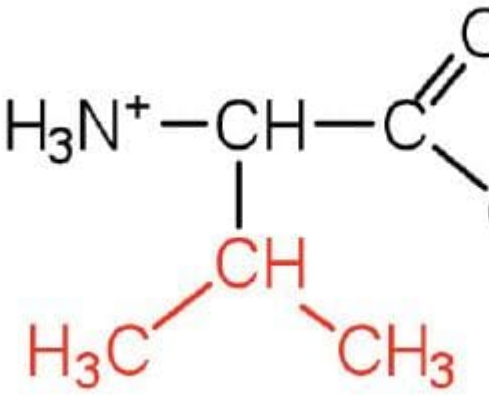
Figure 18.3.1 An α-amino acid. The three parts to an amino acid include the amino group, the carboxyl group, and the side-chain or R group all attached to the α-carbon. The R group is the part that distinguishes one amino acid from the next.

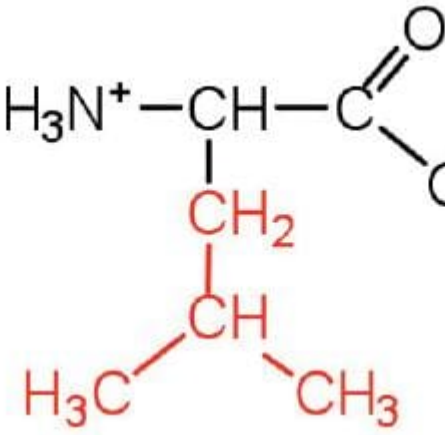
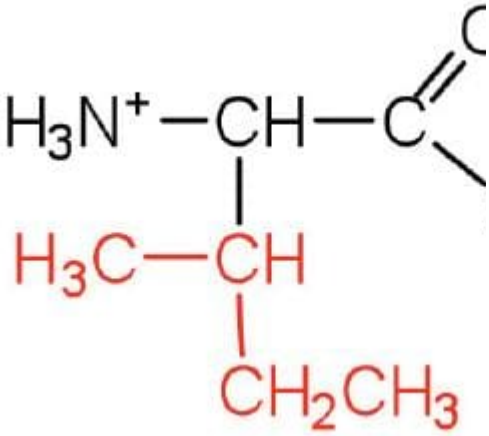
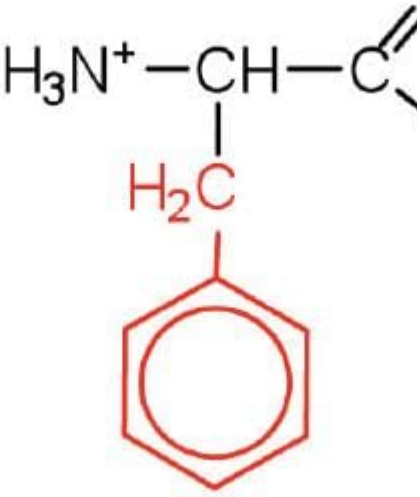
Amino Acid Side Chains

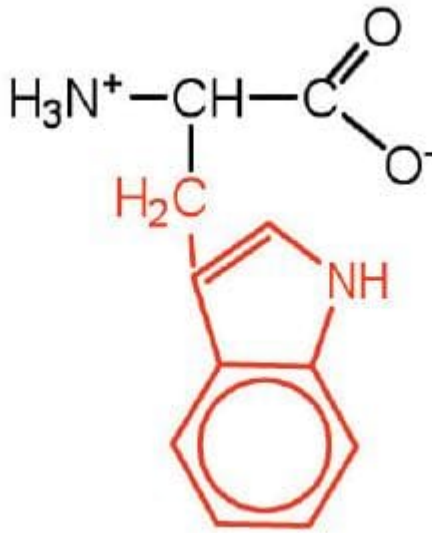
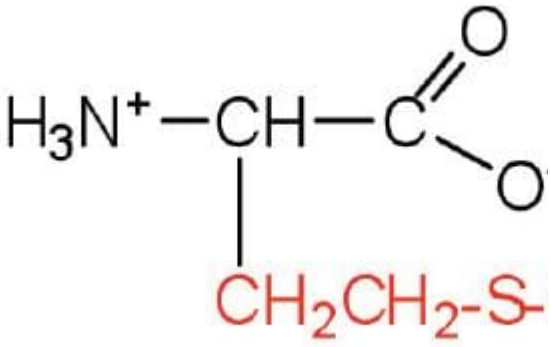
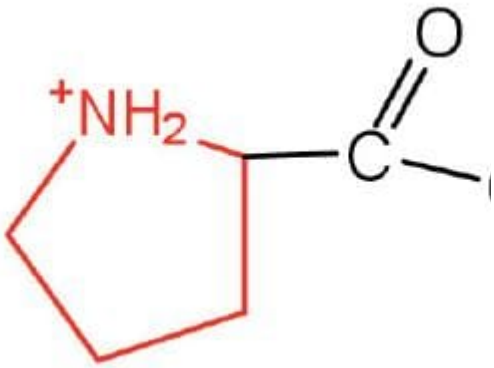
Amino acid side chains or R groups can range from a single hydrogen atom (as in glycine), to a simple hydrocarbon chain, to a hydrocarbon containing a functional group. Each R group has differences in size, shape, solubility, and ionization properties, which contributes to the unique properties of an individual amino acid, and can have an effect on the overall structure and function of a protein.

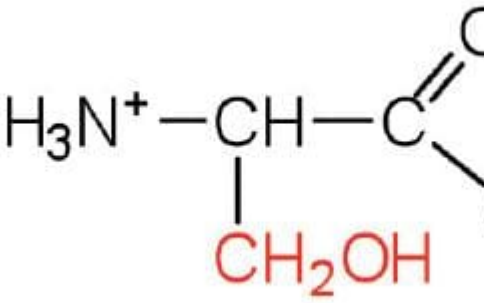
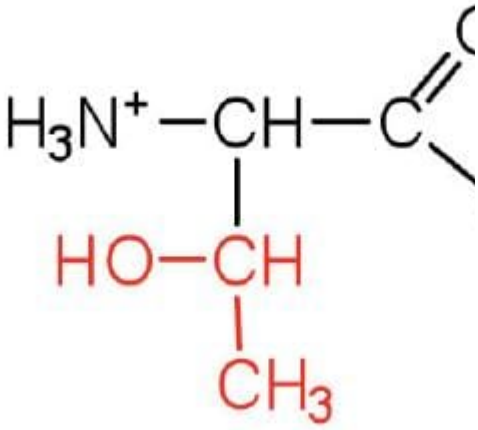
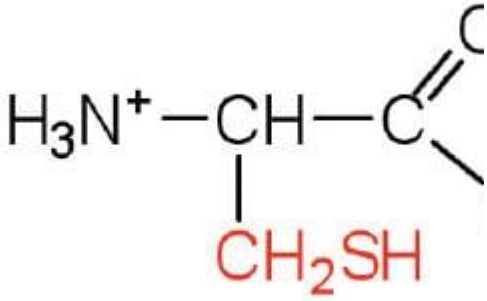
Table 18.3.1 below lists the 20 common amino acids along with their names, their three- and one-letter codes, structures, and distinctive features. The three-letter codes are generally the first three letters of the amino acid name except in a few cases, such as isoleucine (Ile) and tryptophan (Trp). Similarly, the one-letter code is usually the first letter in the amino acid name, but where the letter is not unique, a letter that is phonetically similar the amino acid name is used: F for *F*enylalanine, R for a*R*ginine, and W for t*W*iptophan. This table also groups the amino acids according to whether the side chain at neutral pH is *nonpolar*, *polar uncharged*, *positively charged*, or *negatively charged*.

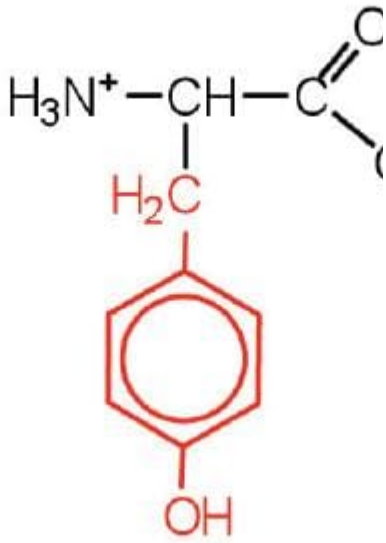
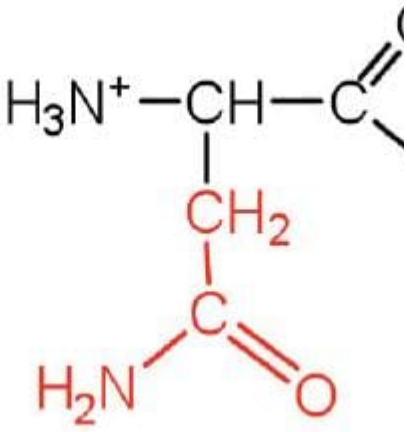
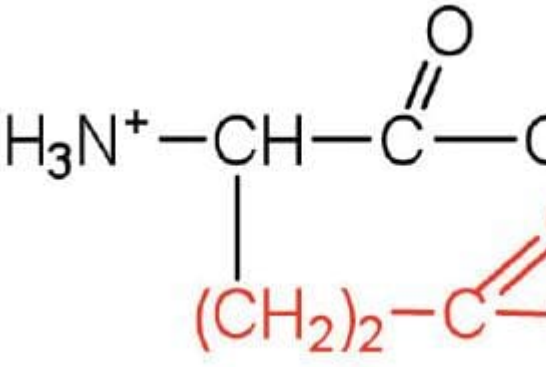
Table 18.3.1*: Common Amino Acids Found in Proteins. (Isoelectric points are explained in a later section.)*

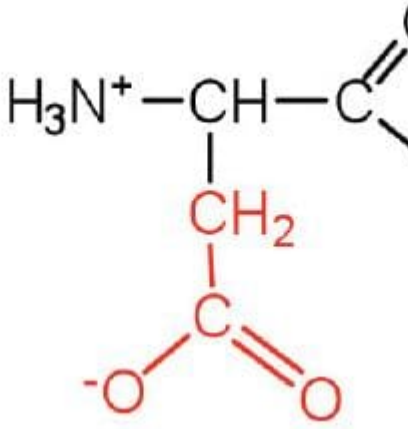
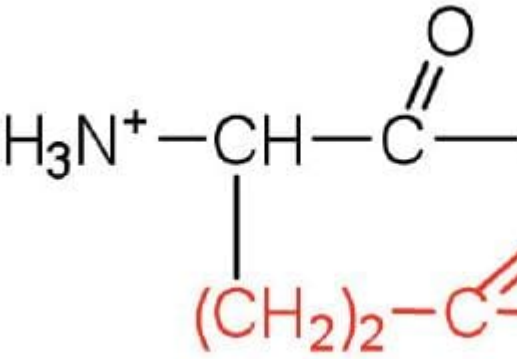
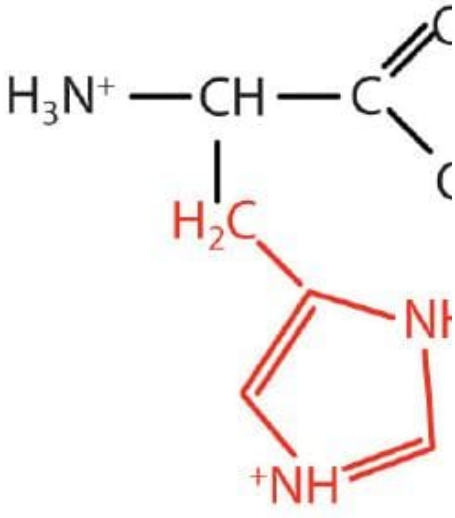
Common Name	Three-letter (one-letter) Code	Systematic (IUPAC) Name	Structural Formula (*at pH 6*)
			Amino acids with a nonpolar R group
glycine	Gly (G)	aminoethanoic acid	
alanine	Ala (A)	2-aminopropanoic acid	
valine	Val (V)	2-amino-3-methylbutanoic acid	

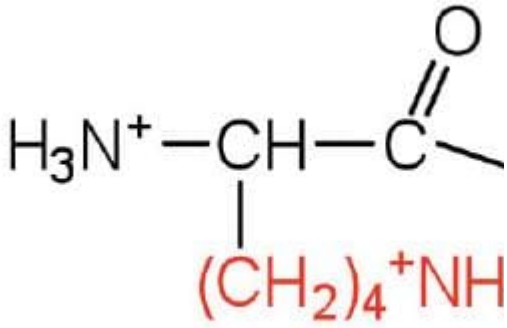
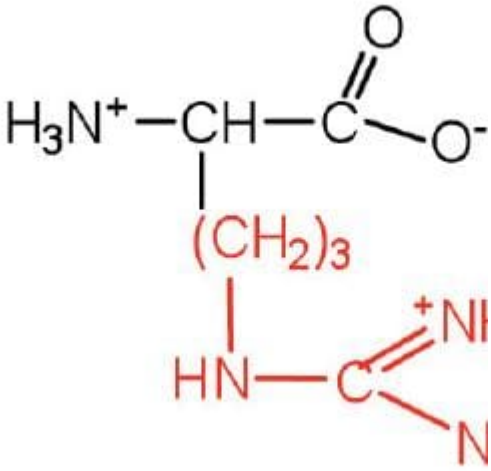
Common Name	Three-letter (one-letter) Code	Systematic (IUPAC) Name	Structural Formula (*at pH 6*)
leucine	Leu (L)	2-amino-4-methylpentanoic acid	
isoleucine	Ile (I)	2-amino-3-methylpentanoic acid	
phenylalanine	Phe (F)	2-amino-3-phenylpropanoic acid	

Common Name	Three-letter (one-letter) Code	Systematic (IUPAC) Name	Structural Formula (*at pH 6*)
tryptophan	Trp (W)	2-Amino-3-(1*H*-indol-3-yl)-propanoic acid	
methionine	Met (M)	2-amino-4-(methylthio)butanoic acid	
proline	Pro (P)	pyrrolidine-2-carboxylic acid	
			Amino acids with a polar but neutral R group

Common Name	Three-letter (one-letter) Code	Systematic (IUPAC) Name	Structural Formula (*at pH 6*)
serine	Ser (S)	2-amino-3-hydroxypropanoic acid	
threonine	Thr (T)	2-amino-3-hydroxybutanoic acid	
cysteine	Cys (C)	2-amino-3-mercaptopropanoic acid	

Common Name	Three-letter (one-letter) Code	Systematic (IUPAC) Name	Structural Formula (*at pH 6*)
tyrosine	Tyr (Y)	2-amino-3-(4-hydroxyphenyl)-propanoic acid	
asparagine	Asn (N)	2-amino-3-carbamoylpropanoic acid	
glutamine	Gln (Q)	2-amino-4-carbamoylbutanoic acid	
			Amino acids with a negatively charged R group

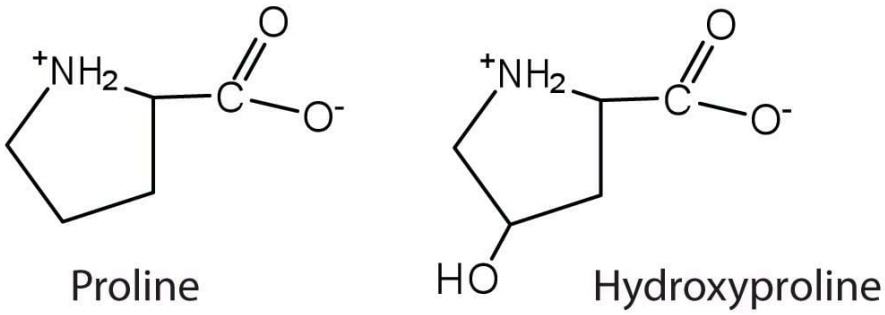
Common Name	Three-letter (one-letter) Code	Systematic (IUPAC) Name	Structural Formula (*at pH 6*)
aspartic acid	Asp (D)	2-aminobutanedioic acid	
glutamic acid	Glu (E)	2-aminopentanedioic acid	
			Amino acids with a positively charged R group
histidine	His (H)	2-Amino-3-(1*H*-imidazol-4-yl)-propanoic acid	

Common Name	Three-letter (one-letter) Code	Systematic (IUPAC) Name	Structural Formula (*at pH 6*)
lysine	Lys (K)	2,6-diaminohexanoic acid	
arginine	Arg (R)	2-amino-5-guanidinopentanoic acid	

Note: Interesting Facts About Amino Acids

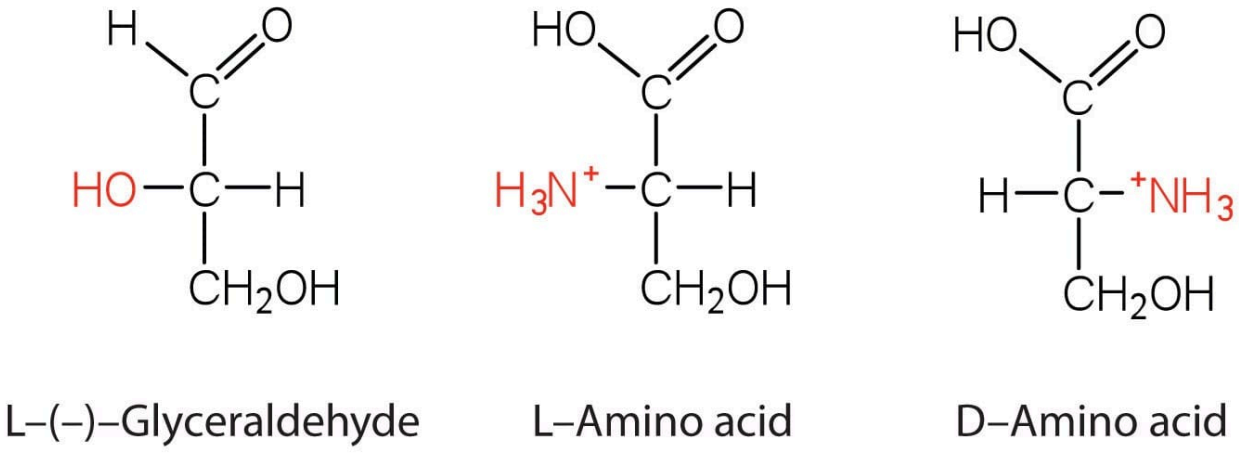
The first amino acid to be isolated was asparagine in 1806. It was obtained from protein found in asparagus juice (hence the name). Glycine, the major amino acid found in gelatin, was named for its sweet taste (Greek *glykys*, meaning “sweet”). Glutamic acid is named as such because it was first isolated from gluten. The crystalline salt of glutamic acid is called monosodium glutamate (MSG), which is naturally occuring in some foods but is also added to as a savory or "umami" flavor enhancer.

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 of proline occurs *after* the amino acid has been assembled into a protein.



Chirality of Amino Acids

Notice in Table 18.3.1 that glycine is the only amino acid whose (\alpha\)-carbon is *not* chiral, in other words the molecule and the mirror-image of glycine are identical. All other amino acids have two forms that are mirror images of each other, they are **enantiomers**. As you can see in the figure below, the "left-handed" form of the molecule is known as the L-amino acid and the "right-handed" form is the D-amino acid.



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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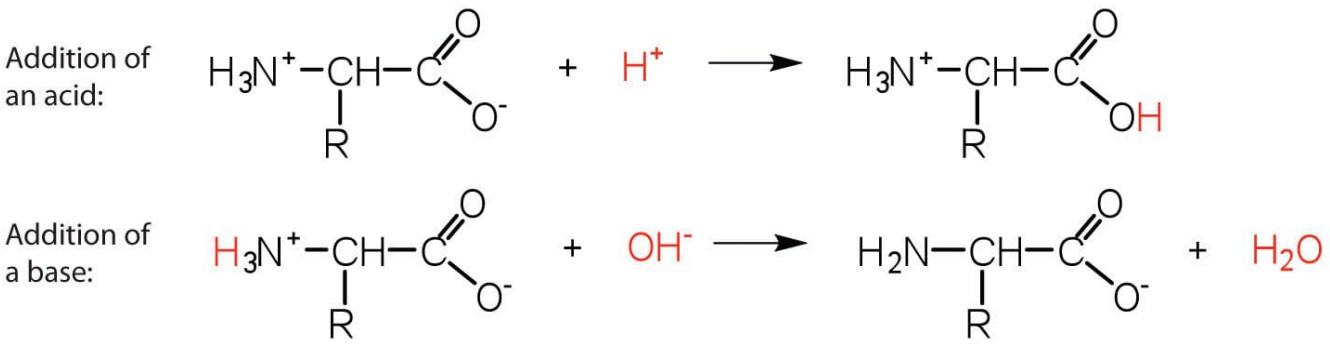
- 18.1: Properties of Amino Acids by Anonymous is licensed CC BY-NC-SA 3.0. Original source: https://2012books.lardbucket.org/books/introduction-to-chemistry-general-organic-and-biological.

18.4: Acid-Base Properties of Amino Acids

Learning Objectives

- To explain how an amino acid can act as both an acid and a base.

The structure of an amino acid allows it to act as both an acid and a base. An amino acid has this ability because at a certain pH value (different for each amino acid) nearly all the amino acid molecules exist as zwitterions. If acid is added to a solution containing the zwitterion, the carboxylate group captures a hydrogen (H^+) ion, and the amino acid becomes positively charged. If base is added, ion removal of the H^+ ion from the amino group of the zwitterion produces a negatively charged amino acid. In both circumstances, the amino acid acts to maintain the pH of the system—that is, to remove the added acid (H^+) or base (OH^-) from solution.

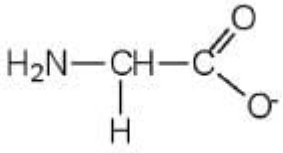


Example 18.4.1

a. Draw the structure for the anion formed when glycine (at neutral pH) reacts with a base.
b. Draw the structure for the cation formed when glycine (at neutral pH) reacts with an acid.

Solution

a. The base removes H^+ from the protonated amine group.



- The acid adds H^+ to the carboxylate group.



Exercise 18.4.1

a. Draw the structure for the cation formed when valine (at neutral pH) reacts with an acid.

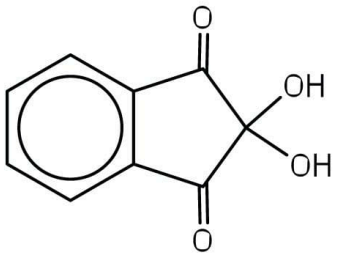
b. Draw the structure for the anion formed when valine (at neutral pH) reacts with a base.

The particular pH at which a given amino acid exists in solution as a zwitterion is called the isoelectric point (pI). At its pI, the positive and negative charges on the amino acid balance, and the molecule as a whole is electrically neutral. The amino acids whose side chains are always neutral have isoelectric points ranging from 5.0 to 6.5. The basic amino acids (which have positively charged side chains at neutral pH) have relatively high examples. Acidic amino acids (which have negatively charged side chains at neutral pH) have quite low examples (Table 18.4.1).

Table 18.4.1: ExampIes of Some Representative Amino Acids

Amino Acid	Classification	pI
alanine	nonpolar	6.0
valine	nonpolar	6.0
serine	polar, uncharged	5.7
threonine	polar, uncharged	6.5
arginine	positively charged (basic)	10.8
histidine	positively charged (basic)	7.6
lysine	positively charged (basic)	9.8
aspartic acid	negatively charged (acidic)	3.0
glutamic acid	negatively charged (acidic)	3.2

Amino acids undergo reactions characteristic of carboxylic acids and amines. The reactivity of these functional groups is particularly important in linking amino acids together to form peptides and proteins, as you will see later in this chapter. Simple chemical tests that are used to detect amino acids take advantage of the reactivity of these functional groups. An example is the ninhydrin test in which the amine functional group of α-amino acids reacts with ninhydrin to form purple-colored compounds. Ninhydrin is used to detect fingerprints because it reacts with amino acids from the proteins in skin cells transferred to the surface by the individual leaving the fingerprint.



Ninhydrin



Summary

Amino acids can act as both an acid and a base due to the presence of the amino and carboxyl functional groups. The pH at which a given amino acid exists in solution as a zwitterion is called the *isoelectric point* (pI).

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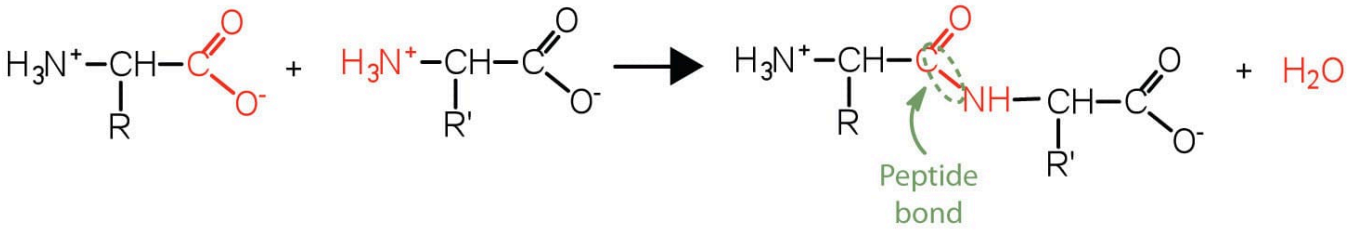
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18.5: Peptides

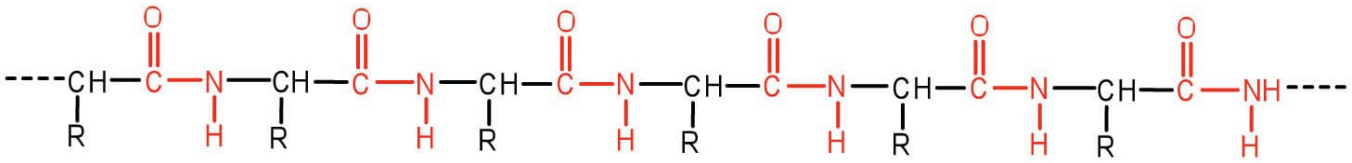
Learning Objectives

- Explain how a peptide is formed from individual amino acids.
- Explain why the sequence of amino acids in a protein is important.

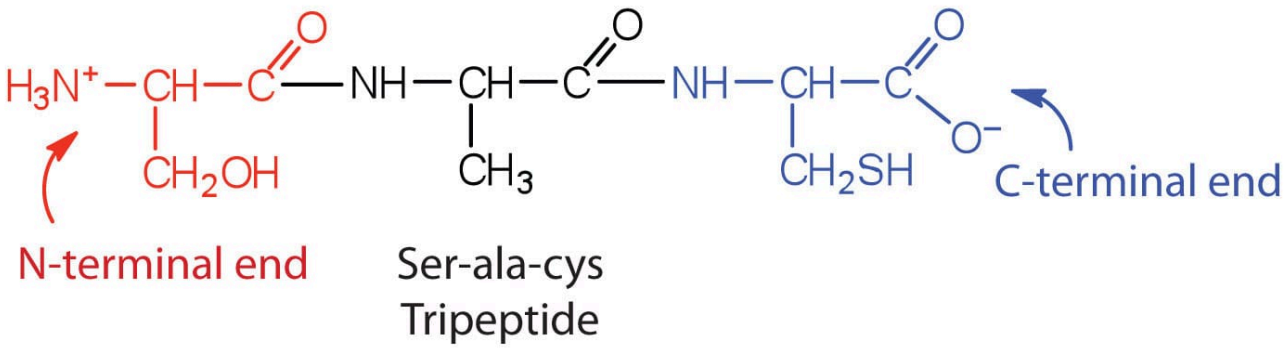
Two or more amino acids can join together into chains called peptides. In an earlier chapter, we discussed the reaction between ammonia and a carboxylic acid to form an amide. In a similar reaction, the amino group on one amino acid molecule reacts with the carboxyl group on another, releasing a molecule of water and forming an amide linkage:



An amide bond joining two amino acid units is called a **peptide bond**. Note that the product molecule still has a reactive amino group on the left and a reactive carboxyl group on the right. These can react with additional amino acids to lengthen the peptide. The process can continue until thousands of units have joined, resulting in large proteins.



A chain consisting of only two amino acid units is called a *dipeptide*; a chain consisting of three is a *tripeptide*. By convention, peptide and protein structures are depicted with the amino acid whose amino group is free (the **amino-terminal** or N-terminal end) on the left and the amino acid with a free carboxyl group (the **carboxyl-terminal** or C-terminal end) to the right. Individual amino acids joined in a chain are called **residues**.



The general term *peptide* refers to an amino acid chain of unspecified length. However, chains of about 50 amino acids or more are usually called proteins or polypeptides. In its physiologically active form, a protein may be composed of one or more polypeptide chains.

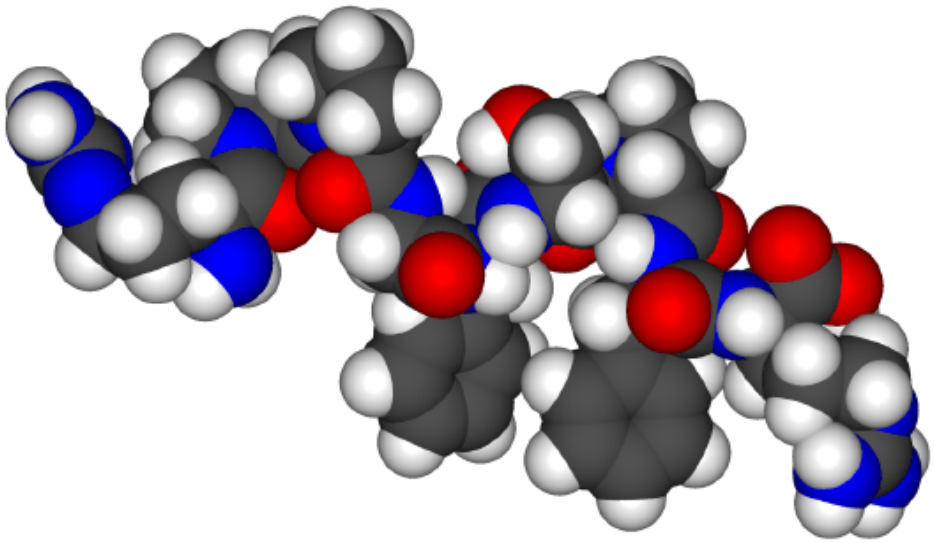


Figure 18.5.1: Space-filling model of bradykinin. (Public Domain; Fvasconcellos)

Note: Order is Important

For peptides and proteins to be physiologically active, it is not enough that they incorporate certain amounts of specific amino acids. The order, or *sequence*, in which the amino acids are connected is also of critical importance. Bradykinin is a nine-amino acid peptide (Figure 18.5.1) produced in the blood that has the following amino acid sequence:

arg-pro-pro-gly-phe-ser-pro-phe-arg

This peptide lowers blood pressure, stimulates smooth muscle tissue, increases capillary permeability, and causes pain. When the order of amino acids in bradykinin is reversed,

arg-phe-pro-ser-phe-gly-pro-pro-arg

the peptide resulting from this synthesis shows none of the activity of bradykinin.

Just as millions of different words are spelled with our 26-letter English alphabet, millions of different proteins are made with the 20 common amino acids. However, just as the English alphabet can be used to write gibberish, amino acids can be put together in the *wrong sequence* to produce nonfunctional proteins. Although the correct sequence is ordinarily of utmost importance, it is not always absolutely required. Just as you can sometimes make sense of incorrectly spelled English words,

a protein with a small percentage of “incorrect” amino acids may continue to function. However, it rarely functions as well as a protein having the correct sequence. There are also instances in which seemingly minor errors of sequence have disastrous effects. For example, in some people, every molecule of hemoglobin (a protein in the blood that transports oxygen) has a single incorrect amino acid unit out of about 300 (a single valine replaces a glutamic acid). That “minor” error is responsible for sickle cell anemia, an inherited condition that usually is fatal.

Summary

The amino group of one amino acid can react with the carboxyl group on another amino acid to form a peptide bond that links the two amino acids together. Additional amino acids can be added on through the formation of addition peptide (amide) bonds. A sequence of amino acids in a peptide or protein is written with the N-terminal amino acid first and the C-terminal amino acid at the end (writing left to right).

Concept Review Exercises

1. Distinguish between the N-terminal amino acid and the C-terminal amino acid of a peptide or protein.
2. Describe the difference between an amino acid and a peptide.
3. Amino acid units in a protein are connected by peptide bonds. What is another name for the functional group linking the amino acids?

Answers

1. The N-terminal end is the end of a peptide or protein whose amino group is free (not involved in the formation of a peptide bond), while the C-terminal end has a free carboxyl group.
2. A peptide is composed of two or more amino acids. Amino acids are the building blocks of peptides.
3. amide bond

Exercises

1. Draw the structure for each peptide.

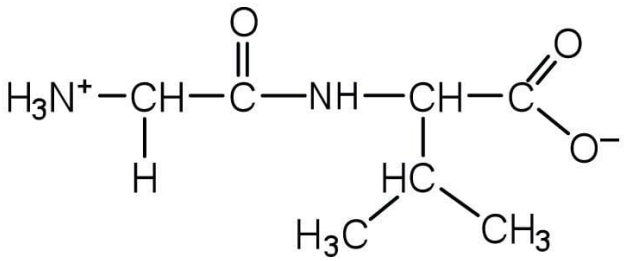
    a. gly-val
    b. val-gly

2. Draw the structure for cys-val-ala.

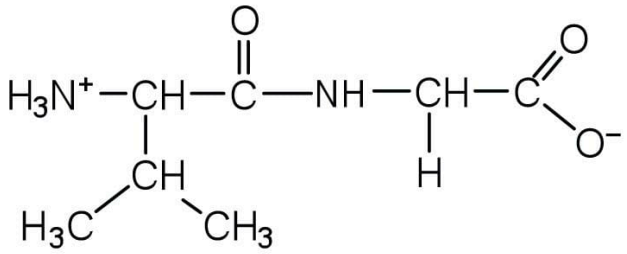
3. Identify the C- and N-terminal amino acids for the peptide lys-val-phe-gly-arg-cys.

4. Identify the C- and N-terminal amino acids for the peptide asp-arg-val-tyr-ile-his-pro-phe.

Answers



1. a.



b.

3. C-terminal amino acid: cys; N-terminal amino acid: lys

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18.6: Protein Structure- An Overview and Primary Protein Structure

Learning Objectives

- Describe primary protein structure.
- Explain how sequence can affect function.

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.

Levels of Protein Structure

The structure of proteins is generally described as having four organizational levels. The first of these is the **primary structure**, which is the number and sequence of amino acids in a protein's polypeptide chain or chains, beginning with the free amino group and maintained by the peptide bonds connecting each amino acid to the next. The primary structure of insulin, composed of 51 amino acids, is shown in Figure 18.6.1.

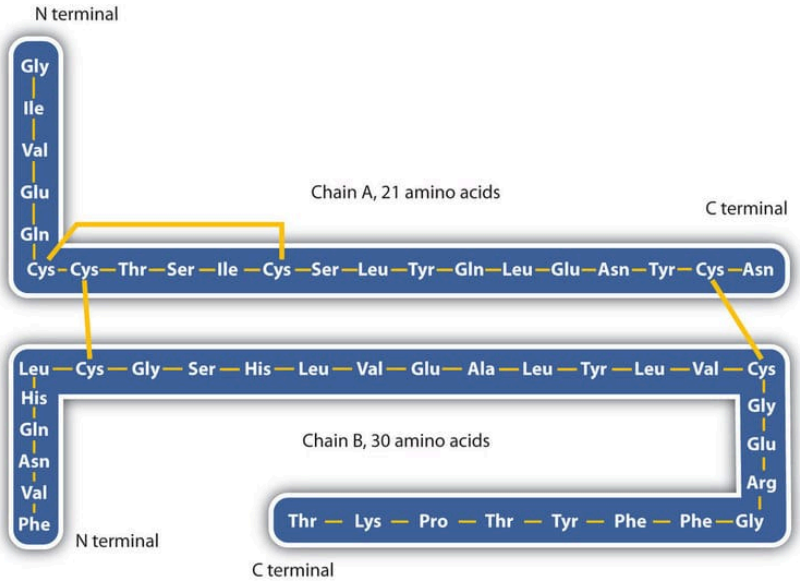


Figure 18.6.1: Primary Structure of Human Insulin. Human insulin, whose amino acid sequence is shown here, is a hormone that is required for the proper metabolism of glucose. (CC BY-SA-NC 3.0; anonymous)

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18.7: Secondary Protein Structure

Learning Objectives

- Objective 1
- Objective 2

A protein molecule is not a random tangle of polypeptide chains. Instead, the chains are arranged in unique but specific conformations. The term **secondary structure** refers to the fixed arrangement of the polypeptide backbone. On the basis of X ray studies, Linus Pauling and Robert Corey postulated that certain proteins or portions of proteins twist into a spiral or a helix. This helix is stabilized by *intrachain* hydrogen bonding between the carbonyl oxygen atom of one amino acid and the amide hydrogen atom four amino acids up the chain (located on the next turn of the helix) and is known as a right-handed α-helix. X ray data indicate that this helix makes one turn for every 3.6 amino acids, and the side chains of these amino acids project outward from the coiled backbone (Figure 18.7.1). The α-keratins, found in hair and wool, are exclusively α-helical in conformation. Some proteins, such as gamma globulin, chymotrypsin, and cytochrome c, have little or no helical structure. Others, such as hemoglobin and myoglobin, are helical in certain regions but not in others.

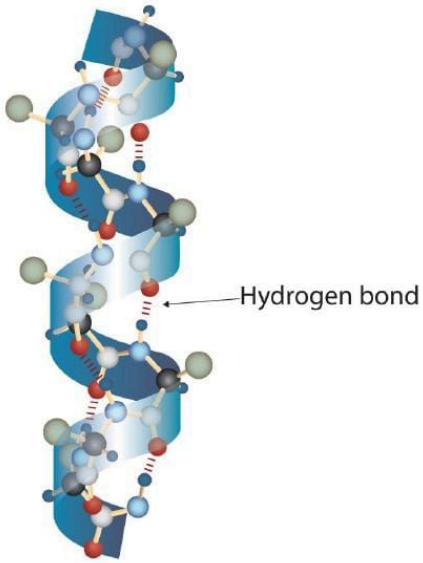


Figure 18.7.1 A Ball-and-Stick Model of an α-Helix. This ball-and-stick model shows the intrachain hydrogen bonding between carbonyl oxygen atoms and amide hydrogen atoms. Each turn of the helix spans 3.6 amino acids. Note that the side chains (represented as green spheres) point out from the helix.

Another common type of secondary structure, called the *β-pleated sheet conformation*, is a sheetlike arrangement in which two or more extended polypeptide chains (or separate regions on the same chain) are aligned side by side. The aligned segments can run either parallel or antiparallel—that is, the N-terminals can face in the same direction on adjacent chains or in different directions—and are connected by *interchain* hydrogen bonding (Figure 18.7.3). The β-pleated sheet is particularly important in structural proteins, such as silk fibroin. It is also seen in portions of many enzymes, such as carboxypeptidase A and lysozyme.

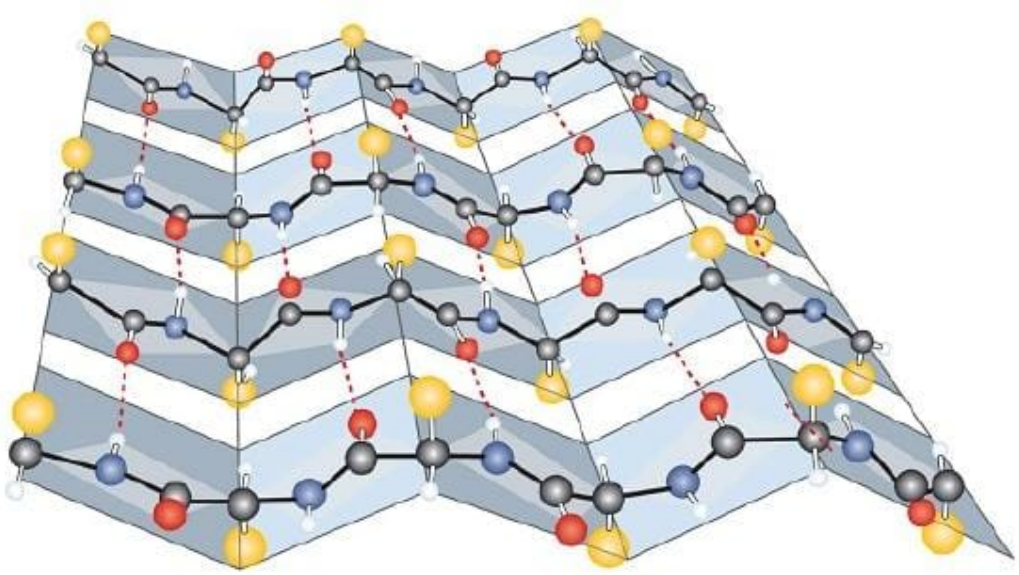


Figure 18.7.3: A Ball-and-Stick Model of the β-Pleated Sheet Structure in Proteins. The side chains extend above or below the sheet and alternate along the chain. The protein chains are held together by interchain hydrogen bonding.

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18.8: Tertiary Protein Structure

Learning Objectives

- Objective 1
- Objective 2

Tertiary structure refers to the unique three-dimensional shape of the protein as a whole, which results from the folding and bending of the protein backbone. The tertiary structure is intimately tied to the proper biochemical functioning of the protein. Figure 18.8.1 shows a depiction of the three-dimensional structure of insulin.

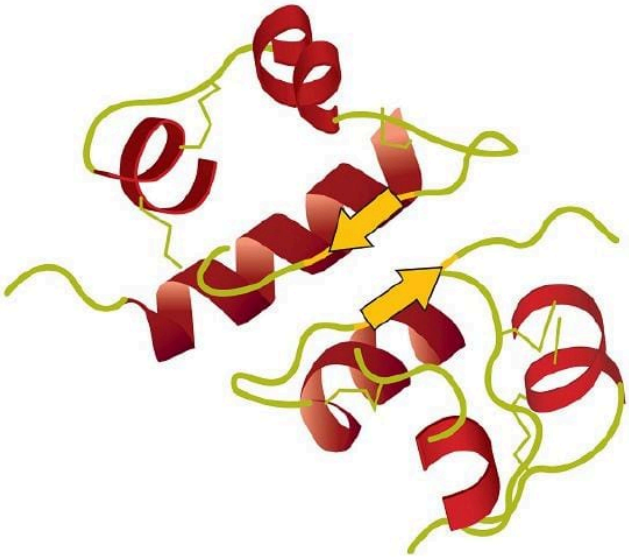
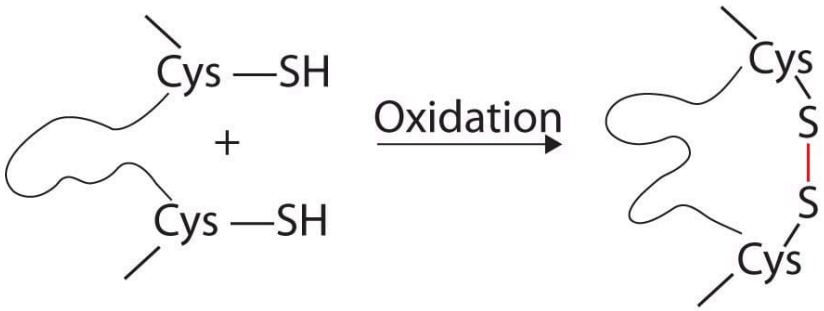


Figure 18.8.1: A Ribbon Model of the Three-Dimensional Structure of Insulin. The spiral regions represent sections of the polypeptide chain that have an α-helical structure, while the broad arrows represent β-pleated sheet structures.

Four major types of attractive interactions determine the shape and stability of the tertiary structure of proteins. You studied several of them previously.

1. Ionic bonding. Ionic bonds result from electrostatic attractions between positively and negatively charged side chains of amino acids. For example, the mutual attraction between an aspartic acid carboxylate ion and a lysine ammonium ion helps to maintain a particular folded area of a protein (part (a) of Figure 18.8.5).
2. Hydrogen bonding. Hydrogen bonding forms between a highly electronegative oxygen atom or a nitrogen atom and a hydrogen atom attached to another oxygen atom or a nitrogen atom, such as those found in polar amino acid side chains. Hydrogen bonding (as well as ionic attractions) is extremely important in both the intra- and intermolecular interactions of proteins (part (b) of Figure 18.8.5).
3. Disulfide linkages. Two cysteine amino acid units may be brought close together as the protein molecule folds. Subsequent oxidation and linkage of the sulfur atoms in the highly reactive sulfhydryl (SH) groups leads to the formation of cystine (part (c) of Figure 18.8.2). Intrachain disulfide linkages are found in many proteins, including insulin (yellow bars in Figure 18.8.1) and have a strong stabilizing effect on the tertiary structure.



4. Dispersion forces. Dispersion forces arise when a normally nonpolar atom becomes momentarily polar due to an uneven distribution of electrons, leading to an instantaneous dipole that induces a shift of electrons in a neighboring nonpolar atom. Dispersion forces are weak but can be important when other types of interactions are either missing or minimal (part (d) of Figure 18.8.2). This is the case with fibroin, the major protein in silk, in which a high proportion of amino acids in the protein have nonpolar side chains. The term *hydrophobic interaction* is often misused as a synonym for dispersion forces. Hydrophobic interactions arise because water molecules engage in hydrogen bonding with other water molecules (or groups in proteins capable of hydrogen bonding). Because nonpolar groups cannot engage in hydrogen bonding, the protein folds in such a way that these groups are buried in the interior part of the protein structure, minimizing their contact with water.

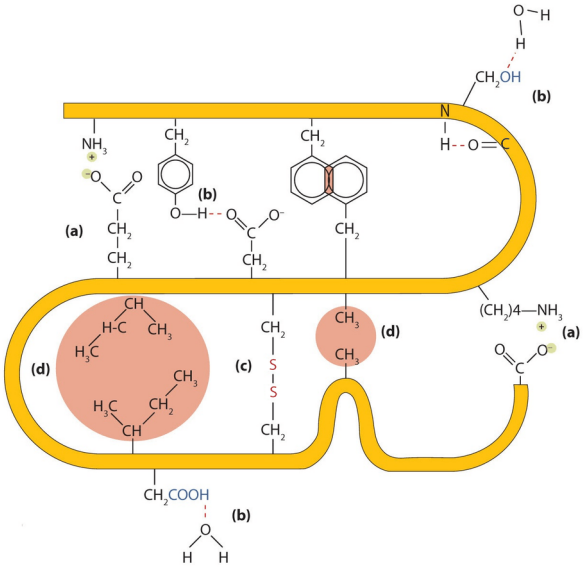


Figure 18.8.2: Tertiary Protein Structure Interactions. Four interactions stabilize the tertiary structure of a protein: (a) ionic bonding, (b) hydrogen bonding, (c) disulfide linkages, and (d) dispersion forces.

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18.9: Quaternary Protein Structure

Learning Objectives

- Objective 1
- Objective 2

When a protein contains more than one polypeptide chain, each chain is called a *subunit*. The arrangement of multiple subunits represents a fourth level of structure, the **quaternary structure** of a protein. Hemoglobin, with four polypeptide chains or subunits, is the most frequently cited example of a protein having quaternary structure (Figure 18.9.1). The quaternary structure of a protein is produced and stabilized by the same kinds of interactions that produce and maintain the tertiary structure. A schematic representation of the four levels of protein structure is in Figure 18.9.2.



Figure 18.9.1 The Quaternary Structure of Hemoglobin. Hemoglobin is a protein that transports oxygen throughout the body.

Source: Image from the RCSB PDB (www.pdb.org) of PDB ID 1I3D (R.D. Kidd, H.M. Baker, A.J. Mathews, T. Brittain, E.N. Baker (2001) Oligomerization and ligand binding in a homotetrameric hemoglobin: two high-resolution crystal structures of hemoglobin Bart's (gamma(4)), a marker for alpha-thalassemia. Protein Sci. 1739–1749).

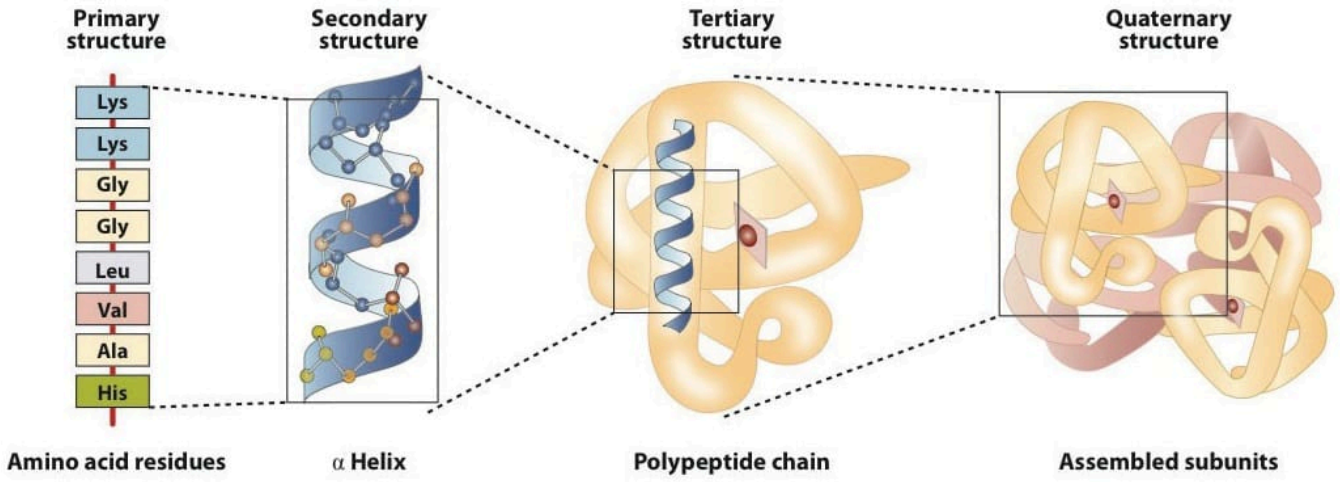


Figure 18.9.2: Levels of Structure in Proteins

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.

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18.10: Chemical Properties of Proteins

Learning Objectives

- Objective 1
- Objective 2

Protein Hydrolysis

Protein Denaturation

The highly organized structures of proteins are truly masterworks of chemical architecture. But highly organized structures tend to have a certain delicacy, and this is true of proteins. Denaturation is the term used for any change in the three-dimensional structure of a protein that renders it incapable of performing its assigned function. A denatured protein cannot do its job. (Sometimes denaturation is equated with the precipitation or coagulation of a protein; our definition is a bit broader.) A wide variety of reagents and conditions, such as heat, organic compounds, pH changes, and heavy metal ions can cause protein denaturation (Figure 18.10.1).

Figure 18.10.1*: Protein Denaturation Methods*

Method	Effect on Protein Structure
Heat above 50°C or ultraviolet (UV) radiation	Heat or UV radiation supplies kinetic energy to protein molecules, causing their atoms to vibrate more rapidly and disrupting relatively weak hydrogen bonding and dispersion forces.
Use of organic compounds, such as ethyl alcohol	These compounds are capable of engaging in intermolecular hydrogen bonding with protein molecules, disrupting intramolecular hydrogen bonding within the protein.
Salts of heavy metal ions, such as mercury, silver, and lead	These ions form strong bonds with the carboxylate anions of the acidic amino acids or SH groups of cysteine, disrupting ionic bonds and disulfide linkages.
Alkaloid reagents, such as tannic acid (used in tanning leather)	These reagents combine with positively charged amino groups in proteins to disrupt ionic bonds.

Anyone who has fried an egg has observed denaturation. The clear egg white turns opaque as the albumin denatures and coagulates. No one has yet reversed that process. However, given the proper circumstances and enough time, a protein that has unfolded under sufficiently gentle conditions can refold and may again exhibit biological activity (Figure 18.10.8). Such evidence suggests that, at least for these proteins, the primary structure determines the secondary and tertiary structure. A given sequence of amino acids seems to adopt its particular three-dimensional arrangement naturally if conditions are right.

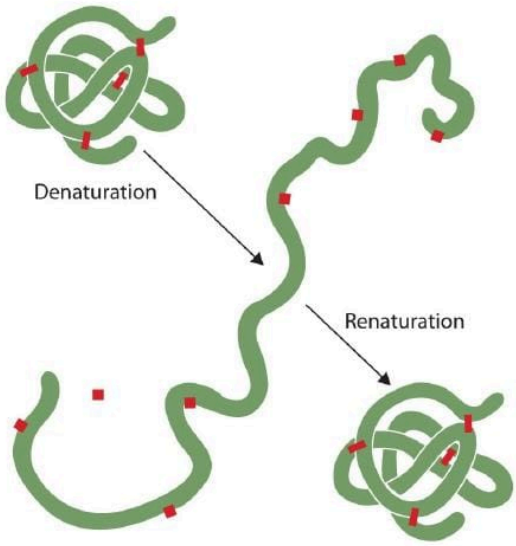


Figure 18.10.8: Denaturation and Renaturation of a Protein. The denaturation (unfolding) and renaturation (refolding) of a protein is depicted. The red boxes represent stabilizing interactions, such as disulfide linkages, hydrogen bonding, and/or ionic bonds.

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.

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19: ENZYMES AND VITAMINS

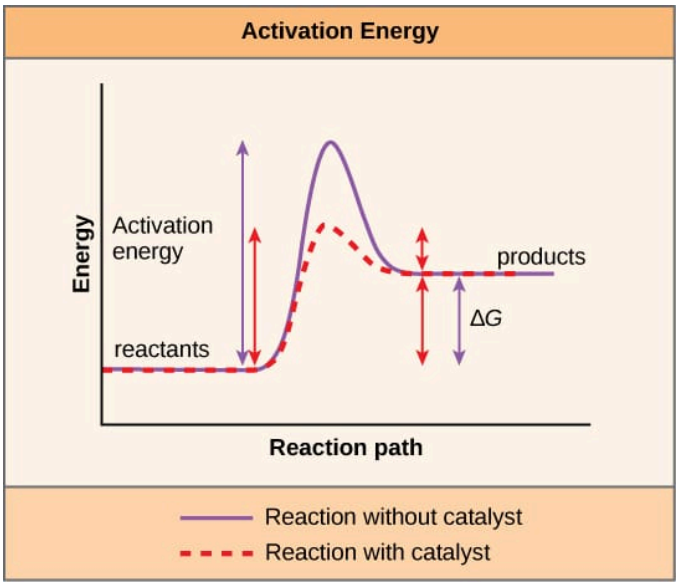
19.1: Catalysis by Enzymes
19.2: Enzyme Cofactors
19.3: Enzyme Classification
19.4: How Enzymes Work
19.5: Factors Affecting Enzyme Activity
19.6: Enzyme Regulation - Inhibition
19.7: Enzyme Regulation- Allosteric Control and Feedback Inhibition
19.8: Enzyme Regulation - Covalent Modification and Genetic Control
19.9: Vitamins, Antioxidants, and Minerals

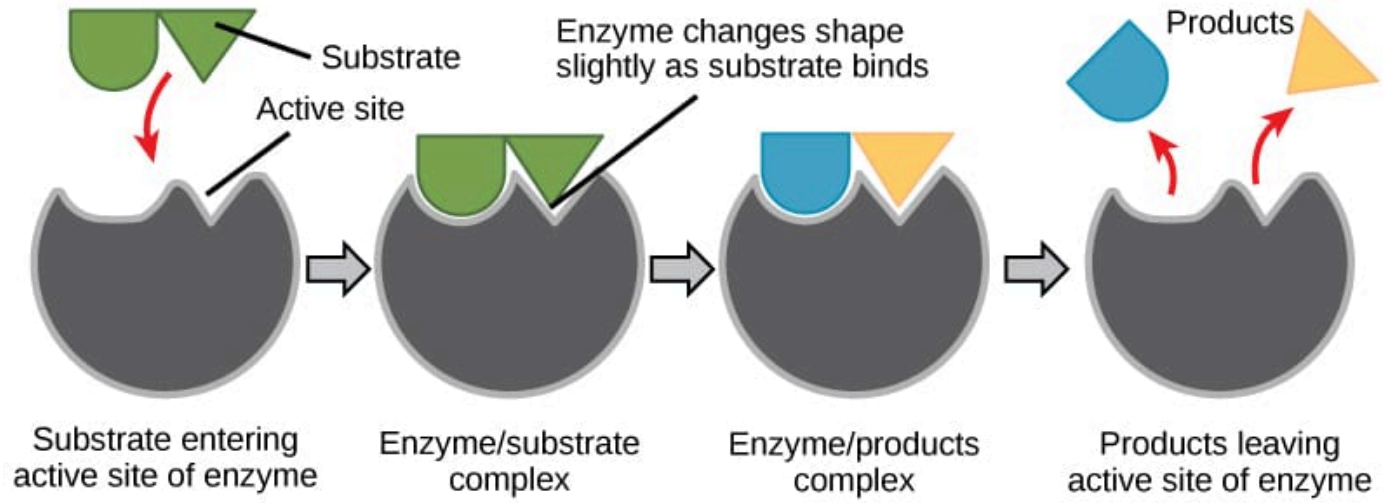
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19.1: Catalysis by Enzymes

Learning Objectives

- Describe how enzymes catalyze biochemical reactions.





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19.2: Enzyme Cofactors

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 19.2.1: 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 19.2.1 and 19.2.2.

Table 19.2.2: 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	Coenzyme	Coenzyme Function	Deficiency Disease
vitamin B_6 (pyridoxine)	pyridoxal phosphate	variety of reactions including the transfer of amino groups	—
vitamin B_{12} (cyanocobalamin)	methylcobalamin or deoxyadenoxylcobalamin	intramolecular rearrangement reactions	pernicious anemia
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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19.3: Enzyme Classification

Learning Objectives

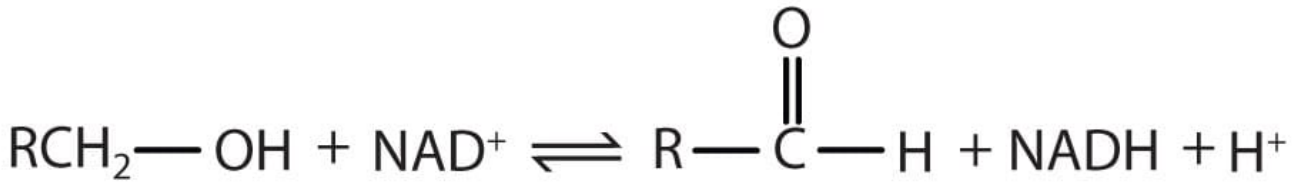
- Objective 1
- Objective 2

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.

Enzyme Nomenclature

Most enzymes can be recognized because they have the family name ending *–ase*. However, 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.

In addition to the family name, more systematic enzyme names will give two sepcific pieces of information: the first part is the *substrate* upon which the enzyme acts, and the second part is the *type of reaction* it catalyzes. For example, alcohol dehydrogenase (Figure 19.3.1) catalyzes the *oxidation* of an *alcohol* to an aldehyde.



Enzyme Classification

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 19.3.1), 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 19.3.2 for alcohol dehydrogenase.

Table 19.3.1: Classes of Enzymes

Main Class	Type of Reaction Catalyzed	Subclasses	Examples
Oxidoreductases	oxidation-reduction reactions	*Dehydrogenases* catalyze oxidation-reduction reactions involving hydrogen.	Alcohol dehydrogenase
		Oxidases catalyze oxidation by addition of O_2 to a substrate.	

Main Class	Type of Reaction Catalyzed	Subclasses	Examples
		Reductases catalyze reactions in which a substrate is reduced.	
Transferases	transfer reactions of functional groups	*Transaminases* catalyze the transfer of amino group.	
		Kinases catalyze the transfer of a phosphate group.	Phosphofructokinase
Hydrolases	reactions that use water to break a chemical bond	*Lipases* catalyze the hydrolysis of lipids	
		Proteases catalyze the hydrolysis of proteins	
		Amylases catalyze the hydrolysis of carbohydrates	
		Nucleases catalyze the hydrolysis of DNA and RNA	
Lyases	reactions in which functional groups are added or removed without hydrolysis	*Decarboxylases* catalyze the removal of carboxyl groups.	
		Deaminases catalyze the removal of amino groups.	
		Dehydratases catalyze the removal of water.	
		Hydratases catalyze the addition of water.	Fumarase
Isomerases	reactions in which a compound is converted to its isomer	*Isomerases* may catalyze the conversion of an aldose to a ketose.	Triose Phosphate Isomerase
		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.	
		Carboxylases catalyze the addition of CO_2 using ATP	Pyruvate Carboxylase

Table 19.3.2: Assignment of an Enzyme Classification Number

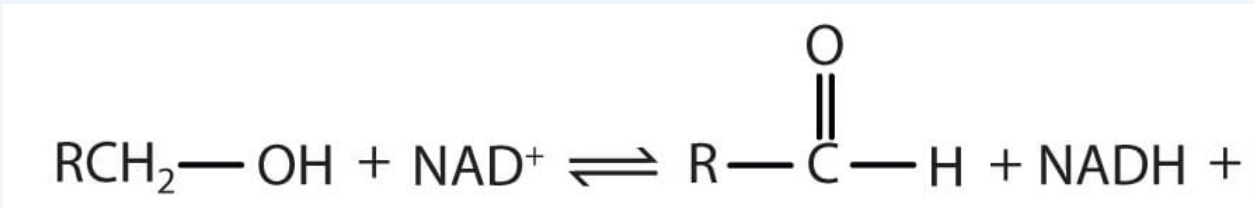
Alcohol Dehydrogenase: EC 1.1.1.1	
The first digit indicates that this enzyme is an oxidoreductase; that is, an enzyme that catalyzes an oxidation-reduction reaction.	
The second digit indicates that this oxidoreductase catalyzes a reaction involving a primary or secondary alcohol.	
The third digit indicates that either the coenzyme NAD^+ or $NADP^+$ is required for this reaction.	
The fourth digit indicates that this was the first enzyme isolated, characterized, and named using this system of nomenclature.	
The systematic name for this enzyme is *alcohol:NAD^+ oxidoreductase*, while the recommended or common name is alcohol dehydr	
Reaction catalyzed:	

Figure 19.3.1***:*** *Structure of the alcohol dehydrogenase protein (E.C.1.1.1.1) (EE ISOZYME) complexed wtih nicotinamide adenini dinulceotide (NAD) and zinc (PDB: 1CDO).*

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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19.4: How Enzymes Work

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 (E) and the substrate molecule or molecules (S) collide and react to form an intermediate compound called the *enzyme-substrate* (ES) *complex*. (This step is reversible because the complex can break apart into the original substrate or substrates and the free enzyme.) Once the ES complex forms, the enzyme is able to catalyze the formation of product (P), which is then released from the enzyme surface:

$$E + S \leftrightarrow ES \tag{19.4.1}$$

$$ES \rightarrow E + P \tag{19.4.2}$$

Hydrogen bonding and other electrostatic interactions hold the enzyme and substrate together in the complex. The structural features or functional groups on the enzyme that participate in these interactions are located in a cleft or pocket on the enzyme surface. This pocket, where the enzyme combines with the substrate and transforms the substrate to product is called the active site of the enzyme (Figure 19.4.1).

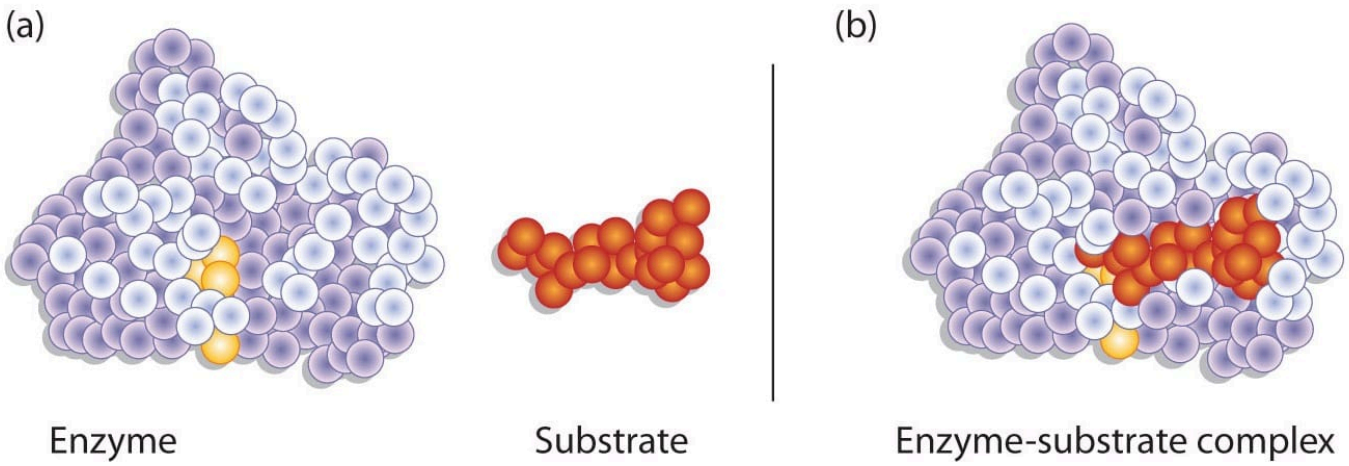


Figure 19.4.1: Substrate Binding to the Active Site of an Enzyme. The enzyme dihydrofolate reductase is shown with one of its substrates: $NADP^+$ (a) unbound and (b) bound. The $NADP^+$ (shown in red) binds to a pocket that is complementary to it in shape and ionic properties.

Models of Enzyme-Substrate Interaction

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 19.4.2). This model portrayed the enzyme as conformationally rigid and able to bond only to substrates that exactly fit the active site.

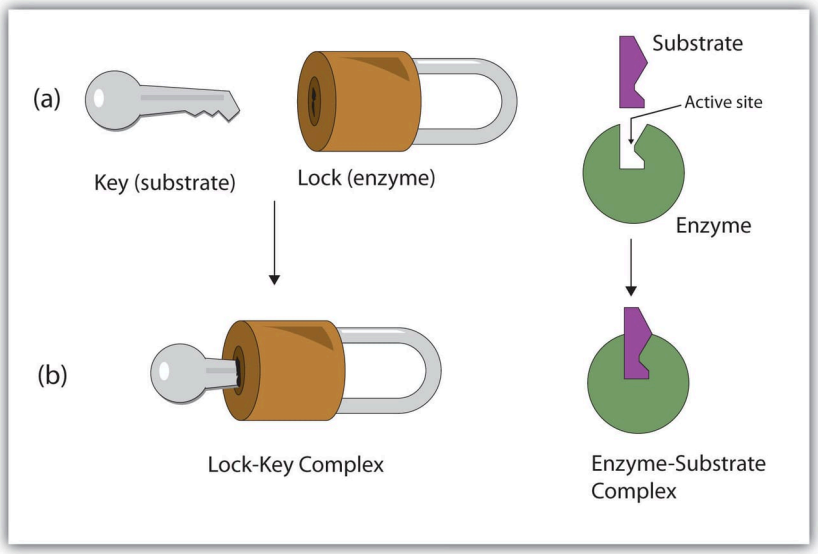


Figure 19.4.2: The Lock-and-Key Model of Enzyme Action. (a) Because the substrate and the active site of the enzyme have complementary structures and bonding groups, they fit together as a key fits a lock. (b) The catalytic reaction occurs while the two are bonded together in the enzyme-substrate complex.

Working out the precise three-dimensional structures of numerous enzymes has enabled chemists to refine the original lock-and-key model of enzyme actions. They discovered that the binding of a substrate often leads to a large conformational change in the enzyme, as well as to changes in the structure of the substrate or substrates. The current theory, known as the **induced-fit model**, says that enzymes can undergo a change in conformation when they bind substrate molecules, and the active site has a shape complementary to that of the substrate only *after* the substrate is bound, as shown for hexokinase in Figure 19.4.3. After catalysis, the enzyme resumes its original structure.

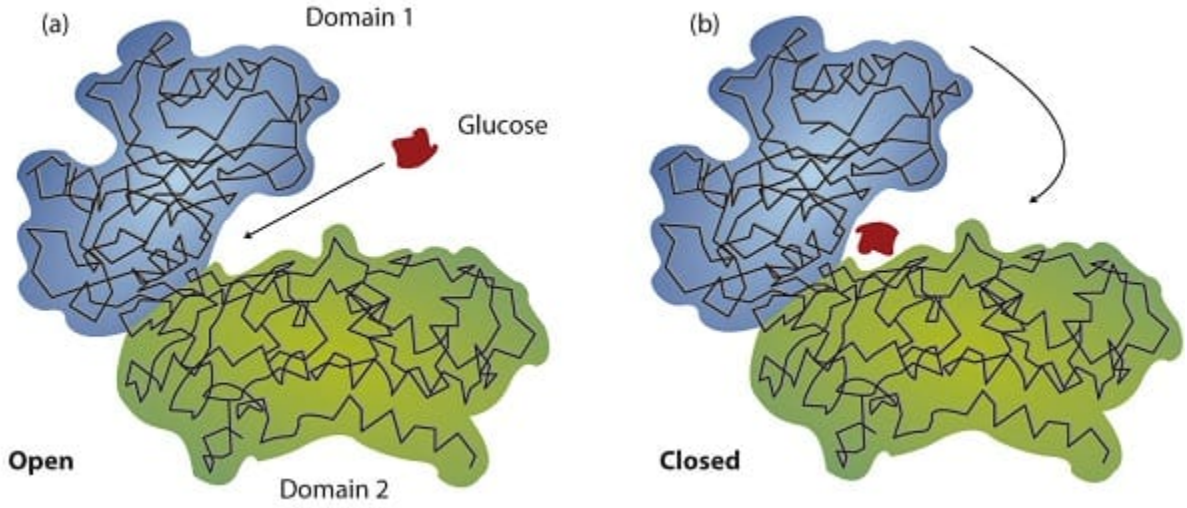


Figure 19.4.3: The Induced-Fit Model of Enzyme Action. (a) The enzyme hexokinase without its substrate (glucose, shown in red) is bound to the active site. (b) The enzyme conformation changes dramatically when the substrate binds to it, resulting in additional interactions between hexokinase and glucose.

The structural changes that occur when an enzyme and a substrate join together bring specific parts of a substrate into alignment with specific parts of the enzyme's active site. Amino acid side chains in or near the binding site can then act as acid or base catalysts, provide binding sites for the transfer of functional groups from one substrate to another or aid in the rearrangement of a substrate. The participating amino acids, which are usually widely separated in the primary sequence of the protein, are brought close together in the active site as a result of the folding and bending of the polypeptide chain or chains when the protein acquires its tertiary and quaternary structure. Binding to enzymes brings reactants close to each other and aligns them properly, which has the same effect as increasing the concentration of the reacting compounds.

Example 19.4.1

a. What type of interaction would occur between an OH group present on a substrate molecule and a functional group in the active site of an enzyme?
b. Suggest an amino acid whose side chain might be in the active site of an enzyme and form the type of interaction you just identified.

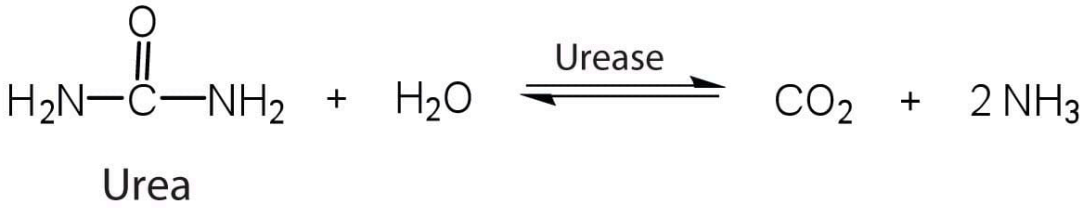
Solution

a. An OH group would most likely engage in hydrogen bonding with an appropriate functional group present in the active site of an enzyme.
b. Several amino acid side chains would be able to engage in hydrogen bonding with an OH group. One example would be asparagine, which has an amide functional group.

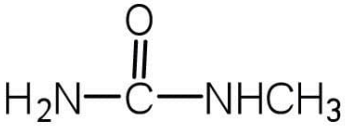
Exercise 19.4.1

a. What type of interaction would occur between an COO^- group present on a substrate molecule and a functional group in the active site of an enzyme?
b. Suggest an amino acid whose side chain might be in the active site of an enzyme and form the type of interaction you just identified.

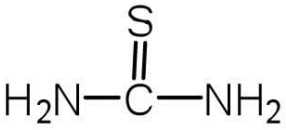
One characteristic that distinguishes an enzyme from all other types of catalysts is its **substrate specificity**. An inorganic acid such as sulfuric acid can be used to increase the reaction rates of many different reactions, such as the hydrolysis of disaccharides, polysaccharides, lipids, and proteins, with complete impartiality. In contrast, enzymes are much more specific. Some enzymes act on a single substrate, while other enzymes act on any of a group of related molecules containing a similar functional group or chemical bond. Some enzymes even distinguish between D- and L-stereoisomers, binding one stereoisomer but not the other. Urease, for example, is an enzyme that catalyzes the hydrolysis of a single substrate—urea—but not the closely related compounds methyl urea, thiourea, or biuret. The enzyme carboxypeptidase, on the other hand, is far less specific. It catalyzes the removal of nearly any amino acid from the carboxyl end of any peptide or protein.



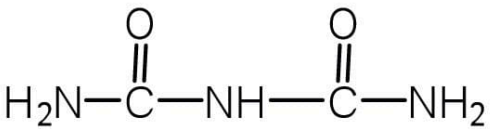
Urea



Methylurea



Thiourea



Biuret

Enzyme specificity results from the uniqueness of the active site in each different enzyme because of the identity, charge, and spatial orientation of the functional groups located there. It regulates cell chemistry so that the proper reactions occur in the proper place at the proper time. Clearly, it is crucial to the proper functioning of the living cell.

Summary

A substrate binds to a specific region on an enzyme known as the active site, where the substrate can be converted to product. The substrate binds to the enzyme primarily through hydrogen bonding and other electrostatic interactions. The induced-fit model says that an enzyme can undergo a conformational change when binding a substrate. Enzymes exhibit varying degrees of substrate specificity.

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19.5: Factors Affecting 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.

Substrate Concentration

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 19.5.1). 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).

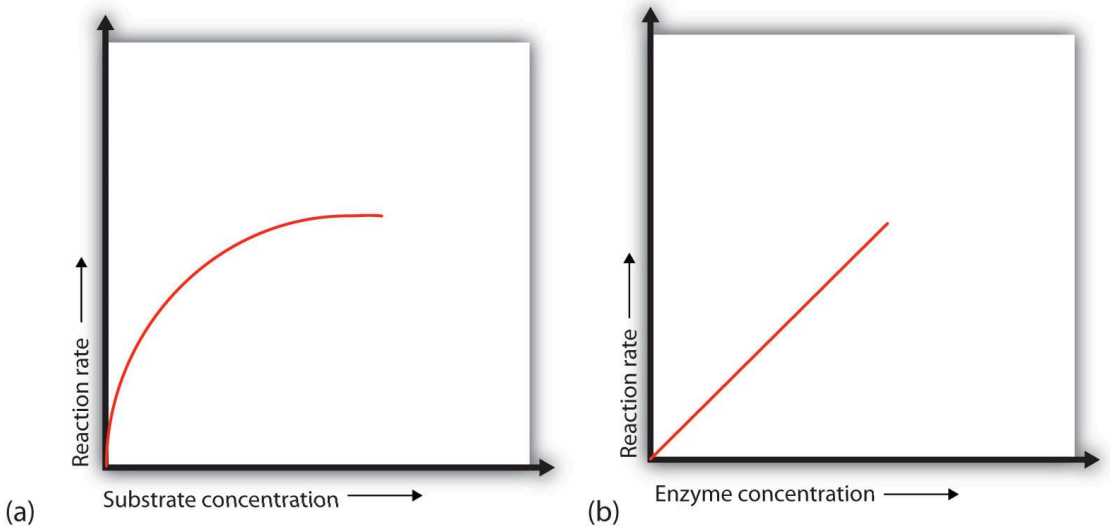


Figure 19.5.1: Concentration versus Reaction Rate. (a) This graph shows the effect of substrate concentration on the rate of a reaction that is catalyzed by a fixed amount of enzyme. (b) This graph shows the effect of enzyme concentration on the reaction rate at a constant level of substrate.

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.

Enzyme Concentration

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 19.5.1). This is true for any catalyst; the reaction rate increases as the concentration of the catalyst is increased.

Effect of Temperature on Activity

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 enzyme reaction rate, due to *denaturation* of the protein structure and disruption of the active site (part (a) of Figure 19.5.2). 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.

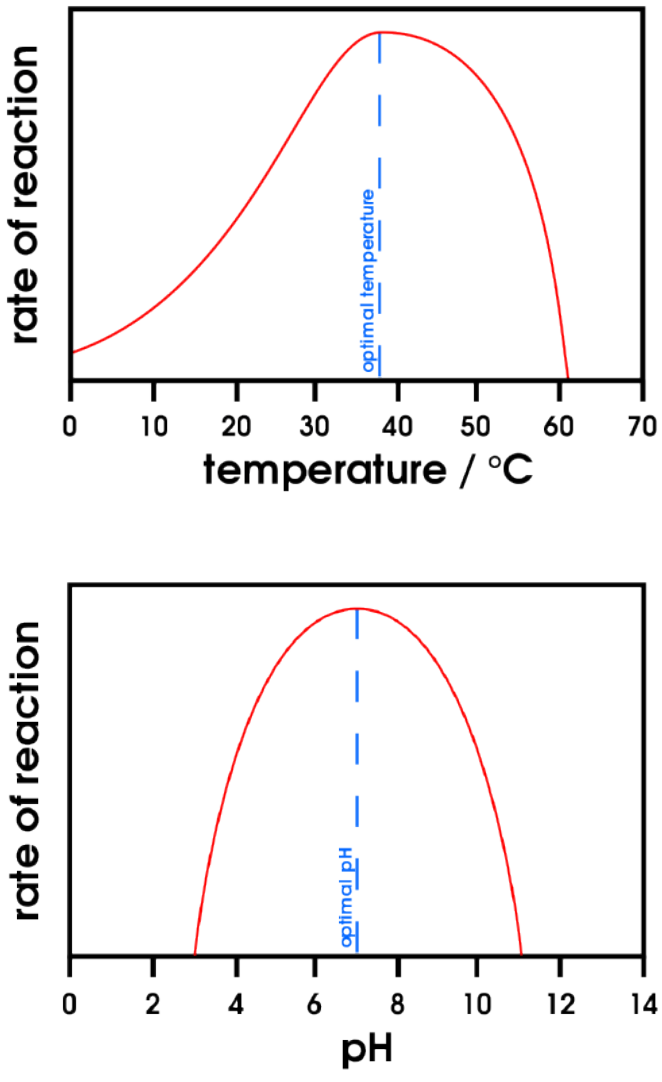


Figure 19.5.2: Temperature and pH versus Concentration. (a) This graph depicts the effect of temperature on the rate of a reaction that is catalyzed by a fixed amount of enzyme. (b) This graph depicts the effect of pH on the rate of a reaction that is catalyzed by a fixed amount of enzyme.

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.

Effect of Hydrogen Ion Concentration (pH) on Activity

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 19.5.2). With the notable exception of gastric juice (the fluids secreted in the stomach), most body fluids have pH values between 6 and 8. Not surprisingly, most enzymes exhibit optimal activity in this pH range. However, a few enzymes have optimum pH values outside this range. For example, the optimum pH for pepsin, an enzyme that is active in the stomach, is 2.0.

Summary

Initially, an increase in substrate concentration leads to an increase in the rate of an enzyme-catalyzed reaction. As the enzyme molecules become saturated with substrate, this increase in reaction rate levels off. The rate of an enzyme-catalyzed reaction increases with an increase in the concentration of an enzyme. At low temperatures, an increase in temperature increases the rate of an enzyme-catalyzed reaction. At higher temperatures, the protein is denatured, and the rate of the reaction dramatically decreases. An enzyme has an optimum pH range in which it exhibits maximum activity.

Concept Review Exercises

1. The concentration of substrate X is low. What happens to the rate of the enzyme-catalyzed reaction if the concentration of X is doubled?
2. What effect does an increase in the enzyme concentration have on the rate of an enzyme-catalyzed reaction?

Answers

1. If the concentration of the substrate is low, increasing its concentration will increase the rate of the reaction.
2. An increase in the amount of enzyme will increase the rate of the reaction (provided sufficient substrate is present).

Exercises

1. In non-enzyme-catalyzed reactions, the reaction rate increases as the concentration of reactant is increased. In an enzyme-catalyzed reaction, the reaction rate initially increases as the substrate concentration is increased but then begins to level off, so that the increase in reaction rate becomes less and less as the substrate concentration increases. Explain this difference.

2. Why do enzymes become inactive at very high temperatures?

3. An enzyme has an optimum pH of 7.4. What is most likely to happen to the activity of the enzyme if the pH drops to 6.3? Explain.

4. An enzyme has an optimum pH of 7.2. What is most likely to happen to the activity of the enzyme if the pH increases to 8.5? Explain.

Answers

1. In an enzyme-catalyzed reaction, the substrate binds to the enzyme to form an enzyme-substrate complex. If more substrate is present than enzyme, all of the enzyme binding sites will have substrate bound, and further increases in substrate concentration cannot increase the rate.

3. The activity will decrease; a pH of 6.3 is more acidic than 7.4, and one or more key groups in the active site may bind a hydrogen ion, changing the charge on that group.

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19.6: Enzyme Regulation - Inhibition

Learning Objectives

- Explain what an enzyme inhibitor is.
- Distinguish between reversible and irreversible inhibitors.
- Distinguish between competitive, noncompetitive, and uncompetitive inhibitors.

Previously, we noted that enzymes can be 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** that slow or stop catalysis. Enzyme inhibition can either be *reversible* or *irreversible*. In reversible inhibition, the inhibitor can bind (usually non-covalently) and dissociate, allowing enzyme activity to return back to its original, uninhibited level. Irreversible inhibitors bind to the enzyme permanently and thus permanently inhibit enzyme activity.

Reversible Inhibition

Reversible enzyme inhibition can be *competitive*, *noncompetitive*, or *uncompetitive*, depending on where the inhibitor binds to the enzyme, substrate, or enzyme-substrate complex.

Competitive inhibition is when an inhibitor reversibly binds to an enzyme at the enzyme active site; competing with the substrate for binding. A competitive inhibitor must be a molecule that is *structurally similar* to the substrate molecule, allowing it to interact with the enzyme active site through similar non-covalent interactions, but it does not, or cannot, undergo the same chemical reaction. When the inhibitor is bound to the active site, it blocks the correct substrate from binding and catalysis from occurring. However, as a reversible inhibitor, it can disassociate from the enzyme eventually allowing for the correct substrate to bind and the catalysis to occur. Because the inhibitor and substrate are in competition for the same active site, inhibition is concentration-dependent. As shown in the below plot of rate of reaction vs. substrate concentration (Figure 19.6.1), the competitive inhibitor slows the rate of reaction, but at higher substrate concentrations, the normal maximum rate can be reached.

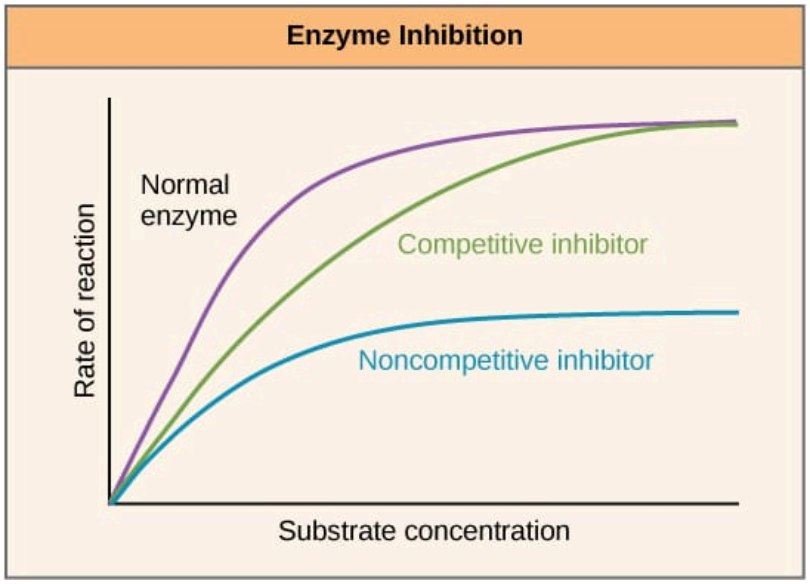


Figure 19.6.1: Plots of reaction rate vs. substrate concentration with and without inhibitors. Competitive inhibitors bind reversibly at the active site and therefore, compete with the substrate for binding. As substrate concentration increases, it can outcompete the inhibitor allowing enzyme activity to reach a normal maximum (green line). A noncompetive inhibitor binds at a site separate from the active site, the enzyme activity can only reach a lower than normal maximum reaction rate even as substrate concentration increases (blue line). Uncompetitive inhibition is not represented on this plot, but would be similar to the noncompetitive inhibitor, reaching a lower maximum rate. (Figure from OpenStax Biology)

Studies of competitive inhibition have provided helpful information about certain enzyme-substrate complexes and the interactions of specific groups at the active sites. As a result, pharmaceutical companies have synthesized drugs that competitively inhibit metabolic processes in bacteria and certain cancer cells. Many drugs are competitive inhibitors of specific enzymes.

A classic example of competitive inhibition is the effect of malonate on the enzyme activity of succinate dehydrogenase (Figure 19.6.2). Malonate and succinate are the anions of dicarboxylic acids and contain three and four carbon atoms, respectively. The malonate molecule binds to the active site because the spacing of its carboxyl groups is not greatly different from that of succinate. However, no catalytic reaction occurs because malonate does not have a CH_2CH_2 group to convert to CH=CH. This reaction will also be discussed in connection with the Krebs cycle and energy production in a later chapter.

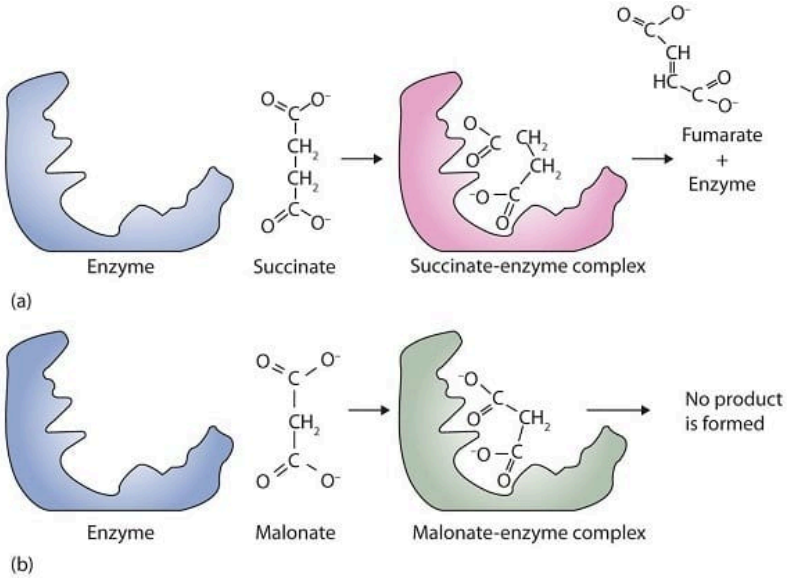


Figure 19.6.2: Competitive Inhibition. (a) Succinate binds to the enzyme succinate dehydrogenase. A dehydrogenation reaction occurs, and the product—fumarate—is released from the enzyme. (b) Malonate, a competitive inhibitor, also binds to the active site of succinate dehydrogenase. In this case, however, no subsequent reaction occurs while malonate remains bound to the enzyme.

In **uncompetitive inhibition**, the inhibitor can only bind the enzyme when the substrate is already bound, in other words it binds the enzyme-substrate complex but not the enzyme alone. The maximum reaction rate in the presence of an uncompetitive inhibitor is lowered, however, unlike with competitive inhibition, the rate cannot be increased by adding more substrate. This type of inhibition is most commonly seen when the enzyme reaction involves two substrates and as long as the concentration of inhibitor remains constant, the maximum reaction rate does not change.

A **noncompetitive inhibitor** can bind to either the free enzyme or the enzyme-substrate complex because its binding site on the enzyme is distinct from the active site. Binding of this kind of inhibitor alters the three-dimensional conformation of the enzyme, changing the configuration of the active site with one of two results. Either the enzyme-substrate complex does not form at its normal rate, or, once formed, it does not yield products at the normal rate (see Figure 19.6.1). Because the inhibitor does not structurally resemble the substrate, nor is it competing with the substrate for the active site, the addition of excess substrate does *not* reverse the inhibitory effect.

Chemotherapy is the strategic use of chemicals (that is, drugs) to destroy infectious microorganisms or cancer cells without causing excessive damage to the other, healthy cells of the host. From bacteria to humans, the metabolic pathways of all living organisms are quite similar, so the search for safe and effective chemotherapeutic agents is a formidable task. Many well-established chemotherapeutic drugs function by inhibiting a critical enzyme in the cells of the invading organism.

An *antibiotic* is a compound that kills bacteria; it may come from a natural source such as molds or be synthesized with a structure analogous to a naturally occurring antibacterial compound. Antibiotics constitute no well-defined class of chemically

related substances, but many of them work by effectively inhibiting a variety of enzymes essential to bacterial growth.

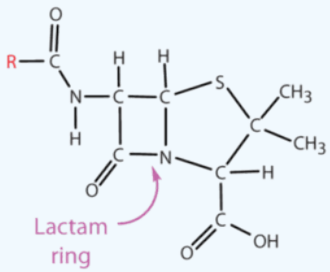
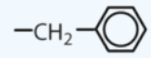
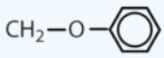
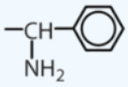
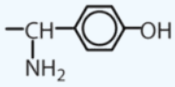
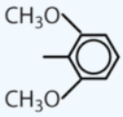
To Your Health: Penicillin

Penicillin, one of the most widely used antibiotics in the world, was fortuitously discovered by Alexander Fleming in 1928, when he noticed antibacterial properties in a mold growing on a bacterial culture plate. In 1938, Ernst Chain and Howard Florey began an intensive effort to isolate penicillin from the mold and study its properties. The large quantities of penicillin needed for this research became available through development of a corn-based nutrient medium that the mold loved and through the discovery of a higher-yielding strain of mold at a United States Department of Agriculture research center near Peoria, Illinois. Even so, it was not until 1944 that large quantities of penicillin were being produced and made available for the treatment of bacterial infections.

Penicillin functions by interfering with the synthesis of cell walls of reproducing bacteria. It does so by inhibiting an enzyme—transpeptidase—that catalyzes the last step in bacterial cell-wall biosynthesis. The defective walls cause bacterial cells to burst. Human cells are not affected because they have cell membranes, not cell walls.

Several naturally occurring penicillins have been isolated. They are distinguished by different R groups connected to a common structure: a four-member cyclic amide (called a lactam ring) fused to a five-member ring. The addition of appropriate organic compounds to the culture medium leads to the production of the different kinds of penicillin.

The penicillins are effective against gram-positive bacteria (bacteria capable of being stained by Gram's stain) and a few gram-negative bacteria (including the intestinal bacterium *Escherichia coli*). They are effective in the treatment of diphtheria, gonorrhea, pneumonia, syphilis, many pus infections, and certain types of boils. Penicillin G was the earliest penicillin to be used on a wide scale. However, it cannot be administered orally because it is quite unstable; the acidic pH of the stomach converts it to an inactive derivative. The major oral penicillins—penicillin V, ampicillin, and amoxicillin—on the other hand, are acid stable.

Penicillin Structure	R Group	Drug Name
		penicillin G
		penicillin V
		ampicillin
		amoxicillin
		methicillin

Some strains of bacteria become resistant to penicillin through a mutation that allows them to synthesize an enzyme—penicillinase—that breaks the antibiotic down (by cleavage of the amide linkage in the lactam ring). To combat these strains, scientists have synthesized penicillin analogs (such as methicillin) that are not inactivated by penicillinase.

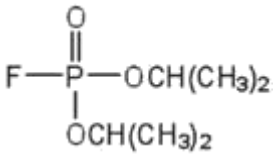
Some people (perhaps 5% of the population) are allergic to penicillin and therefore must be treated with other antibiotics. Their allergic reaction can be so severe that a fatal coma may occur if penicillin is inadvertently administered to them. Fortunately, several other antibiotics have been discovered. Most, including aureomycin and streptomycin, are the products of microbial synthesis. Others, such as the semisynthetic penicillins and tetracyclines, are made by chemical modifications of antibiotics; and some, like chloramphenicol, are manufactured entirely by chemical synthesis. They are as effective as penicillin in destroying infectious microorganisms. Many of these antibiotics exert their effects by blocking protein synthesis in microorganisms.

Initially, antibiotics were considered miracle drugs, substantially reducing the number of deaths from blood poisoning, pneumonia, and other infectious diseases. Some seven decades ago, a person with a major infection almost always died. Today, such deaths are rare. Seven decades ago, pneumonia was a dreaded killer of people of all ages. Today, it kills only the very old or those ill from other causes. Antibiotics have indeed worked miracles in our time, but even miracle drugs have limitations. Not long after the drugs were first used, disease organisms began to develop strains resistant to them. In a race to stay ahead of resistant bacterial strains, scientists continue to seek new antibiotics. The penicillins have now been partially displaced by related compounds, such as the cephalosporins and vancomycin. Unfortunately, some strains of bacteria have already shown resistance to these antibiotics.

Irreversible Inhibition

An **irreversible inhibitor** inactivates an enzyme by bonding covalently to a particular group at the active site. When the inhibitor is bound, the enzyme active site is blocked, the substrate does not bind, and catalysis cannot occur, similar to competitive inhibition. The difference here is that the inhibition is *irreversible*, meaning that the inhibitor remains bound and does not dissociate from the enzyme because the enzyme-inhibitor covalent bonds are not easily broken. In the presence of an irreversible inhibitor, the substrate cannot bind the active site at all, nor can high substrate concentrations outcompete the inhibitor, hence the enzyme is completely inactivated. Many of the known irreversible inhibitors are *poisons* because they inactivate an enzyme completely. Some examples are provided in Table 19.6.1 below.

Table 19.6.1: Poisons as Enzyme Inhibitors

Poison	Formula	Example of Enzyme Inhibited	Action
arsenate	AsO_4^{3-}	glyceraldehyde 3-phosphate dehydrogenase	substitutes for phosphate
iodoacetate	ICH_2COO^-	triose phosphate dehydrogenase	binds to cysteine SH group
diisopropylfluoro-phosphate (DIFP; a nerve poison)		acetylcholinesterase	binds to serine OH group

Summary

An irreversible inhibitor inactivates an enzyme by bonding covalently to a particular group at the active site. A reversible inhibitor inactivates an enzyme through noncovalent, reversible interactions. A competitive inhibitor competes with the substrate for binding at the active site of the enzyme. A noncompetitive inhibitor binds at a site distinct from the active site.

Concept Review Exercises

1. What are the characteristics of an irreversible inhibitor?
2. In what ways does a competitive inhibitor differ from a noncompetitive inhibitor?

Answers

1. It inactivates an enzyme by bonding covalently to a particular group at the active site.
2. A competitive inhibitor structurally resembles the substrate for a given enzyme and competes with the substrate for binding at the active site of the enzyme. A noncompetitive inhibitor binds at a site distinct from the active site and can bind to either the free enzyme or the enzyme-substrate complex.

Exercises

1. What amino acid is present in the active site of all enzymes that are irreversibly inhibited by nerve gases such as DIFP?
2. Oxaloacetate (OOCCH2COCOO) inhibits succinate dehydrogenase. Would you expect oxaloacetate to be a competitive or noncompetitive inhibitor? Explain.

Answer

1. serine

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19.7: Enzyme Regulation- Allosteric Control and Feedback Inhibition

Learning Objectives

- Objective 1
- Objective 2

In the previous section you learned about the different types of enzyme inhibitors and how they can be used to *slow* or *stop* enzyme activity by binding to an enzyme or enzyme-substrate complex. All of these inhibitor types, except noncompetitive inhibitors, work by binding to enzyme active sites. Noncompetitive inhibitors, however, work by binding to an enzyme at a location other than the active site, an *allosteric site*. Inhibitors and other molecules, called activators, that bind to enzymes at allosteric sites are considered an important part of enzyme regulation called **allosteric control**. In this section, we will take a look at allosteric control and feedback control, two ways in which enzyme activity is regulated differently.

Allosteric Control

Allosteric enzymes have both a binding site, for substrate binding and catalysis, and an allosteric site, for regulation of enzyme activity. When a regulator molecule binds to the allosteric site of an enzyme, usually by noncovalent interactions, a conformational change occurs in the enzyme active site, which affects substrate binding and reaction rates. Allosteric regulation of enzyme activity can be either positive, increasing reaction rates, or negative, decreasing reaction rates.

When an enzyme binds a negative regulator (or inhibitor), it will undergo a change in the active site in a way that *prevents* substrate binding, thereby lowering the reaction rate. As illustrated in the left-hand panel in Figure 19.7.1, the active site changes (becomes smaller in this case) and the substrate can no longer bind. Positive regulators (activators) bind to allosteric sites and cause conformational changes that open up an active site to *promote* substrate binding, allowing catalysis or increasing the reaction rate. The right panel of Figure 19.7.1 shows an enzyme that will only bind substrate when the active site is formed after the allosteric activator binds.

Some enzymes will have more than one allosteric site that can interact with one another, which allows for highly-controlled or finely-tuned reaction rates.

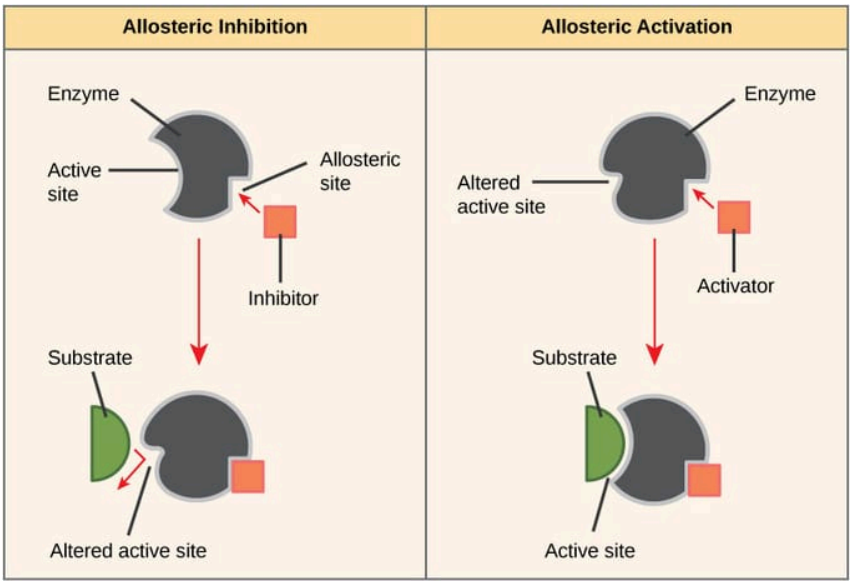


Figure 19.7.1: **Allosteric inhibitors and activators**: Allosteric inhibitors modify the active site of the enzyme so that substrate binding is reduced or prevented. In contrast, allosteric activators modify the active site of the enzyme so that the affinity for the substrate increases.

Feedback Control

Many biological processes involve the sequential action of multiple enzymes, a reaction pathway, in which the product of one reaction is the substrate for the next enzyme and so on until the final product is formed. Positive or negative regulation of these pathways often occurs by **feedback control**, where a product from one of the steps in the path *feedback* to an earlier step in the process to increase or decrease production. It may help to visualize a factory assembly line with each person responsible for one step (catalytic reaction) in making a perfect box of 12 donuts. If the last person in the line, who is responsible for putting 12 donuts in the box, falls behind, donuts will start to pile up. In order to not waste donuts or have less than full boxes at the end, it would be beneficial to signal to the other people to slow down or take a break. The process is similar in biochemical pathways: if too much product is being formed, the pathway needs to be turned off so energy and resources are not wasted.

Consider the pathway shown below in which substrate A is converted to product D through three enzymes and two intermediate products (B and C):

$$A \xrightarrow{Enzyme\ 1} B \xrightarrow{Enzyme\ 2} C \xrightarrow{Enzyme\ 3} D$$

If there is a lot of product D formed, there would be enough to bind to Enzyme 1, which would inhibit formation of products B, and subsequently product C, and D. This type of *feedback control* is useful to prevent waste of substrate A and any energy that is needed for the activity of Enzymes 1-3. As you will see in later chapters, there are many different types of feedback control that can both negatively and positively regulate pathways. Typically, feedback control occurs at points in pathways where it would be energetically unfavorable to proceede if the final product is not needed.

Feedback inhibition is used to regulate the synthesis of many amino acids. For example, bacteria synthesize isoleucine from threonine in a series of five enzyme-catalyzed steps. As the concentration of isoleucine increases, some of it binds as a noncompetitive inhibitor to the first enzyme of the series (threonine deaminase), thus bringing about a decrease in the amount of isoleucine being formed (Figure 19.7.2).

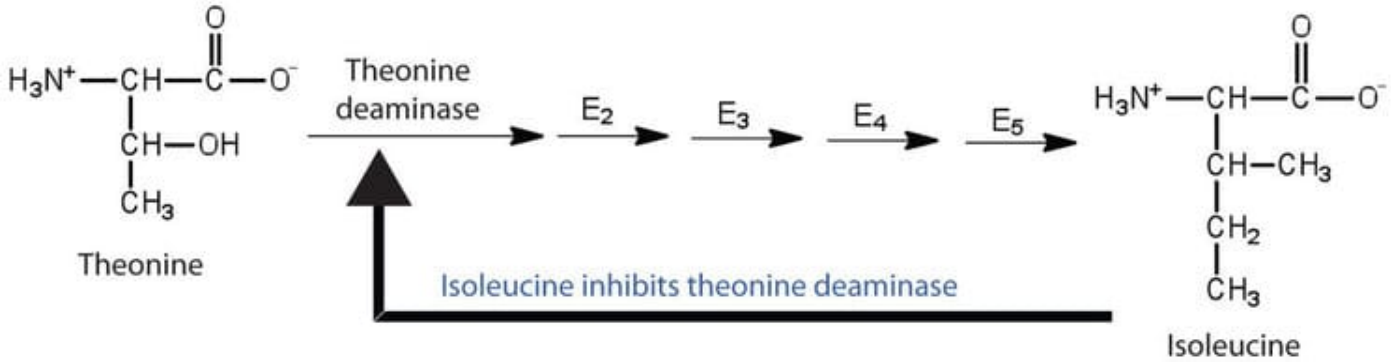


Figure 19.7.2: Feedback Inhibition of Threonine Deaminase by Isoleucine. Threonine deaminase is the first enzyme in the conversion of threonine to isoleucine. Isoleucine inhibits threonine deaminase through feedback inhibition.

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19.8: Enzyme Regulation - Covalent Modification and Genetic Control



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19.9: Vitamins, Antioxidants, and Minerals



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20: CARBOHYDRATES

20.1: An Introduction to Carbohydrates
20.2: Handedness of Carbohydrates
20.3: Structure of Glucose and Other Monosaccharides
20.4: Some Important Monosaccharides
20.5: Reactions of Monosaccharides
20.6: Common Disaccharides
20.7: Some Important Polysaccharides Based on Glucose

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20.1: An Introduction to Carbohydrates



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20.2: Handedness of Carbohydrates



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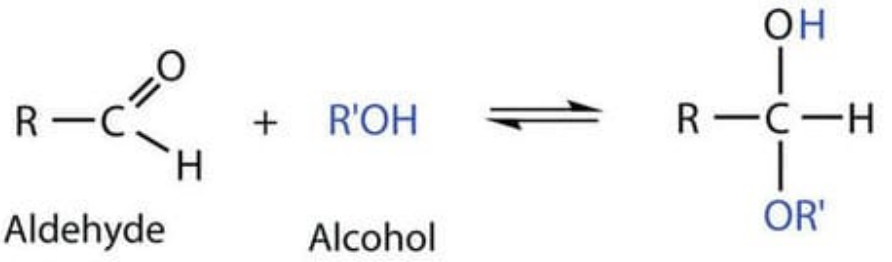
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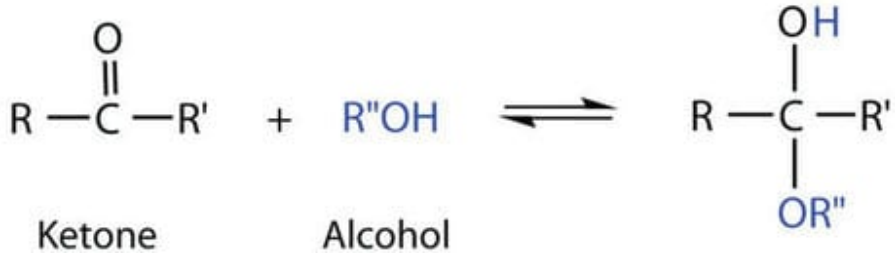
20.3: Structure of Glucose and Other Monosaccharides

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.

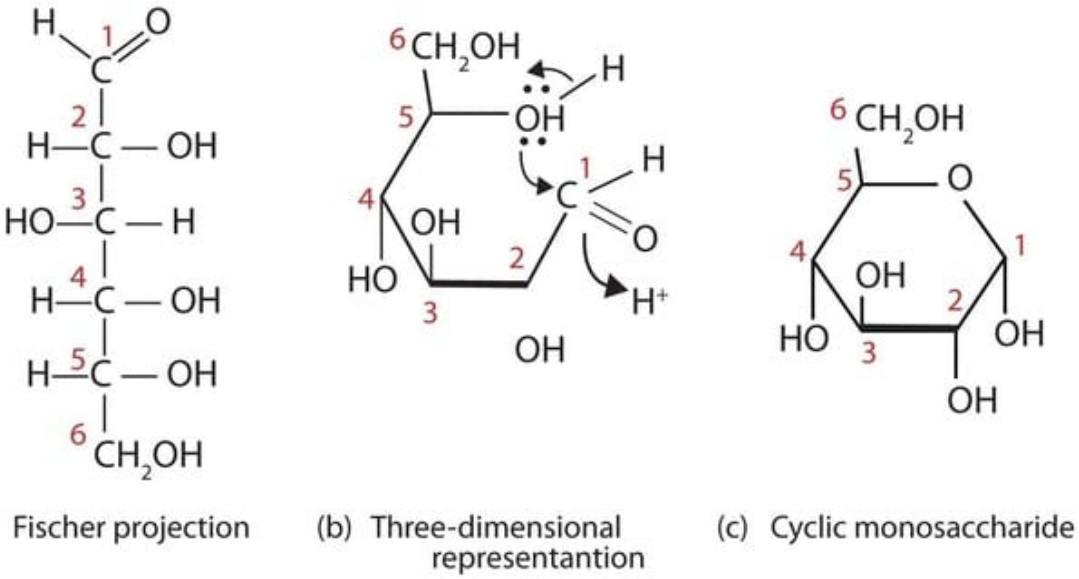


Figure 20.3.1: Cyclization of D-Glucose. D-Glucose can be represented with a Fischer projection (a) or three dimensionally (b). By reacting the OH group on the fifth carbon atom with the aldehyde group, the cyclic monosaccharide (c) is produced.

When a straight-chain monosaccharide, such as any of the structures shown in Figure 20.3.1, forms a cyclic structure, the carbonyl oxygen atom may be pushed either up or down, giving rise to two stereoisomers, as shown in Figure 20.3.2. The structure shown on the left side of Figure 20.3.2, 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 20.3.2). You can start with a pure crystalline sample of glucose consisting entirely of either anomer, but as soon as the molecules dissolve in water, they open to form the carbonyl group and then reclose to form either the α or the β anomer. The opening and closing repeats continuously in an ongoing interconversion between anomeric forms and is referred to as mutarotation (Latin *mutare*, meaning "to change"). At equilibrium, the mixture consists of about 36% α-D-glucose, 64% β-D-glucose, and less than 0.02% of the open-chain aldehyde form. The observed rotation of this solution is +52.7°.

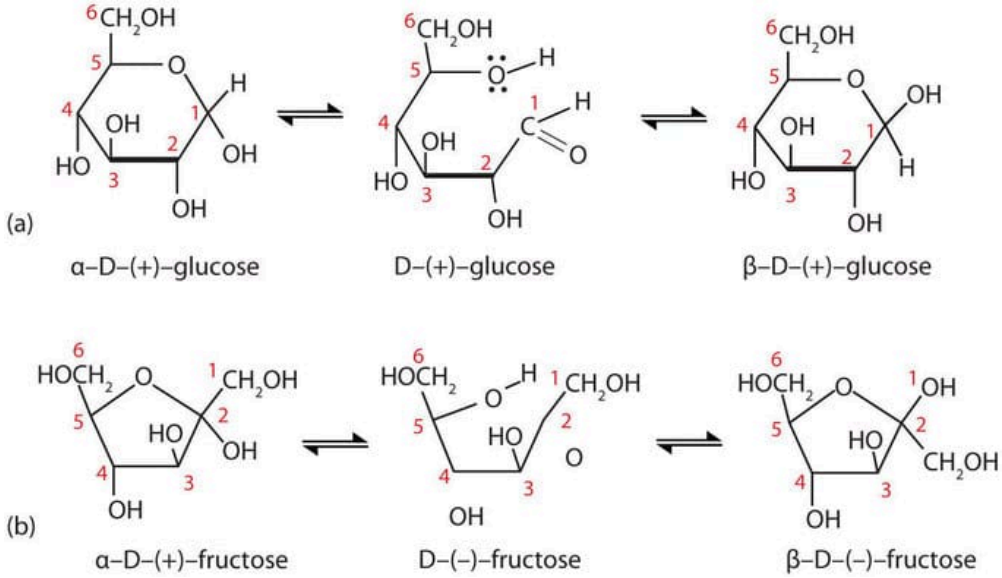


Figure 20.3.2: Monosaccharides. In an aqueous solution, monosaccharides exist as an equilibrium mixture of three forms. The interconversion between the forms is known as *mutarotation*, which is shown for D-glucose (a) and D-fructose (b).

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 20.3.1 and 20.3.2) the cyclic forms of sugars are depicted using a convention first suggested by Walter N. Haworth, an English chemist. The molecules are drawn as planar hexagons with a darkened edge representing the side facing toward the viewer. The structure is simplified to show only the functional groups attached to the carbon atoms. Any group written to the right in a Fischer projection appears below the plane of the ring in a Haworth projection, and any group written to the left in a Fischer projection appears above the plane in a Haworth projection.

The difference between the α and the β forms of sugars may seem trivial, but such structural differences are often crucial in biochemical reactions. This explains why we can get energy from the starch in potatoes and other plants but not from cellulose, even though both starch and cellulose are polysaccharides composed of glucose molecules linked together.

Summary

Monosaccharides that contain five or more carbons atoms form cyclic structures in aqueous solution. Two cyclic stereoisomers can form from each straight-chain monosaccharide; these are known as anomers. In an aqueous solution, an equilibrium mixture

forms between the two anomers and the straight-chain structure of a monosaccharide in a process known as mutarotation.

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20.4: Some Important Monosaccharides

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 20.4.1). Glucose and galactose are both aldohexoses, while fructose is a ketohexose.

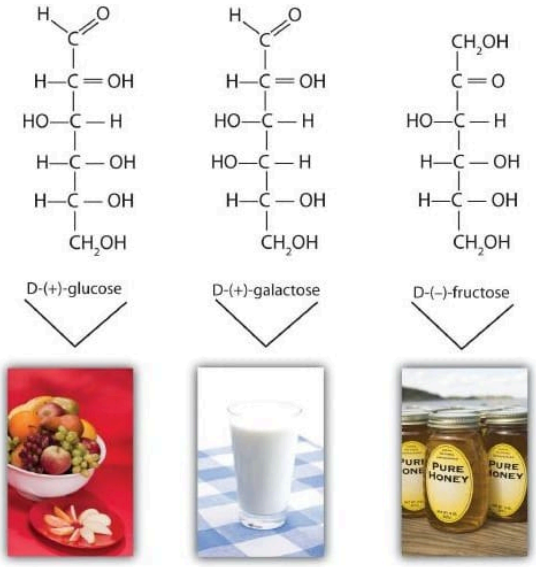


Figure 20.4.1: Structures of Three Important Hexoses. Each hexose is pictured with a food source in which it is commonly found. Source: Photos © Thinkstock.

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.

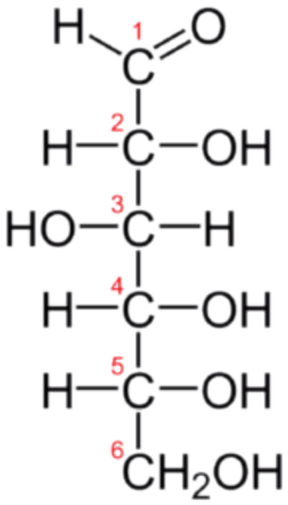


Figure 20.4.2: Fischer projection of D-glucose

The Fischer projection of D-glucose is given in Figure 20.4.2. 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.

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20.5: Reactions of Monosaccharides

Learning Objectives

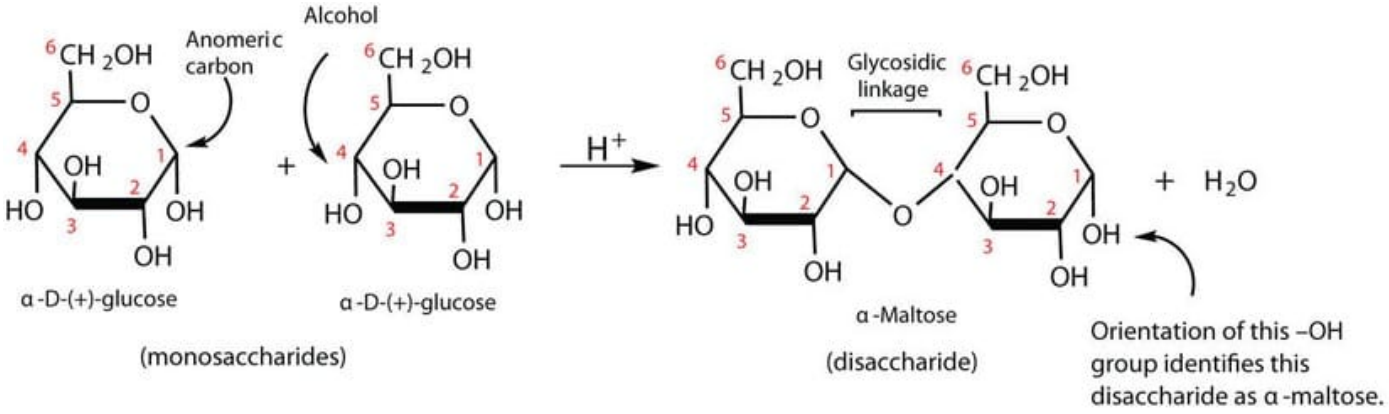
- Identify the structures of sucrose, lactose, and maltose.
- Identify the monosaccharides that are needed to form sucrose, lactose, and maltose
-

Reducing Sugars

Sugar Alcohols

Disaccharide Formation

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.

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20.6: Common Disaccharides

Learning Objectives

- Objective 1
- Objective 2

Maltose

Maltose occurs to a limited extent in sprouting grain. It is formed most often by the partial hydrolysis of starch and glycogen. In the manufacture of beer, maltose is liberated by the action of malt (germinating barley) on starch; for this reason, it is often referred to as *malt sugar*. Maltose is about 30% as sweet as sucrose. The human body is unable to metabolize maltose or any other disaccharide directly from the diet because the molecules are too large to pass through the cell membranes of the intestinal wall. Therefore, an ingested disaccharide must first be broken down by hydrolysis into its two constituent monosaccharide units.

In the body, such hydrolysis reactions are catalyzed by enzymes such as *maltase*. The same reactions can be carried out in the laboratory with dilute acid as a catalyst, although in that case the rate is much slower, and high temperatures are required. Whether it occurs in the body or a glass beaker, the hydrolysis of maltose produces two molecules of D-glucose.

$$\text{maltose} \xrightarrow{\text{H}^+ \text{ or maltase}} 2 \text{ D-glucose} \tag{16.6.2}$$

Maltose is a reducing sugar. Thus, its two glucose molecules must be linked in such a way as to leave one anomeric carbon that can open to form an aldehyde group. The glucose units in maltose are joined in a *head-to-tail* fashion through an α-linkage from the first carbon atom of one glucose molecule to the fourth carbon atom of the second glucose molecule (that is, an α-1,4-glycosidic linkage; see Figure 20.6.1). The bond from the anomeric carbon of the first monosaccharide unit is directed downward, which is why this is known as an α-glycosidic linkage. The OH group on the anomeric carbon of the second glucose can be in either the α or the β position, as shown in Figure 20.6.1.

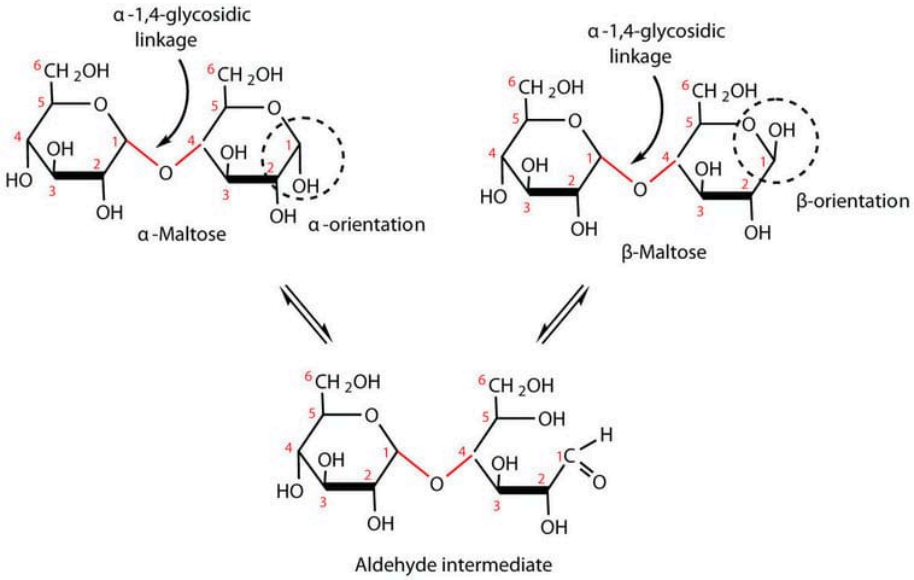


Figure 20.6.1: An Equilibrium Mixture of Maltose Isomers

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20.7: Some Important Polysaccharides Based on Glucose

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 20.7.1). Experimental evidence indicates that amylose is not a straight chain of glucose units but instead is coiled like a spring, with six glucose monomers per turn (part (b) of Figure 20.7.1). When coiled in this fashion, amylose has just enough room in its core to accommodate an iodine molecule. The characteristic blue-violet color that appears when starch is treated with iodine is due to the formation of the amylose-iodine complex. This color test is sensitive enough to detect even minute amounts of starch in solution.

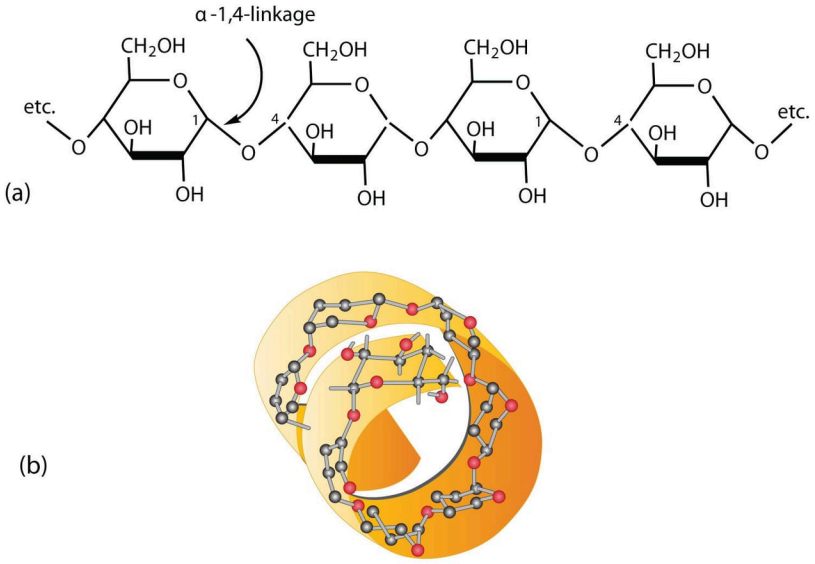


Figure 20.7.1: Amylose. (a) Amylose is a linear chain of α-D-glucose units joined together by α-1,4-glycosidic bonds. (b) Because of hydrogen bonding, amylose acquires a spiral structure that contains six glucose units per turn.

Amylopectin is a branched-chain polysaccharide composed of glucose units linked primarily by α-1,4-glycosidic bonds but with occasional α-1,6-glycosidic bonds, which are responsible for the branching. A molecule of amylopectin may contain many

thousands of glucose units with branch points occurring about every 25–30 units (Figure 20.7.2). The helical structure of amylopectin is disrupted by the branching of the chain, so instead of the deep blue-violet color amylose gives with iodine, amylopectin produces a less intense reddish brown.

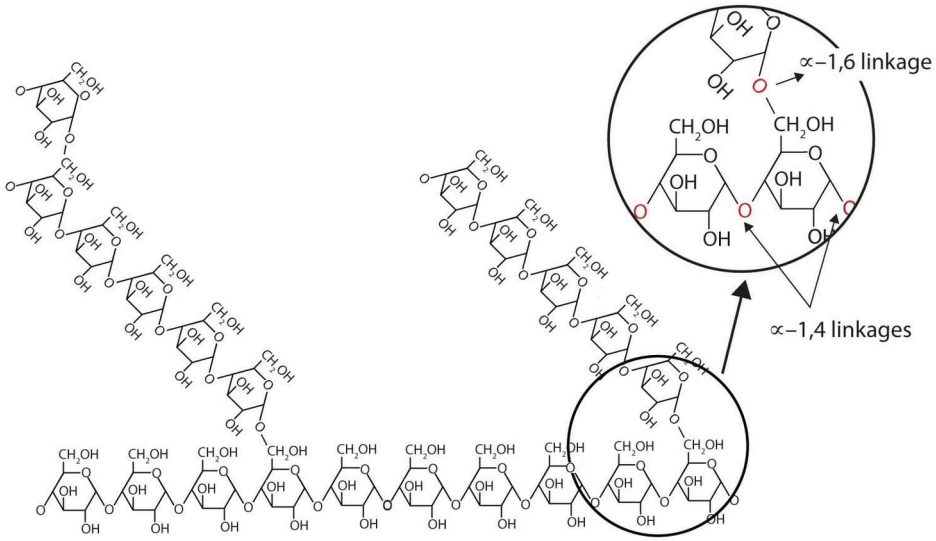


Figure 20.7.2: Representation of the Branching in Amylopectin and Glycogen. Both amylopectin and glycogen contain branch points that are linked through α-1,6-linkages. These branch points occur more often in glycogen.

Dextrins are glucose polysaccharides of intermediate size. The shine and stiffness imparted to clothing by starch are due to the presence of dextrins formed when clothing is ironed. Because of their characteristic stickiness with wetting, dextrins are used as adhesives on stamps, envelopes, and labels; as binders to hold pills and tablets together; and as pastes. Dextrins are more easily digested than starch and are therefore used extensively in the commercial preparation of infant foods.

The complete hydrolysis of starch yields, in successive stages, glucose:

$$\text{starch} \rightarrow \text{dextrins} \rightarrow \text{maltose} \rightarrow \text{glucose}$$

In the human body, several enzymes known collectively as amylases degrade starch sequentially into usable glucose units.

- ## Glycogen

  Glycogen is the energy reserve carbohydrate of animals. Practically all mammalian cells contain some stored carbohydrates in the form of glycogen, but it is especially abundant in the liver (4%–8% by weight of tissue) and in skeletal muscle cells (0.5%–1.0%). Like starch in plants, glycogen is found as granules in liver and muscle cells. When fasting, animals draw on these glycogen reserves during the first day without food to obtain the glucose needed to maintain metabolic balance.

  Glycogen is structurally quite similar to amylopectin, although glycogen is more highly branched (8–12 glucose units between branches) and the branches are shorter. When treated with iodine, glycogen gives a reddish brown color. Glycogen can be broken down into its D-glucose subunits by acid hydrolysis or by the same enzymes that catalyze the breakdown of starch. In animals, the enzyme phosphorylase catalyzes the breakdown of glycogen to phosphate esters of glucose.

  > About 70% of the total glycogen in the body is stored in muscle cells. Although the percentage of glycogen (by weight) is higher in the liver, the much greater mass of skeletal muscle stores a greater total amount of glycogen.

Cellulose

Cellulose, a fibrous carbohydrate found in all plants, is the structural component of plant cell walls. Because the earth is covered with vegetation, cellulose is the most abundant of all carbohydrates, accounting for over 50% of all the carbon found in the vegetable kingdom. Cotton fibrils and filter paper are almost entirely cellulose (about 95%), wood is about 50%

cellulose, and the dry weight of leaves is about 10%–20% cellulose. The largest use of cellulose is in the manufacture of paper and paper products. Although the use of noncellulose synthetic fibers is increasing, rayon (made from cellulose) and cotton still account for over 70% of textile production.

Like amylose, cellulose is a linear polymer of glucose. It differs, however, in that the glucose units are joined by β-1,4-glycosidic linkages, producing a more extended structure than amylose (part (a) of Figure 20.7.3). This extreme linearity allows a great deal of hydrogen bonding between OH groups on adjacent chains, causing them to pack closely into fibers (part (b) of Figure 20.7.3). As a result, cellulose exhibits little interaction with water or any other solvent. Cotton and wood, for example, are completely insoluble in water and have considerable mechanical strength. Because cellulose does not have a helical structure, it does not bind to iodine to form a colored product.

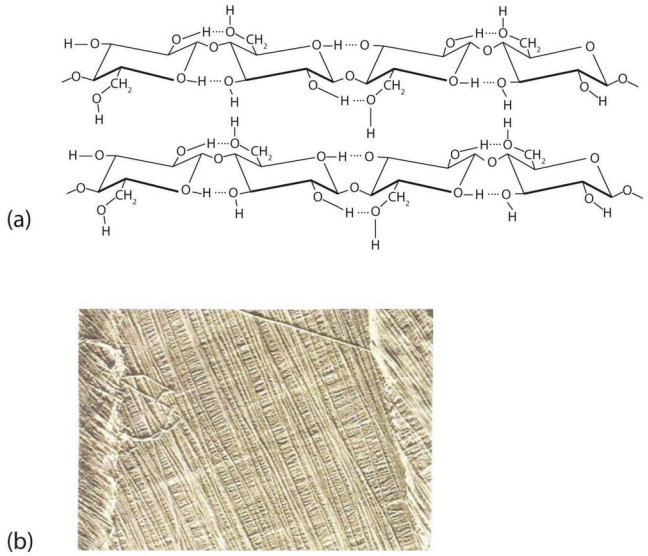


Figure 20.7.3: Cellulose. (a) There is extensive hydrogen bonding in the structure of cellulose. (b) In this electron micrograph of the cell wall of an alga, the wall consists of successive layers of cellulose fibers in parallel arrangement.

Cellulose yields D-glucose after complete acid hydrolysis, yet humans are unable to metabolize cellulose as a source of glucose. Our digestive juices lack enzymes that can hydrolyze the β-glycosidic linkages found in cellulose, so although we can eat potatoes, we cannot eat grass. However, certain microorganisms can digest cellulose because they make the enzyme cellulase, which catalyzes the hydrolysis of cellulose. The presence of these microorganisms in the digestive tracts of herbivorous animals (such as cows, horses, and sheep) allows these animals to degrade the cellulose from plant material into glucose for energy. Termites also contain cellulase-secreting microorganisms and thus can subsist on a wood diet. This example once again demonstrates the extreme stereospecificity of biochemical processes.

Career Focus: Certified Diabetes Educator

Certified diabetes educators come from a variety of health professions, such as nursing and dietetics, and specialize in the education and treatment of patients with diabetes. A diabetes educator will work with patients to manage their diabetes. This involves teaching the patient to monitor blood sugar levels, make good food choices, develop and maintain an exercise program, and take medication, if required.



A certified diabetes educator at Naval Medical Center Portsmouth (left) and a registered dietician at the medical center (center), provide nutritional information to a diabetes patient and her mother at the Diabetes Boot Camp.

Diabetes educators also work with hospital or nursing home staff to improve the care of diabetic patients. Educators must be willing to spend time attending meetings and reading the current literature to maintain their knowledge of diabetes medications, nutrition, and blood monitoring devices so that they can pass this information to their patients.

Summary

Starch is a storage form of energy in plants. It contains two polymers composed of glucose units: amylose (linear) and amylopectin (branched). Glycogen is a storage form of energy in animals. It is a branched polymer composed of glucose units. It is more highly branched than amylopectin. Cellulose is a structural polymer of glucose units found in plants. It is a linear polymer with the glucose units linked through β-1,4-glycosidic bonds.

Concept Review Exercises

Answers

Exercises

Answers

1. What purposes do starch and cellulose serve in plants?
2. What purpose does glycogen serve in animals?
3. Starch is the storage form of glucose (energy) in plants, while cellulose is a structural component of the plant cell wall.
4. Glycogen is the storage form of glucose (energy) in animals.
5. What monosaccharide is obtained from the hydrolysis of each carbohydrate?
    a. starch
    b. cellulose
    c. glycogen

6. For each carbohydrate listed in Exercise 1, indicate whether it is found in plants or mammals.

7. Describe the similarities and differences between amylose and cellulose.

8. Describe the similarities and differences between amylopectin and glycogen.

9. a. glucose
   b. glucose
   c. glucose

10. Amylose and cellulose are both linear polymers of glucose units, but the glycosidic linkages between the glucose units differ. The linkages in amylose are α-1,4-glycosidic linkages, while the linkages in cellulose they are β-1,4-glycosidic linkages.

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21: THE GENERATION OF BIOCHEMICAL ENERGY

21.1: Energy, Life, and Biochemical Reactions
21.2: Cells and Their Structure
21.3: An Overview of Metabolism and Energy Production
21.4: Strategies of Metabolism - ATP and Energy Transfer
21.5: Strategies of Metabolism - Metabolic Pathways and Coupled Reactions
21.6: Strategies of Metabolism- Oxidized and Reduced Coenzymes
21.7: The Citric Acid Cycle
21.8: The Electron-Transport Chain and ATP Production

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21.1: Energy, Life, and Biochemical Reactions

Learning Objectives

- Objective 1
- Objective 2

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.

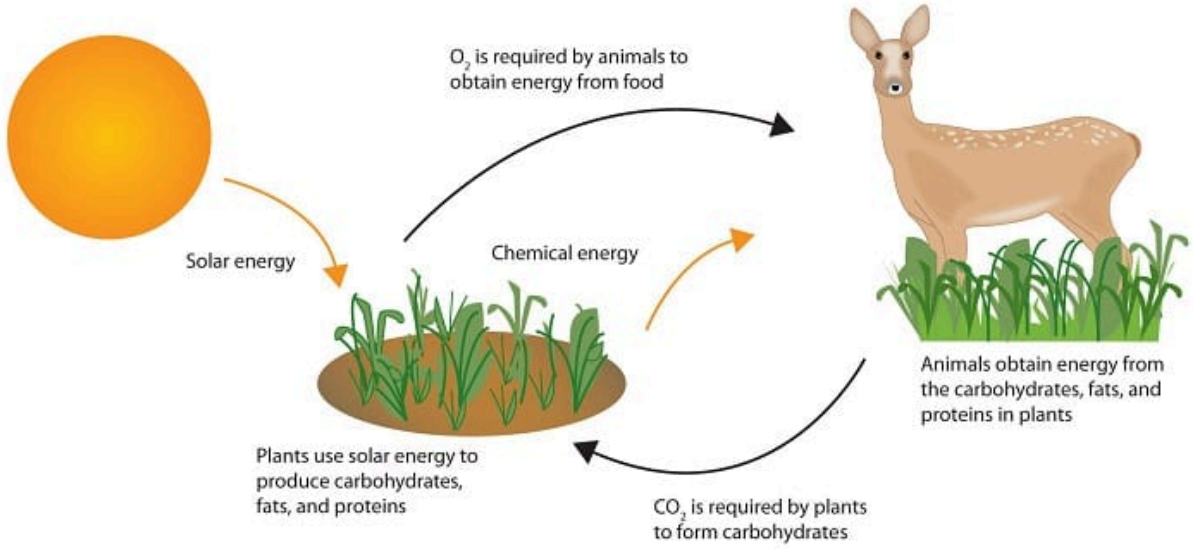


Figure 21.1.2: Some Energy Transformations in Living Systems. Plants and animals exist in a cycle; each requires products of the other.

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:

$$C_6H_{12}O_6 + 6\,O_2 \longrightarrow 6\,CO_2 + 6\,H_2O + 670\,\text{kcal}$$

Lipid:

$$C_{16}H_{32}O_2 + 23\,O_2 \longrightarrow 16\,CO_2 + 16\,H_2O + 2{,}385\,\text{kcal}$$

These two equations summarize the biological combustion of a carbohydrate and a lipid by the cell through respiration. **Respiration** is the collective name for all metabolic processes in which gaseous oxygen is used to oxidize organic matter to carbon dioxide, water, and energy.

Like the combustion of the common fuels we burn in our homes and cars (wood, coal, gasoline), respiration uses oxygen from the air to break down complex organic substances to carbon dioxide and water. But the energy released in the burning of wood is manifested entirely in the form of heat, and excess heat energy is not only useless but also injurious to the living cell. Living organisms instead conserve much of the energy respiration releases by channeling it into a series of stepwise reactions that produce adenosine triphosphate (ATP) or other compounds that ultimately lead to the synthesis of ATP. The remainder of the energy is released as heat and manifested as body temperature.

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21.2: Cells and Their Structure

Learning Objectives

- Describe the two types of cell: prokaryotic and eukaryotic.
- Explain the function of each cellular component.

Cells fall into one of two broad categories: prokaryotic and eukaryotic. Only the predominantly single-celled organisms of the domains Bacteria and Archaea are classified as prokaryotes (pro- = "before"; -kary- = "nucleus"). Cells of animals, plants, fungi, and protists are all eukaryotes (eu- = "true") and are made up of eukaryotic cells.

Components of Prokaryotic Cells

All cells share four common components: 1) a plasma membrane, an outer covering that separates the cell's interior from its surrounding environment; 2) cytoplasm, consisting of a jelly-like cytosol within the cell in which other cellular components are found; 3) DNA, the genetic material of the cell; and 4) ribosomes, which synthesize proteins. However, prokaryotes differ from eukaryotic cells in several ways.

A prokaryote is a simple, mostly single-celled (unicellular) organism that lacks a nucleus, or any other membrane-bound organelle. We will shortly come to see that this is significantly different in eukaryotes. Prokaryotic DNA is found in a central part of the cell: the nucleoid (Figure 21.2.1).

Figure 21.2.1: This figure shows the generalized structure of a prokaryotic cell. All prokaryotes have chromosomal DNA localized in a nucleoid, ribosomes, a cell membrane, and a cell wall. The other structures shown are present in some, but not all, bacteria.

Unlike prokaryotic cells, eukaryotic cells have: 1) a membrane-bound nucleus; 2) numerous membrane-bound organelles such as the endoplasmic reticulum, Golgi apparatus, chloroplasts, mitochondria, and others; and 3) several, rod-shaped chromosomes. Because a eukaryotic cell's nucleus is surrounded by a membrane, it is often said to have a "true nucleus." The word "organelle" means "little organ," and, as already mentioned, organelles have specialized cellular functions, just as the organs of your body have specialized functions.

At this point, it should be clear to you that eukaryotic cells have a more complex structure than prokaryotic cells. Organelles allow different functions to be compartmentalized in different areas of the cell. Before turning to organelles, let's first examine two important components of the cell: the plasma membrane and the **cytoplasm**.

Figure 21.2.2: These figures show the major organelles and other cell components of a general eukaryotic cell.

Mitochondria (singular = mitochondrion) are often called the "powerhouses" or "energy factories" of a cell because they are responsible for making **adenosine triphosphate (ATP)**, the cell's main energy-carrying molecule. ATP represents the short-term stored energy of the cell. Cellular respiration is the process of making ATP using the chemical energy found in glucose and other nutrients. In mitochondria, this process uses oxygen and produces carbon dioxide as a waste product. In fact, the carbon dioxide that you exhale with every breath comes from the cellular reactions that produce carbon dioxide as a byproduct.

Mitochondria are oval-shaped, double membrane organelles (Figure 21.2.3) that have their own ribosomes and DNA. Each membrane is a phospholipid bilayer embedded with proteins. The inner layer has folds called cristae. The area surrounded by the folds is called the **mitochondrial matrix**. The cristae and the matrix have different roles in cellular respiration.

Figure 21.2.3: This electron micrograph shows a mitochondrion as viewed with a transmission electron microscope. This organelle has an outer membrane and an inner membrane. The inner membrane contains folds, called cristae, which increase its surface area. The space between the two membranes is called the intermembrane space, and the space inside the inner membrane is called the mitochondrial matrix. ATP synthesis takes place on the inner membrane. (credit: modification of work by Matthew Britton; scale-bar data from Matt Russell)

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21.3: An Overview of Metabolism and Energy Production

Learning Objectives

- Describe the stages of catabolism from food to ATP.

Metabolism describes all of the chemical reactions that take place in an organism. A *metabolic pathway* is a series of interconnected biochemical reactions that convert a substrate molecule or molecules, step-by-step, through a series of metabolic intermediates, eventually yielding a final product or products. In the case of sugar metabolism, the first metabolic pathway synthesized sugar from smaller molecules, and the other pathway broke sugar down into smaller molecules. These two opposite processes—the first requiring energy and the second producing energy—are referred to as anabolic (building) and catabolic (breaking down) pathways, respectively. Consequently, metabolism is composed of building (**anabolism**) and degradation (**catabolism**).

It is important to know that the chemical reactions of metabolic pathways don't take place spontaneously. Each reaction step is facilitated, or catalyzed, by enzymes. Enzymes are important for catalyzing all types of biological reactions—those that require energy as well as those that release energy. See a simple graphic below, (Figure 21.3.1).

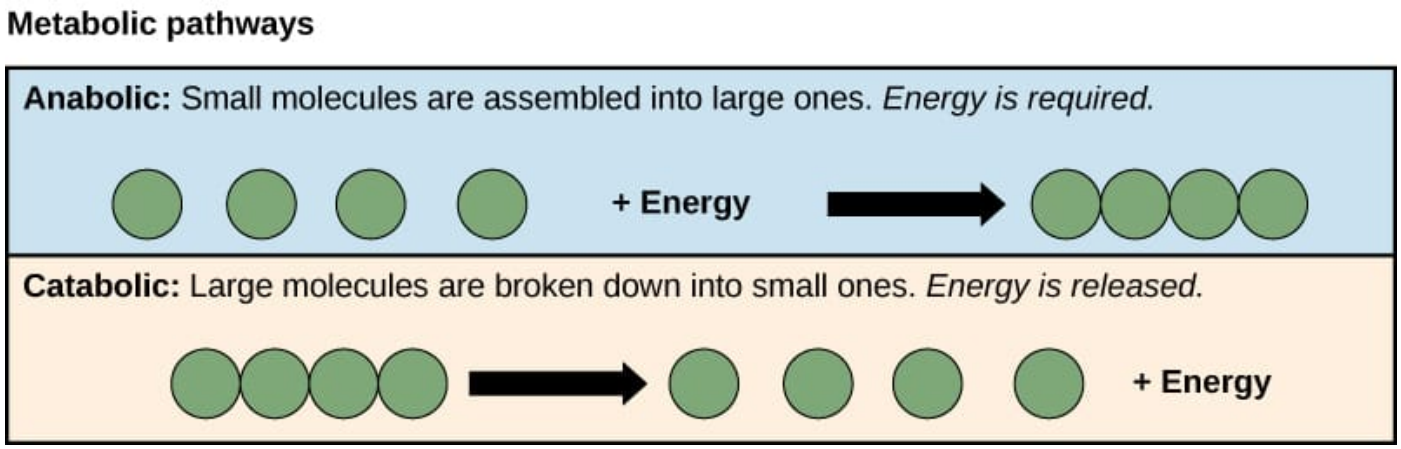


Figure 21.3.1: Anabolic pathways are those that require energy to synthesize larger molecules. Catabolic pathways are those that generate energy by breaking down larger molecules. Both types of pathways are required for maintaining the cell's energy balance.

We can think of catabolism as occurring in three stages (Figure 21.3.1). 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, **Acetyl-coenzyme A**, 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.

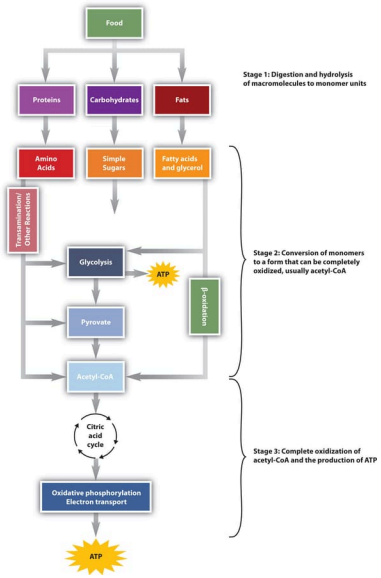


Figure 21.3.1: Energy Conversions. The conversion of food into cellular energy (as ATP) occurs in three stages.

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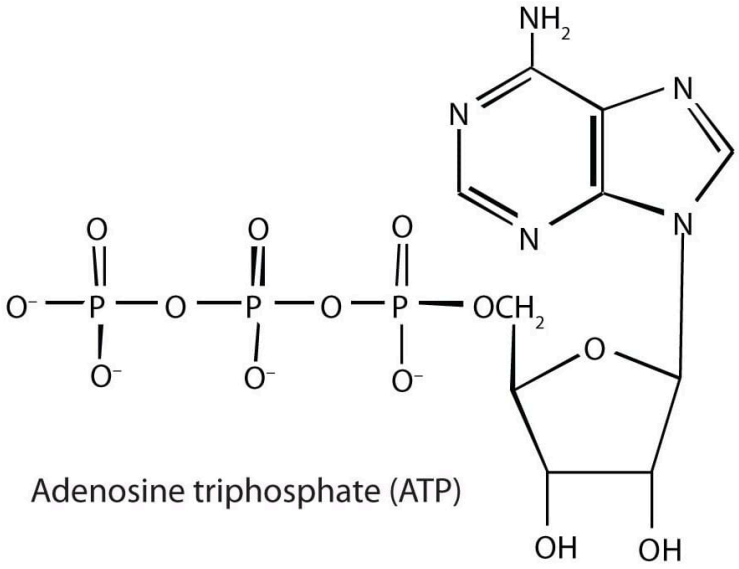
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21.4: Strategies of Metabolism - ATP and Energy Transfer

Learning Objectives

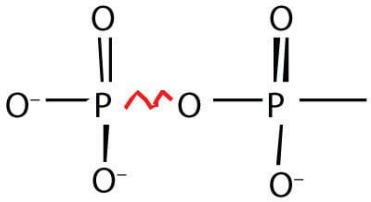
- To describe the importance of ATP as a source of energy in living organisms.

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.



Adenosine triphosphate (ATP)

Energy-rich compounds are substances having particular structural features that lead to a release of energy after hydrolysis. As a result, these compounds are able to supply energy for biochemical processes that require energy. The structural feature important in ATP is the phosphoric acid anhydride, or pyrophosphate, linkage:



The pyrophosphate bond, symbolized by a squiggle (~), is hydrolyzed when ATP is converted to adenosine diphosphate (ADP). In this hydrolysis reaction, the products contain less energy than the reactants; there is a release of energy (> 7 kcal/mol). One reason for the amount of energy released is that hydrolysis relieves the electron-electron repulsions experienced by the negatively charged phosphate groups when they are bonded to each other (Figure 20.1.1).

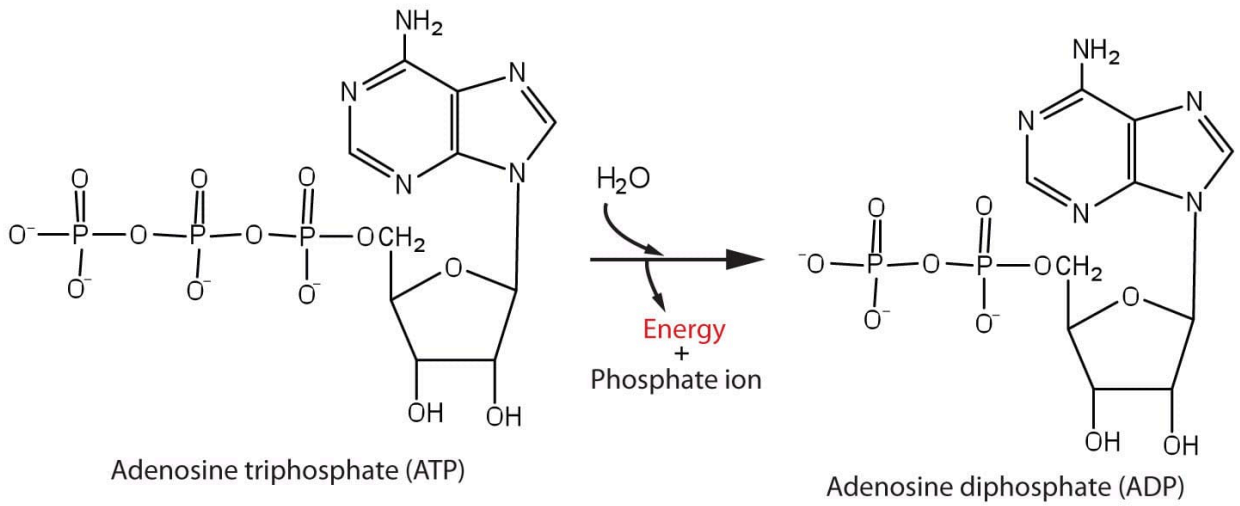


Figure 21.4.1: Hydrolysis of ATP to Form ADP

Energy is released because the products (ADP and phosphate ion) have less energy than the reactants [ATP and water (H_2O)].

The general equation for ATP hydrolysis is as follows:

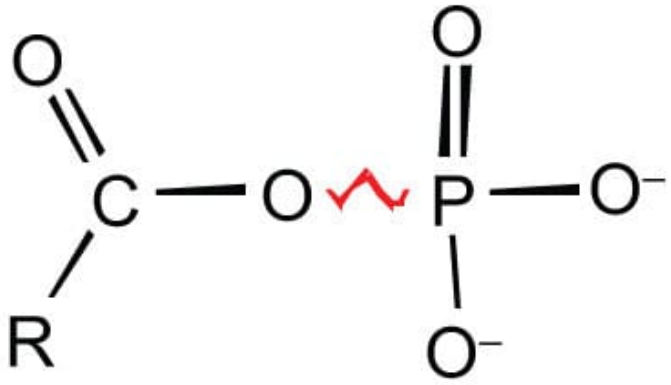
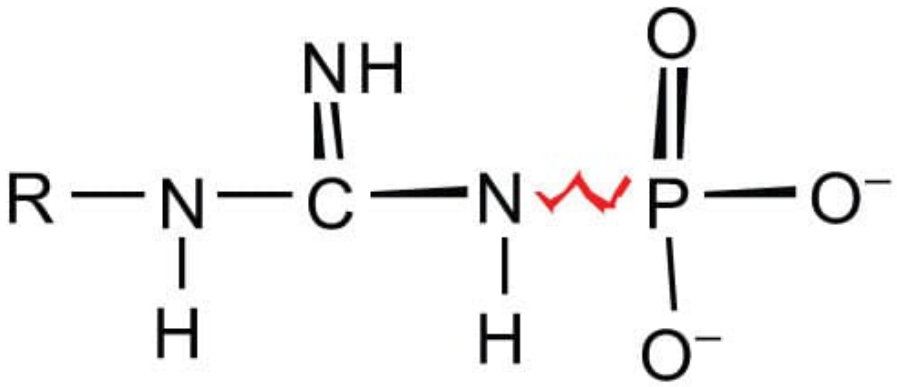
$$ATP + H_2O \rightarrow ADP + P_i + 7.4\ kcal/mol$$

If the hydrolysis of ATP releases energy, its synthesis (from ADP) requires energy. In the cell, ATP is produced by those processes that supply energy to the organism (absorption of radiant energy from the sun in green plants and breakdown of food in animals), and it is hydrolyzed by those processes that require energy (the syntheses of carbohydrates, lipids, proteins; the transmission of nerve impulses; muscle contractions). In fact, ATP is the principal medium of energy exchange in biological systems. Many scientists call it the energy currency of cells.

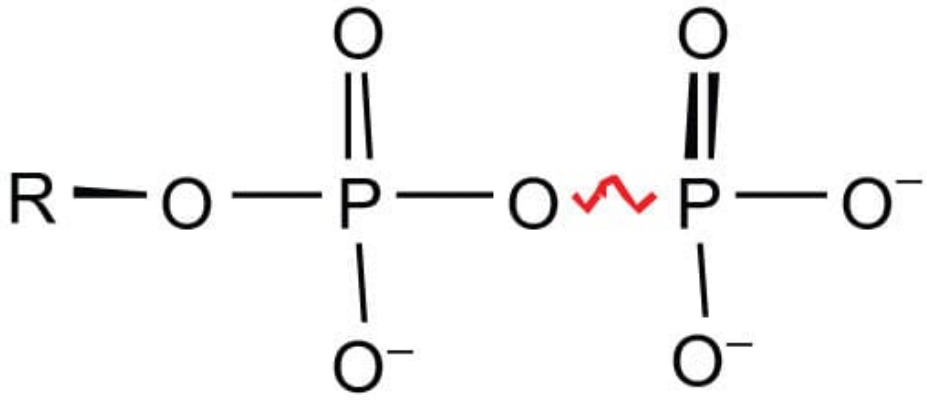
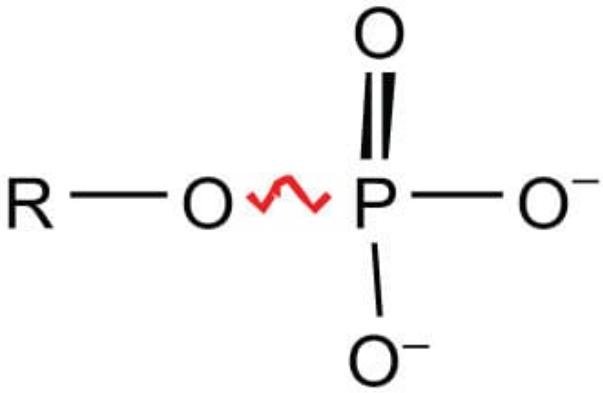
P_i is the symbol for the inorganic phosphate anions $H_2PO_4^-$ and HPO_4^{2-}.

ATP is not the only high-energy compound needed for metabolism. Several others are listed in Table 21.4.1. 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 21.4.1: Energy Released by Hydrolysis of Some Phosphate Compounds

Type
acyl phosphate 
guanidine phosphates 

***PP_i is the pyrophosphate ion.**

Type	
pyrophosphates	
sugar phosphates	

***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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21.5: Strategies of Metabolism - Metabolic Pathways and Coupled Reactions



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21.6: Strategies of Metabolism- Oxidized and Reduced Coenzymes



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21.7: The Citric Acid Cycle

Learning Objectives

- Describe the reactions of the citric acid cycle.
- Describe the function of the citric acid cycle and identify the products produced.

The acetyl group enters a cyclic sequence of reactions known collectively as the citric acid cycle (or Krebs cycle or tricarboxylic acid [TCA] cycle). The cyclical design of this complex series of reactions, which bring about the oxidation of the acetyl group of acetyl-CoA to carbon dioxide and water, was first proposed by Hans Krebs in 1937. (He was awarded the 1953 Nobel Prize in Physiology or Medicine.) Acetyl-CoA's entrance into the citric acid cycle is the beginning of stage III of catabolism. The citric acid cycle produces adenosine triphosphate (ATP), reduced nicotinamide adenine dinucleotide (NADH), reduced flavin adenine dinucleotide ($FADH_2$), and metabolic intermediates for the synthesis of needed compounds.

Steps of the Citric Acid Cycle

At first glance, the citric acid cycle appears rather complex (Figure 21.7.1). 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 21.7.1, 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.

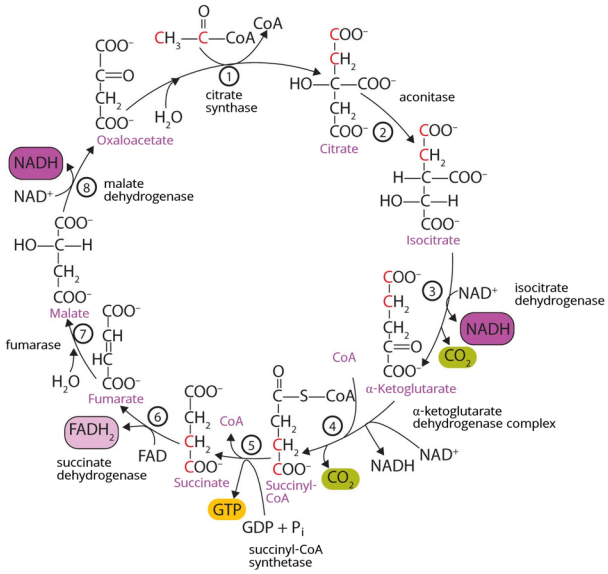


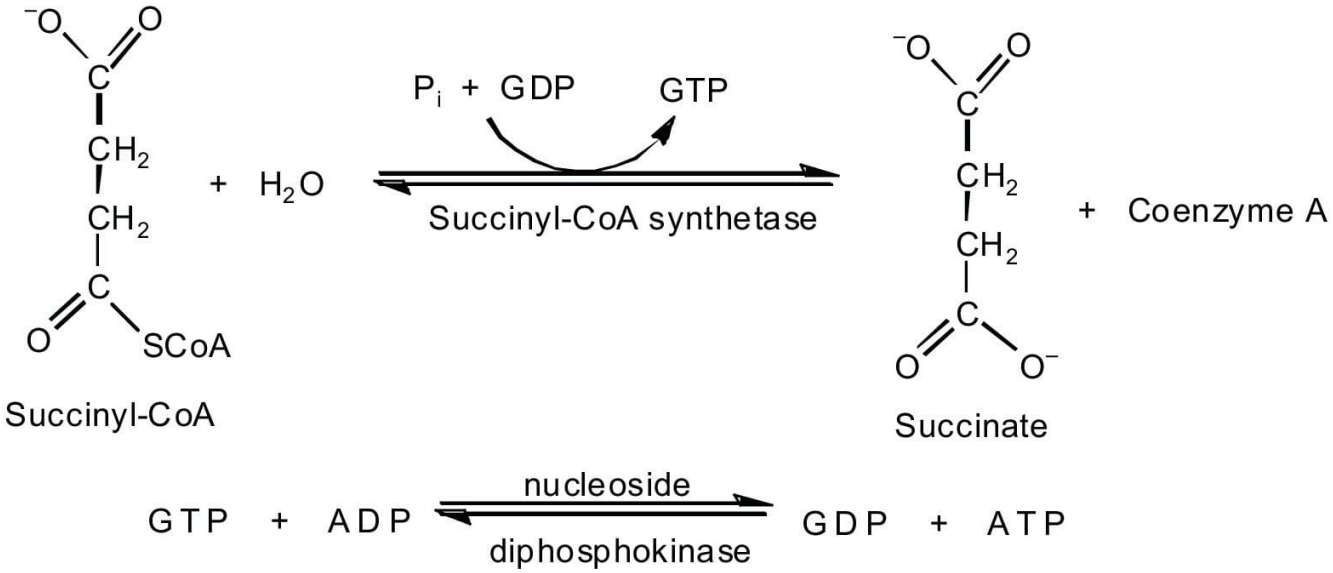
Figure 21.7.1: Reactions of the Citric Acid Cycle

1. In the first step, acetyl-CoA enters the citric acid cycle, and the acetyl group is transferred onto oxaloacetate, yielding citrate. Note that this step releases coenzyme A. The reaction is catalyzed by *citrate synthase*.
2. In the next step, *aconitase* catalyzes the isomerization of citrate to isocitrate. In this reaction, a tertiary alcohol, which cannot be oxidized, is converted to a secondary alcohol, which can be oxidized in the next step.
3. Isocitrate then undergoes a reaction known as oxidative decarboxylation because the alcohol is oxidized and the molecule is shortened by one carbon atom with the release of carbon dioxide (decarboxylation). The reaction is catalyzed by *isocitrate dehydrogenase*, and the product of the reaction is α-ketoglutarate. An important reaction linked to this is the reduction of the coenzyme nicotinamide adenine dinucleotide (NAD^+) to NADH. The NADH is ultimately reoxidized, and the energy released is used in the synthesis of ATP, as we shall see.
4. The fourth step is another oxidative decarboxylation. This time α-ketoglutarate is converted to succinyl-CoA, and another

molecule of NAD^+ is reduced to NADH. The *α-ketoglutarate dehydrogenase complex* catalyzes this reaction. This is the only irreversible reaction in the citric acid cycle. As such, it prevents the cycle from operating in the reverse direction, in which acetyl-CoA would be synthesized from carbon dioxide.

So far, in the first four steps, two carbon atoms have entered the cycle as an acetyl group, and two carbon atoms have been released as molecules of carbon dioxide. The remaining reactions of the citric acid cycle use the four carbon atoms of the succinyl group to resynthesize a molecule of oxaloacetate, which is the compound needed to combine with an incoming acetyl group and begin another round of the cycle.

In the fifth reaction, the energy released by the hydrolysis of the high-energy thioester bond of succinyl-CoA is used to form guanosine triphosphate (GTP) from guanosine diphosphate (GDP) and inorganic phosphate in a reaction catalyzed by *succinyl-CoA synthetase*. This step is the only reaction in the citric acid cycle that directly forms a high-energy phosphate compound. GTP can readily transfer its terminal phosphate group to adenosine diphosphate (ADP) to generate ATP in the presence of *nucleoside diphosphokinase*.



Succinate dehydrogenase then catalyzes the removal of two hydrogen atoms from succinate, forming fumarate. This oxidation-reduction reaction uses flavin adenine dinucleotide (FAD), rather than NAD^+, as the oxidizing agent. Succinate dehydrogenase is the only enzyme of the citric acid cycle located within the inner mitochondrial membrane. We will see soon the importance of this.

In the following step, a molecule of water is added to the double bond of fumarate to form L-malate in a reaction catalyzed by *fumarase*.

One revolution of the cycle is completed with the oxidation of L-malate to oxaloacetate, brought about by *malate dehydrogenase*. This is the third oxidation-reduction reaction that uses NAD^+ as the oxidizing agent. Oxaloacetate can accept an acetyl group from acetyl-CoA, allowing the cycle to begin again.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Video: "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.

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21.8: The Electron-Transport Chain and ATP Production

Learning Outcomes

- Summarize the electron transport chain.
- Recognize that electron transport chain is the third and final stage of aerobic cellular respiration.
- Identify the products of the citric acid cycle.

What do trains, trucks, boats, and planes all have in common? They are ways to transport. And they all use a lot of energy. To make ATP, energy must be "transported" - first from glucose to NADH, and then somehow passed to ATP. How is this done? With an electron transport chain, the third stage of aerobic respiration. This third stage uses energy to make energy.

The Electron Transport Chain: ATP for Life in the Fast Lane

At the end of the Krebs Cycle, energy from the chemical bonds of glucose is stored in diverse energy carrier molecules: four ATPs, but also two $FADH_2$ and ten NADH molecules. The primary task of the last stage of cellular respiration, the **electron transport chain**, is to transfer energy from the electron carriers to even more ATP molecules, the "batteries" which power work within the cell.

Pathways for making ATP in stage 3 of aerobic respiration closely resemble the electron transport chains used in photosynthesis. In both electron transport chains, energy carrier molecules are arranged in sequence within a membrane so that energy-carrying electrons cascade from one to another, losing a little energy in each step. In both photosynthesis and aerobic respiration, the energy lost is harnessed to pump hydrogen ions into a compartment, creating an **electrochemical gradient** or **chemiosmotic gradient** across the enclosing membrane. And in both processes, the energy stored in the chemiosmotic gradient is used with **ATP synthase** to build ATP.

For aerobic respiration, the electron transport chain or "respiratory chain" is embedded in the inner membrane of the mitochondria (see figure below). The $FADH_2$ and NADH molecules produced in glycolysis and the Krebs Cycle, donate high-energy electrons to energy carrier molecules within the membrane. As they pass from one carrier to another, the energy they lose is used to pump hydrogen ions into the mitochondrial intermembrane space, creating an electrochemical gradient. Hydrogen ions flow "down" the gradient - from outer to inner compartment - through the ion channel/enzyme ATP synthase, which transfers their energy to ATP. Note the paradox that it requires energy to create and maintain a concentration gradient of hydrogen ions that are then used by ATP synthase to create stored energy (ATP). In broad terms, it takes energy to make energy. Coupling the electron transport chain to ATP synthesis with a hydrogen ion gradient is **chemiosmosis**, first described by Nobel laureate Peter D. Mitchell. This process, the use of energy to phosphorylate ADP and produce ATP is also known as **oxidative phosphorylation**.

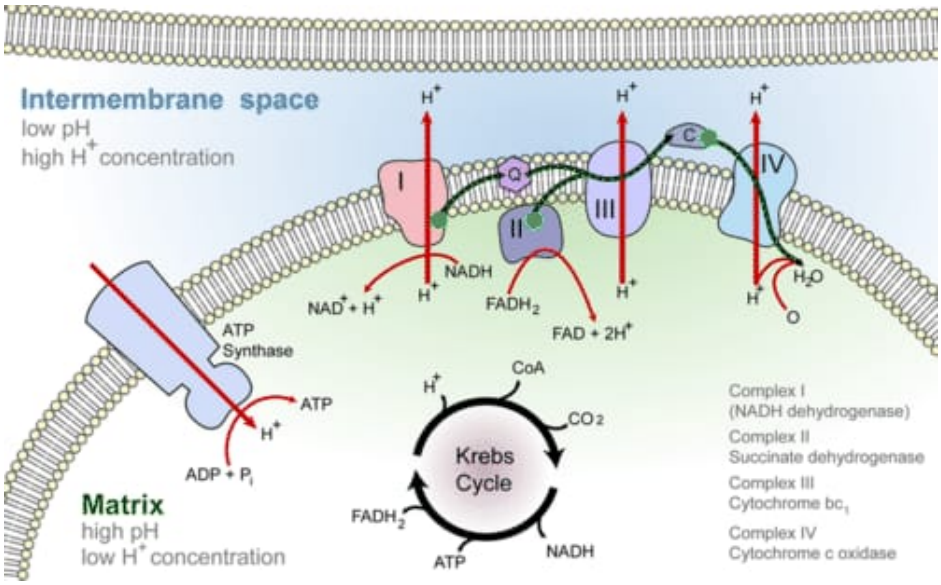


Figure 21.8.1: The third stage of cellular respiration uses the energy stored during the earlier stages in NADH and $FADH_2$ to make ATP. Electron transport chains embedded in the mitochondrial inner membrane capture high-energy electrons from the carrier molecules and use them to concentrate hydrogen ions in the intermembrane space. Hydrogen ions flow down their electrochemical gradient back into the matrix through ATP synthase channels which capture their energy to convert ADP to ATP. Notice that the process regenerates NAD^+, supplying the electron acceptor molecule needed in glycolysis. (CC BY-NC 3.0; Mariana Ruiz Villarreal (LadyofHats) for the CK-12 Foundation).

After passing through the electron transport chain, low-energy electrons and low-energy hydrogen ions combine with oxygen to form water. Thus, oxygen's role is to drive the entire set of ATP-producing reactions within the mitochondrion by accepting "spent" hydrogens. Oxygen is the final electron acceptor, no part of the process - from the Krebs Cycle through the electron transport chain- can happen without oxygen.

The electron transport chain can convert the energy from one glucose molecule's worth of $FADH_2$ and $NADH + H^+$ into as many as 34 ATP. When the four ATP produced in glycolysis and the Krebs Cycle are added, the total of 38 ATP fits the overall equation for aerobic cellular respiration:

$$6\,O_2 + \underbrace{C_6H_{12}O_6}_{\text{stored chemical energy}} + 38\,ADP + 39\ P_i \rightarrow \underbrace{38\,ATP}_{\text{stored chemical energy}} + 6\,CO_2 + 6\,H_2O \tag{21.8.1}$$

Aerobic respiration is complete. If oxygen is available, cellular respiration transfers the energy from one molecule of glucose to 38 molecules of ATP, releasing carbon dioxide and water as waste. "Deliverable" food energy has become energy which can be used for work within the cell - transport within the cell, pumping ions and molecules across membranes, and building large organic molecules. Can you see how this could lead to "life in the fast lane" compared to anaerobic respiration (glycolysis alone)?

Contributors and Attributions

-

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22: CARBOHYDRATE METABOLISM

22.1: Digestion of Carbohydrates
22.2: Glucose Metabolism - An Overview
22.3: Glycolysis
22.4: Entry of Other Sugars into Glycolysis
22.5: The Fate of Pyruvate
22.6: Energy Output in Complete Glucose Catabolism
22.7: Regulation of Glucose Metabolism and Metabolism During Stress
22.8: Glycogen Metabolism- Glycogenesis and Glycogenolysis
22.9: Gluconeogenesis- Glucose Synthesis from Noncarbohydrates

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22.1: Digestion of Carbohydrates

Learning Objectives

- Describe digestion of carbohydrates.

The first stage of catabolism is **digestion**, in which food molecules are broken down into smaller molecules. Carbohydrate digestion begins in the mouth (Figure 22.1.1) where salivary α-amylase attacks the α-glycosidic linkages in starch, the main carbohydrate ingested by humans. Cleavage of the glycosidic linkages produces a mixture of dextrins, maltose, and glucose. The α-amylase mixed into the food remains active as the food passes through the esophagus, but it is rapidly inactivated in the acidic environment of the stomach.

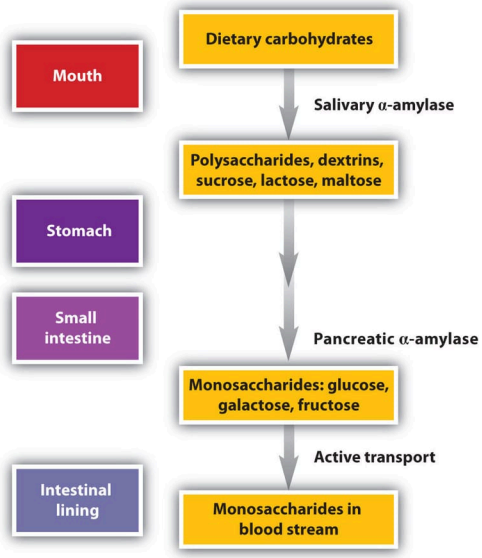


Figure 22.1.1: The Principal Events and Sites of Carbohydrate Digestion

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.

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22.2: Glucose Metabolism - An Overview



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22.3: Glycolysis

Learning Objectives

- Objective 1
- Objective 2

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.

Introduction

There are two phases of Glycolysis:

1. the "priming phase" because it requires an input of energy in the form of 2 ATPs per glucose molecule and
2. the "pay off phase" because energy is released in the form of 4 ATPs, 2 per glyceraldehyde molecule.

The end result of Glycolysis is two new pyruvate molecules which can then be fed into the Citric Acid cycle (also known as the Kreb's Cycle) if oxygen is present, or can be reduced to lactate or ethanol in the absence of of oxygen using a process known as Fermentation. 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 the following diagram:

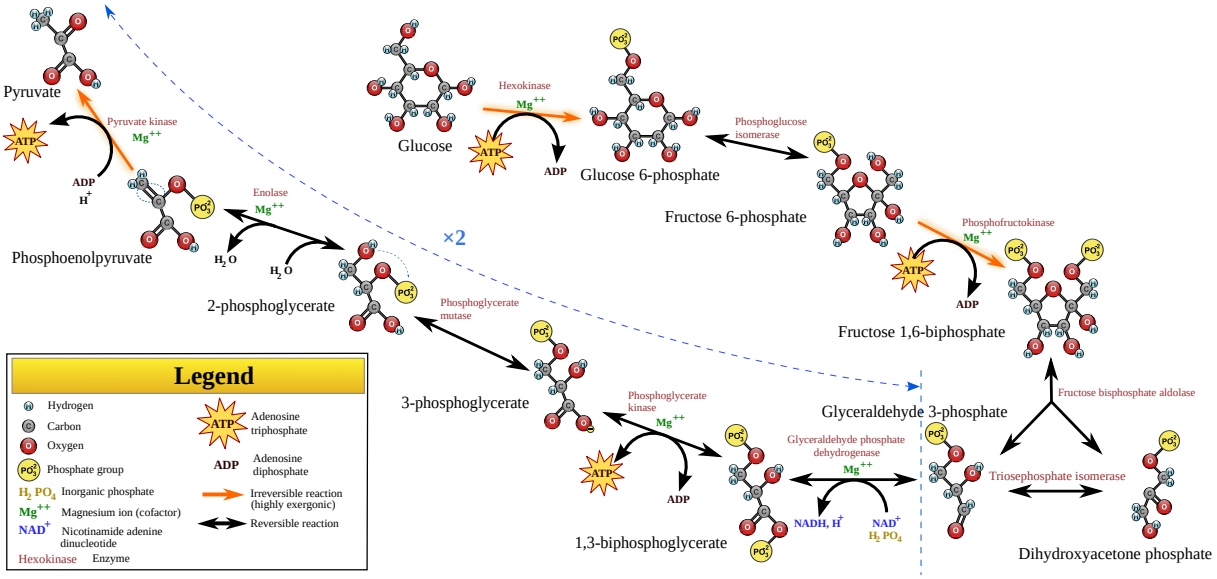


Figure 1: Glycolysis pathway. from Wikipedia (CCBY-SA 3.0; YassineMrabet).

Phase 1: The "Priming Step"

The first phase of Glycolysis requires an input of energy in the form of ATP (adenosine triphosphate).

1. alpha-D-Glucose is phosphorolated at the 6 carbon by ATP via the enzyme Hexokinase (Class: Transferase) to yield alpha-D-Glucose-6-phosphate (G-6-P). This is a regulatory step which is negatively regulated by the presence of glucose-6-phosphate.
2. alpha-D-Glucose-6-phosphate is then converted into D-Fructose-6-phosphate (F-6-P) by Phosphoglucoisomerase (Class: Isomerase)

3. D-Fructose-6-phosphate is once again phosphorolated this time at the 1 carbon position by ATP via the enzyme Phosphofructokinase (Class: Transferase) to yield D-Fructose-1,6-bisphosphate (FBP). This is the committed step of glycolysis because of its large ΔG value.
4. D-Fructose-1,6-bisphosphate is then cleaved into two, three carbon molecules; Dihydroxyacetone phosphate (DHAP) and D-Glyceraldehyde-3-phosphate (G-3-P) by the enzyme Fructose bisphosphate aldolase (Class: Lyase)
5. Because the next portion of Glycolysis requires the molecule D-Glyceraldehyde-3-phosphate to continue Dihydroxyacetone phosphate is converted into D-Glyceraldehyde-3-phosphate by the enzyme Triose phosphate isomerase (Class: Isomerase)

Phase 2: The "Pay Off Step"

The second phase of Glycolysis where 4 molecules of ATP are produced per molecule of glucose. Enzymes appear in red:

1. D-Glyceraldehyde-3-phosphate is phosphorolated at the 1 carbon by the enzyme Glyceraldehyde-3-phosphate dehodrogenase to yield the high energy molecule 1,3-Bisphosphoglycerate (BPG)
2. ADP is then phosphorolated at the expense of 1,3-Bisphosphoglycerate by the enzyme Phosphoglycerate kinase (Class: Transferase) to yield ATP and 3-Phosphoglycerate (3-PG)
3. 3-Phosphoglycerate is then converted into 2-Phosphoglycerate by Phosphoglycerate mutase in preparation to yield another high energy molecule
4. 2-Phosphoglycerate is then converted to phosphoenolpyruvate (PEP) by Enolase. H_2O, potassium, and magnesium are all released as a result.
5. ADP is once again phosphorolated, this time at the expense of PEP by the enzyme pyruvate kinase to yield another molecule of ATP and and pyruvate. This step is regulated by the energy in the cell. The higher the energy of the cell the more inhibited pyruvate kinase becomes. Indicators of high energy levels within the cell are high concentrations of ATP, Acetyl-CoA, Alanine, and cAMP.

Because Glucose is split to yield two molecules of D-Glyceraldehyde-3-phosphate, each step in the "Pay Off" phase occurs twice per molecule of glucose.

References

1. Garrett, H., Reginald and Charles Grisham. Biochemistry. Boston: Twayne Publishers, 2008.
2. Raven, Peter. Biology. Boston: Twayne Publishers, 2005.

Problems

1. What is the net yield of Glycolysis as far as ATP?
2. Name the enzymes that are key regulatory sites in Glycolysis.
3. Why are the enzymes in the previous question targets for regulation?
4. Why is the priming phase necessary?
5. Draw the entire pathway for glycolysis including enzymes, reactants and products for each step.

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22.4: Entry of Other Sugars into Glycolysis



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22.5: The Fate of Pyruvate



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22.6: Energy Output in Complete Glucose Catabolism



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22.7: Regulation of Glucose Metabolism and Metabolism During Stress



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22.8: Glycogen Metabolism- Glycogenesis and Glycogenolysis



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22.9: Gluconeogenesis- Glucose Synthesis from Noncarbohydrates



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23: LIPIDS

23.1: Structure and Classification of Lipids
23.2: Fatty Acids and Their Esters
23.3: Properties of Fats and Oils
23.4: Chemical Reactions of Triacylglycerols
23.5: Phospholipids and Glycolipids
23.6: Steroids
23.7: Cell Membranes- Structure and Transport

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23.1: Structure and Classification of Lipids

Learning Objectives

- Define lipids and recognize the different classes.

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 23.1.1 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.

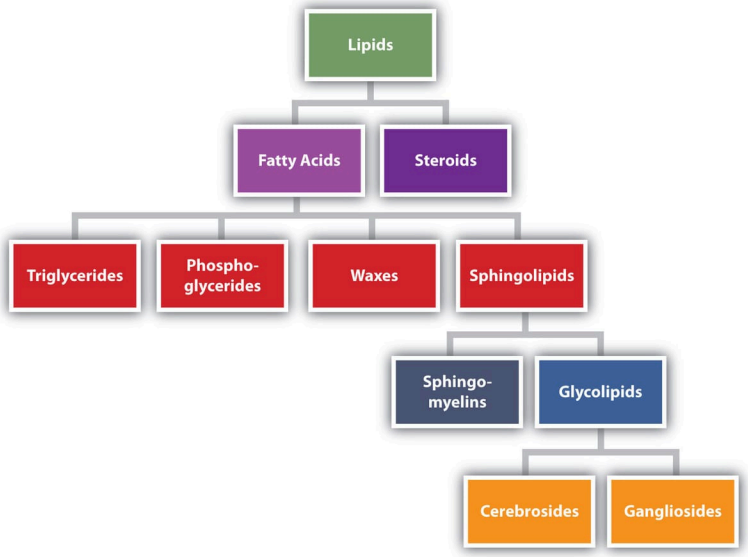


Figure 23.1.1: Lipid Organization Based on Structural Relationships

Lipids Formed from Fatty Acids

Fatty acids are carboxylic acids with 12-22 carbon atoms connected in a long, unbranched chain. As shown in the diagram above, most lipids are classified as *esters* or *amides* of fatty acids.

- *Waxes* are esters formed from long-chain fatty acids and long-chain alcohols. Most natural waxes are mixtures of such esters.
- *Triacylglycerol* (triglycerides) are esters of glycerol, a trialcohol, and three fatty acids. Many organisms store energy in this form.
- *Glycerophospholipids* are esters of glycerol formed from two fatty acid chains and a charged phosphate.

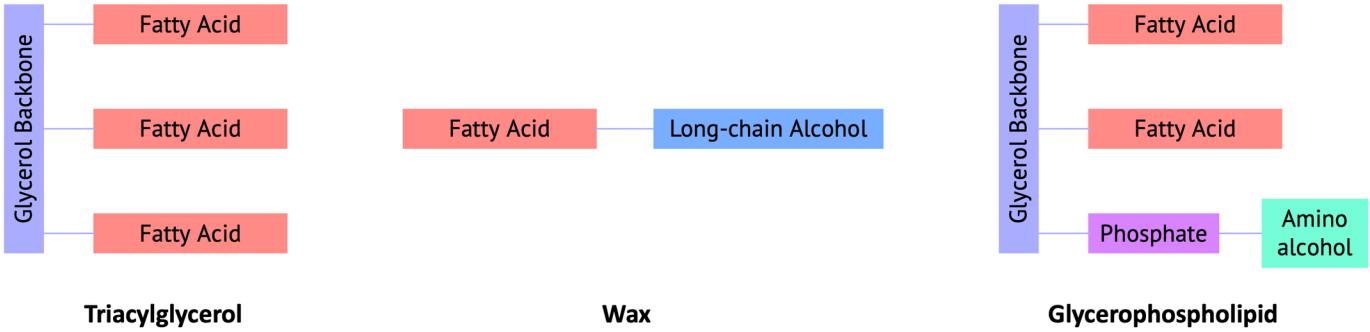


Figure 23.1.2: Esters of Fatty Acids: Triglycerides, Waxes, and Glycerophospholipids.

- *Sphingolipids* are fatty acid amides formed from a fatty acid attached to an amino alcohol backbone, called sphingosine, along with either a phosphate (*sphingomyelin*) or a carbohydrate (*glycolipid*). These along with glycerophospholipids are important for the structure and function of cellular membranes.

Other Lipids

Not all lipids contain fatty acid groups:

- *Sterols* (also classified as steroids) all contain the steroid nucleus, which is four fused rings. *Cholesterol* is the most commonly known sterol and is also an important lipid in cell membranes.
- *Eicosanoids* are important chemical messengers that include *prostaglandins*, which have a five-member ring and a carboxylic acid chain.

Chemical diagram Prostaglandin - Wikipedia

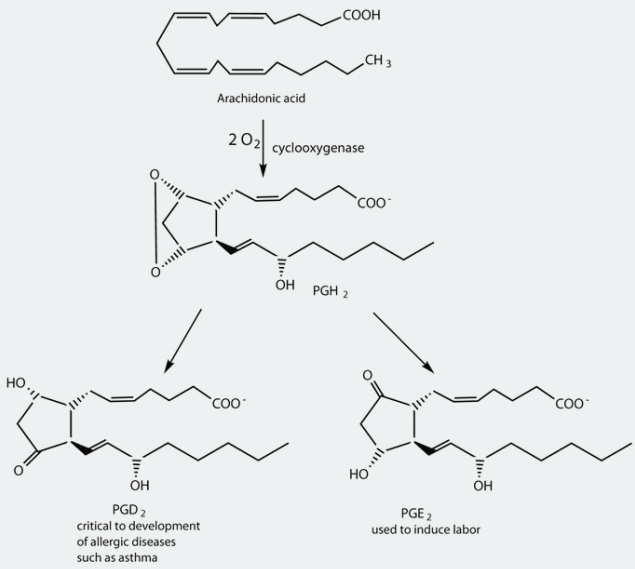
Figure 23.1.3: Other Lipids: Cholesterol contains the steroid nucleus (top) and a prostaglandin (bottom).

In the next sections of this chapter you will learn more about the structure, properties, and functions of each of these types of lipid.

To Your Health: Prostaglandins

Prostaglandins are chemical messengers synthesized in the cells in which their physiological activity is expressed. They are unsaturated fatty acids containing 20 carbon atoms and are synthesized from arachidonic acid—a polyunsaturated fatty acid—when needed by a particular cell. They are called *prostaglandins* because they were originally isolated from semen found in the prostate gland. It is now known that they are synthesized in nearly all mammalian tissues and affect almost all organs in the body. The five major classes of prostaglandins are designated as PGA, PGB, PGE, PGF, and PGI. Subscripts are attached at the end of these abbreviations to denote the number of double bonds outside the five-carbon ring in a given prostaglandin.

The prostaglandins are among the most potent biological substances known. Slight structural differences give them highly distinct biological effects; however, all prostaglandins exhibit some ability to induce smooth muscle contraction, lower blood pressure, and contribute to the inflammatory response. Aspirin and other nonsteroidal anti-inflammatory agents, such as ibuprofen, obstruct the synthesis of prostaglandins by inhibiting cyclooxygenase, the enzyme needed for the initial step in the conversion of arachidonic acid to prostaglandins.



Their wide range of physiological activity has led to the synthesis of hundreds of prostaglandins and their analogs. Derivatives of PGE_2 are now used in the United States to induce labor. Other prostaglandins have been employed clinically to lower or increase blood pressure, inhibit stomach secretions, relieve nasal congestion, relieve asthma, and prevent the formation of blood clots, which are associated with heart attacks and strokes.

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23.2: Fatty Acids and Their Esters

Learning Objectives

- To recognize the structures of common fatty acids and classify them as saturated, monounsaturated, or polyunsaturated.
- Describe characteristics of fatty acid esters.

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, Fatty acids may be **saturated**, containing all carbon-carbon *single* bonds, or **unsaturated**, containing at least one or more carbon-carbon *double* bonds. Saturated fatty acids are *saturated with hydrogens*; in other words, the number of hydrogen atoms attached to the carbon skeleton is maximized. Stearic acid is an example of a saturated fatty acid (Figure 23.2.1).

When the hydrocarbon chain contains a double bond, there are less hydrogens attached to the carbon skeleton and the fatty acid is said to be unsaturated. Oleic acid is an example of a *monounsaturated* fatty acid (Figure 23.2.1), because it contains one double bond. A fatty acid with two or more double bonds is a *polyunsaturated* fat. The atoms or groups around the double bonds in unsaturated fatty acids can be arranged in either the *cis* or *trans* isomeric form, compare *cis* vs. *trans* oleic acid in (Figure 23.2.1). Naturally occurring fatty acids are generally in the *cis* configuration.

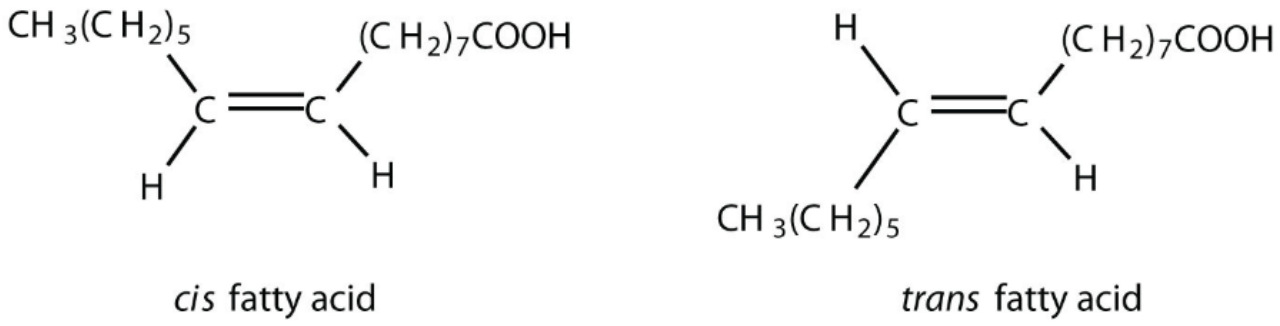


Figure 23.2.1: Saturated fatty acids have hydrocarbon chains connected by single bonds only. Unsaturated fatty acids have one or more double bonds. Each double bond may be in a *cis* or *trans* configuration. In the *cis* configuration, both hydrogens are on the same side of the hydrocarbon chain. In the *trans* configuration, the hydrogens are on opposite sides. A *cis* double bond causes a kink in the chain.

Table 23.2.1 lists some common fatty acids. Chemists use a shorthand notation for fatty acids rather than the common name because they are all carboxylic acids with different numbers of carbons and **degree of unsaturation** (number of double bonds). This notation gives the number of carbons followed by the number of double bonds present. For example: palmitic acid, a 16 carbon saturated fatty acid, would be represented by C16:0 and palmitoleic acid, a 16 carbon monounsaturated fatty acid, would be C16:1.

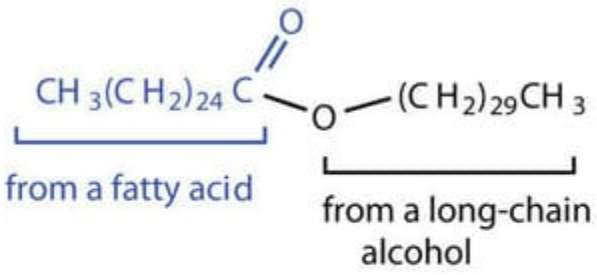
Table 23.2.1: Some Common Fatty Acids Found in Natural Fats

Name	Number of Carbons	Number of Double Bonds	Condensed Structural Formula	Melting Point (°C)	Shorthand Notation	Source
lauric acid	12	0	$CH_3(CH_2)_{10}COOH$	44	C12:0	palm kernel oil
myristic acid	14	0	$CH_3(CH_2)_{12}COOH$	58	C14:0	oil of nutmeg
palmitic acid	16	0	$CH_3(CH_2)_{14}COOH$	63	C16:0	palm oil
palmitoleic acid	16	1	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$	0.5	C16:1	macadamia oil
stearic acid	18	0	$CH_3(CH_2)_{16}COOH$	70	C18:0	cocoa butter
oleic acid	18	1	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	16	C18:1	olive oil
linoleic acid	18	2	$CH_3(CH_2)_3(CH_2CH{=}CH)_2(CH_2)_7COOH$	−5	C18:2	canola oil
α-linolenic acid	18	3	$CH_3(CH_2CH{=}CH)_3(CH_2)_7COOH$	−11	C18:3	flaxseed
arachidonic acid	20	4	$CH_3(CH_2)_4(CH_2CH{=}CH)_4(CH_2)_2COOH$	−50	C20:4	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.

Waxes

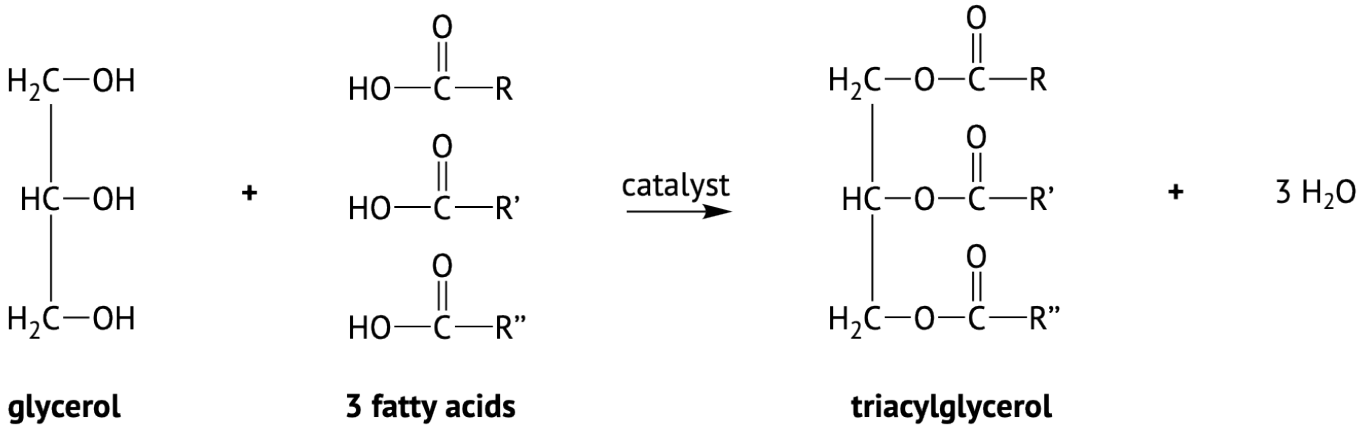
Waxes are esters formed from long-chain fatty acids and long-chain alcohols. Most natural waxes are mixtures of such esters. Plant waxes on the surfaces of leaves, stems, flowers, and fruits protect the plant from dehydration and invasion by harmful microorganisms. Carnauba wax, used extensively in floor waxes, automobile waxes, and furniture polish, is largely myricyl cerotate, obtained from the leaves of certain Brazilian palm trees. Animals also produce waxes that serve as protective coatings, keeping the surfaces of feathers, skin, and hair pliable and water repellent. In fact, if the waxy coating on the feathers of a water bird is dissolved as a result of the bird swimming in an oil slick, the feathers become wet and heavy, and the bird, unable to maintain its buoyancy, drowns.



Myricyl cerotate
(found in carnauba wax)

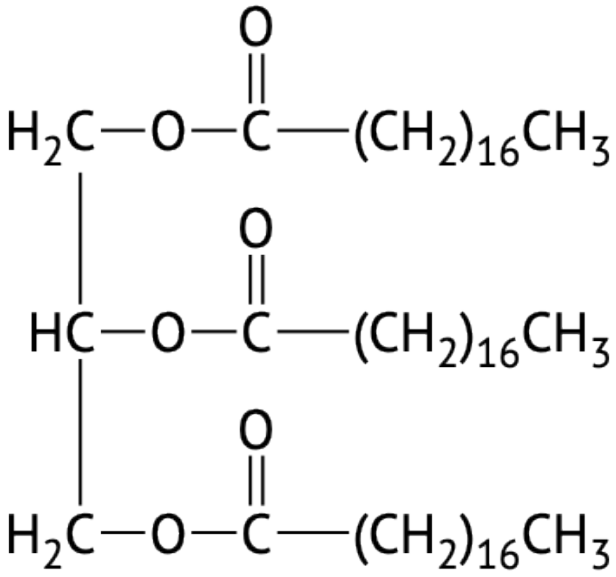
Triacylglycerols

Animal fats and vegetable oils are called *triacylcylgerols* (or triglycerides) because they are esters composed of three fatty acid units joined to *glycerol*, a trihydroxy alcohol:

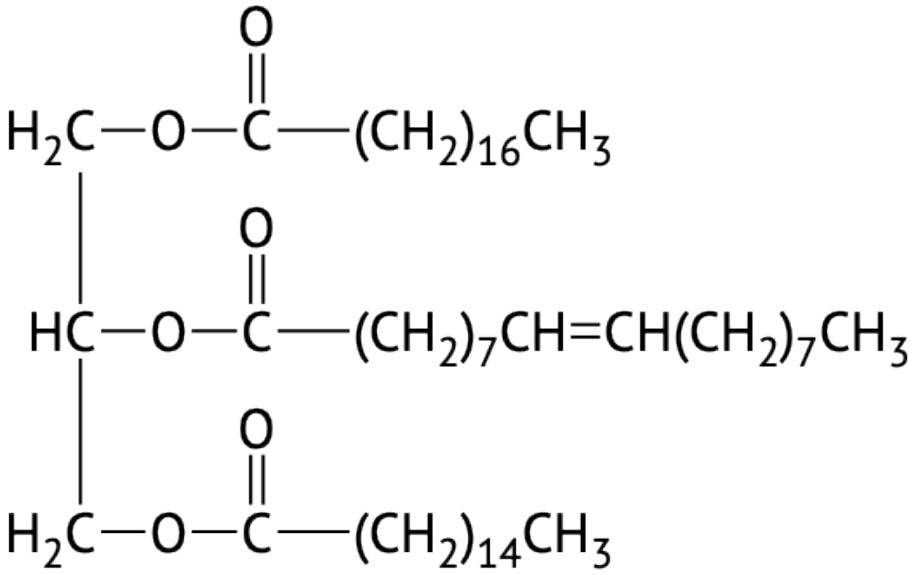


glycerol **3 fatty acids** **triacylglycerol**

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 triacylglycerols 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 triacylglycerol 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 23.2.2 shows the fatty acid compositions of some common fats and oils. The composition of any given fat or oil can vary depending on the plant or animal species it comes from as well as on dietetic and climatic factors. To cite just one example, lard from corn-fed hogs is more highly saturated than lard from peanut-fed hogs. Palmitic acid is the most abundant of the saturated fatty acids, while oleic acid is the most abundant unsaturated fatty acid.

*Table 23.2.2: Average Fatty Acid Composition of Some Common Fats and Oils (%)**

Source	Lauric (C12:0)	Myristic (C14:0)	Palmitic (C16:0)	Stearic (C18:0)	Oleic (C18:1)	Linoleic (C18:2)	Linolenic (C18:3)
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

***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.

Source	Lauric (C12:0)	Myristic (C14:0)	Palmitic (C16:0)	Stearic (C18:0)	Oleic (C18:1)	Linoleic (C18:2)	Linolenic (C18:3)
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.

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23.3: Properties of Fats and Oils



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23.4: Chemical Reactions of Triacylglycerols



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23.5: Phospholipids and Glycolipids



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23.6: 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).

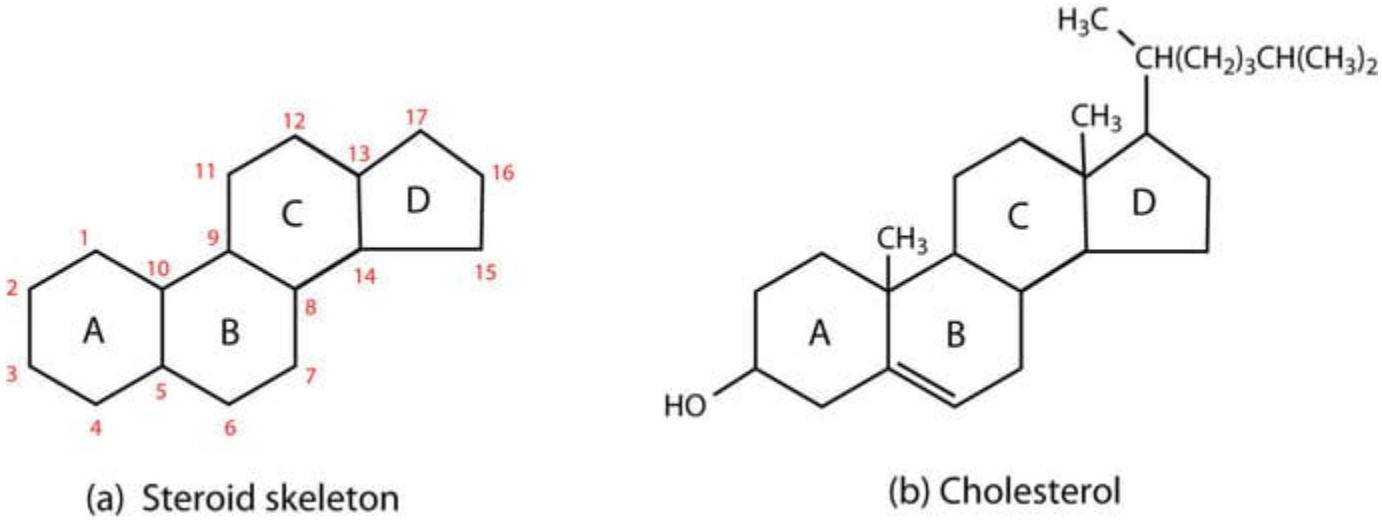


Figure 23.6.1 Steroids. (a) The four-fused-ring steroid skeleton uses letter designations for each ring and the numbering of the carbon atoms. (b) The cholesterol molecule follows this pattern.

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 23.6.1*a*. Slight variations in this structure or in the atoms or groups attached to it produce profound differences in biological activity.

Cholesterol

Cholesterol (Figure 23.6.1*b*) does not occur in plants, but it is the most abundant steroid in the human body (240 g is a typical amount). Excess cholesterol is believed to be a primary factor in the development of atherosclerosis and heart disease, which are major health problems in the United States today. About half of the body's cholesterol is interspersed in the lipid bilayer of cell membranes. Much of the rest is converted to cholic acid, which is used in the formation of bile salts. Cholesterol is also a precursor in the synthesis of sex hormones, adrenal hormones, and vitamin D.

Excess cholesterol not metabolized by the body is released from the liver and transported by the blood to the gallbladder. Normally, it stays in solution there until being secreted into the intestine (as a component of bile) to be eliminated. Sometimes, however, cholesterol in the gallbladder precipitates in the form of gallstones (Figure 23.6.2). Indeed, the name *cholesterol* is derived from the Greek *chole*, meaning "bile," and *stereos*, meaning "solid."



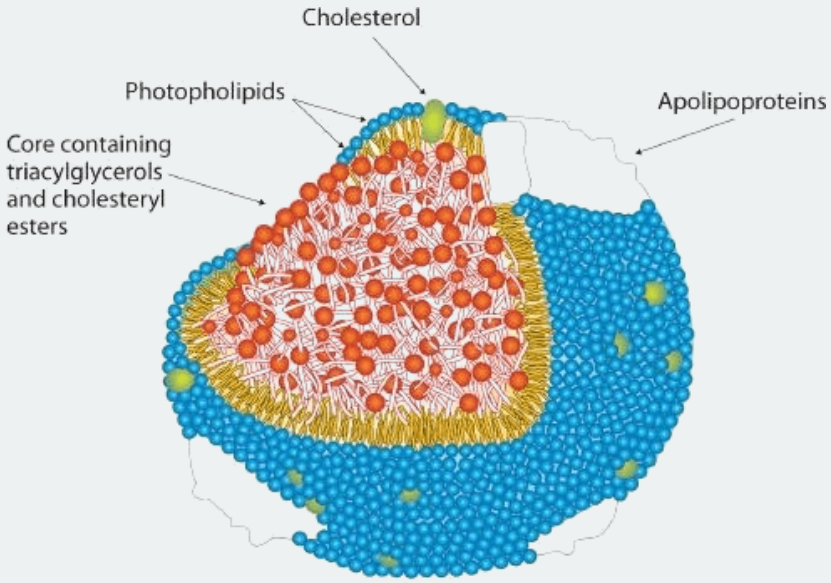
Figure 23.6.2: Numerous small gallstones made up largely of cholesterol, all removed in one patient. Grid scale 1 mm

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.

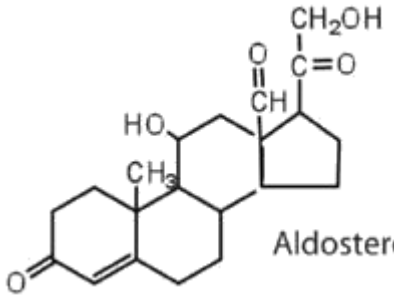
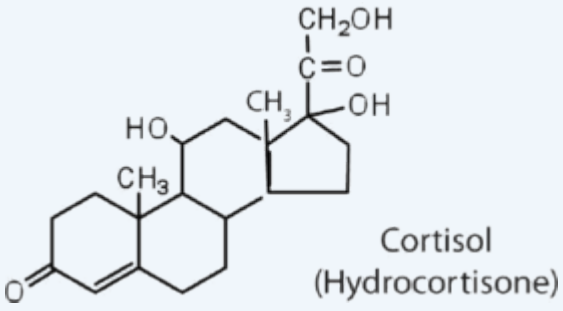
Dietary modifications and increased physical activity can help lower total cholesterol and improve the LDL:HDL ratio. The average American consumes about 600 mg of cholesterol from animal products each day and also synthesizes approximately 1 g of cholesterol each day, mostly in the liver. The amount 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.

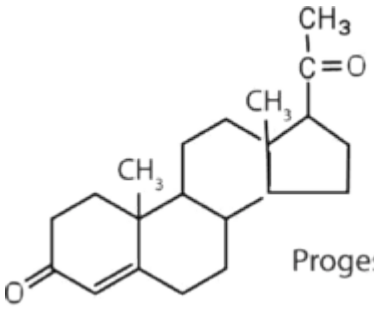
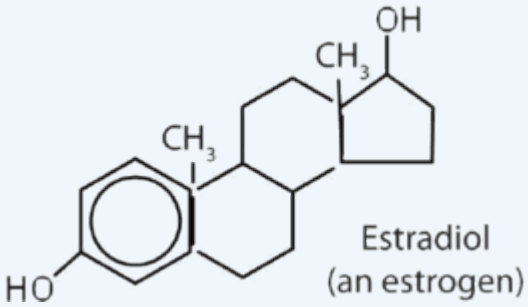
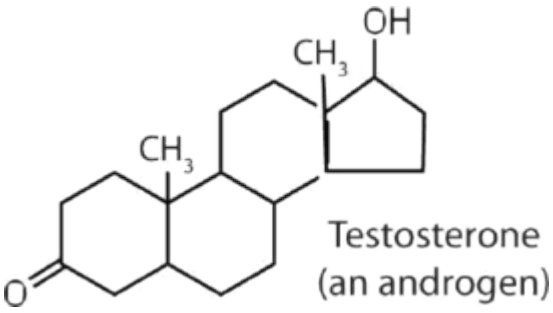
Steroid Hormones

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 23.6.1), 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 23.6.1: Representative Steroid Hormones and Their Physiological Effects

Hormone	Effect
	regulates salt metabolism; stimulates kidneys to retain sodium and excrete potassium
	stimulates the conversion of proteins to carbohydrates

Hormone	Effect
	regulates the menstrual cycle; maintains pregnancy
	stimulates female sex characteristics; regulates changes during the menstrual cycle
	stimulates and maintains male sex characteristics

The sex hormones are a class of steroid hormones secreted by the gonads (ovaries or testes), the placenta, and the adrenal glands. Testosterone and androstenedione are the primary male sex hormones, or *androgens*, controlling the primary sexual characteristics of males, or the development of the male genital organs and the continuous production of sperm. Androgens are also responsible for the development of secondary male characteristics, such as facial hair, deep voice, and muscle strength. Two kinds of sex hormones are of particular importance in females: progesterone, which prepares the uterus for pregnancy and prevents the further release of eggs from the ovaries during pregnancy, and the estrogens, which are mainly responsible for the development of female secondary sexual characteristics, such as breast development and increased deposition of fat tissue in the breasts, the buttocks, and the thighs. Both males and females produce androgens and estrogens, differing in the amounts of secreted hormones rather than in the presence or absence of one or the other.

Sex hormones, both natural and synthetic, are sometimes used therapeutically. For example, a woman who has had her ovaries removed may be given female hormones to compensate. Some of the earliest chemical compounds employed in cancer chemotherapy were sex hormones. For example, estrogens are one treatment option for prostate cancer because they block the release and activity of testosterone. Testosterone enhances prostate cancer growth. Sex hormones are also administered in preparation for sex-change operations, to promote the development of the proper secondary sexual characteristics. Oral contraceptives are synthetic derivatives of the female sex hormones; they work by preventing ovulation.

Bile Salts

Bile is a yellowish green liquid (pH 7.8–8.6) produced in the liver. The most important constituents of bile are bile salts, which are sodium salts of amidelike combinations of bile acids, such as cholic acid (part (a) of Figure $23.6.3$) and an amine such as the amino acid glycine (part (b) of Figure $23.6.3$). 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.

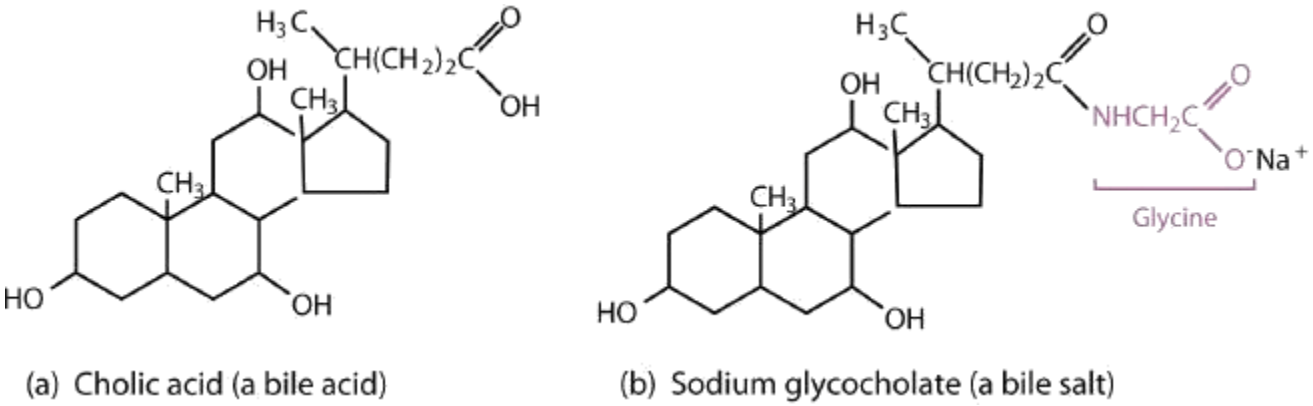


Figure 23.6.3 Bile Acids. (a) Cholic acid is an example of a bile acid. (b) Sodium glycocholate is a bile salt synthesized from cholic acid and glycine.

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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23.7: Cell Membranes- Structure and Transport

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 $23.7.1A$) and animal cells (Figure $23.7.1B$) 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.

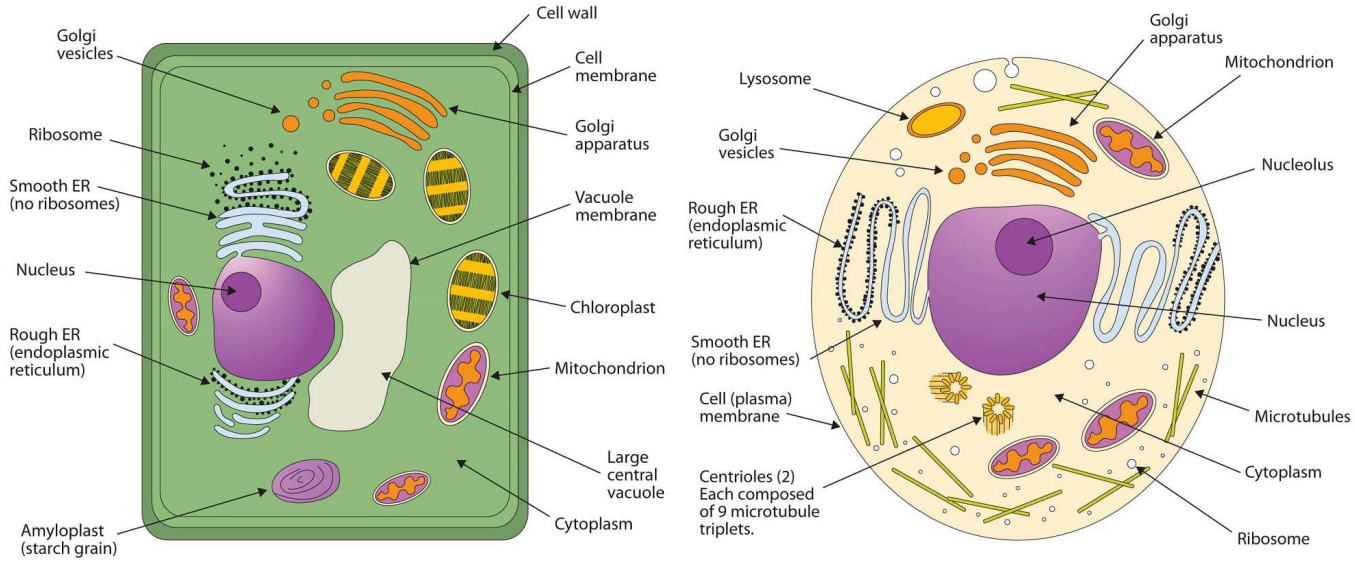


Figure $23.7.1$: (A) An Idealized Plant Cell. Not all the structures shown here occur in every type of plant cell. (B) An Idealized Animal Cell. The structures shown here will seldom all be found in a single animal cell.

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). Molecules that have both polar and nonpolar parts are called **amphipathic**. When allowed to float freely in water, lipids spontaneously cluster together in different arrangements: micelles, liposomes, monolayers, or bilayers (Figure $23.7.2$).

Figure $23.7.2$: Aggregation of Membrane Lipids. In polar solvents like water, amphipathic lipids will aggregate the polar heads and nonpolar tails forming monolayers, bilayers, micelles, and liposomes.

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 $23.7.3$).

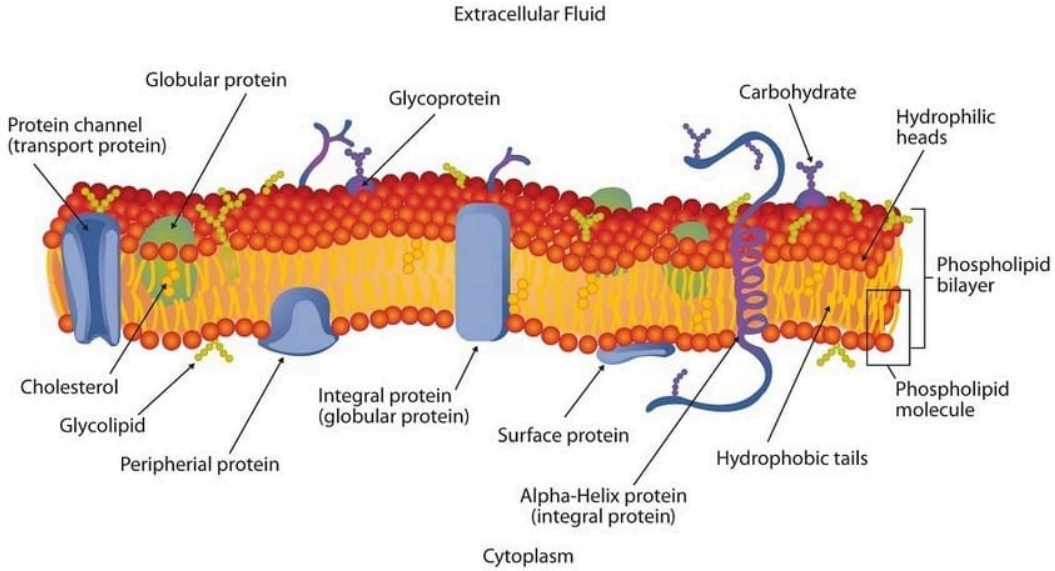


Figure 23.7.3: Schematic Diagram of a Cell Membrane. The membrane enclosing a typical animal cell is a phospholipid bilayer with embedded cholesterol and protein molecules. Short oligosaccharide chains are attached to the outer surface.

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.

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 23.7.3). Peripheral proteins may be attached to integral proteins, to the polar head groups of phospholipids, or to both by hydrogen bonding and electrostatic forces.

Transport Across Cell Membranes

Plasma membranes must allow certain substances to enter and leave a cell, and prevent some harmful materials from entering and some essential materials from leaving. In other words, plasma membranes are **selectively permeable**—they allow some substances to pass through, but not others. If they were to lose this selectivity, the cell would no longer be able to sustain itself, and it would be destroyed. Some cells require larger amounts of specific substances than do other cells; they must have a way of obtaining these materials from extracellular fluids. This may happen passively, as certain materials move back and forth, or the cell may have special mechanisms that facilitate transport. Some materials are so important to a cell that it spends some of its energy, hydrolyzing adenosine triphosphate (ATP), to obtain these materials. Red blood cells use some of their energy doing just that. All cells spend the majority of their energy to maintain an imbalance of sodium and potassium ions between the interior and exterior of the cell.

There are two primary modes of transport across membranes. **Passive transport** is a naturally occurring phenomenon and does not require the cell to exert any of its energy to accomplish the movement. In passive transport, substances move from an area of higher concentration to an area of lower concentration. **Active transport** mechanisms require the use of the cell’s energy, usually in the form of adenosine triphosphate (ATP). If a substance must move into the cell against its concentration gradient—that is, if the concentration of the substance inside the cell is greater than its concentration in the extracellular fluid (and vice versa)—the cell must use energy to move the substance.

File:Passive vs Active Membrane Transport.svg

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24: LIPID METABOLISM

24.1: Digestion of Triacylglycerols

24.2: Lipoproteins for Lipid Transport

24.3: Triacylglycerol Metabolism - An Overview

24.4: Storage and Mobilization of Triacylglycerols

24.5: Oxidation of Fatty Acids

24.6: Ketone Bodies and Ketoacidosis

24.7: Biosynthesis of Fatty Acids

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24.1: Digestion of Triacylglycerols

Learning Objectives

- Describe the process of digestion of lipids and their transport into the bloodstream.

Lipid digestion begins in the upper portion of the small intestine. 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.

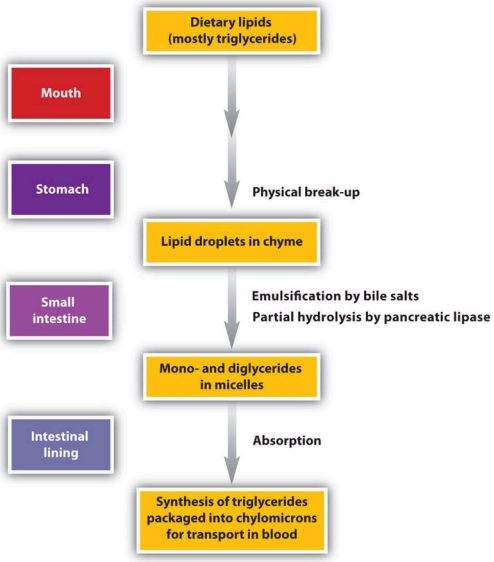


Figure 24.1.1: The Principal Events and Sites of Lipid (Primarily Triglyceride) Digestion

The lipases in pancreatic juice catalyze the digestion of triglycerides first to diglycerides and then to 2-monoglycerides and fatty acids:

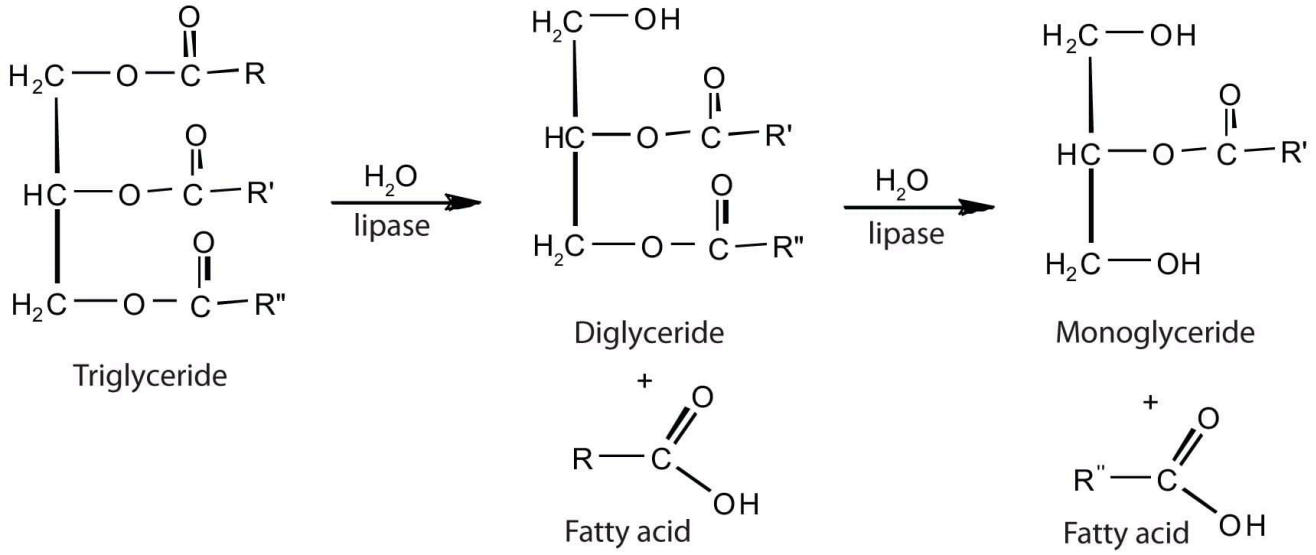


Figure 24.1.2: Digestion of triglycerides.

The large and hydrophobic long-chain fatty acids and monoacylglycerides are not so easily suspended in the watery intestinal chyme. However, bile salts and lecithin resolve this issue by enclosing them in a **micelle**, which is a tiny sphere with polar (hydrophilic) ends facing the watery environment and hydrophobic tails turned to the interior, creating a receptive environment for the long-chain fatty acids. The core also includes cholesterol and fat-soluble vitamins. Without micelles, lipids would sit on the surface of chyme and never come in contact with the absorptive surfaces of the epithelial cells. Micelles can easily squeeze between microvilli and get very near the luminal cell surface. At this point, lipid substances exit the micelle and are absorbed via simple diffusion.

The free fatty acids and monoacylglycerides that enter the epithelial cells are reincorporated into triglycerides. The triglycerides are mixed with phospholipids and cholesterol, and surrounded with a protein coat. This new complex, called a **chylomicron**, (see Figure 24.1.3), is a water-soluble lipoprotein.

File:2512 Chylomicrons Contain Triglycerides Cholesterol Molecules and Other Lipids.jpg

Figure 24.1.3: Lipoproteins (chylomicrons) package triacylglycrols and cholesterol for transport to cells.

After being processed by the Golgi apparatus, chylomicrons are released from the cell. Too big to pass through the basement membranes of blood capillaries, chylomicrons instead enter the large pores of lacteals. The lacteals come together to form the lymphatic vessels. The chylomicrons are transported in the lymphatic vessels and empty through the thoracic duct into the circulatory system (Figure 24.1.4).

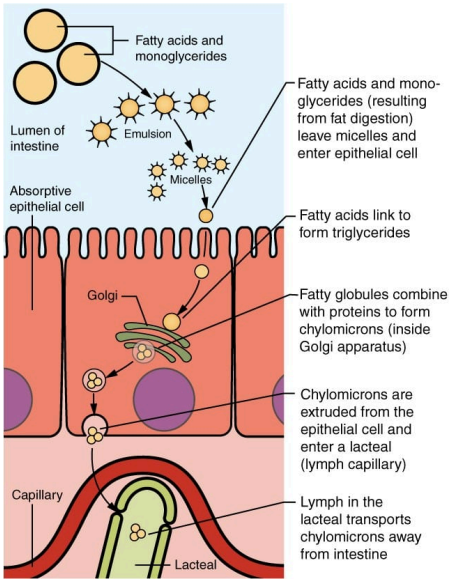


Figure 24.1.4: Pathways of Lipids

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24.2: Lipoproteins for Lipid Transport

Learning Objectives

- Describe the difference in composition and function between the five classes of lipoproteins.

During times of feasting, lipids enter the body's metabolic pathways through the process of digestion. Any excess energy will be stored in adipose tissues. If food has not been eaten for a while, fasting, lipids mobilized from stored adipose tissue and synthesized in the liver can be used for energy. Transportation of nonpolar lipids through the bloodstream requires binding to water-soluble proteins like serum albumin or packaging in lipoproteins. There are five categories of lipoprotein defined by their composition and density, or the ratio of lipid to protein. Chylomicrons, which have the highest lipid to protein ratio, have the lowest-density, are responsible for transporting lipids from digestion into the blood and eventually to the liver. Following is a list of the remaining four lipoproteins and their functions:

- *Very low-density lipoproteins (VLDLs)* (0.96-1.006 g/cm^3) are made in the liver from remnants of chylomicrons and transport triglycerides from the liver to various tissues in the body for energy or storage. As the VLDLs travel through the circulatory system, the lipoprotein lipase strips the VLDL of triglycerides. As triglyceride removal persists, the VLDLs become intermediate-density lipoproteins.
- *Intermediate-density lipoproteins (IDLs)* (1.007-1.019 g/cm^3) transport a variety of fats and cholesterol left from VLDLs from the tissues to the liver where they are transformed into low-density lipoprotein.
- *Low-density lipoproteins (LDLs)* (1.020-1.062 g/cm^3) carry cholesterol and other lipids from the liver to tissue throughout the body. LDLs are comprised of very small amounts of triglycerides, and house over 50 percent cholesterol and cholesterol esters. Once inside the cell, the LDL is taken apart and its cholesterol is released and used for membrane formation, steroid synthesis, or if in excess forming arterial plaques.
- *High-density lipoproteins (HDLs)* (1.063-1.210 g/cm^3) are responsible for carrying cholesterol out of the bloodstream and into the liver, where it is either reused or removed from the body with bile.

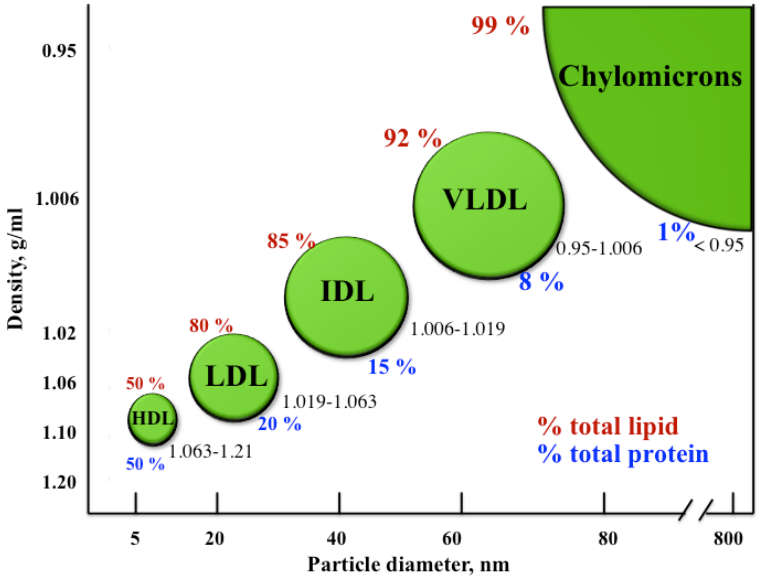


Figure 24.2.1: Lipoprotein Classes The classification of the major types of lipoproteins are based on their densities. Density range is shown as well as lipid (red) and protein (blue) content. (Diagram not to scale) / CC BY 3.0

Note To Your Health: Good vs. Bad Cholesterol

You are probably familiar with HDL and LDL being referred to as "good cholesterol" and "bad cholesterol," respectively. This is an oversimplification to help the public interpret their blood lipid values, because cholesterol is cholesterol; it's not good or bad. LDL and HDL are lipoproteins, and as a result you can't consume good or bad cholesterol, you consume cholesterol. A more appropriate descriptor for these lipoproteins would be HDL "good cholesterol transporter" and LDL "bad cholesterol transporter."

For healthy total blood cholesterol, the desired range you would want to maintain is under 200 mg/dL. More specifically, when looking at individual lipid profiles, a low amount of LDL and a high amount of HDL prevents excess buildup of cholesterol in the arteries and wards off potential health hazards. An LDL level of less than 100 milligrams per deciliter is ideal while an LDL level above 160 mg/dL would be considered high. In contrast, a low value of HDL is a telltale sign that a person is living with major risks for disease. Values of less than 40 mg/dL for men and 50 mg/dL for women mark a risk factor for developing heart disease. In short, elevated LDL blood lipid profiles indicate an increased risk of heart attack, while elevated HDL blood lipid profiles indicate a reduced risk.The University of Maryland Medical Center reports that omega-3 fatty acids promote lower total cholesterol and lower triglycerides in people with high cholesterol.[1]

It is suggested that people consume omega-3 fatty acids such as alpha-linolenic acid in their diets regularly. Polyunsaturated fatty acids are especially beneficial to consume because they both lower LDL and elevate HDL, thus contributing to healthy blood cholesterol levels. The study also reveals that saturated and trans fatty acids serve as catalysts for the increase of LDL cholesterol. Additionally, trans fatty acids decrease HDL levels, which can impact negatively on total blood cholesterol.

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1. Omega-3 fatty acids. University of Maryland Medical Center. http://www.umm.edu/altmed/articles/omega-3-000316.htm. Updated August 5, 2015. Accessed September 28, 2017. ↵

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24.3: Triacylglycerol Metabolism - An Overview

Learning Objectives

- Identify the main metabolic pathways of triacylglycerols.

In the body, triacylglycerols are essential for long-term energy storage as well as for insulation and protection. Triacylglycerols can be ingested directly or synthesized from extra dietary protein or carbohydrates. Figure 24.3.1 is a summary of the metabolic pathways of triacylglycerols that will be discussed in more detail in the following sections.

Dietary Triacylglycerols

Dietary triacylglycerols are transported through the bloodstream in chylomicrons. When a chylomicron encounters the enzyme **lipoprotein lipase**, triacylglycerols are broken down by hydrolysis into fatty acids and glycerol. These breakdown products then pass through capillary walls to be used for energy by cells or stored in adipose tissue as fat. Liver cells combine the remaining chylomicron remnants with proteins, forming lipoproteins that transport cholesterol in the blood.

Stored Triacylglycerols

When energy is needed, lipases in adipose tissue (fat cells) are activated to hydrolyze stored triacylglycerols into fatty acids and glycerol and release them into the bloodstream. Once the fatty acids reach their destination (muscle or liver cells) they are used to generate acetyl-CoA and eventually ATP.

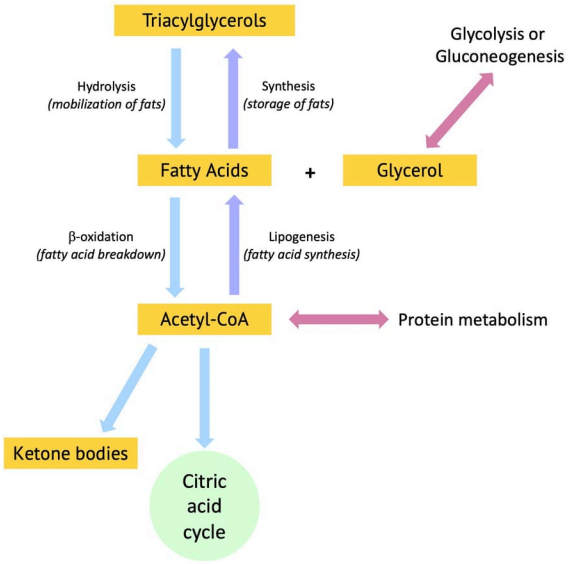


Figure 24.3.1: Overview of Triacylglycerol Metabolism

Glycerol from Triacylglycerols

The hydrolysis of triacylglycerols produce fatty acids, that are used for energy, and glycerol. The glycerol can be used to regenerate triacylglycerol or it can enter glycolysis or gluconeogenesis in the form dihydroxyacetone phosphate (DHAP).

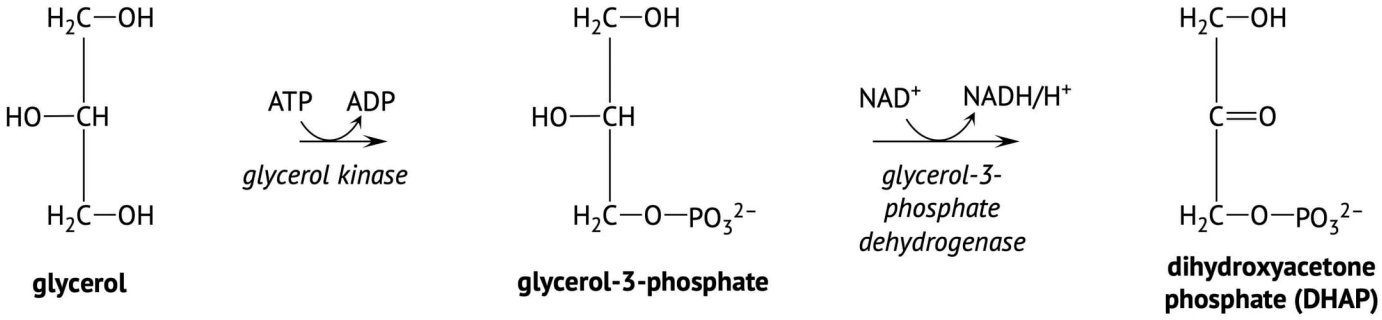


Figure 24.3.2: Conversion of Glycerol to DHAP: Lipid metabolism and carbohydrate metabolism are linked through glycerol and DHAP.

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24.4: Storage and Mobilization of Triacylglycerols

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24.5: Oxidation of Fatty Acids

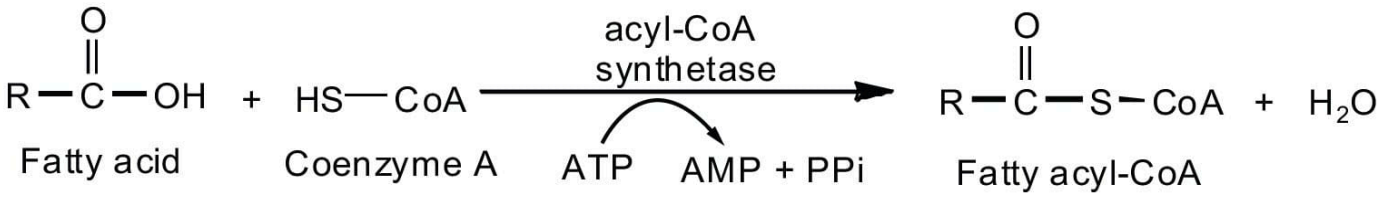
Learning Objectives

- Describe the steps of fatty acid oxidation.
- Calculate the yield of ATP from fatty acid oxidation.

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.

Activation of Fatty Acids

Fatty acid oxidation is initiated in the cytosol. 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]):



Transport into the Mitochondrial Matrix

The fatty acyl-CoA cannot cross the membrane by diffusion and therefore must be transported into the mitochondrial matrix using a carrier molecule known as *carnitine*. At the outer mitochondrial membrane, fatty acyl-CoA is attached to the hydroxyl group of carnitine in a transesterification reaction catalyzed by carnitine acyltransferase I (also called carnitine palmitoyl transferase I, CPTI). The acyl-carnitine derivative is transported into the mitochondrial matrix by facilitated diffusion through a translocase protein (carnitine-acylcarnitine translocase). Once in the matrix, the acyl-carnitine is converted back to the fatty acyl-CoA and carnitine in a reaction catalyzed by carnitine acyltransferase II (also called carnitine palmitoyl transferase II, CPTI).

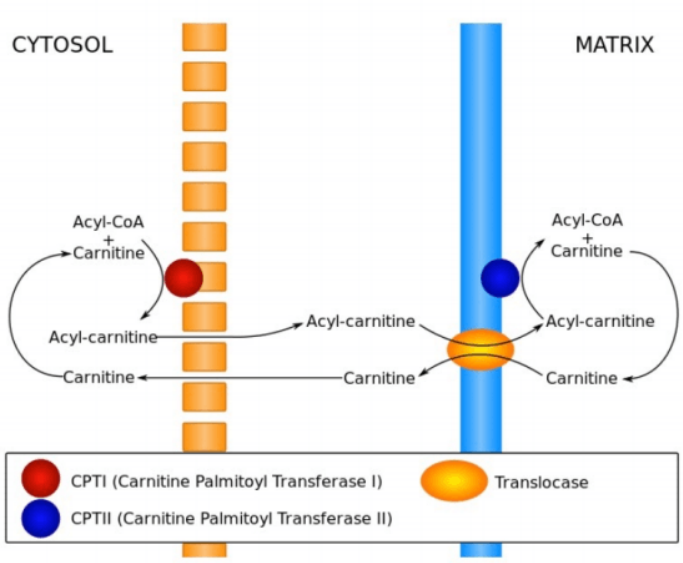


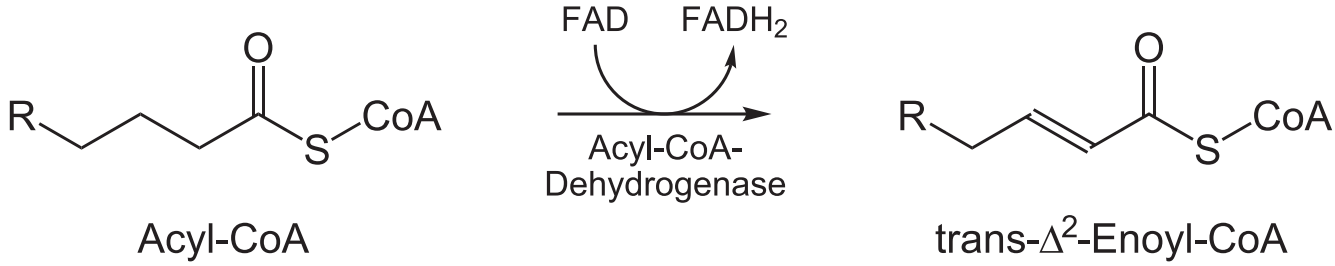
Figure 24.5.1: Movement of Acyl-CoAs into the Mitochondrial Matrix

Oxidation of Fatty Acyl-CoA

Once inside the mitochondria the fatty acyl-CoA can enter into beta-oxidation, which is a four-step cycle that removes carbons from the fatty acid two at a time to form acetyl-CoA (which eventually yields energy in the form of ATP).

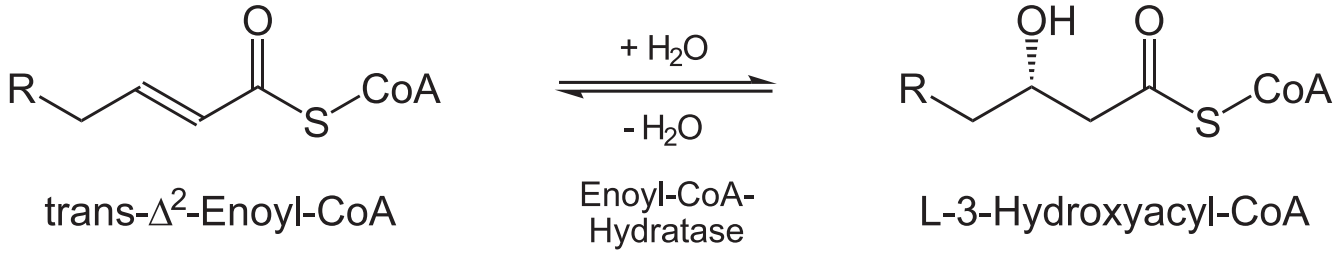
STEP 1: First β-oxidation (dehydrogenation of an alkane)

A fatty acyl-CoA is oxidized by the enzyme, *Acyl-CoA dehydrogenase,* to yield a trans double bond between the α- and β- carbons (the first and second carbons attached to the carbonyl group). The coenzyme FAD is reduced by accepting two hydrogen atoms and their electrons forming $FADH_2$, which moves into the electron transport chain.



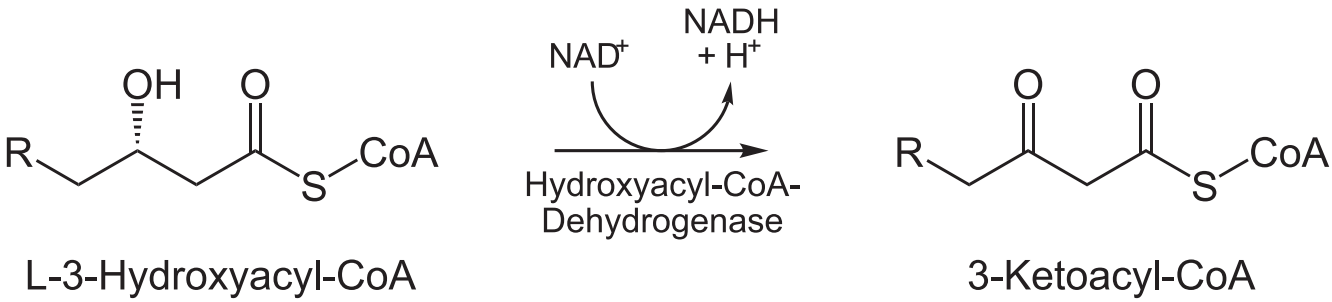
STEP 2: Hydration (addition of water across the double bond)

The trans alkene is then hydrated with the help of Enoyl-CoA hydratase. The hydroxyl group is placed on the β-carbon.



STEP 3: Second β-oxidation (oxidation of an alcohol)

The alcohol of the hydroxyacly-CoA is then oxidized to a carbonyl with the help of *β-hydroxyacyl-CoA dehydrogenase* and the coenzyme by NAD^+.

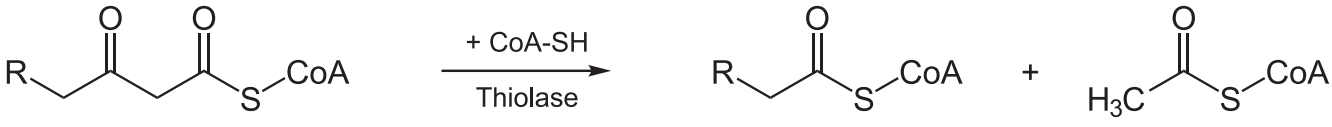


L-3-Hydroxyacyl-CoA

3-Ketoacyl-CoA

STEP 4: Thiolytic Cleavage

The enzyme *thiolase* (*acyl-CoA acetyltransferase*) cleaves off the acetyl-CoA and attaches a new coenzyme A to the chain to yield an acyl-CoA that is two carbons shorter than before. The acyl-CoA will continue through the cycle and start back at step 1. The cleaved acetyl-CoA can then enter into the the citric acid cycle and electron transport chain because it is already within the mitochondria.



3-Ketoacyl-CoA Acyl-CoA Acetyl-CoA

Additional steps are required for unsaturated fatty acids and those with an even number of carbons. The amount of energy released by a fatty acid is determined by the amount of ATP produced from the acetyl-CoA entering the citric acid cycle and from the reduced coenzymes NADH and $FADH_2$ entering the electron transport chain.

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 of 1 mol of palmitic acid requires 1 mol of ATP (for activation) and forms 8 mol of acetyl-CoA. Recall from 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 coenzymes through respiration yields 2.5–3 and 1.5–2 mol of ATP, respectively. The energy calculations can be summarized as follows:

1 mol of ATP is split to AMP and $2P_i$	–2 ATP
8 mol of acetyl-CoA formed (8 × 12)	96 ATP
7 mol of $FADH_2$ formed (7 × 2)	14 ATP
7 mol of NADH formed (7 × 3)	21 ATP
Total	129 ATP

The number of times β-oxidation is repeated for a fatty acid containing n carbon atoms is n/2 – 1 because the final turn yields two acetyl-CoA molecules.

The combustion of 1 mol of palmitic acid releases a considerable amount of energy:

$$C_{16}H_{32}O_2 + 23O_2 \rightarrow 16CO_2 + 16H_2O + 2,340\ kcal$$

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%.

> 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.

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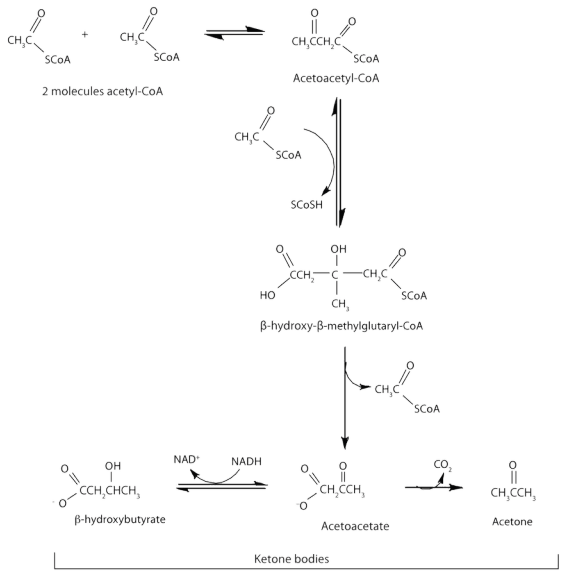
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24.6: Ketone Bodies and Ketoacidosis

Learning Objectives

- Describe the structure and function of 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.

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24.7: Biosynthesis of Fatty Acids

Learning Objectives

- Describe how fatty acids are synthesized and compare to fatty acid break-down.

Lipogenesis or the synthesis of fatty acids occurs in the cytoplasm and endoplasmic reticulum of the cell and is chemically similar to the beta-oxidation process, but with a couple of key differences. The first of these occur in preparing substrates for the reactions that grow the fatty acid. Transport of acetyl-CoA from the mitochondria occurs when it begins to build up. Two molecules can play roles in moving it to the cytoplasm – citrate and acetylcarnitine. Joining of oxaloacetate with acetyl-CoA in the mitochondrion creates citrate which moves across the membrane, followed by action of citrate lyase in the cytoplasm of the cell to release acetyl-CoA and oxaloacetate. Additionally, when free acetyl-CoA accumulates in the mitochondrion, it may combine with carnitine and be transported out to the cytoplasm.

The fatty acid chain is built two carbons at a time (opposite of beta-oxidation), beginning with two acetyl-CoA molecules. One is converted to malonyl-CoA by carboxylation, catalyzed by the enzyme acetyl-CoA carboxylase (ACC), the only regulatory enzyme of fatty acid synthesis (Figure 24.7.1). Next, both acetyl-CoA molecules have their CoA portions replaced by a carrier protein known as ACP (acyl-carrier protein) to form acetyl-ACP and malonyl-ACP. Joining of a fatty acyl-ACP (in this case, acetyl-ACP) with malonyl-ACP splits out the carboxyl that was added and creates the intermediate at the upper right in the figure at left.

Figure 24.7.1: *Fatty Acid Synthesis*

From this point forward, the chemical reactions resemble those of beta oxidation reversed. First, the ketone is reduced to a hydroxyl using NADPH. In contrast to the hydroxylated intermediate of beta oxidation, the beta intermediate here is in the D-configuration. Next, water is removed from carbons 2 and 3 of the hydroxyl intermediate to produce a trans doubled bonded molecule. Last, the double bond is hydrogenated to yield a saturated intermediate. The process cycles with the addition of another malonyl-ACP to the growing chain until ultimately an intermediate with 16 carbons is produced (palmitoyl-CoA). At this point, the cytoplasmic synthesis ceases.

Enzymes of Fatty Acid Synthesis

Acetyl-CoA carboxylase, which catalyzes synthesis of malonyl-CoA, is the only regulated enzyme in fatty acid synthesis. Its regulation involves both allosteric control and covalent modification. The enzyme is known to be phosphorylated by both AMP Kinase and Protein Kinase A. Dephosphorylation is stimulated by phosphatases activated by insulin binding. Dephosphorylation activates the enzyme and favors its assembly into a long polymer, while phosphorylation reverses the process.Citrate acts as an allosteric activator and may also favor polymerization. Palmitoyl-CoA allosterically inactivates it.

Figure 24.7.2: Fatty Acid Synthase (FAS) revised model with positions of polypeptides, three catalytic domains and their corresponding reactions, visualization by Kosi Gramatikoff. Note that FAS is only active as a homodimer rather than the monomer pictured. (Public Domain; Kosigrim)

In animals, six different catalytic activities necessary for the remaining catalytic actions to fully make palmitoyl-CoA are contained in a single complex called Fatty Acid Synthase (Figure 24.7.2). These include transacylases for swapping CoA with ACP on acetyl-CoA and malonyl-CoA; a synthase to catalyze addition of the two carbon unit from the three carbon malonyl-ACP in the first step of the elongation process; a reductase to reduce the ketone; a dehydrase to catalyze removal of water, and a reductase to reduce the trans double bond. In bacteria, these activities are found on separate enzymes and are not part of a complex.

Elongation of Fatty Acids

Elongation to make fatty acids longer than 16 carbons occurs in the endoplasmic reticulum and is catalyzed by enzymes described as elongases. Mitochondria also can elongate fatty acids, but their starting materials are generally shorter than 16 carbons long.

The mechanisms in both environments are similar to those in the cytoplasm (a malonyl group is used to add two carbons, for example), but CoA is attached to the intermediates, not ACP. Further, whereas cytoplasmic synthesis employs the fatty acid synthase complex (Figure 24.7.2), the enzymes in these organelles are separable and not part of a complex.

Desaturation of Fatty Acids

Fatty acids are synthesized in the saturated form and desaturation occurs later. Enzymes called desaturases catalyze the formation of cis double bonds in mature fatty acids. These enzymes are found in the endoplasmic reticulum. Animals are limited in the desaturated fatty acids they can make, due to an inability to catalyze reactions beyond carbons 9 and 10. Thus, humans can make oleic acid, but cannot synthesis linoleic acid or linolenic acid. Consequently, these two must be provided in the diet and are referred to as essential fatty acids.

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25: PROTEIN AND AMINO ACID METABOLISM

25.1: Digestion of Proteins
25.2: Amino Acid Metabolism - An Overview
25.3: Amino Acid Catabolism - The Amino Group
25.4: The Urea Cycle
25.5: Amino Acid Catabolism - The Carbon Atoms
25.6: Biosynthesis of Nonessential Amino Acids

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25.1: Digestion of Proteins

Learning Objectives

- List the steps of protein digestion.

Protein digestion begins in the stomach (Figure 25.1.1), 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.

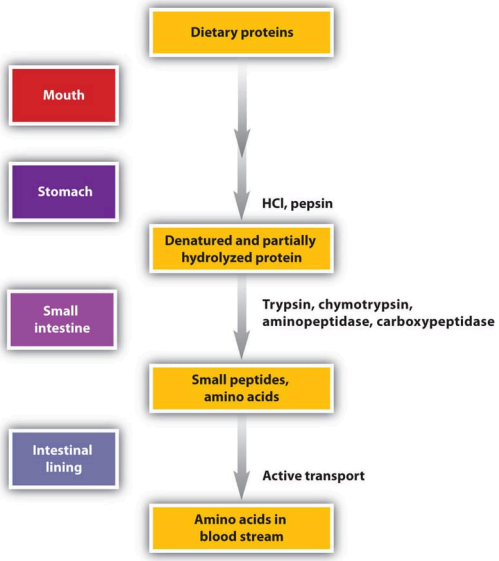


Figure 25.1.1: The Principal Events and Sites of Protein Digestion

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 25.1.2): 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.

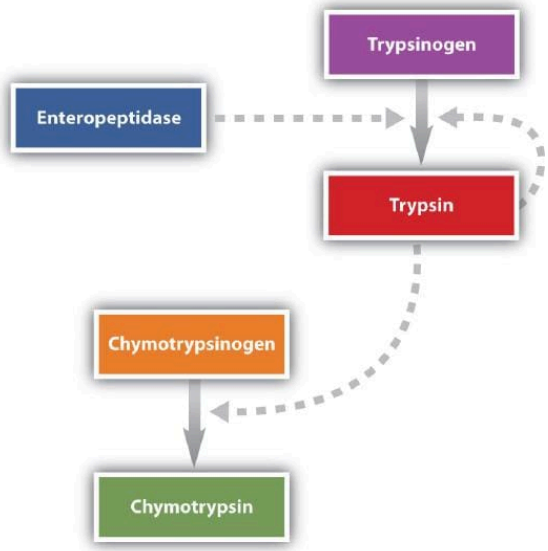


Figure 25.1.2: Activation of Some Pancreatic Enzymes in the Small Intestine

Aminopeptidases in the intestinal juice remove amino acids from the N-terminal end of peptides and proteins possessing a free amino group. Figure 25.1.3 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.

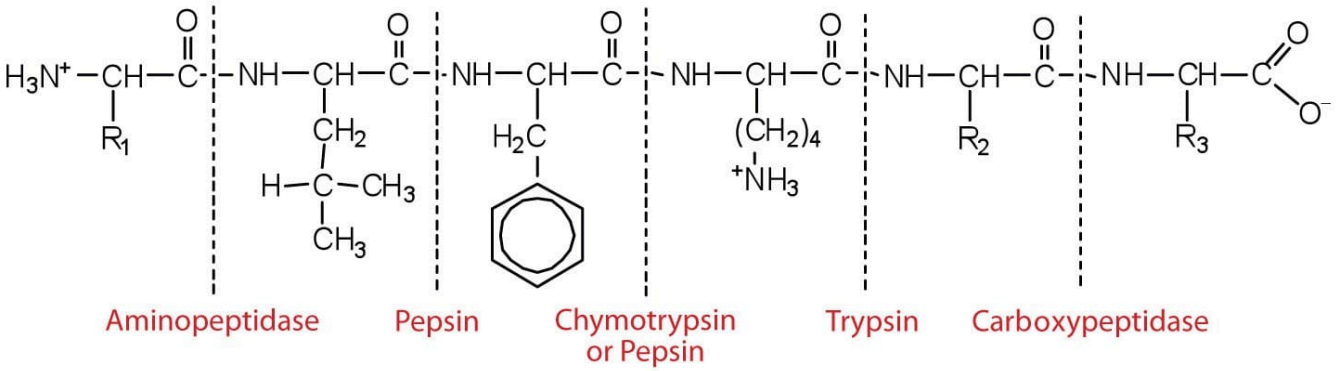


Figure 25.1.3: Hydrolysis of a Peptide by Several Peptidases

This diagram illustrates where in a peptide the different peptidases we have discussed would catalyze hydrolysis the peptide bonds.

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25.2: Amino Acid Metabolism - An Overview

Learning Objectives

- Objective 1
- Objective 2

Once the proteins in the diet have been hydrolyzed, the free amino acids join the non-essential amino acid synthesized in the liver and the amino acids recycled from the body's own proteins, constituting the **amino acid pool** now available for metabolic processes. Most of the amino acid pool is used for the synthesis of protein and other nitrogen-containing compounds such as DNA bases, neurotransmitters, hormones, etc. Under certain metabolic situations, amino acids can also be used as a source of energy by the body. It is worth mentioning that the *human body cannot store amino acid*s. If the amino acids in the amino acid pool are not used for biological processes, they are degraded and the nitrogen excreted in the urine as urea.

Protein turnover

A balance between protein synthesis and protein degradation is required for good health and normal protein metabolism. Not all the amino acids needed for the biological function of the body need to be incorporated through the diet. When the proteins already present in the metabolism have complete their lifespan, they are also recycled. **Protein turnover** refers to the replacement of older proteins as they are broken down within the cell. Different types of proteins have very different turnover rates, depending on their particular function. Structural proteins such as college tend to have long half-life periods (in the range of years), while enzymatic protein have a shorter life span to adapt to the metabolic requirements of the body.

Example protein half-lives

Name	Half-Life
Collagen	117 years
Eye lens crystallin	>70 years
Replication factor C subunit 1	9 hours
40S ribosomal protein S8	3 hours
Ornithine decarboxylase	11 minutes

Once the protein have been hydrolyzed and amino acids recycled, these amino acids are added to the amino acid pool for further utilization.

Note To Your Health: Complete and Incomplete Proteins

Amino acids are classified into three groups namely: essential amino acids and nonessential amino acids

ESSENTIAL AMINO ACIDS

- Essential amino acids cannot be made by the body. As a result, they must come from food.
- The 9 essential amino acids are: histidine, isoleucine, leucine, lysine, methionine, phenylalanine, threonine, tryptophan, and valine.

NONESSENTIAL AMINO ACIDS

Nonessential means that our bodies produce an amino acid, even if we do not get it from the food we eat. Nonessential amino acids include: alanine, arginine, asparagine, aspartic acid, cysteine, glutamic acid, glutamine, glycine, proline, serine, and tyrosine.

Based on this classification of amino acids, proteins can also be classified as either complete or incomplete. **Complete proteins** provide adequate amounts of all nine essential amino acids. Animal proteins such as meat, fish, milk, and eggs are good examples of complete proteins. **Incomplete proteins** do not contain adequate amounts of one or more of the essential amino acids. For example, if a protein doesn't provide enough of the essential amino acid leucine it would be considered incomplete. Leucine would be referred to as the limiting amino acid, because there is not enough of it for the protein to be complete. Most plant foods are incomplete proteins, with a few exceptions such as soy. Table 25.2.1 shows the limiting amino acids in some plant foods.

Food	Amino Acid(s)
Beans and Most Legumes	Methionine, Tryptophan
Tree Nuts and Seeds	Methionine, Lysine
Grains	Lysine
Vegetables	Methionine, Lysine

Table 25.2.1 *Limiting Amino Acids in Some Common Plant Foods.*

Even though most plant foods do not contain complete proteins, it does not mean that they should be sworn off as protein sources. It is possible to pair foods containing incomplete proteins with different limiting amino acids to provide adequate amounts of the essential amino acids. These two proteins are called **complementary proteins**, because they supply the amino acid(s) missing in the other protein. A simple analogy would be that of a 4 piece puzzle. If one person has 2 pieces of a puzzle, and another person has 2 remaining pieces, neither of them have a complete puzzle. But when they are combined, the two individuals create a complete puzzle.

Two examples of complementary proteins are shown below.



Figure 25.2.1 *.Two complementary protein examples*

It should be noted that complementary proteins do not need to be consumed at the same time or meal. It is currently recommended that essential amino acids be met on a daily basis, meaning that if a grain is consumed at one meal, a legume could be consumed at a later meal, and the proteins would still complement one another.

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25.3: Amino Acid Catabolism - The Amino Group

Learning Objectives

- Describe how nitrogen is conserved from amino acids.

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 $alpha$-keto acid to alanine, aspartate, or glutamate, respectively. Transamination reactions are catalyzed by specific transaminases (also called aminotransferases), which require pyridoxal phosphate as a coenzyme.

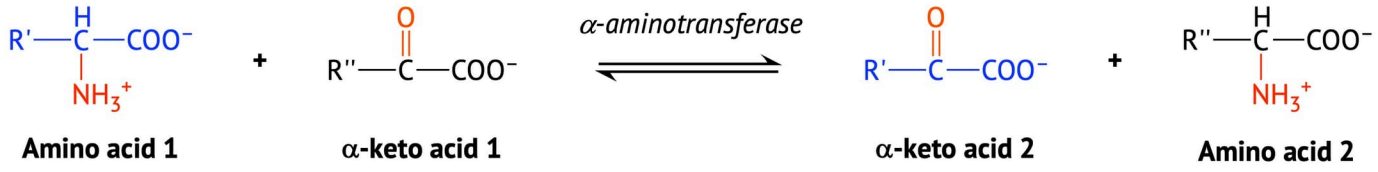


Figure 25.3.1): Transamination involves the interchange of an amino group and keto group.

In an $alpha$-keto acid, the carbonyl or keto group is located on the carbon atom adjacent to the carboxyl group of the acid.

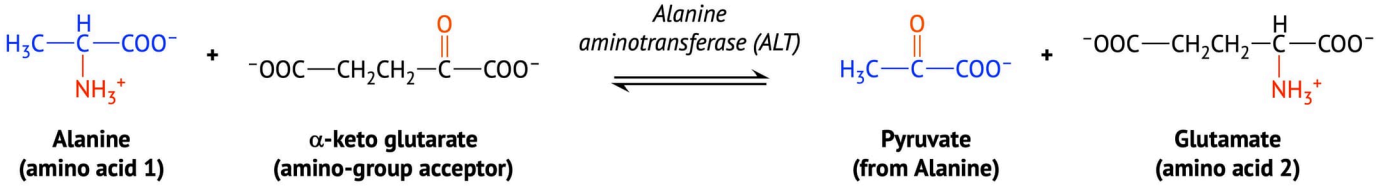
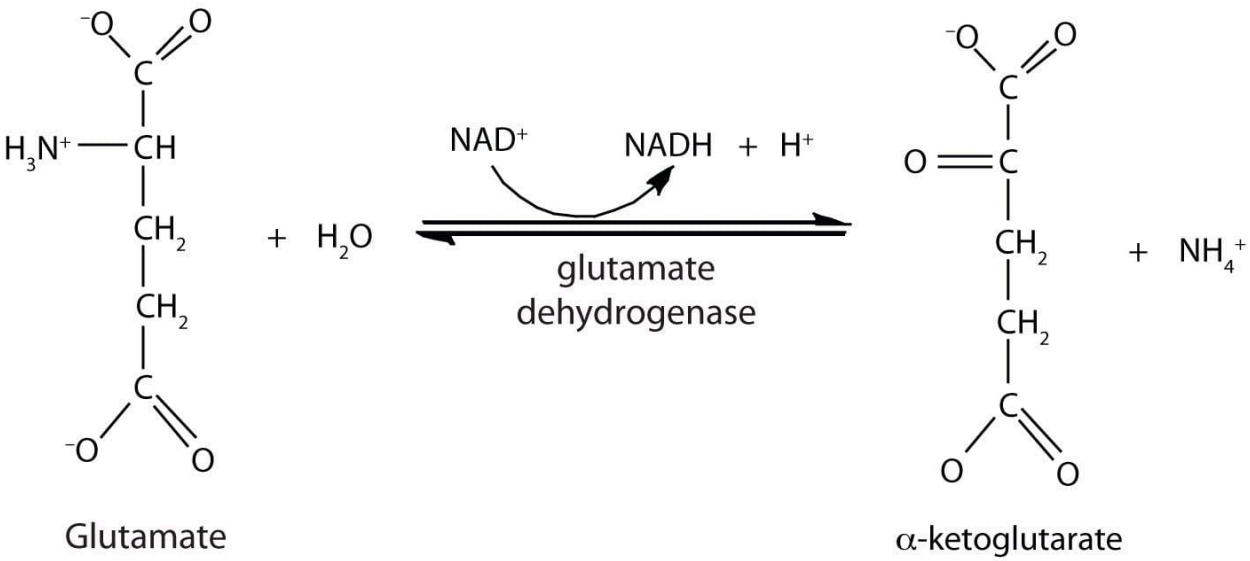


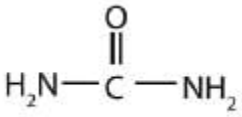
Figure 25.3.2: Alanine aminotransferase (ALT) catalyzes the transfer of an amino group from alanine to $alpha$-ketoglutarate, forming pyruvate and glutamate.

Oxidative Deamination

In the breakdown of amino acids for energy, the final acceptor of the $alpha$-amino group is $alpha$-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 $alpha$-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.

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25.4: The Urea Cycle

Learning Objectives

- Describe the urea cycle reactions.

Deamination of amino acids results in the production of **ammonia** (as well as the ammonium ion, NH_4^+). Ammonia is an extremely toxic base and its accumulation in the body would quickly be fatal. Animals that live in aquatic environments tend to release ammonia into the water. Terrestrial organisms have evolved other mechanisms to excrete nitrogenous wastes. These animals must detoxify ammonia by converting it into a relatively nontoxic form such as urea or uric acid. Mammals, including humans, produce urea through the **urea cycle**, whereas reptiles and many terrestrial invertebrates produce uric acid. Animals that secrete urea as the primary nitrogenous waste material are called ureotelic animals.

The Urea Cycle

The urea cycle is the primary mechanism by which mammals convert ammonia to urea. Urea is made in the liver and excreted in urine. The overall chemical reaction by which ammonia is converted to urea is 2 NH_3 (ammonia) + CO_2 + 3 ATP + H_2O → $H_2N\text{-}CO\text{-}NH_2$ (urea) + 2 ADP + 4 P_i + AMP.

The urea cycle utilizes five intermediate steps, catalyzed by five different enzymes, to convert ammonia to urea, as shown in Figure 25.4.1. The amino acid L-ornithine gets converted into different intermediates before being regenerated at the end of the urea cycle. Hence, the urea cycle is also referred to as the ornithine cycle. The enzyme ornithine transcarbamylase catalyzes a key step in the urea cycle and its deficiency can lead to accumulation of toxic levels of ammonia in the body. The first two reactions occur in the mitochondria and the last three reactions occur in the cytosol. Urea concentration in the blood, called blood urea nitrogen or BUN, is used as an indicator of kidney function.

Figure 25.4.1: The urea cycle converts ammonia to urea.

Note Everyday Connection: Gout

Mammals use uric acid crystals as an antioxidant in their cells. However, too much uric acid tends to form kidney stones and may also cause a painful condition called gout, where uric acid crystals accumulate in the joints, as illustrated in Figure 25.4.2. Food choices that reduce the amount of nitrogenous bases in the diet help reduce the risk of gout. For example, tea, coffee, and chocolate have purine-like compounds, called xanthines, and should be avoided by people with gout and kidney stones.

Figure 25.4.2: Gout causes the inflammation visible in this person's left big toe joint. (credit: "Gonzosft"/Wikimedia Commons)

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25.5: Amino Acid Catabolism - The Carbon Atoms

Learning Objectives

- Objective 1
- Objective 2

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-coenzymeA (CoA) and then to acetyl-CoA before it enters the citric acid cycle.

File:Amino acid catabolism revised.png

Figure 25.5.1: Fates of the Carbon Skeletons of Amino Acids (https://commons.wikimedia.org/wiki/F...sm_revised.png)

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 25.5.1 summarizes the ultimate fates of the carbon skeletons of the 20 amino acids.

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25.6: Biosynthesis of Nonessential Amino Acids

Learning Objectives

- Objective 1
- Objective 2

In humans, only half of the standard amino acids (Glu, Gln, Pro, Asp, Asn, Ala, Gly, Ser, Tyr, Cys) can be synthesized (Figure 25.6.12 and 13), and are thus classified the **nonessential amino acids**. Within this group, the first three, glutamate, glutamine, and proline, have a shared anabolic pathway. It begins with glutamate dehydrogenase, which adds ammonia to α-ketoglutarate in the presence of NADPH to form glutamate. This is a key reaction for all amino acid synthesis: glutamate is a nitrogen (amino group) donor for the production of all the other amino acids.

Glutamine synthetase catalyzes the formation of glutamine from glutamate and ammonia. This is an important biochemical reaction for a completely different reason: it is the primary route for ammonia detoxification.

Proline is synthesized from glutamate in a two-step process that begins with the reduction of glutamate to a semialdehyde form that spontaneously cyclizes to D-pyrroline-5-carboxylate. This is reduced by pyrroline carboxylate reductase to proline.

Alanine and Aspartate are the products of glutamate-based transamination of pyruvate and oxaloacetate, respectively.

Asparagine is synthesized through one of two known pathways. In bacteria, an asparagine synthetase combines aspartate and ammonia. However, in mammals, the aspartate gets its amino group from glutamine.

The synthesis of serine begins with the metabolic intermediate 3-phosphoglycerate (glycolysis). Phosphoglycerate dehydrogenase oxidizes it to 3-phosphohydroxypyruvate. An amino group is donated by glutamate in a reaction catalyzed by phosphoserine transaminase, forming 3-phosphoserine, and finally the phosphate is removed by phosphoserine phosphatase to produce serine.

Serine is the immediate precursor to glycine, which is formed by serine hydroxymethyltransferase. This enzyme requires the coenzyme tetrahydrofolate (THF), which is a derivative of vitamin B_9 (folic acid).

Serine is also a precursor for cysteine, although the synthesis of cysteine actually begins with the essential amino acid methionine. Methionine is converted to S-adenosylmethionine by methionine adenosyltransferase. This is then converted to S-adenosylhomocysteine by a member of the SAM-dependent methylase family. The sugar is removed by adenosylhomocysteinase, and the resultant homocysteine is connected by cystathionine synthase to the serine molecule to form cystathionine. Finally, cystathionine-g-lyase catalyzes the production of cysteine.

Tyrosine is another amino acid that depends on an essential amino acid as a precursor. In this case, phenylalanine oxygenase reduces phenylalanine to produce the tyrosine.

In general, the synthesis of essential amino acids, usually in microorganisms, is much more complex than for the nonessential amino acids and is best left to a full-fledged biochemistry course.

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26: NUCLEIC ACIDS AND PROTEIN SYNTHESIS

26.1: DNA, Chromosomes, and Genes

26.2: Composition of Nucleic Acids

26.3: The Structure of Nucleic Acid Chains

26.4: Base Pairing in DNA- The Watson-Crick Model

26.5: Nucleic Acids and Heredity

26.6: Replication of DNA

26.7: Structure and Function of RNA

26.8: Transcription - RNA Synthesis

26.9: The Genetic Code

26.10: Translation- tRNA and Protein Synthesis

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26.1: DNA, Chromosomes, and Genes



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26.2: Composition of Nucleic Acids



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26.3: The Structure of Nucleic Acid Chains



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26.4: Base Pairing in DNA- The Watson-Crick Model



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26.5: Nucleic Acids and Heredity



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26.6: Replication of DNA



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26.7: Structure and Function of RNA



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26.8: Transcription - RNA Synthesis



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26.9: The Genetic Code



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26.10: Translation- tRNA and Protein Synthesis



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27: GENOMICS

27.1: Mapping the Human Genome
27.2: DNA and Chromosomes
27.3: Mutations and Polymorphisms
27.4: Recombinant DNA
27.5: Genomics- Using What We Know

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27.1: Mapping the Human Genome



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27.2: DNA and Chromosomes



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27.3: Mutations and Polymorphisms



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27.4: Recombinant DNA



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27.5: Genomics- Using What We Know

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28: CHEMICAL MESSENGERS- HORMONES, NEUROTRANSMITTERS, AND DRUGS

28.1: Messenger Molecules
28.2: Hormones and the Endocrine System
28.3: How Hormones Work - Epinephrine and Fight-or-Flight
28.4: Amino Acid Derivatives and Polypeptides as Hormones
28.5: Neurotransmitters
28.6: How Neurotransmitters Work- Acetylcholine, Its Agonists and Antagonists
28.7: Histamines, Antihistamines, and Important Neurotransmitters

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28.1: Messenger Molecules



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28.2: Hormones and the Endocrine System



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28.3: How Hormones Work - Epinephrine and Fight-or-Flight



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28.4: Amino Acid Derivatives and Polypeptides as Hormones



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28.5: Neurotransmitters



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28.6: How Neurotransmitters Work- Acetylcholine, Its Agonists and Antagonists

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28.7: Histamines, Antihistamines, and Important Neurotransmitters

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29: BODY FLUIDS

29.1: Body Water and Its Solutes
29.2: Fluid Balance
29.3: Blood
29.4: Plasma Proteins, White Blood Cells, and Immunity
29.5: Blood Clotting
29.6: Red Blood Cells and Blood Gases
29.7: The Kidney and Urine Formation
29.8: Urine Composition and Function

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29.1: Body Water and Its Solutes

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29.2: Fluid Balance



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29.3: Blood

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29.4: Plasma Proteins, White Blood Cells, and Immunity

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29.5: Blood Clotting

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29.6: Red Blood Cells and Blood Gases



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29.7: The Kidney and Urine Formation



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29.8: Urine Composition and Function

Learning Objectives

- Describe how normal urine consists of water, urea, salts and pigment

Urine is a liquid byproduct of the body secreted by the kidneys through a process called urination and excreted through the urethra. The normal chemical composition of urine is mainly water content, but it also includes nitrogenous molecules, such as urea, as well as creatinine and other metabolic waste components. Other substances may be excreted in urine due to injury or infection of the glomeruli of the kidneys, which can alter the ability of the nephron to reabsorb or filter the different components of blood plasma.

Normal Chemical Composition of Urine

Urine is an aqueous solution of greater than 95% water, with a minimum of these remaining constituents, in order of decreasing concentration:

- Urea 9.3 g/L.
- Chloride 1.87 g/L.
- Sodium 1.17 g/L.
- Potassium 0.750 g/L.
- Creatinine 0.670 g/L .
- Other dissolved ions, inorganic and organic compounds (proteins, hormones, metabolites).

Urine is sterile until it reaches the urethra, where epithelial cells lining the urethra are colonized by facultatively anaerobic gram-negative rods and cocci. Urea is essentially a processed form of ammonia that is non-toxic to mammals, unlike ammonia, which can be highly toxic. It is processed from ammonia and carbon dioxide in the liver.

Abnormal Types of Urine

There are several conditions that can cause abnormal components to be excreted in urine or present as abnormal characteristics of urine. They are mostly referred to by the suffix -uria. Some of the more common types of abnormal urine include:

- Proteinuria—Protein content in urine, often due to leaky or damaged glomeruli.
- Oliguria—An abnormally small amount of urine, often due to shock or kidney damage.
- Polyuria—An abnormally large amount of urine, often caused by diabetes.
- Dysuria—Painful or uncomfortable urination, often from urinary tract infections.
- Hematuria—Red blood cells in urine, from infection or injury.
- Glycosuria—Glucose in urine, due to excess plasma glucose in diabetes, beyond the amount able to be reabsorbed in the proximal convoluted tubule.

Summary

Urine is a liquid by-product of the body secreted by the kidneys through a process called urination and excreted through the urethra. It is an aqueous solution of greater than 95% water. Other constituents include urea, chloride, sodium, potassium, creatinine and other dissolved ions, and inorganic and organic compounds. Urea is a non-toxic molecule made of toxic ammonia and carbon dioxide. Any abnormal constituents found in urine are an indication of disease.

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INDEX

A

abnormal urine
29.8: Urine Composition and Function

absolute temperature
8.6: Charles's Law- The Relation between Volume and Temperature

Absorption
22.1: Digestion of Carbohydrates
24.1: Digestion of Triacylglycerols

acetaldehyde
15.4: Some Common Aldehydes and Ketones

acetoacetate
24.6: Ketone Bodies and Ketoacidosis
25.5: Amino Acid Catabolism - The Carbon Atoms

acetylcholine
28: Chemical Messengers- Hormones, Neurotransmitters, and Drugs

acid
10.10: Buffer Solutions
10.4: Water as Both an Acid and a Base
10.6: Working with pH
5.4: Acids, Bases, and Neutralization Reactions

acid dissociation constant
10.3: Acid Dissociation Constants

acid ionization constants
10.3: Acid Dissociation Constants

acid rain
10.5: Measuring Acidity in Aqueous Solutions- The pH Scale

acid strength
10.3: Acid Dissociation Constants

acidic
10.9: Acidity and Basicity of Salt Solutions

acidic base reactions
5: Classification and Balancing of Chemical Reactions

acidic hydrolysis
17.4: Hydrolysis of Esters and Amides

acidity
10: Acids and Bases
14: Some Compounds with Oxygen, Sulfur, or a Halogen
17: Carboxylic Acids and their Derivatives
17.2: Acidity of Carboxylic Acids

acids
10: Acids and Bases
10.1: Acids and Bases Definitions
10.5: Measuring Acidity in Aqueous Solutions- The pH Scale
3.11: $H^{\oplus}$ and $OH^{\ominus}$ Ions - An Introduction to Acids and Bases

activation energy
7.5: How Do Chemical Reactions Occur? Reaction Rates
7.6: Effects of Temperature, Concentration, and Catalysts on Reaction Rates

active site
19.4: How Enzymes Work

actual yield
6.5: Limiting Reagent and Percent Yield

addictive alkaloids
16.7: Amines in Plants- Alkaloids

addition
1.9: Rounding Off Numbers
15: Aldehydes and Ketones

addition polymerization
13.7: Alkene Polymers

addition reactions
13: Alkenes, Alkynes, and Aromatic Compounds
13.6: Addition Reactions of Alkenes

adenosine triphosphate
17.6: Phosphoric Acid Derivatives
21.4: Strategies of Metabolism - ATP and Energy Transfer

adipose tissue
24.3: Triacylglycerol Metabolism - An Overview
25.3: Amino Acid Catabolism - The Amino Group

ADP
21.4: Strategies of Metabolism - ATP and Energy Transfer

aerobic cellular respiration
21.8: The Electron-Transport Chain and ATP Production

agonists
28: Chemical Messengers- Hormones, Neurotransmitters, and Drugs

AIDS
19.3: Enzyme Classification

alcohol
14.7: Ethers
14.9: Halogen-Containing Compounds

alcohol production
8.11: Partial Pressure and Dalton's Law

alcohol synthesis
13.6: Addition Reactions of Alkenes

alcohols
12.2: Families of Organic Molecules - Functional Groups
14: Some Compounds with Oxygen, Sulfur, or a Halogen
14.4: Reactions of Alcohols
15.3: Properties of Aldehydes and Ketones
15.5: Oxidation of Aldehydes
16.3: Properties of Amines
17.3: Reactions of Carboxylic Acids - Ester and Amide Formation
17.4: Hydrolysis of Esters and Amides

aldehyde
15.1: The Carbonyl Group

aldehydes
15: Aldehydes and Ketones
15.2: Naming Aldehydes and Ketones
15.3: Properties of Aldehydes and Ketones
15.4: Some Common Aldehydes and Ketones
15.5: Oxidation of Aldehydes
20.3: Structure of Glucose and Other Monosaccharides

aldohexoses
20.4: Some Important Monosaccharides

aliphatic
16.2: Naming and Drawing Amines

aliphatic compounds
15.1: The Carbonyl Group

alkali metals
2.5: Some Characteristics of Different Groups
3.3: Ions of Some Common Elements

alkaline earth metals
2.5: Some Characteristics of Different Groups
3.3: Ions of Some Common Elements

alkaloids
16: Amines

alkanes
12: Introduction to Organic Chemistry - Alkanes
12.2: Families of Organic Molecules - Functional Groups
12.3: The Structure of Organic Molecules - Alkanes and Their Isomers
12.6: Naming Alkanes
12.7: Properties of Alkanes
12.8: Reactions of Alkanes
15.3: Properties of Aldehydes and Ketones
16.3: Properties of Amines

alkene properties
13.3: The Structure of Alkenes- Cis-Trans Isomerism

alkenes
12.2: Families of Organic Molecules - Functional Groups
13: Alkenes, Alkynes, and Aromatic Compounds
13.1: Alkenes and Alkynes
13.2: Naming Alkenes and Alkynes
13.3: The Structure of Alkenes- Cis-Trans Isomerism
13.4: Properties of Alkenes and Alkynes
13.6: Addition Reactions of Alkenes

alkyl groups
16.1: Classifying Amines

alkyl halide
14.9: Halogen-Containing Compounds

alkynes
12.2: Families of Organic Molecules - Functional Groups
13: Alkenes, Alkynes, and Aromatic Compounds
13.1: Alkenes and Alkynes

allosteric control
19: Enzymes and Vitamins
19.7: Enzyme Regulation- Allosteric Control and Feedback Inhibition

allosteric enzymes
19.7: Enzyme Regulation- Allosteric Control and Feedback Inhibition

alpha emission
11.4: Nuclear Decay

alpha form
20.3: Structure of Glucose and Other Monosaccharides

amide formation
17: Carboxylic Acids and their Derivatives

amides
17: Carboxylic Acids and their Derivatives
17.3: Reactions of Carboxylic Acids - Ester and Amide Formation
17.4: Hydrolysis of Esters and Amides

amine
16.2: Naming and Drawing Amines
16.5: Basicity of Amines

amine salts
16: Amines

amines
16.1: Classifying Amines
17.3: Reactions of Carboxylic Acids - Ester and Amide Formation
18.4: Acid-Base Properties of Amino Acids
amines in plants
16: Amines
amino acid
18.5: Peptides
18.9: Quaternary Protein Structure
amino acid derivatives
28: Chemical Messengers- Hormones, Neurotransmitters, and Drugs
amino acids
14.8: Thiols and Disulfides
18: Amino Acids and Proteins
18.10: Chemical Properties of Proteins
18.3: Amino Acids
18.4: Acid-Base Properties of Amino Acids
18.6: Protein Structure- An Overview and Primary Protein Structure
18.7: Secondary Protein Structure
25: Protein and Amino Acid Metabolism
25.2: Amino Acid Metabolism - An Overview
25.3: Amino Acid Catabolism - The Amino Group
25.5: Amino Acid Catabolism - The Carbon Atoms
25.6: Biosynthesis of Nonessential Amino Acids
amino group
16.1: Classifying Amines
ammonia
25.4: The Urea Cycle
4.6: Molecular Formulas and Lewis Structures
ammonium
16.5: Basicity of Amines
ammonium ion
3.6: Polyatomic Ions
amorphous
8.13: Solids
amount of substance
1.6: Physical Quantities - Units and Scientific Notation
amphipathic
23.7: Cell Membranes- Structure and Transport
amylase
22.1: Digestion of Carbohydrates
anabolism
21.1: Energy, Life, and Biochemical Reactions
21.3: An Overview of Metabolism and Energy Production
analyte
10.11: Titration
anatomy
14.8: Thiols and Disulfides
anion
16.5: Basicity of Amines
3.1: Ions
3.4: Periodic Properties and Ion Formation
3.7: Ionic Bonds
3.9: Naming Ionic Compounds
anions
3.2: Ions and the Octet Rule
3.5: Naming Monoatomic Ions
3.6: Polyatomic Ions
3.8: Formulas of Ionic Compounds
anomeric carbon
20.3: Structure of Glucose and Other Monosaccharides
anomers
20.3: Structure of Glucose and Other Monosaccharides
antioxidants
19.2: Enzyme Cofactors
antiseptics
14.5: Phenols
aqueous solution
9.8: Ions in Solution - Electrolytes
aqueous solutions
5.7: Net Ionic Equations
archaeology
11.5: Radioactive Half-Life
arithmetic operations
1.9: Rounding Off Numbers
aromatic compounds
13: Alkenes, Alkynes, and Aromatic Compounds
13.9: Naming Aromatic Compounds
14.5: Phenols
aromatic hydrocarbons
13.8: Aromatic Compounds and the Structure of Benzene
Arrhenius
10.1: Acids and Bases Definitions
atherosclerosis
23.6: Steroids
atmospheric pressure
8.12: Liquids
8.4: Pressure
atomic counts
5.2: Balancing Chemical Equations
atomic decay
11.2: The Discovery and Nature of Radioactivity
atomic mass
2.3: Isotopes and Atomic Weight
2.4: The Periodic Table
atomic masses
6.1: The Mole and Avogadro's Number
atomic number
11.1: Nuclear Reactions
2: Atoms and the Periodic Table
2.1: Atomic Theory and the Structure of Atoms
2.2: Elements and Atomic Number
2.3: Isotopes and Atomic Weight
2.7: Electron Configurations
2.8: Electron Configurations and the Periodic Table
atomic properties
2.5: Some Characteristics of Different Groups
atomic radius
3.4: Periodic Properties and Ion Formation
atomic structure
11.2: The Discovery and Nature of Radioactivity
2.1: Atomic Theory and the Structure of Atoms
2.2: Elements and Atomic Number
2.7: Electron Configurations
atomic theory
2: Atoms and the Periodic Table
2.2: Elements and Atomic Number
atomic weight
2.3: Isotopes and Atomic Weight
atoms
2.6: Electronic Structure of Atoms
3.1: Ions
4.6: Molecular Formulas and Lewis Structures
ATP
17.6: Phosphoric Acid Derivatives
21: The Generation of Biochemical Energy
21.1: Energy, Life, and Biochemical Reactions
21.3: An Overview of Metabolism and Energy Production
21.4: Strategies of Metabolism - ATP and Energy Transfer
21.7: The Citric Acid Cycle
22.3: Glycolysis
24.3: Triacylglycerol Metabolism - An Overview
ATP production
21.8: The Electron-Transport Chain and ATP Production
ATP yield
24.5: Oxidation of Fatty Acids
attractive interactions
18.8: Tertiary Protein Structure
3.7: Ionic Bonds
Aufbau principle
2.7: Electron Configurations
Avogadro
6: Chemical Reactions - Mole and Mass Relationships
avogadro's law
8.9: Avogadro's Law - The Relation between Volume and Molar Amount
Avogadro's number
6.1: The Mole and Avogadro's Number

B

balanced chemical reaction
6.3: Mole Relationships and Chemical Equations
balanced equation
5.1: Chemical Equations
balanced equations
6.4: Mass Relationships and Chemical Equations
balancing chemical equations
6.3: Mole Relationships and Chemical Equations
balancing equations
5: Classification and Balancing of Chemical Reactions
5.2: Balancing Chemical Equations
5.7: Net Ionic Equations
band of stability
11.3: Stable and Unstable Isotopes
base
10.10: Buffer Solutions
10.4: Water as Both an Acid and a Base
10.6: Working with pH
5.4: Acids, Bases, and Neutralization Reactions
base pairing
26: Nucleic Acids and Protein Synthesis
bases
10: Acids and Bases
10.1: Acids and Bases Definitions
10.5: Measuring Acidity in Aqueous Solutions- The pH Scale
3.11: H⊕ and OH⊖ Ions - An Introduction to Acids and Bases
basic
10.9: Acidity and Basicity of Salt Solutions
basic hydrolysis
17.4: Hydrolysis of Esters and Amides
basicity
10: Acids and Bases

basicity of amines
16: Amines
battery chemistry
5.5: Redox Reactions
benzene
13: Alkenes, Alkynes, and Aromatic Compounds
13.8: Aromatic Compounds and the Structure of Benzene
13.9: Naming Aromatic Compounds
beryllium
2.9: Electron-Dot Symbols
beta emission
11.4: Nuclear Decay
beta form
20.3: Structure of Glucose and Other Monosaccharides
bilayers
23.7: Cell Membranes- Structure and Transport
bile
24.1: Digestion of Triacylglycerols
binary
4.11: Naming Binary Molecular Compounds
binding energy
11.9: Nuclear Fission and Nuclear Fusion
biochemical compounds
20: Carbohydrates
biochemical functioning
18.8: Tertiary Protein Structure
biochemical processes
21.4: Strategies of Metabolism - ATP and Energy Transfer
biochemical reactions
19.1: Catalysis by Enzymes
19.5: Factors Affecting Enzyme Activity
20.4: Some Important Monosaccharides
21: The Generation of Biochemical Energy
21.3: An Overview of Metabolism and Energy Production
25.6: Biosynthesis of Nonessential Amino Acids
biochemistry
1.1: Chemistry - The Central Science
16.4: Heterocyclic Nitrogen Compounds
17.6: Phosphoric Acid Derivatives
18: Amino Acids and Proteins
18.1: An Introduction to Biochemistry
19.1: Catalysis by Enzymes
20.5: Reactions of Monosaccharides
4.9: Polar Covalent Bonds and Electronegativity
6.2: Gram-Mole Conversions
biological activity
18.10: Chemical Properties of Proteins
biological catalyst
19.3: Enzyme Classification
biological effectiveness
11.7: Detecting and Measuring Radiation
biological fats
23.2: Fatty Acids and Their Esters
biological systems
9.10: Osmosis and Osmotic Pressure
biological tissues
11.6: Ionizing Radiation
biomolecules
12.2: Families of Organic Molecules - Functional Groups
18.1: An Introduction to Biochemistry
23.1: Structure and Classification of Lipids
blood
29: Body Fluids
29.3: Blood
blood clotting
29: Body Fluids
blood components
29.3: Blood
blood gases
29: Body Fluids
bloodstream
22.1: Digestion of Carbohydrates
body fluids
9.2: The Solution Process
body water
29: Body Fluids
boiling point
1.11: Temperature, Heat, and Energy
1.2: States of Matter
12.7: Properties of Alkanes
8.12: Liquids
boiling point elevation
9.9: Properties of Solutions
boiling points
12.1: The Nature of Organic Molecules
13.4: Properties of Alkenes and Alkynes
14.7: Ethers
16.3: Properties of Amines
4.5: Characteristics of Molecular Compounds
8.2: Intermolecular Forces
bond angle
12.9: Cycloalkanes
bond angles
13.2: Naming Alkenes and Alkynes
4.8: The Shapes of Molecules
bond characteristics
4.10: Polar Molecules
bond dissociation energies
7.3: Exothermic and Endothermic Reactions
bond dissociation energy
7.2: Heat Changes during Chemical Reactions
bond energies
7.2: Heat Changes during Chemical Reactions
bond length
4.1: Covalent Bonds
4.10: Polar Molecules
bond polarity
4: Molecular Compounds
4.10: Polar Molecules
bonding
12.1: The Nature of Organic Molecules
3: Ionic Compounds
4.8: The Shapes of Molecules
bonding pairs
4.7: Drawing Lewis Structures
bonds
7: Chemical Reactions - Energy, Rates, and Equilibrium
boron
2.9: Electron-Dot Symbols
boron trifluoride
4.4: Coordinate Covalent Bonds
Boyle's law
8: Gases, Liquids, and Solids
8.7: Gay-Lussac's Law- The Relationship Between Pressure and Temperature
8.8: The Combined Gas Law
boyles law
8.5: Boyle's Law - The Relation between Volume and Pressure
breathing cycle
8.5: Boyle's Law - The Relation between Volume and Pressure
bromine test
13.6: Addition Reactions of Alkenes
buffer
10.10: Buffer Solutions
buffers
10: Acids and Bases
build
19.8: Enzyme Regulation - Covalent Modification and Genetic Control
building
12.5: The Shapes of Organic Molecules
13.10: Reactions of Aromatic Compounds
13.5: Types of Organic Reactions
15.6: Reduction of Aldehydes and Ketones
16.6: Amine Salts
19.9: Vitamins, Antioxidants, and Minerals
22.6: Energy Output in Complete Glucose Catabolism
22.7: Regulation of Glucose Metabolism and Metabolism During Stress
26.8: Transcription - RNA Synthesis
building materials
26.7: Structure and Function of RNA
burette
10.11: Titration
butane
12.8: Reactions of Alkanes

C

calcium carbonate
7.7: Reversible Reactions and Chemical Equilibrium
calcium oxide
7.7: Reversible Reactions and Chemical Equilibrium
calculation
10.6: Working with pH
calculations
1.12: Density and Specific Gravity
1.9: Rounding Off Numbers
calorimetry
8.14: Changes of State Calculations
carbohydrates
18.1: An Introduction to Biochemistry
20: Carbohydrates
20.4: Some Important Monosaccharides
20.5: Reactions of Monosaccharides
20.7: Some Important Polysaccharides Based on Glucose
21.1: Energy, Life, and Biochemical Reactions
21.3: An Overview of Metabolism and Energy Production
22: Carbohydrate Metabolism
22.1: Digestion of Carbohydrates
23.1: Structure and Classification of Lipids
carbon
4.3: Multiple Covalent Bonds
carbon atoms
12.10: Drawing and Naming Cycloalkanes
13.8: Aromatic Compounds and the Structure of Benzene
carbon chain
12.6: Naming Alkanes
14.9: Halogen-Containing Compounds
carbon chains
13.2: Naming Alkenes and Alkynes

carbon compounds
12.1: The Nature of Organic Molecules
carbon dioxide
7.7: Reversible Reactions and Chemical Equilibrium
9.5: The Effect of Pressure on Solubility - Henry's Law
carbon monoxide
12.8: Reactions of Alkanes
4.4: Coordinate Covalent Bonds
carbonated beverages
8.11: Partial Pressure and Dalton's Law
carbonation
8.11: Partial Pressure and Dalton's Law
carbonyl compounds
15.4: Some Common Aldehydes and Ketones
carbonyl group
15: Aldehydes and Ketones
15.1: The Carbonyl Group
15.2: Naming Aldehydes and Ketones
15.3: Properties of Aldehydes and Ketones
15.5: Oxidation of Aldehydes
carboxylic acids
15.5: Oxidation of Aldehydes
17: Carboxylic Acids and their Derivatives
17.2: Acidity of Carboxylic Acids
17.3: Reactions of Carboxylic Acids - Ester and Amide Formation
17.4: Hydrolysis of Esters and Amides
17.6: Phosphoric Acid Derivatives
18.4: Acid-Base Properties of Amino Acids
23.2: Fatty Acids and Their Esters
carcinogens
13.9: Naming Aromatic Compounds
cardiovascular health
23.6: Steroids
catabolism
21.1: Energy, Life, and Biochemical Reactions
21.3: An Overview of Metabolism and Energy Production
22.1: Digestion of Carbohydrates
22.3: Glycolysis
25: Protein and Amino Acid Metabolism
25.5: Amino Acid Catabolism - The Carbon Atoms
catalysis
19: Enzymes and Vitamins
19.1: Catalysis by Enzymes
19.4: How Enzymes Work
catalyst
7.6: Effects of Temperature, Concentration, and Catalysts on Reaction Rates
7.9: Le Chatelier's Principle- The Effect of Changing Conditions on Equilibria
catalysts
13.6: Addition Reactions of Alkenes
catalytic activity
19.5: Factors Affecting Enzyme Activity
cation
16.5: Basicity of Amines
3.1: Ions
3.4: Periodic Properties and Ion Formation
3.7: Ionic Bonds
3.9: Naming Ionic Compounds
cations
3.2: Ions and the Octet Rule
3.5: Naming Monoatomic Ions
3.6: Polyatomic Ions
3.8: Formulas of Ionic Compounds
cell membrane
23.7: Cell Membranes- Structure and Transport
cell membranes
23: Lipids
cells
21: The Generation of Biochemical Energy
21.2: Cells and Their Structure
cellular components
21.2: Cells and Their Structure
cellular metabolism
21.4: Strategies of Metabolism - ATP and Energy Transfer
cellular respiration
21.2: Cells and Their Structure
cellulose
20.7: Some Important Polysaccharides Based on Glucose
Celsius
1.11: Temperature, Heat, and Energy
central atom
4.7: Drawing Lewis Structures
chain reactions
11.9: Nuclear Fission and Nuclear Fusion
champagnes
8.11: Partial Pressure and Dalton's Law
charge balance
5.5: Redox Reactions
5.7: Net Ionic Equations
charges
3.8: Formulas of Ionic Compounds
Charles's Law
8: Gases, Liquids, and Solids
8.6: Charles's Law- The Relation between Volume and Temperature
8.7: Gay-Lussac's Law- The Relationship Between Pressure and Temperature
8.8: The Combined Gas Law
chemical
5.3: Precipitation Reactions and Solubility Guidelines
7: Chemical Reactions - Energy, Rates, and Equilibrium
chemical behavior
2.5: Some Characteristics of Different Groups
chemical bond
4.9: Polar Covalent Bonds and Electronegativity
chemical bonding
12.4: Drawing Organic Structures
13.8: Aromatic Compounds and the Structure of Benzene
2.9: Electron-Dot Symbols
4.5: Characteristics of Molecular Compounds
4.8: The Shapes of Molecules
chemical bonds
3: Ionic Compounds
chemical change
1.1: Chemistry - The Central Science
chemical composition
6.1: The Mole and Avogadro's Number
chemical compounds
1.4: Chemical Elements and Symbols
13.2: Naming Alkenes and Alkynes
2.1: Atomic Theory and the Structure of Atoms
3.5: Naming Monoatomic Ions
4.6: Molecular Formulas and Lewis Structures
chemical elements
1: Matter and Measurements
chemical equation
1.5: Chemical Reactions - Examples of Chemical Change
5.1: Chemical Equations
5.4: Acids, Bases, and Neutralization Reactions
6.3: Mole Relationships and Chemical Equations
chemical equations
1.4: Chemical Elements and Symbols
10.1: Acids and Bases Definitions
10.4: Water as Both an Acid and a Base
5: Classification and Balancing of Chemical Reactions
5.2: Balancing Chemical Equations
5.5: Redox Reactions
6: Chemical Reactions - Mole and Mass Relationships
6.4: Mass Relationships and Chemical Equations
chemical equilibrium
10.10: Buffer Solutions
10.2: Acid and Base Strength
7.7: Reversible Reactions and Chemical Equilibrium
chemical formula
1.5: Chemical Reactions - Examples of Chemical Change
3.10: Some Properties of Ionic Compounds
3.8: Formulas of Ionic Compounds
4.7: Drawing Lewis Structures
chemical formulas
1.4: Chemical Elements and Symbols
12.10: Drawing and Naming Cycloalkanes
5.1: Chemical Equations
5.2: Balancing Chemical Equations
6.1: The Mole and Avogadro's Number
chemical kinetics
7.5: How Do Chemical Reactions Occur? Reaction Rates
chemical messengers
18.1: An Introduction to Biochemistry
chemical nomenclature
3: Ionic Compounds
chemical notation
12.4: Drawing Organic Structures
chemical processes
7.3: Exothermic and Endothermic Reactions
8.1: States of Matter and Their Changes
chemical properties
1: Matter and Measurements
1.1: Chemistry - The Central Science
1.3: Classification of Matter
1.5: Chemical Reactions - Examples of Chemical Change
12.1: The Nature of Organic Molecules
12.3: The Structure of Organic Molecules - Alkanes and Their Isomers
13.9: Naming Aromatic Compounds
15.1: The Carbonyl Group
18.1: An Introduction to Biochemistry
2.4: The Periodic Table
2.6: Electronic Structure of Atoms
2.8: Electron Configurations and the Periodic Table
chemical reaction
19.3: Enzyme Classification
5.1: Chemical Equations
5.5: Redox Reactions
6.5: Limiting Reagent and Percent Yield
7.2: Heat Changes during Chemical Reactions
7.8: Equilibrium Equations and Equilibrium Constants

chemical reactions
1: Matter and Measurements
1.5: Chemical Reactions - Examples of Chemical Change
10.5: Measuring Acidity in Aqueous Solutions- The pH Scale
13.6: Addition Reactions of Alkenes
14.4: Reactions of Alcohols
14.9: Halogen-Containing Compounds
17.2: Acidity of Carboxylic Acids
17.5: Polyamides and Polyesters
21.1: Energy, Life, and Biochemical Reactions
23: Lipids
5: Classification and Balancing of Chemical Reactions
5.2: Balancing Chemical Equations
5.6: Recognizing Redox Reactions
5.7: Net Ionic Equations
6.4: Mass Relationships and Chemical Equations
7.4: Why Do Chemical Reactions Occur? Free Energy
7.6: Effects of Temperature, Concentration, and Catalysts on Reaction Rates
9.6: Units of Concentration
chemical reactivity
12.2: Families of Organic Molecules - Functional Groups
4.2: Covalent Bonds and the Periodic Table
chemical structure
1.5: Chemical Reactions - Examples of Chemical Change
13: Alkenes, Alkynes, and Aromatic Compounds
14.5: Phenols
15.2: Naming Aldehydes and Ketones
chemical structures
12.10: Drawing and Naming Cycloalkanes
12.6: Naming Alkanes
13.3: The Structure of Alkenes- Cis-Trans Isomerism
chemical substances
3.11: H⊕ and OH⊖ Ions - An Introduction to Acids and Bases
chemical symbols
1.4: Chemical Elements and Symbols
chemicalequilibrium
7.9: Le Chatelier's Principle- The Effect of Changing Conditions on Equilibria
chemiosmosis
21.8: The Electron-Transport Chain and ATP Production
chemistry
1: Matter and Measurements
1.1: Chemistry - The Central Science
10.6: Working with pH
11.8: Artificial Transmutation
13.7: Alkene Polymers
14.8: Thiols and Disulfides
16.5: Basicity of Amines
2.3: Isotopes and Atomic Weight
3.1: Ions
4.11: Naming Binary Molecular Compounds
4.6: Molecular Formulas and Lewis Structures
5.6: Recognizing Redox Reactions
6.2: Gram-Mole Conversions
8.10: The Ideal Gas Law
8.11: Partial Pressure and Dalton's Law
chemistry education
12.4: Drawing Organic Structures
14.5: Phenols
chlorine
3.1: Ions
cholesterol
23.1: Structure and Classification of Lipids
23.6: Steroids
24.2: Lipoproteins for Lipid Transport
chromosomes
26: Nucleic Acids and Protein Synthesis
27: Genomics
chylomicrons
24.1: Digestion of Triacylglycerols
24.2: Lipoproteins for Lipid Transport
chymotrypsinogen
25.1: Digestion of Proteins
circulatory system
29.3: Blood
citric acid cycle
21: The Generation of Biochemical Energy
21.7: The Citric Acid Cycle
24.6: Ketone Bodies and Ketoacidosis
25.5: Amino Acid Catabolism - The Carbon Atoms
classification
16.1: Classifying Amines
18.3: Amino Acids
classification of matter
1.3: Classification of Matter
classification of mixtures
9.1: Mixtures and Solutions
classifying amines
16: Amines
codeine
16.7: Amines in Plants- Alkaloids
coefficients
5.1: Chemical Equations
5.2: Balancing Chemical Equations
6.3: Mole Relationships and Chemical Equations
coenzymes
19.2: Enzyme Cofactors
collaboration
10.8: Some Common Acid-Base Reactions
22.2: Glucose Metabolism - An Overview
23.3: Properties of Fats and Oils
26.3: The Structure of Nucleic Acid Chains
26.6: Replication of DNA
26.8: Transcription - RNA Synthesis
26.9: The Genetic Code
27.4: Recombinant DNA
28.1: Messenger Molecules
28.2: Hormones and the Endocrine System
28.3: How Hormones Work - Epinephrine and Fight-or-Flight
29.2: Fluid Balance
29.7: The Kidney and Urine Formation
collaborative learning
14.6: Acidity of Alcohols and Phenols
23.4: Chemical Reactions of Triacylglycerols
23.5: Phospholipids and Glycolipids
26.1: DNA, Chromosomes, and Genes
26.5: Nucleic Acids and Heredity
27.2: DNA and Chromosomes
28.4: Amino Acid Derivatives and Polypeptides as Hormones
29.6: Red Blood Cells and Blood Gases
colligative properties
9.9: Properties of Solutions
collision theory
7.5: How Do Chemical Reactions Occur? Reaction Rates
7.6: Effects of Temperature, Concentration, and Catalysts on Reaction Rates
collisions
8.3: Gases and the Kinetic-Molecular Theory
colloids
9.1: Mixtures and Solutions
combined gas law
8: Gases, Liquids, and Solids
8.8: The Combined Gas Law
combustion
1.5: Chemical Reactions - Examples of Chemical Change
12.8: Reactions of Alkanes
common aldehydes
15: Aldehydes and Ketones
common ions
3.3: Ions of Some Common Elements
common ketones
15: Aldehydes and Ketones
competitive
19.6: Enzyme Regulation - Inhibition
complete
19.8: Enzyme Regulation - Covalent Modification and Genetic Control
complete proteins
25.2: Amino Acid Metabolism - An Overview
completed
22.5: The Fate of Pyruvate
22.7: Regulation of Glucose Metabolism and Metabolism During Stress
completion
16.6: Amine Salts
19.9: Vitamins, Antioxidants, and Minerals
compound naming
16.1: Classifying Amines
compounds
1.3: Classification of Matter
4.11: Naming Binary Molecular Compounds
5.3: Precipitation Reactions and Solubility Guidelines
5.6: Recognizing Redox Reactions
concentrated
9.3: Solubility
concentration
10.11: Titration
10.6: Working with pH
7.6: Effects of Temperature, Concentration, and Catalysts on Reaction Rates
7.7: Reversible Reactions and Chemical Equilibrium
7.8: Equilibrium Equations and Equilibrium Constants
9: Solutions
9.3: Solubility
9.5: The Effect of Pressure on Solubility - Henry's Law
9.6: Units of Concentration
9.7: Dilution
concentrationchanges
7.9: Le Chatelier's Principle- The Effect of Changing Conditions on Equilibria
concentrations
10.10: Buffer Solutions
condensation
8.12: Liquids
condensation polymers
17.3: Reactions of Carboxylic Acids - Ester and Amide Formation
17.5: Polyamides and Polyesters
condensed structures
12.4: Drawing Organic Structures

conductivity
3.10: Some Properties of Ionic Compounds
9.8: Ions in Solution - Electrolytes
conjugate acid
10.2: Acid and Base Strength
conjugate base
10.2: Acid and Base Strength
conservation of energy
7.1: Energy and Chemical Bonds
constant R
8.10: The Ideal Gas Law
content availability
29.6: Red Blood Cells and Blood Gases
content creation
26.5: Nucleic Acids and Heredity
content development
14.10: Stereochemistry and Chirality
20.1: An Introduction to Carbohydrates
26.6: Replication of DNA
conversion factors
6.4: Mass Relationships and Chemical Equations
conversions
1.8: Measurement and Significant Figures
6: Chemical Reactions - Mole and Mass Relationships
6.2: Gram-Mole Conversions
cooking
9.9: Properties of Solutions
coordinate covalent bond
4.4: Coordinate Covalent Bonds
counting methods
1.8: Measurement and Significant Figures
covalent
4.11: Naming Binary Molecular Compounds
8.13: Solids
covalent bond
4.3: Multiple Covalent Bonds
4.4: Coordinate Covalent Bonds
covalent bonds
12.1: The Nature of Organic Molecules
4: Molecular Compounds
4.1: Covalent Bonds
4.2: Covalent Bonds and the Periodic Table
7.2: Heat Changes during Chemical Reactions
covalent compounds
4.10: Polar Molecules
6.1: The Mole and Avogadro's Number
covalent modification
19: Enzymes and Vitamins
critical mass
11.9: Nuclear Fission and Nuclear Fusion
crystal lattice
3.10: Some Properties of Ionic Compounds
crystal structure
3.7: Ionic Bonds
crystalline
8.13: Solids
cyclic compounds
12.10: Drawing and Naming Cycloalkanes
16.4: Heterocyclic Nitrogen Compounds
cyclic hydrocarbons
12.9: Cycloalkanes
cyclic structures
20.3: Structure of Glucose and Other Monosaccharides
cycloalkanes
12: Introduction to Organic Chemistry - Alkanes
12.10: Drawing and Naming Cycloalkanes
12.9: Cycloalkanes
cycloalkenes
13.2: Naming Alkenes and Alkynes

D

d block
2.8: Electron Configurations and the Periodic Table
Dalton's atomic theory
6.1: The Mole and Avogadro's Number
decarboxylation
21.7: The Citric Acid Cycle
decay
11.5: Radioactive Half-Life
decompression sickness
9.5: The Effect of Pressure on Solubility - Henry's Law
deficiency diseases
19.2: Enzyme Cofactors
dehydration prevention
9.2: The Solution Process
dehydrogenation
24.5: Oxidation of Fatty Acids
denaturation
18.10: Chemical Properties of Proteins
density
1.10: Problem Solving - Unit Conversions and Estimating Answers
1.12: Density and Specific Gravity
12.7: Properties of Alkanes
desaturation
24.7: Biosynthesis of Fatty Acids
detoxification
25.4: The Urea Cycle
development
22.2: Glucose Metabolism - An Overview
dextrins
22.1: Digestion of Carbohydrates
diabetes mellitus
24.6: Ketone Bodies and Ketoacidosis
dialysis
9.11: Dialysis
diatomic molecules
4.2: Covalent Bonds and the Periodic Table
dietary fats
23.2: Fatty Acids and Their Esters
24.3: Triacylglycerol Metabolism - An Overview
dietary fiber
20.7: Some Important Polysaccharides Based on Glucose
dietary modifications
23.6: Steroids
dietary nutrients
19.2: Enzyme Cofactors
dietary proteins
25.2: Amino Acid Metabolism - An Overview
diffusion
9.10: Osmosis and Osmotic Pressure
digestion
20.6: Common Disaccharides
22: Carbohydrate Metabolism
22.1: Digestion of Carbohydrates
24: Lipid Metabolism
24.2: Lipoproteins for Lipid Transport
25: Protein and Amino Acid Metabolism
digestive enzymes
25.1: Digestion of Proteins
dilute
9.3: Solubility
dilution
9: Solutions
9.6: Units of Concentration
9.7: Dilution
dilution equation
9.7: Dilution
dimensional analysis
1.10: Problem Solving - Unit Conversions and Estimating Answers
dioxide
4.11: Naming Binary Molecular Compounds
dipeptide
18.5: Peptides
dipole moment
4.10: Polar Molecules
disaccharide
20.6: Common Disaccharides
disaccharides
20: Carbohydrates
20.5: Reactions of Monosaccharides
disinfectants
14.5: Phenols
dispersion forces
18.8: Tertiary Protein Structure
dissociation
10.2: Acid and Base Strength
9.8: Ions in Solution - Electrolytes
dissociation equation
3.10: Some Properties of Ionic Compounds
disubstituted benzenes
13.9: Naming Aromatic Compounds
disulfide linkages
18.8: Tertiary Protein Structure
disulfides
14: Some Compounds with Oxygen, Sulfur, or a Halogen
14.8: Thiols and Disulfides
division
1.9: Rounding Off Numbers
DNA
21.2: Cells and Their Structure
26: Nucleic Acids and Protein Synthesis
27: Genomics
domain
22.7: Regulation of Glucose Metabolism and Metabolism During Stress
dosage calculations
9.7: Dilution
dose
11.7: Detecting and Measuring Radiation
double bond
4.3: Multiple Covalent Bonds
double bonds
13.2: Naming Alkenes and Alkynes
13.3: The Structure of Alkenes- Cis-Trans Isomerism

drawing amines
16: Amines
drawing cycloalkanes
12: Introduction to Organic Chemistry - Alkanes
drug design
19.3: Enzyme Classification
drug mechanisms
16.4: Heterocyclic Nitrogen Compounds
dynamic equilibrium
7.8: Equilibrium Equations and Equilibrium Constants
dynamic process
7.7: Reversible Reactions and Chemical Equilibrium

E

E/Z nomenclature
13.3: The Structure of Alkenes- Cis-Trans Isomerism
education
13.10: Reactions of Aromatic Compounds
15.6: Reduction of Aldehydes and Ketones
16.6: Amine Salts
26.6: Replication of DNA
26.8: Transcription - RNA Synthesis
26.9: The Genetic Code
27.4: Recombinant DNA
28.1: Messenger Molecules
29.2: Fluid Balance
educational
14.1: Alcohols, Phenols, and Ethers
22.6: Energy Output in Complete Glucose Catabolism
educational content
21.6: Strategies of Metabolism- Oxidized and Reduced Coenzymes
26.9: The Genetic Code
educational materials
21.6: Strategies of Metabolism- Oxidized and Reduced Coenzymes
29.7: The Kidney and Urine Formation
elastic collisions
8.3: Gases and the Kinetic-Molecular Theory
electrical conductance
9.8: Ions in Solution - Electrolytes
electrical conductivity
4.5: Characteristics of Molecular Compounds
electrolyte balance
3.5: Naming Monoatomic Ions
electrolytes
9: Solutions
9.2: The Solution Process
electron affinity
3.4: Periodic Properties and Ion Formation
electron arrangement
2.7: Electron Configurations
electron arrangements
2.6: Electronic Structure of Atoms
electron capture
11.4: Nuclear Decay
electron configurations
2.7: Electron Configurations
2.8: Electron Configurations and the Periodic Table
3: Ionic Compounds
3.2: Ions and the Octet Rule
electron deficiency
4.4: Coordinate Covalent Bonds
electron dot symbol
2.9: Electron-Dot Symbols
electron groups
4.8: The Shapes of Molecules
electron sharing
4.1: Covalent Bonds
4.2: Covalent Bonds and the Periodic Table
4.4: Coordinate Covalent Bonds
electron transfer
3.7: Ionic Bonds
3.8: Formulas of Ionic Compounds
5.5: Redox Reactions
5.6: Recognizing Redox Reactions
electron transport chain
21.8: The Electron-Transport Chain and ATP Production
electronegativity
4.10: Polar Molecules
4.7: Drawing Lewis Structures
4.9: Polar Covalent Bonds and Electronegativity
Electrons
11.1: Nuclear Reactions
2: Atoms and the Periodic Table
2.1: Atomic Theory and the Structure of Atoms
2.2: Elements and Atomic Number
2.6: Electronic Structure of Atoms
3.1: Ions
electrostatic force
3.7: Ionic Bonds
element
2.2: Elements and Atomic Number
elemental state
5.6: Recognizing Redox Reactions
elements
1.3: Classification of Matter
1.4: Chemical Elements and Symbols
2.4: The Periodic Table
2.9: Electron-Dot Symbols
4.11: Naming Binary Molecular Compounds
6.2: Gram-Mole Conversions
elimination
14.9: Halogen-Containing Compounds
empirical formula
3.8: Formulas of Ionic Compounds
emulsification
24.1: Digestion of Triacylglycerols
endocrine system
28: Chemical Messengers- Hormones, Neurotransmitters, and Drugs
endothermic
7: Chemical Reactions - Energy, Rates, and Equilibrium
7.2: Heat Changes during Chemical Reactions
7.9: Le Chatelier's Principle- The Effect of Changing Conditions on Equilibria
endothermic reaction
7.5: How Do Chemical Reactions Occur? Reaction Rates
endothermic reactions
7.3: Exothermic and Endothermic Reactions
7.4: Why Do Chemical Reactions Occur? Free Energy
energy
1: Matter and Measurements
1.2: States of Matter
20.4: Some Important Monosaccharides
21: The Generation of Biochemical Energy
21.1: Energy, Life, and Biochemical Reactions
21.2: Cells and Their Structure
21.4: Strategies of Metabolism - ATP and Energy Transfer
22: Carbohydrate Metabolism
22.3: Glycolysis
23.1: Structure and Classification of Lipids
7: Chemical Reactions - Energy, Rates, and Equilibrium
7.1: Energy and Chemical Bonds
8.14: Changes of State Calculations
energy as product
7.3: Exothermic and Endothermic Reactions
energy as reactant
7.3: Exothermic and Endothermic Reactions
energy carriers
21.8: The Electron-Transport Chain and ATP Production
energy change
7.2: Heat Changes during Chemical Reactions
energy changes
3.4: Periodic Properties and Ion Formation
8.1: States of Matter and Their Changes
energy levels
2.6: Electronic Structure of Atoms
energy production
21: The Generation of Biochemical Energy
energy release
24.5: Oxidation of Fatty Acids
energy requirement
24.6: Ketone Bodies and Ketoacidosis
energy storage
20.7: Some Important Polysaccharides Based on Glucose
24.3: Triacylglycerol Metabolism - An Overview
energy transfer
1.11: Temperature, Heat, and Energy
21: The Generation of Biochemical Energy
enthalpy
7.4: Why Do Chemical Reactions Occur? Free Energy
8.1: States of Matter and Their Changes
8.14: Changes of State Calculations
enthalpy change
7.2: Heat Changes during Chemical Reactions
7.3: Exothermic and Endothermic Reactions
entropy
7.4: Why Do Chemical Reactions Occur? Free Energy
environment
13.4: Properties of Alkenes and Alkynes
environmental chemistry
10.5: Measuring Acidity in Aqueous Solutions- The pH Scale
environmental science
11.5: Radioactive Half-Life
enzymatic
22.3: Glycolysis
enzyme
18.2: Proteins and Their Functions- An Overview
19.4: How Enzymes Work
19.6: Enzyme Regulation - Inhibition

enzyme activity
19: Enzymes and Vitamins
19.5: Factors Affecting Enzyme Activity
19.6: Enzyme Regulation - Inhibition
19.7: Enzyme Regulation- Allosteric Control and Feedback Inhibition
enzyme catalysis
25.6: Biosynthesis of Nonessential Amino Acids
enzyme catalysts
14.4: Reactions of Alcohols
enzyme classification
19: Enzymes and Vitamins
19.3: Enzyme Classification
enzyme cofactor
19: Enzymes and Vitamins
enzyme concentration
19.5: Factors Affecting Enzyme Activity
enzyme inhibitors
19.7: Enzyme Regulation- Allosteric Control and Feedback Inhibition
enzyme kinetics
19.4: How Enzymes Work
enzyme nomenclature
19.3: Enzyme Classification
enzyme reactions
21.4: Strategies of Metabolism - ATP and Energy Transfer
enzyme regulation
19: Enzymes and Vitamins
19.7: Enzyme Regulation- Allosteric Control and Feedback Inhibition
enzyme specificity
19.4: How Enzymes Work
enzymes
18.7: Secondary Protein Structure
19: Enzymes and Vitamins
19.1: Catalysis by Enzymes
19.2: Enzyme Cofactors
19.3: Enzyme Classification
20.6: Common Disaccharides
21.3: An Overview of Metabolism and Energy Production
25.4: The Urea Cycle
epinephrine
28: Chemical Messengers- Hormones, Neurotransmitters, and Drugs
equations
5.3: Precipitation Reactions and Solubility Guidelines
equilibrium
10: Acids and Bases
10.10: Buffer Solutions
10.4: Water as Both an Acid and a Base
8.12: Liquids
9.5: The Effect of Pressure on Solubility - Henry's Law
equilibrium constant
7.8: Equilibrium Equations and Equilibrium Constants
equilibrium equation
7.7: Reversible Reactions and Chemical Equilibrium
equilibrium expression
10.3: Acid Dissociation Constants
7.8: Equilibrium Equations and Equilibrium Constants
equivalence point
10.11: Titration
essential amino acids
18.3: Amino Acids
25.2: Amino Acid Metabolism - An Overview
essential fatty acids
23.2: Fatty Acids and Their Esters
24.7: Biosynthesis of Fatty Acids
ester formation
17: Carboxylic Acids and their Derivatives
esterification
17.3: Reactions of Carboxylic Acids - Ester and Amide Formation
esters
17: Carboxylic Acids and their Derivatives
17.3: Reactions of Carboxylic Acids - Ester and Amide Formation
17.4: Hydrolysis of Esters and Amides
ether
14.7: Ethers
ethers
14: Some Compounds with Oxygen, Sulfur, or a Halogen
16.3: Properties of Amines
eukaryotic
21.2: Cells and Their Structure
evaporation
8.12: Liquids
exact values
1.8: Measurement and Significant Figures
example
5.1: Chemical Equations
exothermic
7: Chemical Reactions - Energy, Rates, and Equilibrium
7.2: Heat Changes during Chemical Reactions
7.9: Le Chatelier's Principle- The Effect of Changing Conditions on Equilibria
exothermic reaction
7.5: How Do Chemical Reactions Occur? Reaction Rates
exothermic reactions
7.3: Exothermic and Endothermic Reactions
7.4: Why Do Chemical Reactions Occur? Free Energy
extraction
16.7: Amines in Plants- Alkaloids

F

f block
2.8: Electron Configurations and the Periodic Table
factors affecting reaction rates
7.5: How Do Chemical Reactions Occur? Reaction Rates
FADH2
21.7: The Citric Acid Cycle
21.8: The Electron-Transport Chain and ATP Production
Fahrenheit
1.11: Temperature, Heat, and Energy
fats
21.3: An Overview of Metabolism and Energy Production
23.1: Structure and Classification of Lipids
25: Protein and Amino Acid Metabolism
fatty acid classification
23.2: Fatty Acids and Their Esters
Fatty Acid Oxidation
24.5: Oxidation of Fatty Acids
24.6: Ketone Bodies and Ketoacidosis
fatty acid synthase
24.7: Biosynthesis of Fatty Acids
fatty acids
23: Lipids
23.2: Fatty Acids and Their Esters
24: Lipid Metabolism
24.3: Triacylglycerol Metabolism - An Overview
24.7: Biosynthesis of Fatty Acids
feedback control
19.7: Enzyme Regulation- Allosteric Control and Feedback Inhibition
feedback inhibition
19: Enzymes and Vitamins
fermentation
20.6: Common Disaccharides
22.3: Glycolysis
8.11: Partial Pressure and Dalton's Law
fibrous proteins
18.2: Proteins and Their Functions- An Overview
filtration
9.11: Dialysis
final concentration
9.7: Dilution
finished
14.2: Naming Alcohols
19.8: Enzyme Regulation - Covalent Modification and Genetic Control
20.2: Handedness of Carbohydrates
finished pages
28.5: Neurotransmitters
first 20 elements
2.7: Electron Configurations
fission products
11.9: Nuclear Fission and Nuclear Fusion
fluid balance
29: Body Fluids
formaldehyde
15.4: Some Common Aldehydes and Ketones
forward reaction
7.7: Reversible Reactions and Chemical Equilibrium
fractional distillation
12.8: Reactions of Alkanes
free energy
7.4: Why Do Chemical Reactions Occur? Free Energy
free radicals
4.2: Covalent Bonds and the Periodic Table
freezing
8.14: Changes of State Calculations
freezing point
1.11: Temperature, Heat, and Energy
freezing point depression
9.9: Properties of Solutions
fuels
12.8: Reactions of Alkanes
fumarate
25.5: Amino Acid Catabolism - The Carbon Atoms
functional group
14.4: Reactions of Alcohols
14.9: Halogen-Containing Compounds
16.2: Naming and Drawing Amines

functional group isomers
12.3: The Structure of Organic Molecules - Alkanes and Their Isomers
functional groups
12: Introduction to Organic Chemistry - Alkanes
12.2: Families of Organic Molecules - Functional Groups
13.1: Alkenes and Alkynes
15.1: The Carbonyl Group
15.2: Naming Aldehydes and Ketones
15.3: Properties of Aldehydes and Ketones
15.5: Oxidation of Aldehydes
16.1: Classifying Amines
17.5: Polyamides and Polyesters
18.4: Acid-Base Properties of Amino Acids
functional roles
18.2: Proteins and Their Functions- An Overview

G

gallbladder
24.1: Digestion of Triacylglycerols
gamma emission
11.4: Nuclear Decay
gamma rays
11.2: The Discovery and Nature of Radioactivity
11.6: Ionizing Radiation
gas
1.2: States of Matter
gas amount
8.9: Avogadro's Law - The Relation between Volume and Molar Amount
gas calculations
8.6: Charles's Law- The Relation between Volume and Temperature
gas law
8.5: Boyle's Law - The Relation between Volume and Pressure
gas laws
8: Gases, Liquids, and Solids
8.10: The Ideal Gas Law
8.4: Pressure
8.6: Charles's Law- The Relation between Volume and Temperature
8.7: Gay-Lussac's Law- The Relationship Between Pressure and Temperature
8.8: The Combined Gas Law
8.9: Avogadro's Law - The Relation between Volume and Molar Amount
gas phase
8.12: Liquids
gas pressure
8.11: Partial Pressure and Dalton's Law
8.4: Pressure
8.7: Gay-Lussac's Law- The Relationship Between Pressure and Temperature
gas properties
8.3: Gases and the Kinetic-Molecular Theory
8.5: Boyle's Law - The Relation between Volume and Pressure
8.9: Avogadro's Law - The Relation between Volume and Molar Amount
gas solubility
9.4: The Effect of Temperature on Solubility
9.5: The Effect of Pressure on Solubility - Henry's Law
gas temperature
8.6: Charles's Law- The Relation between Volume and Temperature
gas volume
8.5: Boyle's Law - The Relation between Volume and Pressure
8.6: Charles's Law- The Relation between Volume and Temperature
gases
8.3: Gases and the Kinetic-Molecular Theory
gastric juice
25.1: Digestion of Proteins
Genes
26: Nucleic Acids and Protein Synthesis
genetic
11.7: Detecting and Measuring Radiation
genome
27: Genomics
genomics
27: Genomics
geological formations
11.5: Radioactive Half-Life
geometric isomers
13.3: The Structure of Alkenes- Cis-Trans Isomerism
germicide
14.5: Phenols
Gibbs Free Energy
7.4: Why Do Chemical Reactions Occur? Free Energy
globular proteins
18.2: Proteins and Their Functions- An Overview
gluconeogenesis
22: Carbohydrate Metabolism
glucose
20.6: Common Disaccharides
20.7: Some Important Polysaccharides Based on Glucose
22: Carbohydrate Metabolism
22.1: Digestion of Carbohydrates
22.3: Glycolysis
glucose metabolism
18.6: Protein Structure- An Overview and Primary Protein Structure
glutamate
25.6: Biosynthesis of Nonessential Amino Acids
glycerol
24.3: Triacylglycerol Metabolism - An Overview
glycogen
20.7: Some Important Polysaccharides Based on Glucose
22: Carbohydrate Metabolism
glycolaldehyde
15.4: Some Common Aldehydes and Ketones
glycolipids
23: Lipids
glycolysis
22: Carbohydrate Metabolism
22.3: Glycolysis
24.3: Triacylglycerol Metabolism - An Overview
glycosidic linkage
20.5: Reactions of Monosaccharides
20.6: Common Disaccharides
gravity
1.7: Measuring Mass, Length, and Volume
greenhouse effect
12.8: Reactions of Alkanes

H

H+
5.4: Acids, Bases, and Neutralization Reactions
halogen
14: Some Compounds with Oxygen, Sulfur, or a Halogen
14.9: Halogen-Containing Compounds
halogenation
13.6: Addition Reactions of Alkenes
halogens
2.5: Some Characteristics of Different Groups
3.3: Ions of Some Common Elements
HCl
9.4: The Effect of Temperature on Solubility
HDLs
24.2: Lipoproteins for Lipid Transport
health
11.7: Detecting and Measuring Radiation
23.6: Steroids
6.2: Gram-Mole Conversions
health effects
13.8: Aromatic Compounds and the Structure of Benzene
14.5: Phenols
15.4: Some Common Aldehydes and Ketones
3.5: Naming Monoatomic Ions
health nutrition
25.2: Amino Acid Metabolism - An Overview
heart disease
23.6: Steroids
heat
1.11: Temperature, Heat, and Energy
7: Chemical Reactions - Energy, Rates, and Equilibrium
heat flow
7.3: Exothermic and Endothermic Reactions
heat of fusion
8.14: Changes of State Calculations
heat of reaction
7.2: Heat Changes during Chemical Reactions
7.3: Exothermic and Endothermic Reactions
heat transfer
8.14: Changes of State Calculations
helium
2.9: Electron-Dot Symbols
hematology
29.3: Blood
hemodialysis
9.11: Dialysis
hemoglobin
18.9: Quaternary Protein Structure
Henry's law
9: Solutions
9.5: The Effect of Pressure on Solubility - Henry's Law
Heredity
26: Nucleic Acids and Protein Synthesis
heroin
16.7: Amines in Plants- Alkaloids
heterocyclic
16.5: Basicity of Amines
heterocyclic amines
16.4: Heterocyclic Nitrogen Compounds
heterocyclic nitrogen compounds
16: Amines
heterogeneous
9.1: Mixtures and Solutions

heterogeneous mixtures
1.3: Classification of Matter
hexoses
20.4: Some Important Monosaccharides
HIV
19.3: Enzyme Classification
homogeneous
9.1: Mixtures and Solutions
homogeneous mixtures
1.3: Classification of Matter
hormone
18.2: Proteins and Their Functions- An Overview
hormone functions
23.6: Steroids
hormones
28: Chemical Messengers- Hormones, Neurotransmitters, and Drugs
human
27: Genomics
human biology
29.3: Blood
Hund's rule
2.7: Electron Configurations
hybridization
13.2: Naming Alkenes and Alkynes
hydration
13.6: Addition Reactions of Alkenes
24.5: Oxidation of Fatty Acids
9.2: The Solution Process
hydrocarbon
16.2: Naming and Drawing Amines
hydrocarbons
12.1: The Nature of Organic Molecules
12.10: Drawing and Naming Cycloalkanes
12.2: Families of Organic Molecules - Functional Groups
12.3: The Structure of Organic Molecules - Alkanes and Their Isomers
12.6: Naming Alkanes
12.7: Properties of Alkanes
12.9: Cycloalkanes
13.1: Alkenes and Alkynes
13.4: Properties of Alkenes and Alkynes
13.8: Aromatic Compounds and the Structure of Benzene
13.9: Naming Aromatic Compounds
hydrochloric acid
25.1: Digestion of Proteins
3.11: H⊕ and OH⊖ Ions - An Introduction to Acids and Bases
hydrofluoric acid
10.9: Acidity and Basicity of Salt Solutions
hydrogen
2.9: Electron-Dot Symbols
hydrogen bonding
16.3: Properties of Amines
18.10: Chemical Properties of Proteins
18.7: Secondary Protein Structure
18.8: Tertiary Protein Structure
4.5: Characteristics of Molecular Compounds
8.2: Intermolecular Forces
9.2: The Solution Process
hydrogen ions
3.11: H⊕ and OH⊖ Ions - An Introduction to Acids and Bases
hydrogen molecule
4.1: Covalent Bonds
hydrogen peroxide
7.6: Effects of Temperature, Concentration, and Catalysts on Reaction Rates
hydrogenation
13.6: Addition Reactions of Alkenes
hydrolysis
17: Carboxylic Acids and their Derivatives
17.4: Hydrolysis of Esters and Amides
18.10: Chemical Properties of Proteins
20.6: Common Disaccharides
21.4: Strategies of Metabolism - ATP and Energy Transfer
hydronium
10.4: Water as Both an Acid and a Base
5.4: Acids, Bases, and Neutralization Reactions
hydronium concentration
10.6: Working with pH
hydronium ion
10.1: Acids and Bases Definitions
3.6: Polyatomic Ions
hydrophilic
23.7: Cell Membranes- Structure and Transport
hydrophobic
23.7: Cell Membranes- Structure and Transport
hydroxide
10.4: Water as Both an Acid and a Base
hydroxide ion
10.1: Acids and Bases Definitions
3.6: Polyatomic Ions
hydroxide ions
3.11: H⊕ and OH⊖ Ions - An Introduction to Acids and Bases
hypertonic solutions
9.10: Osmosis and Osmotic Pressure
hypothesis
1.1: Chemistry - The Central Science

I

ideal gas
8.3: Gases and the Kinetic-Molecular Theory
ideal gas law
8: Gases, Liquids, and Solids
8.10: The Ideal Gas Law
8.9: Avogadro's Law - The Relation between Volume and Molar Amount
IDLs
24.2: Lipoproteins for Lipid Transport
immunity
29: Body Fluids
important monosaccharides
20: Carbohydrates
incomplete
10.7: Acid and Base Equivalents
12.5: The Shapes of Organic Molecules
14.1: Alcohols, Phenols, and Ethers
15.7: Addition of Alcohols - Hemiacetals and Acetals
21.5: Strategies of Metabolism - Metabolic Pathways and Coupled Reactions
incomplete work
13.10: Reactions of Aromatic Compounds
indicator
10.11: Titration
industrial applications
13.7: Alkene Polymers
inhibition
19: Enzymes and Vitamins
inhibitor
19.6: Enzyme Regulation - Inhibition
inorganic acids
17.6: Phosphoric Acid Derivatives
inorganic compounds
4.6: Molecular Formulas and Lewis Structures
insoluble in water
13.4: Properties of Alkenes and Alkynes
insulin
18.6: Protein Structure- An Overview and Primary Protein Structure
integral proteins
23.7: Cell Membranes- Structure and Transport
intermolecular forces
4.5: Characteristics of Molecular Compounds
8: Gases, Liquids, and Solids
8.1: States of Matter and Their Changes
8.12: Liquids
8.2: Intermolecular Forces
intermolecular hydrogen bonding
14.7: Ethers
intrachain bonding
18.7: Secondary Protein Structure
ion
3.1: Ions
ion charge
3.3: Ions of Some Common Elements
ion charges
3.5: Naming Monoatomic Ions
ion formulas
3.6: Polyatomic Ions
ion names
3.6: Polyatomic Ions
ion product
10.4: Water as Both an Acid and a Base
ionic
5.3: Precipitation Reactions and Solubility Guidelines
8.13: Solids
ionic bond
3.7: Ionic Bonds
3.8: Formulas of Ionic Compounds
4.9: Polar Covalent Bonds and Electronegativity
ionic bonding
18.8: Tertiary Protein Structure
ionic bonds
3: Ionic Compounds
ionic compound
10.9: Acidity and Basicity of Salt Solutions
3.7: Ionic Bonds
3.8: Formulas of Ionic Compounds
ionic compounds
3.10: Some Properties of Ionic Compounds
3.11: H⊕ and OH⊖ Ions - An Introduction to Acids and Bases
3.9: Naming Ionic Compounds
4.5: Characteristics of Molecular Compounds
5: Classification and Balancing of Chemical Reactions
6.1: The Mole and Avogadro's Number
9.2: The Solution Process
9.9: Properties of Solutions
ionic equations
5.7: Net Ionic Equations
ionic solute
9.8: Ions in Solution - Electrolytes

ionization
10: Acids and Bases
10.2: Acid and Base Strength
10.3: Acid Dissociation Constants
17.2: Acidity of Carboxylic Acids
ionization energy
3.4: Periodic Properties and Ion Formation
ionizing radiation
11: Nuclear Chemistry
11.6: Ionizing Radiation
ions
2.2: Elements and Atomic Number
3: Ionic Compounds
3.2: Ions and the Octet Rule
irreversible
19.6: Enzyme Regulation - Inhibition
isoelectric point
18.4: Acid-Base Properties of Amino Acids
isomer classification
13.3: The Structure of Alkenes- Cis-Trans Isomerism
isomerism
13: Alkenes, Alkynes, and Aromatic Compounds
isomers
12: Introduction to Organic Chemistry - Alkanes
12.3: The Structure of Organic Molecules - Alkanes and Their Isomers
12.4: Drawing Organic Structures
12.6: Naming Alkanes
13.1: Alkenes and Alkynes
isotonic solutions
9.10: Osmosis and Osmotic Pressure
isotopes
11: Nuclear Chemistry
11.1: Nuclear Reactions
11.5: Radioactive Half-Life
11.8: Artificial Transmutation
2: Atoms and the Periodic Table
2.2: Elements and Atomic Number
2.3: Isotopes and Atomic Weight
IUPAC
12.6: Naming Alkanes
13.2: Naming Alkenes and Alkynes
13.9: Naming Aromatic Compounds
15.2: Naming Aldehydes and Ketones

J

John Dalton
2.1: Atomic Theory and the Structure of Atoms

K

K_a
10.3: Acid Dissociation Constants
Kelvin
1.11: Temperature, Heat, and Energy
Kelvin scale
8.6: Charles's Law- The Relation between Volume and Temperature
ketohexose
20.4: Some Important Monosaccharides
ketone
15.1: The Carbonyl Group
Ketone bodies
24: Lipid Metabolism
24.6: Ketone Bodies and Ketoacidosis
ketones
15: Aldehydes and Ketones
15.2: Naming Aldehydes and Ketones
15.3: Properties of Aldehydes and Ketones
15.4: Some Common Aldehydes and Ketones
15.5: Oxidation of Aldehydes
20.3: Structure of Glucose and Other Monosaccharides
ketosis
24.6: Ketone Bodies and Ketoacidosis
key takeaway
6.3: Mole Relationships and Chemical Equations
kidney
25: Protein and Amino Acid Metabolism
25.3: Amino Acid Catabolism - The Amino Group
29: Body Fluids
kidney function
25.4: The Urea Cycle
kidneys
29.8: Urine Composition and Function
9.11: Dialysis
kinetic energy
7.1: Energy and Chemical Bonds
8.1: States of Matter and Their Changes
kinetic theory
8: Gases, Liquids, and Solids
8.3: Gases and the Kinetic-Molecular Theory
KNO3
9.4: The Effect of Temperature on Solubility
Krebs cycle
21.7: The Citric Acid Cycle
21.8: The Electron-Transport Chain and ATP Production
Kw
10.4: Water as Both an Acid and a Base

L

laboratory measurements
1.12: Density and Specific Gravity
lactose
20.5: Reactions of Monosaccharides
law of conservation of matter
5.1: Chemical Equations
laws of physics
1.12: Density and Specific Gravity
LDLs
24.2: Lipoproteins for Lipid Transport
learning
1.7: Measuring Mass, Length, and Volume
19.3: Enzyme Classification
5.3: Precipitation Reactions and Solubility Guidelines
learning objective
9.7: Dilution
learning objectives
1.10: Problem Solving - Unit Conversions and Estimating Answers
1.6: Physical Quantities - Units and Scientific Notation
11.6: Ionizing Radiation
12.2: Families of Organic Molecules - Functional Groups
12.3: The Structure of Organic Molecules - Alkanes and Their Isomers
12.7: Properties of Alkanes
12.8: Reactions of Alkanes
13.4: Properties of Alkenes and Alkynes
14.4: Reactions of Alcohols
14.7: Ethers
16.7: Amines in Plants- Alkaloids
17.2: Acidity of Carboxylic Acids
17.3: Reactions of Carboxylic Acids - Ester and Amide Formation
17.4: Hydrolysis of Esters and Amides
17.6: Phosphoric Acid Derivatives
18.8: Tertiary Protein Structure
19.1: Catalysis by Enzymes
19.7: Enzyme Regulation- Allosteric Control and Feedback Inhibition
2.1: Atomic Theory and the Structure of Atoms
2.4: The Periodic Table
2.5: Some Characteristics of Different Groups
2.6: Electronic Structure of Atoms
20.3: Structure of Glucose and Other Monosaccharides
23.6: Steroids
25.2: Amino Acid Metabolism - An Overview
3.8: Formulas of Ionic Compounds
4.2: Covalent Bonds and the Periodic Table
4.3: Multiple Covalent Bonds
4.8: The Shapes of Molecules
5.7: Net Ionic Equations
6.1: The Mole and Avogadro's Number
6.3: Mole Relationships and Chemical Equations
7.3: Exothermic and Endothermic Reactions
8.1: States of Matter and Their Changes
8.3: Gases and the Kinetic-Molecular Theory
8.4: Pressure
8.6: Charles's Law- The Relation between Volume and Temperature
8.7: Gay-Lussac's Law- The Relationship Between Pressure and Temperature
8.8: The Combined Gas Law
8.9: Avogadro's Law - The Relation between Volume and Molar Amount
9.2: The Solution Process
9.3: Solubility
9.5: The Effect of Pressure on Solubility - Henry's Law
9.9: Properties of Solutions
learning outcomes
21.8: The Electron-Transport Chain and ATP Production
7.6: Effects of Temperature, Concentration, and Catalysts on Reaction Rates
lechatelierprinciple
7.9: Le Chatelier's Principle- The Effect of Changing Conditions on Equilibria
length
1.6: Physical Quantities - Units and Scientific Notation
1.7: Measuring Mass, Length, and Volume
Lewis structure
4.2: Covalent Bonds and the Periodic Table
Lewis structures
4: Molecular Compounds
4.1: Covalent Bonds
4.3: Multiple Covalent Bonds
4.7: Drawing Lewis Structures

Lewis Symbols
2.9: Electron-Dot Symbols
LibreTexts
10.7: Acid and Base Equivalents
10.8: Some Common Acid-Base Reactions
12.5: The Shapes of Organic Molecules
13.10: Reactions of Aromatic Compounds
13.5: Types of Organic Reactions
14.1: Alcohols, Phenols, and Ethers
14.10: Stereochemistry and Chirality
14.2: Naming Alcohols
14.3: Properties of Alcohols
14.6: Acidity of Alcohols and Phenols
15.6: Reduction of Aldehydes and Ketones
15.7: Addition of Alcohols - Hemiacetals and Acetals
16.6: Amine Salts
19.8: Enzyme Regulation - Covalent Modification and Genetic Control
19.9: Vitamins, Antioxidants, and Minerals
20.1: An Introduction to Carbohydrates
20.2: Handedness of Carbohydrates
21.5: Strategies of Metabolism - Metabolic Pathways and Coupled Reactions
21.6: Strategies of Metabolism- Oxidized and Reduced Coenzymes
22.2: Glucose Metabolism - An Overview
22.4: Entry of Other Sugars into Glycolysis
22.5: The Fate of Pyruvate
22.6: Energy Output in Complete Glucose Catabolism
22.7: Regulation of Glucose Metabolism and Metabolism During Stress
22.8: Glycogen Metabolism- Glycogenesis and Glycogenolysis
22.9: Gluconeogenesis- Glucose Synthesis from Noncarbohydrates
23.3: Properties of Fats and Oils
23.4: Chemical Reactions of Triacylglycerols
23.5: Phospholipids and Glycolipids
26.1: DNA, Chromosomes, and Genes
26.10: Translation- tRNA and Protein Synthesis
26.2: Composition of Nucleic Acids
26.3: The Structure of Nucleic Acid Chains
26.4: Base Pairing in DNA- The Watson-Crick Model
26.5: Nucleic Acids and Heredity
26.6: Replication of DNA
26.7: Structure and Function of RNA
26.8: Transcription - RNA Synthesis
26.9: The Genetic Code
27.2: DNA and Chromosomes
27.3: Mutations and Polymorphisms
27.4: Recombinant DNA
28.1: Messenger Molecules
28.2: Hormones and the Endocrine System
28.3: How Hormones Work - Epinephrine and Fight-or-Flight
28.4: Amino Acid Derivatives and Polypeptides as Hormones
28.5: Neurotransmitters
29.2: Fluid Balance
29.6: Red Blood Cells and Blood Gases
29.7: The Kidney and Urine Formation
limiting reagent
6: Chemical Reactions - Mole and Mass Relationships
6.5: Limiting Reagent and Percent Yield
line structures
12.4: Drawing Organic Structures
Linus Pauling
4.9: Polar Covalent Bonds and Electronegativity
lipases
24.1: Digestion of Triacylglycerols
lipid digestion
24.1: Digestion of Triacylglycerols
lipid metabolism
23.6: Steroids
24.3: Triacylglycerol Metabolism - An Overview
lipid transport
24: Lipid Metabolism
lipids
15.4: Some Common Aldehydes and Ketones
18.1: An Introduction to Biochemistry
21.1: Energy, Life, and Biochemical Reactions
23: Lipids
23.1: Structure and Classification of Lipids
23.2: Fatty Acids and Their Esters
24.5: Oxidation of Fatty Acids
Lipogenesis
24.7: Biosynthesis of Fatty Acids
lipoproteins
24: Lipid Metabolism
24.2: Lipoproteins for Lipid Transport
liposomes
23.7: Cell Membranes- Structure and Transport
liquid
1.2: States of Matter
liquids
8.12: Liquids
lithium
2.9: Electron-Dot Symbols
liver
24.6: Ketone Bodies and Ketoacidosis
25: Protein and Amino Acid Metabolism
25.3: Amino Acid Catabolism - The Amino Group
25.4: The Urea Cycle
living organisms
18.1: An Introduction to Biochemistry
London dispersion forces
8.2: Intermolecular Forces
lone pair
4.4: Coordinate Covalent Bonds
lone pairs
4.8: The Shapes of Molecules

M

macronutrients
7.1: Energy and Chemical Bonds
macroscopic gas properties
8.4: Pressure
magnesium
1.4: Chemical Elements and Symbols
main group elements
2.4: The Periodic Table
3.9: Naming Ionic Compounds
maltase
20.6: Common Disaccharides
maltose
20.5: Reactions of Monosaccharides
20.6: Common Disaccharides
22.1: Digestion of Carbohydrates
mammals
25.4: The Urea Cycle
manganese
1.4: Chemical Elements and Symbols
manganese oxide
7.6: Effects of Temperature, Concentration, and Catalysts on Reaction Rates
mapping
27: Genomics
maps
10.7: Acid and Base Equivalents
10.8: Some Common Acid-Base Reactions
12.5: The Shapes of Organic Molecules
13.10: Reactions of Aromatic Compounds
13.5: Types of Organic Reactions
14.1: Alcohols, Phenols, and Ethers
14.10: Stereochemistry and Chirality
14.2: Naming Alcohols
14.3: Properties of Alcohols
14.6: Acidity of Alcohols and Phenols
15.6: Reduction of Aldehydes and Ketones
15.7: Addition of Alcohols - Hemiacetals and Acetals
16.6: Amine Salts
19.8: Enzyme Regulation - Covalent Modification and Genetic Control
19.9: Vitamins, Antioxidants, and Minerals
20.1: An Introduction to Carbohydrates
20.2: Handedness of Carbohydrates
21.5: Strategies of Metabolism - Metabolic Pathways and Coupled Reactions
21.6: Strategies of Metabolism- Oxidized and Reduced Coenzymes
22.2: Glucose Metabolism - An Overview
22.4: Entry of Other Sugars into Glycolysis
22.5: The Fate of Pyruvate
22.6: Energy Output in Complete Glucose Catabolism
22.7: Regulation of Glucose Metabolism and Metabolism During Stress
22.8: Glycogen Metabolism- Glycogenesis and Glycogenolysis
22.9: Gluconeogenesis- Glucose Synthesis from Noncarbohydrates
23.3: Properties of Fats and Oils
23.4: Chemical Reactions of Triacylglycerols
23.5: Phospholipids and Glycolipids
26.1: DNA, Chromosomes, and Genes
26.10: Translation- tRNA and Protein Synthesis
26.2: Composition of Nucleic Acids
26.3: The Structure of Nucleic Acid Chains
26.4: Base Pairing in DNA- The Watson-Crick Model
26.5: Nucleic Acids and Heredity
26.6: Replication of DNA
26.7: Structure and Function of RNA
26.8: Transcription - RNA Synthesis
26.9: The Genetic Code
27.2: DNA and Chromosomes
27.3: Mutations and Polymorphisms
27.4: Recombinant DNA
28.1: Messenger Molecules
28.2: Hormones and the Endocrine System
28.3: How Hormones Work - Epinephrine and Fight-or-Flight
28.4: Amino Acid Derivatives and Polypeptides as Hormones
28.5: Neurotransmitters
29.2: Fluid Balance
29.6: Red Blood Cells and Blood Gases
29.7: The Kidney and Urine Formation
mass
1.12: Density and Specific Gravity
1.6: Physical Quantities - Units and Scientific Notation
1.7: Measuring Mass, Length, and Volume
6.2: Gram-Mole Conversions
mass number
11.1: Nuclear Reactions
2: Atoms and the Periodic Table
2.2: Elements and Atomic Number
mass relationships
6: Chemical Reactions - Mole and Mass Relationships
Matching
22.5: The Fate of Pyruvate

matching materials
10.8: Some Common Acid-Base Reactions
14.6: Acidity of Alcohols and Phenols

materials
1.12: Density and Specific Gravity
10.7: Acid and Base Equivalents
10.8: Some Common Acid-Base Reactions
12.5: The Shapes of Organic Molecules
13.10: Reactions of Aromatic Compounds
13.5: Types of Organic Reactions
14.1: Alcohols, Phenols, and Ethers
14.10: Stereochemistry and Chirality
14.2: Naming Alcohols
14.3: Properties of Alcohols
15.6: Reduction of Aldehydes and Ketones
15.7: Addition of Alcohols - Hemiacetals and Acetals
16.6: Amine Salts
19.8: Enzyme Regulation - Covalent Modification and Genetic Control
19.9: Vitamins, Antioxidants, and Minerals
20.1: An Introduction to Carbohydrates
20.2: Handedness of Carbohydrates
21.5: Strategies of Metabolism - Metabolic Pathways and Coupled Reactions
22.2: Glucose Metabolism - An Overview
22.4: Entry of Other Sugars into Glycolysis
22.5: The Fate of Pyruvate
22.6: Energy Output in Complete Glucose Catabolism
22.7: Regulation of Glucose Metabolism and Metabolism During Stress
22.8: Glycogen Metabolism- Glycogenesis and Glycogenolysis
22.9: Gluconeogenesis- Glucose Synthesis from Noncarbohydrates
23.3: Properties of Fats and Oils
26.10: Translation- tRNA and Protein Synthesis
26.2: Composition of Nucleic Acids
26.4: Base Pairing in DNA- The Watson-Crick Model
26.6: Replication of DNA
26.8: Transcription - RNA Synthesis
27.2: DNA and Chromosomes
27.3: Mutations and Polymorphisms
27.4: Recombinant DNA
28.1: Messenger Molecules
28.2: Hormones and the Endocrine System
28.3: How Hormones Work - Epinephrine and Fight-or-Flight
28.5: Neurotransmitters
29.2: Fluid Balance
29.7: The Kidney and Urine Formation

mathematical formula
8.5: Boyle's Law - The Relation between Volume and Pressure

matter
1: Matter and Measurements
1.1: Chemistry - The Central Science
1.2: States of Matter
1.3: Classification of Matter
1.4: Chemical Elements and Symbols

matter properties
8: Gases, Liquids, and Solids

measurement
1: Matter and Measurements
1.7: Measuring Mass, Length, and Volume
1.8: Measurement and Significant Figures

measurements
1.10: Problem Solving - Unit Conversions and Estimating Answers
1.6: Physical Quantities - Units and Scientific Notation

measuring radiation
11.7: Detecting and Measuring Radiation

medical importance
16.4: Heterocyclic Nitrogen Compounds

medical terminology
14.8: Thiols and Disulfides

medicinal chemistry
14.7: Ethers

medicinal plants
16.7: Amines in Plants- Alkaloids

melting point
1.2: States of Matter

melting points
12.1: The Nature of Organic Molecules
3.10: Some Properties of Ionic Compounds
4.5: Characteristics of Molecular Compounds
8.2: Intermolecular Forces

membrane
9.11: Dialysis

membrane lipids
23.7: Cell Membranes- Structure and Transport

membrane proteins
18.2: Proteins and Their Functions- An Overview

membranes
23.1: Structure and Classification of Lipids

mercury column
8.4: Pressure

messenger molecules
28: Chemical Messengers- Hormones, Neurotransmitters, and Drugs

metabolic fuel
24.6: Ketone Bodies and Ketoacidosis

metabolic intermediates
21.7: The Citric Acid Cycle

metabolic pathways
21: The Generation of Biochemical Energy
21.3: An Overview of Metabolism and Energy Production
24.2: Lipoproteins for Lipid Transport
24.7: Biosynthesis of Fatty Acids
25.6: Biosynthesis of Nonessential Amino Acids

metabolic processes
19.5: Factors Affecting Enzyme Activity

metabolic reactions
7.1: Energy and Chemical Bonds

metabolic waste
29.8: Urine Composition and Function

metabolism
15.4: Some Common Aldehydes and Ketones
19.2: Enzyme Cofactors
19.6: Enzyme Regulation - Inhibition
20.7: Some Important Polysaccharides Based on Glucose
21: The Generation of Biochemical Energy
21.1: Energy, Life, and Biochemical Reactions
21.3: An Overview of Metabolism and Energy Production
22: Carbohydrate Metabolism
24.3: Triacylglycerol Metabolism - An Overview
25: Protein and Amino Acid Metabolism
25.3: Amino Acid Catabolism - The Amino Group
25.6: Biosynthesis of Nonessential Amino Acids

metabolites
21.1: Energy, Life, and Biochemical Reactions

metallic
8.13: Solids

metalloids
2.4: The Periodic Table

metals
2.4: The Periodic Table

methane
12.8: Reactions of Alkanes

methanol
4.6: Molecular Formulas and Lewis Structures

methylamine
16.5: Basicity of Amines

metric system
1.10: Problem Solving - Unit Conversions and Estimating Answers
1.6: Physical Quantities - Units and Scientific Notation
1.8: Measurement and Significant Figures

micelles
23.7: Cell Membranes- Structure and Transport

missing
14.2: Naming Alcohols
19.8: Enzyme Regulation - Covalent Modification and Genetic Control
22.7: Regulation of Glucose Metabolism and Metabolism During Stress

missing pages
23.4: Chemical Reactions of Triacylglycerols

mitochondria
21.2: Cells and Their Structure

mixtures
1.3: Classification of Matter
9: Solutions
9.1: Mixtures and Solutions

mobilization
24: Lipid Metabolism

modern atomic theory
2.1: Atomic Theory and the Structure of Atoms

molar mass
13.4: Properties of Alkenes and Alkynes
6.1: The Mole and Avogadro's Number
6.2: Gram-Mole Conversions
6.4: Mass Relationships and Chemical Equations
6.5: Limiting Reagent and Percent Yield
9.6: Units of Concentration

molar volume
8.9: Avogadro's Law - The Relation between Volume and Molar Amount

molarity
7.8: Equilibrium Equations and Equilibrium Constants
9.6: Units of Concentration
9.7: Dilution

mole
6: Chemical Reactions - Mole and Mass Relationships

molecular
4.11: Naming Binary Molecular Compounds
8.13: Solids

molecular bonding
4.1: Covalent Bonds
4.4: Coordinate Covalent Bonds

molecular compounds
4: Molecular Compounds
4.5: Characteristics of Molecular Compounds
9.9: Properties of Solutions

molecular equation
5.7: Net Ionic Equations

molecular formula
12.3: The Structure of Organic Molecules - Alkanes and Their Isomers
4.6: Molecular Formulas and Lewis Structures

molecular formulas
12.4: Drawing Organic Structures
4: Molecular Compounds

molecular geometry
13.3: The Structure of Alkenes- Cis-Trans Isomerism
4.10: Polar Molecules
4.8: The Shapes of Molecules
molecular ions
4.7: Drawing Lewis Structures
molecular mass
6.1: The Mole and Avogadro's Number
molecular polarity
4.10: Polar Molecules
Molecular Shapes
4.8: The Shapes of Molecules
molecular structure
12.4: Drawing Organic Structures
12.9: Cycloalkanes
molecules
3: Ionic Compounds
moles
6.2: Gram-Mole Conversions
6.4: Mass Relationships and Chemical Equations
8.10: The Ideal Gas Law
9.6: Units of Concentration
moles of solute
9.7: Dilution
monatomic ions
3.5: Naming Monoatomic Ions
5.6: Recognizing Redox Reactions
monomers
13.7: Alkene Polymers
monosaccharides
20: Carbohydrates
20.3: Structure of Glucose and Other Monosaccharides
20.4: Some Important Monosaccharides
20.5: Reactions of Monosaccharides
morphine
16.7: Amines in Plants- Alkaloids
motion
8.3: Gases and the Kinetic-Molecular Theory
multiple covalent bonds
4: Molecular Compounds
multiplication
1.9: Rounding Off Numbers
muscles
25: Protein and Amino Acid Metabolism
25.3: Amino Acid Catabolism - The Amino Group
mutations
27: Genomics

N

NaCl
9.4: The Effect of Temperature on Solubility
NADH
21.7: The Citric Acid Cycle
21.8: The Electron-Transport Chain and ATP Production
naming
12.10: Drawing and Naming Cycloalkanes
14: Some Compounds with Oxygen, Sulfur, or a Halogen
15: Aldehydes and Ketones
4.11: Naming Binary Molecular Compounds
naming alkanes
12: Introduction to Organic Chemistry - Alkanes
naming amines
16: Amines
naming compounds
13.9: Naming Aromatic Compounds
naming conventions
15.1: The Carbonyl Group
15.2: Naming Aldehydes and Ketones
naming ionic compounds
3.9: Naming Ionic Compounds
naming ions
3.1: Ions
3.5: Naming Monoatomic Ions
naming organic compounds
13: Alkenes, Alkynes, and Aromatic Compounds
natural compounds
16.4: Heterocyclic Nitrogen Compounds
negative regulation
19.7: Enzyme Regulation- Allosteric Control and Feedback Inhibition
negatively charged amino acids
18.3: Amino Acids
neon
1.4: Chemical Elements and Symbols
nephron
29.8: Urine Composition and Function
9.11: Dialysis
net ionic equations
5.7: Net Ionic Equations
neurotransmitters
16.4: Heterocyclic Nitrogen Compounds
28: Chemical Messengers- Hormones, Neurotransmitters, and Drugs
neutral solution
10.5: Measuring Acidity in Aqueous Solutions- The pH Scale
neutralization
17.2: Acidity of Carboxylic Acids
5.4: Acids, Bases, and Neutralization Reactions
neutralization reactions
5: Classification and Balancing of Chemical Reactions
neutrons
11.1: Nuclear Reactions
2: Atoms and the Periodic Table
2.1: Atomic Theory and the Structure of Atoms
2.2: Elements and Atomic Number
2.3: Isotopes and Atomic Weight
NH3
9.4: The Effect of Temperature on Solubility
NH4NO3
3.10: Some Properties of Ionic Compounds
nicotine
16.7: Amines in Plants- Alkaloids
ninhydrin test
18.4: Acid-Base Properties of Amino Acids
nitric acid
17.6: Phosphoric Acid Derivatives
nitrogen
1.4: Chemical Elements and Symbols
16.2: Naming and Drawing Amines
25.3: Amino Acid Catabolism - The Amino Group
4.11: Naming Binary Molecular Compounds
4.3: Multiple Covalent Bonds
4.4: Coordinate Covalent Bonds
nitrogen atom
16.1: Classifying Amines
nitrogen excretion
25.2: Amino Acid Metabolism - An Overview
nitrogenous wastes
25.4: The Urea Cycle
Nobel Prize
4.9: Polar Covalent Bonds and Electronegativity
noble gas configuration
3.2: Ions and the Octet Rule
3.4: Periodic Properties and Ion Formation
noble gases
2.5: Some Characteristics of Different Groups
nomenclature
12.6: Naming Alkanes
13.2: Naming Alkenes and Alkynes
14.9: Halogen-Containing Compounds
15.2: Naming Aldehydes and Ketones
3.5: Naming Monoatomic Ions
noncompetitive
19.6: Enzyme Regulation - Inhibition
nonelectrolytes
9.8: Ions in Solution - Electrolytes
nonessential amino acids
25.6: Biosynthesis of Nonessential Amino Acids
nonionizing radiation
11.6: Ionizing Radiation
nonmetal atoms
4.1: Covalent Bonds
nonmetals
2.4: The Periodic Table
nonpolar
12.7: Properties of Alkanes
nonpolar amino acids
18.3: Amino Acids
nonpolar bond
4.9: Polar Covalent Bonds and Electronegativity
nonpolar molecules
12.8: Reactions of Alkanes
8.2: Intermolecular Forces
normal urine composition
29.8: Urine Composition and Function
nuclear accidents
11.9: Nuclear Fission and Nuclear Fusion
nuclear chemistry
11: Nuclear Chemistry
11.1: Nuclear Reactions
nuclear equations
11.4: Nuclear Decay
nuclear fission
11: Nuclear Chemistry
11.9: Nuclear Fission and Nuclear Fusion
nuclear fusion
11: Nuclear Chemistry
11.9: Nuclear Fission and Nuclear Fusion
nuclear medicine
11.8: Artificial Transmutation
nuclear physics
11.2: The Discovery and Nature of Radioactivity
11.8: Artificial Transmutation
nuclear power
11.9: Nuclear Fission and Nuclear Fusion
nuclear reaction
11.1: Nuclear Reactions

nuclear reactions
- 11: Nuclear Chemistry
- 11.3: Stable and Unstable Isotopes
- 11.4: Nuclear Decay
- 11.6: Ionizing Radiation
- 11.8: Artificial Transmutation

nuclear structure
- 11.1: Nuclear Reactions

nuclear symbol
- 2.3: Isotopes and Atomic Weight

nucleic acids
- 18.1: An Introduction to Biochemistry
- 26: Nucleic Acids and Protein Synthesis

numerical relationships
- 6.3: Mole Relationships and Chemical Equations

nutrients
- 25.6: Biosynthesis of Nonessential Amino Acids

nutrition
- 20: Carbohydrates

nylon
- 17.5: Polyamides and Polyesters

O

objectives
- 19.3: Enzyme Classification
- 5.3: Precipitation Reactions and Solubility Guidelines

octet rule
- 3: Ionic Compounds
- 3.2: Ions and the Octet Rule
- 3.3: Ions of Some Common Elements
- 4: Molecular Compounds
- 4.1: Covalent Bonds
- 4.2: Covalent Bonds and the Periodic Table
- 4.3: Multiple Covalent Bonds
- 4.7: Drawing Lewis Structures

oils
- 23.1: Structure and Classification of Lipids

online learning
- 26.5: Nucleic Acids and Heredity

open materials
- 22.9: Gluconeogenesis- Glucose Synthesis from Noncarbohydrates
- 23.3: Properties of Fats and Oils
- 23.4: Chemical Reactions of Triacylglycerols
- 23.5: Phospholipids and Glycolipids
- 26.1: DNA, Chromosomes, and Genes
- 26.10: Translation- tRNA and Protein Synthesis
- 26.2: Composition of Nucleic Acids
- 26.3: The Structure of Nucleic Acid Chains
- 26.5: Nucleic Acids and Heredity
- 26.7: Structure and Function of RNA
- 26.8: Transcription - RNA Synthesis
- 26.9: The Genetic Code
- 27.3: Mutations and Polymorphisms
- 28.1: Messenger Molecules
- 28.2: Hormones and the Endocrine System
- 28.4: Amino Acid Derivatives and Polypeptides as Hormones
- 28.5: Neurotransmitters
- 29.6: Red Blood Cells and Blood Gases

optimum pH
- 19.5: Factors Affecting Enzyme Activity

organelles
- 21.2: Cells and Their Structure

organic chemistry
- 12.1: The Nature of Organic Molecules
- 12.10: Drawing and Naming Cycloalkanes
- 12.4: Drawing Organic Structures
- 12.6: Naming Alkanes
- 12.9: Cycloalkanes
- 13: Alkenes, Alkynes, and Aromatic Compounds
- 13.2: Naming Alkenes and Alkynes
- 13.6: Addition Reactions of Alkenes
- 13.8: Aromatic Compounds and the Structure of Benzene
- 13.9: Naming Aromatic Compounds
- 14.5: Phenols
- 14.7: Ethers
- 14.9: Halogen-Containing Compounds
- 15.1: The Carbonyl Group
- 15.2: Naming Aldehydes and Ketones
- 15.3: Properties of Aldehydes and Ketones
- 15.5: Oxidation of Aldehydes
- 16.2: Naming and Drawing Amines
- 16.4: Heterocyclic Nitrogen Compounds
- 17.2: Acidity of Carboxylic Acids
- 17.4: Hydrolysis of Esters and Amides
- 18.1: An Introduction to Biochemistry
- 20: Carbohydrates

organic compounds
- 12.3: The Structure of Organic Molecules - Alkanes and Their Isomers
- 12.7: Properties of Alkanes
- 14.8: Thiols and Disulfides
- 4.6: Molecular Formulas and Lewis Structures

organic molecules
- 12: Introduction to Organic Chemistry - Alkanes
- 12.2: Families of Organic Molecules - Functional Groups

organic salts
- 17.2: Acidity of Carboxylic Acids

organic structures
- 12: Introduction to Organic Chemistry - Alkanes

osmolarity
- 9.10: Osmosis and Osmotic Pressure

osmosis
- 9: Solutions
- 9.10: Osmosis and Osmotic Pressure
- 9.11: Dialysis

osmotic pressure
- 9.10: Osmosis and Osmotic Pressure
- 9.9: Properties of Solutions

oxidation
- 14.4: Reactions of Alcohols
- 15: Aldehydes and Ketones
- 15.3: Properties of Aldehydes and Ketones
- 15.5: Oxidation of Aldehydes
- 21.7: The Citric Acid Cycle
- 24: Lipid Metabolism
- 5.5: Redox Reactions
- 5.6: Recognizing Redox Reactions

oxidation numbers
- 5.6: Recognizing Redox Reactions

oxidation reduction
- 5: Classification and Balancing of Chemical Reactions

oxidative phosphorylation
- 21.8: The Electron-Transport Chain and ATP Production

oxidizing agent
- 5.5: Redox Reactions

oxygen
- 4.3: Multiple Covalent Bonds

P

p block
- 2.8: Electron Configurations and the Periodic Table

page availability
- 21.6: Strategies of Metabolism- Oxidized and Reduced Coenzymes

pages
- 10.7: Acid and Base Equivalents
- 14.1: Alcohols, Phenols, and Ethers
- 14.2: Naming Alcohols
- 15.7: Addition of Alcohols - Hemiacetals and Acetals
- 16.6: Amine Salts
- 19.9: Vitamins, Antioxidants, and Minerals
- 20.2: Handedness of Carbohydrates
- 21.5: Strategies of Metabolism - Metabolic Pathways and Coupled Reactions
- 22.4: Entry of Other Sugars into Glycolysis
- 22.5: The Fate of Pyruvate
- 22.7: Regulation of Glucose Metabolism and Metabolism During Stress
- 22.8: Glycogen Metabolism- Glycogenesis and Glycogenolysis

pancreas
- 24.1: Digestion of Triacylglycerols

pancreatic juice
- 25.1: Digestion of Proteins

patient care
- 9.11: Dialysis

Pauli exclusion principle
- 2.7: Electron Configurations

penetrating power
- 11.2: The Discovery and Nature of Radioactivity

pepsin
- 25.1: Digestion of Proteins

pepsinogen
- 25.1: Digestion of Proteins

peptide
- 18.5: Peptides

peptide bond
- 18.5: Peptides

peptide bonds
- 18.10: Chemical Properties of Proteins
- 18.6: Protein Structure- An Overview and Primary Protein Structure

peptide chain
- 18.9: Quaternary Protein Structure

peptides
- 18: Amino Acids and Proteins
- 18.4: Acid-Base Properties of Amino Acids

percent yield
- 6: Chemical Reactions - Mole and Mass Relationships
- 6.5: Limiting Reagent and Percent Yield

periodic table
- 2: Atoms and the Periodic Table
- 2.3: Isotopes and Atomic Weight
- 2.4: The Periodic Table
- 2.5: Some Characteristics of Different Groups
- 2.6: Electronic Structure of Atoms
- 2.7: Electron Configurations
- 2.8: Electron Configurations and the Periodic Table
- 3: Ionic Compounds
- 3.2: Ions and the Octet Rule
- 3.3: Ions of Some Common Elements
- 3.4: Periodic Properties and Ion Formation
- 4: Molecular Compounds

periodic trends
2.5: Some Characteristics of Different Groups
3.4: Periodic Properties and Ion Formation
personal dosimeter
11.7: Detecting and Measuring Radiation
PET
17.3: Reactions of Carboxylic Acids - Ester and Amide Formation
petrochemical
13.1: Alkenes and Alkynes
pH
10.10: Buffer Solutions
10.6: Working with pH
18.4: Acid-Base Properties of Amino Acids
19.5: Factors Affecting Enzyme Activity
pH calculation
10.5: Measuring Acidity in Aqueous Solutions- The pH Scale
pH scale
10: Acids and Bases
10.5: Measuring Acidity in Aqueous Solutions- The pH Scale
10.6: Working with pH
pharmaceutical
1.10: Problem Solving - Unit Conversions and Estimating Answers
pharmacology
16.4: Heterocyclic Nitrogen Compounds
19.6: Enzyme Regulation - Inhibition
phase changes
8.1: States of Matter and Their Changes
8.14: Changes of State Calculations
8.2: Intermolecular Forces
phases
8.13: Solids
phenols
14: Some Compounds with Oxygen, Sulfur, or a Halogen
14.5: Phenols
phenylalanine
25.5: Amino Acid Catabolism - The Carbon Atoms
phosphate
21.4: Strategies of Metabolism - ATP and Energy Transfer
phosphate ion
3.6: Polyatomic Ions
phosphoanhydride bonds
17.6: Phosphoric Acid Derivatives
phospholipids
23: Lipids
phosphoric acid
17.6: Phosphoric Acid Derivatives
phosphoric acid derivatives
17: Carboxylic Acids and their Derivatives
phosphorylation
21.4: Strategies of Metabolism - ATP and Energy Transfer
photosynthesis
7.1: Energy and Chemical Bonds
physical change
1.1: Chemistry - The Central Science
physical characteristics
14.7: Ethers
physical properties
1: Matter and Measurements
1.1: Chemistry - The Central Science
1.2: States of Matter
1.3: Classification of Matter
12.1: The Nature of Organic Molecules
12.7: Properties of Alkanes
13.4: Properties of Alkenes and Alkynes
15.1: The Carbonyl Group
2.6: Electronic Structure of Atoms
3.10: Some Properties of Ionic Compounds
8.10: The Ideal Gas Law
8.2: Intermolecular Forces
8.8: The Combined Gas Law
9.1: Mixtures and Solutions
physical state
1.5: Chemical Reactions - Examples of Chemical Change
physics
11.8: Artificial Transmutation
physiological activity
18.5: Peptides
physiological effects
16.7: Amines in Plants- Alkaloids
physiology
14.8: Thiols and Disulfides
29.3: Blood
pKa
17.2: Acidity of Carboxylic Acids
plant cell walls
20.7: Some Important Polysaccharides Based on Glucose
plasma
29.3: Blood
plasma proteins
29: Body Fluids
platelets
29.3: Blood
polar amino acids
18.3: Amino Acids
polar bond
4.9: Polar Covalent Bonds and Electronegativity
polar interactions
4.5: Characteristics of Molecular Compounds
Polar Molecules
23.7: Cell Membranes- Structure and Transport
4.10: Polar Molecules
8.2: Intermolecular Forces
pollution
10.5: Measuring Acidity in Aqueous Solutions- The pH Scale
polyamides
17.5: Polyamides and Polyesters
Polyatomic Ions
3.6: Polyatomic Ions
4.7: Drawing Lewis Structures
5.2: Balancing Chemical Equations
polycyclic aromatic hydrocarbons
13.9: Naming Aromatic Compounds
polyesters
17.5: Polyamides and Polyesters
polyethylene
13.7: Alkene Polymers
polyethylene terephthalate
17.3: Reactions of Carboxylic Acids - Ester and Amide Formation
polymer
13.1: Alkenes and Alkynes
polymer synthesis
17.5: Polyamides and Polyesters
polymerization
17.5: Polyamides and Polyesters
polymers
13: Alkenes, Alkynes, and Aromatic Compounds
13.7: Alkene Polymers
polymorphisms
27: Genomics
polypeptide
18.5: Peptides
18.9: Quaternary Protein Structure
polypeptide chain
18.6: Protein Structure- An Overview and Primary Protein Structure
polypeptide chains
18.7: Secondary Protein Structure
polypeptides
28: Chemical Messengers- Hormones, Neurotransmitters, and Drugs
polypropylene
13.7: Alkene Polymers
polyprotic acids
10.3: Acid Dissociation Constants
polysaccharides
20: Carbohydrates
20.7: Some Important Polysaccharides Based on Glucose
polytetrafluoroethylene
13.7: Alkene Polymers
polyvinyl chloride
13.7: Alkene Polymers
positive regulation
19.7: Enzyme Regulation- Allosteric Control and Feedback Inhibition
positron emission
11.4: Nuclear Decay
potential energy
7.1: Energy and Chemical Bonds
precipitation
5.3: Precipitation Reactions and Solubility Guidelines
precipitation reaction
5.7: Net Ionic Equations
precipitation reactions
5: Classification and Balancing of Chemical Reactions
precision
1.8: Measurement and Significant Figures
1.9: Rounding Off Numbers
prefixes
4.11: Naming Binary Molecular Compounds
pressure
8.10: The Ideal Gas Law
8.5: Boyle's Law - The Relation between Volume and Pressure
8.8: The Combined Gas Law
9.5: The Effect of Pressure on Solubility - Henry's Law
pressure calculations
8.4: Pressure
8.7: Gay-Lussac's Law- The Relationship Between Pressure and Temperature
pressure volume relationship
8.6: Charles's Law- The Relation between Volume and Temperature
8.9: Avogadro's Law - The Relation between Volume and Molar Amount

pressurechanges
7.9: Le Chatelier's Principle- The Effect of Changing Conditions on Equilibria
primary
16.2: Naming and Drawing Amines
primary alcohol
14.4: Reactions of Alcohols
primary amines
16.1: Classifying Amines
16.3: Properties of Amines
primary structure
18: Amino Acids and Proteins
18.6: Protein Structure- An Overview and Primary Protein Structure
problem solving
1.10: Problem Solving - Unit Conversions and Estimating Answers
products
1.5: Chemical Reactions - Examples of Chemical Change
5.1: Chemical Equations
5.2: Balancing Chemical Equations
6: Chemical Reactions - Mole and Mass Relationships
6.3: Mole Relationships and Chemical Equations
7.5: How Do Chemical Reactions Occur? Reaction Rates
7.8: Equilibrium Equations and Equilibrium Constants
project
10.7: Acid and Base Equivalents
12.5: The Shapes of Organic Molecules
13.5: Types of Organic Reactions
14.1: Alcohols, Phenols, and Ethers
14.10: Stereochemistry and Chirality
14.2: Naming Alcohols
15.6: Reduction of Aldehydes and Ketones
15.7: Addition of Alcohols - Hemiacetals and Acetals
16.6: Amine Salts
19.8: Enzyme Regulation - Covalent Modification and Genetic Control
19.9: Vitamins, Antioxidants, and Minerals
20.1: An Introduction to Carbohydrates
20.2: Handedness of Carbohydrates
21.5: Strategies of Metabolism - Metabolic Pathways and Coupled Reactions
22.2: Glucose Metabolism - An Overview
22.4: Entry of Other Sugars into Glycolysis
22.5: The Fate of Pyruvate
22.6: Energy Output in Complete Glucose Catabolism
22.7: Regulation of Glucose Metabolism and Metabolism During Stress
22.8: Glycogen Metabolism- Glycogenesis and Glycogenolysis
22.9: Gluconeogenesis- Glucose Synthesis from Noncarbohydrates
23.3: Properties of Fats and Oils
26.10: Translation- tRNA and Protein Synthesis
26.2: Composition of Nucleic Acids
26.6: Replication of DNA
26.8: Transcription - RNA Synthesis
27.3: Mutations and Polymorphisms
28.1: Messenger Molecules
28.2: Hormones and the Endocrine System
28.3: How Hormones Work - Epinephrine and Fight-or-Flight
28.5: Neurotransmitters
29.2: Fluid Balance
project completion
10.8: Some Common Acid-Base Reactions
14.6: Acidity of Alcohols and Phenols
21.6: Strategies of Metabolism- Oxidized and Reduced Coenzymes
23.4: Chemical Reactions of Triacylglycerols
26.3: The Structure of Nucleic Acid Chains
26.4: Base Pairing in DNA- The Watson-Crick Model
26.7: Structure and Function of RNA
27.4: Recombinant DNA
28.4: Amino Acid Derivatives and Polypeptides as Hormones
29.6: Red Blood Cells and Blood Gases
29.7: The Kidney and Urine Formation
project development
14.3: Properties of Alcohols
26.1: DNA, Chromosomes, and Genes
26.5: Nucleic Acids and Heredity
26.9: The Genetic Code
project management
13.10: Reactions of Aromatic Compounds
prokaryotic
21.2: Cells and Their Structure
propanone
15.1: The Carbonyl Group
properties
1.12: Density and Specific Gravity
14: Some Compounds with Oxygen, Sulfur, or a Halogen
15: Aldehydes and Ketones
17: Carboxylic Acids and their Derivatives
8.13: Solids
properties of alkanes
12: Introduction to Organic Chemistry - Alkanes
properties of amines
16: Amines
properties of amino acids
18.3: Amino Acids
properties of elements
2.5: Some Characteristics of Different Groups
properties of fats
23: Lipids
properties of matter
8.1: States of Matter and Their Changes
protein
18.10: Chemical Properties of Proteins
18.5: Peptides
18.7: Secondary Protein Structure
18.9: Quaternary Protein Structure
protein degradation
25.2: Amino Acid Metabolism - An Overview
protein digestion
25.1: Digestion of Proteins
protein folding
18.8: Tertiary Protein Structure
protein function
18.6: Protein Structure- An Overview and Primary Protein Structure
protein functions
18.10: Chemical Properties of Proteins
protein levels
18.6: Protein Structure- An Overview and Primary Protein Structure
protein metabolism
25.2: Amino Acid Metabolism - An Overview
protein stability
18.8: Tertiary Protein Structure
protein structure
18: Amino Acids and Proteins
18.10: Chemical Properties of Proteins
18.3: Amino Acids
18.6: Protein Structure- An Overview and Primary Protein Structure
19.4: How Enzymes Work
4.9: Polar Covalent Bonds and Electronegativity
protein synthesis
25.2: Amino Acid Metabolism - An Overview
proteins
14.8: Thiols and Disulfides
18: Amino Acids and Proteins
18.1: An Introduction to Biochemistry
18.2: Proteins and Their Functions- An Overview
18.4: Acid-Base Properties of Amino Acids
21.3: An Overview of Metabolism and Energy Production
25: Protein and Amino Acid Metabolism
proteinuria
29.8: Urine Composition and Function
proton acceptor
10.1: Acids and Bases Definitions
proton donor
10.1: Acids and Bases Definitions
protons
11: Nuclear Chemistry
11.1: Nuclear Reactions
2: Atoms and the Periodic Table
2.1: Atomic Theory and the Structure of Atoms
2.2: Elements and Atomic Number
2.3: Isotopes and Atomic Weight
3.1: Ions
psychotropic effects
16.7: Amines in Plants- Alkaloids
public
22.7: Regulation of Glucose Metabolism and Metabolism During Stress

public domain
10.7: Acid and Base Equivalents
10.8: Some Common Acid-Base Reactions
12.5: The Shapes of Organic Molecules
13.5: Types of Organic Reactions
14.1: Alcohols, Phenols, and Ethers
14.10: Stereochemistry and Chirality
14.2: Naming Alcohols
14.3: Properties of Alcohols
14.6: Acidity of Alcohols and Phenols
15.7: Addition of Alcohols - Hemiacetals and Acetals
16.6: Amine Salts
19.9: Vitamins, Antioxidants, and Minerals
20.1: An Introduction to Carbohydrates
20.2: Handedness of Carbohydrates
21.5: Strategies of Metabolism - Metabolic Pathways and Coupled Reactions
22.2: Glucose Metabolism - An Overview
22.4: Entry of Other Sugars into Glycolysis
22.5: The Fate of Pyruvate
22.8: Glycogen Metabolism- Glycogenesis and Glycogenolysis
22.9: Gluconeogenesis- Glucose Synthesis from Noncarbohydrates
23.3: Properties of Fats and Oils
23.5: Phospholipids and Glycolipids
26.10: Translation- tRNA and Protein Synthesis
26.2: Composition of Nucleic Acids
26.3: The Structure of Nucleic Acid Chains
26.4: Base Pairing in DNA- The Watson-Crick Model
26.5: Nucleic Acids and Heredity
26.6: Replication of DNA
26.7: Structure and Function of RNA
27.2: DNA and Chromosomes
27.3: Mutations and Polymorphisms
27.4: Recombinant DNA
28.1: Messenger Molecules
28.2: Hormones and the Endocrine System
28.3: How Hormones Work - Epinephrine and Fight-or-Flight
28.4: Amino Acid Derivatives and Polypeptides as Hormones
28.5: Neurotransmitters
29.2: Fluid Balance
29.6: Red Blood Cells and Blood Gases
29.7: The Kidney and Urine Formation
pure substances
1.3: Classification of Matter
pyruvate
22: Carbohydrate Metabolism
22.3: Glycolysis
25.3: Amino Acid Catabolism - The Amino Group

Q

quantitative analysis
6.4: Mass Relationships and Chemical Equations
quantities
1.7: Measuring Mass, Length, and Volume
quantum mechanics
2.6: Electronic Structure of Atoms
quantum numbers
2.6: Electronic Structure of Atoms
2.7: Electron Configurations
quaternary structure
18: Amino Acids and Proteins
18.9: Quaternary Protein Structure

R

radiation
11.2: The Discovery and Nature of Radioactivity
radiation absorbed dose
11.7: Detecting and Measuring Radiation
radiation exposure
11.7: Detecting and Measuring Radiation
radiation penetration
11.6: Ionizing Radiation
radiation types
11.2: The Discovery and Nature of Radioactivity
radiation units
11.7: Detecting and Measuring Radiation
radioactive decay
11: Nuclear Chemistry
11.1: Nuclear Reactions
11.3: Stable and Unstable Isotopes
11.4: Nuclear Decay
11.5: Radioactive Half-Life
11.8: Artificial Transmutation
radioactive isotopes
11.5: Radioactive Half-Life
radioactivity
11: Nuclear Chemistry
11.2: The Discovery and Nature of Radioactivity
11.3: Stable and Unstable Isotopes
radioisotopes
11.3: Stable and Unstable Isotopes
radiological safety
11.7: Detecting and Measuring Radiation
radiometric dating
11.5: Radioactive Half-Life
radionuclides
11.8: Artificial Transmutation
reactants
1.5: Chemical Reactions - Examples of Chemical Change
5: Classification and Balancing of Chemical Reactions
5.1: Chemical Equations
5.2: Balancing Chemical Equations
6: Chemical Reactions - Mole and Mass Relationships
6.3: Mole Relationships and Chemical Equations
7.5: How Do Chemical Reactions Occur? Reaction Rates
7.8: Equilibrium Equations and Equilibrium Constants
reaction
5.4: Acids, Bases, and Neutralization Reactions
reaction completion
6.5: Limiting Reagent and Percent Yield
reaction rate
19.5: Factors Affecting Enzyme Activity
7.5: How Do Chemical Reactions Occur? Reaction Rates
7.6: Effects of Temperature, Concentration, and Catalysts on Reaction Rates
reaction spontaneity
7.4: Why Do Chemical Reactions Occur? Free Energy
reactions
13.1: Alkenes and Alkynes
13.8: Aromatic Compounds and the Structure of Benzene
14: Some Compounds with Oxygen, Sulfur, or a Halogen
15.3: Properties of Aldehydes and Ketones
16.3: Properties of Amines
16.5: Basicity of Amines
17: Carboxylic Acids and their Derivatives
3.11: H⃞ and OH⃞ Ions - An Introduction to Acids and Bases
5.3: Precipitation Reactions and Solubility Guidelines
7: Chemical Reactions - Energy, Rates, and Equilibrium
reactions of alkanes
12: Introduction to Organic Chemistry - Alkanes
reactions of monosaccharides
20: Carbohydrates
reactionshift
7.9: Le Chatelier's Principle- The Effect of Changing Conditions on Equilibria
reactive molecules
4.4: Coordinate Covalent Bonds
reactivity
14.7: Ethers
reactor safety
11.9: Nuclear Fission and Nuclear Fusion
reagent
10.11: Titration
recombinant
27: Genomics
red blood cells
29: Body Fluids
29.3: Blood
redox
5.5: Redox Reactions
redox reactions
5: Classification and Balancing of Chemical Reactions
5.6: Recognizing Redox Reactions
reducing agent
5.5: Redox Reactions
reducing sugar
20.6: Common Disaccharides
reducing sugars
20.5: Reactions of Monosaccharides
reduction
15: Aldehydes and Ketones
5.5: Redox Reactions
5.6: Recognizing Redox Reactions
refolding
18.10: Chemical Properties of Proteins
regulation
22: Carbohydrate Metabolism
22.3: Glycolysis
regulatory mechanisms
19.7: Enzyme Regulation- Allosteric Control and Feedback Inhibition
Replication
26: Nucleic Acids and Protein Synthesis
representation of molecules
4.6: Molecular Formulas and Lewis Structures
respiration
21.1: Energy, Life, and Biochemical Reactions
8.5: Boyle's Law - The Relation between Volume and Pressure

respiratory system
8.5: Boyle's Law - The Relation between Volume and Pressure
restricted rotation
12.9: Cycloalkanes
reverse reaction
7.7: Reversible Reactions and Chemical Equilibrium
reversible
19.6: Enzyme Regulation - Inhibition
reversible reaction
7.7: Reversible Reactions and Chemical Equilibrium
ribosomes
21.2: Cells and Their Structure
ring strain
12.9: Cycloalkanes
RNA
26: Nucleic Acids and Protein Synthesis
rounding
1.9: Rounding Off Numbers

S

s block
2.8: Electron Configurations and the Periodic Table
safety
8.7: Gay-Lussac's Law- The Relationship Between Pressure and Temperature
salt
5.4: Acids, Bases, and Neutralization Reactions
salt hydrolysis
10.9: Acidity and Basicity of Salt Solutions
salt solution
10.9: Acidity and Basicity of Salt Solutions
salts
16.5: Basicity of Amines
saponification
17.4: Hydrolysis of Esters and Amides
saturated
13.1: Alkenes and Alkynes
23.2: Fatty Acids and Their Esters
9.3: Solubility
saturated compounds
12.9: Cycloalkanes
saturated hydrocarbons
12.3: The Structure of Organic Molecules - Alkanes and Their Isomers
Science
1.1: Chemistry - The Central Science
1.7: Measuring Mass, Length, and Volume
scientific method
1: Matter and Measurements
1.1: Chemistry - The Central Science
8.3: Gases and the Kinetic-Molecular Theory
scientific notation
1.6: Physical Quantities - Units and Scientific Notation
1.8: Measurement and Significant Figures
1.9: Rounding Off Numbers
secondary
16.2: Naming and Drawing Amines
secondary alcohol
14.4: Reactions of Alcohols
secondary amines
16.1: Classifying Amines
16.3: Properties of Amines
secondary structure
18: Amino Acids and Proteins
18.7: Secondary Protein Structure
18.9: Quaternary Protein Structure
semipermeable
9.11: Dialysis
semipermeable membranes
9.10: Osmosis and Osmotic Pressure
SI base units
1.6: Physical Quantities - Units and Scientific Notation
SI units
1.10: Problem Solving - Unit Conversions and Estimating Answers
side chains
18.3: Amino Acids
significant figure rules
1.8: Measurement and Significant Figures
significant figures
1.10: Problem Solving - Unit Conversions and Estimating Answers
1.8: Measurement and Significant Figures
1.9: Rounding Off Numbers
10.6: Working with pH
6.4: Mass Relationships and Chemical Equations
silver mirror
15.5: Oxidation of Aldehydes
small intestine
24.1: Digestion of Triacylglycerols
25: Protein and Amino Acid Metabolism
25.1: Digestion of Proteins
25.3: Amino Acid Catabolism - The Amino Group
SO2
9.4: The Effect of Temperature on Solubility
sodium
3.1: Ions
sodium acetate
9.4: The Effect of Temperature on Solubility
sodium bicarbonate
3.11: H⊕ and OH⊖ Ions - An Introduction to Acids and Bases
sodium chloride
3.10: Some Properties of Ionic Compounds
3.7: Ionic Bonds
3.8: Formulas of Ionic Compounds
sodium hydroxide
10.9: Acidity and Basicity of Salt Solutions
3.11: H⊕ and OH⊖ Ions - An Introduction to Acids and Bases
solar energy
7.1: Energy and Chemical Bonds
solid
1.2: States of Matter
8.13: Solids
solubility
12.7: Properties of Alkanes
15.3: Properties of Aldehydes and Ketones
16.3: Properties of Amines
16.5: Basicity of Amines
5.3: Precipitation Reactions and Solubility Guidelines
9: Solutions
9.2: The Solution Process
9.3: Solubility
9.4: The Effect of Temperature on Solubility
soluble in organic solvents
13.4: Properties of Alkenes and Alkynes
solute
9: Solutions
9.1: Mixtures and Solutions
9.10: Osmosis and Osmotic Pressure
9.2: The Solution Process
9.3: Solubility
9.4: The Effect of Temperature on Solubility
9.5: The Effect of Pressure on Solubility - Henry's Law
9.6: Units of Concentration
solutes
9.8: Ions in Solution - Electrolytes
Solution
9.5: The Effect of Pressure on Solubility - Henry's Law
9.6: Units of Concentration
solution preparation
9.7: Dilution
solutions
10.6: Working with pH
9: Solutions
9.1: Mixtures and Solutions
9.3: Solubility
9.9: Properties of Solutions
solvent
9: Solutions
9.1: Mixtures and Solutions
9.10: Osmosis and Osmotic Pressure
9.2: The Solution Process
9.3: Solubility
solvents
15.4: Some Common Aldehydes and Ketones
sparkling wines
8.11: Partial Pressure and Dalton's Law
specific gravity
1.12: Density and Specific Gravity
specific heat
8.14: Changes of State Calculations
spectator ions
5.7: Net Ionic Equations
spontaneous reactions
7.4: Why Do Chemical Reactions Occur? Free Energy
stability
11.3: Stable and Unstable Isotopes
11.8: Artificial Transmutation
stable bonds
4.1: Covalent Bonds
stable compounds
4.2: Covalent Bonds and the Periodic Table
stable ions
3.2: Ions and the Octet Rule
standard temperature and pressure
8.9: Avogadro's Law - The Relation between Volume and Molar Amount
starch
20.7: Some Important Polysaccharides Based on Glucose
22.1: Digestion of Carbohydrates
states of matter
1: Matter and Measurements
1.2: States of Matter
8: Gases, Liquids, and Solids
8.1: States of Matter and Their Changes
stereoisomers
20.3: Structure of Glucose and Other Monosaccharides
steroids
23: Lipids
23.6: Steroids

stimulants
16.4: Heterocyclic Nitrogen Compounds
stock solution
9.7: Dilution
stock system
3.5: Naming Monoatomic Ions
3.9: Naming Ionic Compounds
stoichiometric coefficients
1.5: Chemical Reactions - Examples of Chemical Change
stoichiometry
5.2: Balancing Chemical Equations
6.3: Mole Relationships and Chemical Equations
6.4: Mass Relationships and Chemical Equations
6.5: Limiting Reagent and Percent Yield
8.10: The Ideal Gas Law
8.9: Avogadro's Law - The Relation between Volume and Molar Amount
9.6: Units of Concentration
storage
23.1: Structure and Classification of Lipids
24: Lipid Metabolism
storage protein
18.2: Proteins and Their Functions- An Overview
strength
10: Acids and Bases
strength of acids
10.2: Acid and Base Strength
stressequilibrium
7.9: Le Chatelier's Principle- The Effect of Changing Conditions on Equilibria
strong acid
10.10: Buffer Solutions
10.2: Acid and Base Strength
10.9: Acidity and Basicity of Salt Solutions
strong base
10.2: Acid and Base Strength
strong electrolytes
9.8: Ions in Solution - Electrolytes
structural analysis
4.8: The Shapes of Molecules
structural classes
18.2: Proteins and Their Functions- An Overview
structural difference
14.7: Ethers
structural formula
4.6: Molecular Formulas and Lewis Structures
structural formulas
12.4: Drawing Organic Structures
12.9: Cycloalkanes
13.3: The Structure of Alkenes- Cis-Trans Isomerism
15.2: Naming Aldehydes and Ketones
structural isomers
12.3: The Structure of Organic Molecules - Alkanes and Their Isomers
structural properties
12.1: The Nature of Organic Molecules
structural proteins
18.7: Secondary Protein Structure
structure
18.9: Quaternary Protein Structure
structure of atoms
2: Atoms and the Periodic Table
structure of glucose
20: Carbohydrates
study guides
21.6: Strategies of Metabolism- Oxidized and Reduced Coenzymes
subshells
2.8: Electron Configurations and the Periodic Table
substance characterization
1.12: Density and Specific Gravity
substituent groups
12.10: Drawing and Naming Cycloalkanes
substituents
12.6: Naming Alkanes
substitution
14.9: Halogen-Containing Compounds
Substrate
19.4: How Enzymes Work
substrate concentration
19.5: Factors Affecting Enzyme Activity
subtraction
1.9: Rounding Off Numbers
subunit
18.9: Quaternary Protein Structure
sucrose
20.5: Reactions of Monosaccharides
sugar
8.11: Partial Pressure and Dalton's Law
sugar structure
20.5: Reactions of Monosaccharides
sulfate ion
3.6: Polyatomic Ions
sulfur
14.8: Thiols and Disulfides
sulfuric acid
10.3: Acid Dissociation Constants
17.6: Phosphoric Acid Derivatives
suspensions
9.1: Mixtures and Solutions
synthesis
16.2: Naming and Drawing Amines
25.6: Biosynthesis of Nonessential Amino Acids
synthetic polymers
13.7: Alkene Polymers
systematic naming
12.6: Naming Alkanes

T

TCA cycle
21.7: The Citric Acid Cycle
temperature
1.11: Temperature, Heat, and Energy
1.2: States of Matter
1.6: Physical Quantities - Units and Scientific Notation
19.5: Factors Affecting Enzyme Activity
7: Chemical Reactions - Energy, Rates, and Equilibrium
7.6: Effects of Temperature, Concentration, and Catalysts on Reaction Rates
7.8: Equilibrium Equations and Equilibrium Constants
8.10: The Ideal Gas Law
8.12: Liquids
8.13: Solids
8.14: Changes of State Calculations
8.4: Pressure
8.5: Boyle's Law - The Relation between Volume and Pressure
8.7: Gay-Lussac's Law- The Relationship Between Pressure and Temperature
8.8: The Combined Gas Law
9.4: The Effect of Temperature on Solubility
temperature conversion
1.11: Temperature, Heat, and Energy
temperature effects
8.1: States of Matter and Their Changes
temperature scale
8.6: Charles's Law- The Relation between Volume and Temperature
temperaturechanges
7.9: Le Chatelier's Principle- The Effect of Changing Conditions on Equilibria
tertiary
16.2: Naming and Drawing Amines
tertiary alcohol
14.4: Reactions of Alcohols
tertiary amines
16.1: Classifying Amines
16.3: Properties of Amines
tertiary structure
18: Amino Acids and Proteins
18.8: Tertiary Protein Structure
18.9: Quaternary Protein Structure
textbook
14.1: Alcohols, Phenols, and Ethers
14.10: Stereochemistry and Chirality
14.3: Properties of Alcohols
21.6: Strategies of Metabolism- Oxidized and Reduced Coenzymes
26.1: DNA, Chromosomes, and Genes
26.8: Transcription - RNA Synthesis
28.2: Hormones and the Endocrine System
28.3: How Hormones Work - Epinephrine and Fight-or-Flight
29.2: Fluid Balance
textbook development
23.4: Chemical Reactions of Triacylglycerols
27.2: DNA and Chromosomes
textbooks
26.2: Composition of Nucleic Acids
26.6: Replication of DNA
27.4: Recombinant DNA
28.1: Messenger Molecules
textiles
17.5: Polyamides and Polyesters
theoretical yield
6.5: Limiting Reagent and Percent Yield
thermal energy
1.11: Temperature, Heat, and Energy
thermochemistry
7.2: Heat Changes during Chemical Reactions

thermodynamic temperature
8.7: Gay-Lussac's Law- The Relationship Between Pressure and Temperature
thermodynamics
7: Chemical Reactions - Energy, Rates, and Equilibrium
7.1: Energy and Chemical Bonds
7.4: Why Do Chemical Reactions Occur? Free Energy
7.5: How Do Chemical Reactions Occur? Reaction Rates
8.14: Changes of State Calculations
thiols
14: Some Compounds with Oxygen, Sulfur, or a Halogen
14.8: Thiols and Disulfides
time
1.6: Physical Quantities - Units and Scientific Notation
titrant
10.11: Titration
titration
10: Acids and Bases
10.11: Titration
Tollens reagent
15.5: Oxidation of Aldehydes
toxicity
13.8: Aromatic Compounds and the Structure of Benzene
14.5: Phenols
transamination
25.3: Amino Acid Catabolism - The Amino Group
25.5: Amino Acid Catabolism - The Carbon Atoms
25.6: Biosynthesis of Nonessential Amino Acids
transcription
26: Nucleic Acids and Protein Synthesis
transfer
7: Chemical Reactions - Energy, Rates, and Equilibrium
transition metals
2.4: The Periodic Table
3.3: Ions of Some Common Elements
3.9: Naming Ionic Compounds
transmutation
11.4: Nuclear Decay
11.8: Artificial Transmutation
transport
23: Lipids
transport protein
18.2: Proteins and Their Functions- An Overview
trends
12.7: Properties of Alkanes
13.4: Properties of Alkenes and Alkynes
triacylglycerol metabolism
24: Lipid Metabolism
triacylglycerols
23: Lipids
24: Lipid Metabolism
24.3: Triacylglycerol Metabolism - An Overview
triglycerides
23.1: Structure and Classification of Lipids
23.2: Fatty Acids and Their Esters
24.1: Digestion of Triacylglycerols
24.2: Lipoproteins for Lipid Transport
24.5: Oxidation of Fatty Acids
tripeptide
18.5: Peptides
triple bond
4.3: Multiple Covalent Bonds
trypsinogen
25.1: Digestion of Proteins
Type I ionic compounds
3.9: Naming Ionic Compounds
Type II ionic compounds
3.9: Naming Ionic Compounds
types of reactions
14.4: Reactions of Alcohols

U

uncertainty
1.8: Measurement and Significant Figures
unfinished
14.10: Stereochemistry and Chirality
14.6: Acidity of Alcohols and Phenols
20.1: An Introduction to Carbohydrates
unfinished pages
10.8: Some Common Acid-Base Reactions
unfinished projects
27.2: DNA and Chromosomes
unit conversion
1.10: Problem Solving - Unit Conversions and Estimating Answers
6.2: Gram-Mole Conversions
9.6: Units of Concentration
units
1.7: Measuring Mass, Length, and Volume
units of pressure
8.4: Pressure
unsaturated
13.1: Alkenes and Alkynes
9.3: Solubility
unsaturated fats
23.2: Fatty Acids and Their Esters
unsaturated hydrocarbons
13.8: Aromatic Compounds and the Structure of Benzene
unstable nuclei
11.4: Nuclear Decay
urea
29.8: Urine Composition and Function
urea cycle
25.4: The Urea Cycle
ureotelic animals
25.4: The Urea Cycle
uric acid
25.4: The Urea Cycle
urinary system
29.8: Urine Composition and Function
urinary tract infections
29.8: Urine Composition and Function
urine
29.8: Urine Composition and Function

V

valence electron
3.7: Ionic Bonds
valence electrons
2.8: Electron Configurations and the Periodic Table
2.9: Electron-Dot Symbols
3: Ionic Compounds
3.2: Ions and the Octet Rule
3.3: Ions of Some Common Elements
3.4: Periodic Properties and Ion Formation
4: Molecular Compounds
4.1: Covalent Bonds
4.2: Covalent Bonds and the Periodic Table
4.3: Multiple Covalent Bonds
4.7: Drawing Lewis Structures
valence shell
3.2: Ions and the Octet Rule
vapor pressure
8.12: Liquids
vapor pressure depression
9.9: Properties of Solutions
variable charge
3.9: Naming Ionic Compounds
variable charges
3.3: Ions of Some Common Elements
vitamin A
19.2: Enzyme Cofactors
vitamin C
19.2: Enzyme Cofactors
4.9: Polar Covalent Bonds and Electronegativity
vitamin D
19.2: Enzyme Cofactors
vitamins
19.2: Enzyme Cofactors
VLDLs
24.2: Lipoproteins for Lipid Transport
volume
1.12: Density and Specific Gravity
1.7: Measuring Mass, Length, and Volume
8.10: The Ideal Gas Law
8.4: Pressure
8.8: The Combined Gas Law
volumetric
10.11: Titration
VSEPR Theory
4.10: Polar Molecules
4.8: The Shapes of Molecules

W

waste disposal
6.5: Limiting Reagent and Percent Yield
waste removal
9.11: Dialysis
water
10.4: Water as Both an Acid and a Base
4: Molecular Compounds
5.4: Acids, Bases, and Neutralization Reactions
water formation
5.1: Chemical Equations
water solubility
4.5: Characteristics of Molecular Compounds
water solution
3.10: Some Properties of Ionic Compounds
weak acid
10.10: Buffer Solutions
10.2: Acid and Base Strength
10.3: Acid Dissociation Constants
weak acids
10.3: Acid Dissociation Constants
17.2: Acidity of Carboxylic Acids

weak base
10.2: Acid and Base Strength
10.9: Acidity and Basicity of Salt Solutions
weak electrolytes
9.8: Ions in Solution - Electrolytes
weight
1.7: Measuring Mass, Length, and Volume
white blood cells
29: Body Fluids
29.3: Blood
work
7.1: Energy and Chemical Bonds
work in progress
21.6: Strategies of Metabolism- Oxidized and Reduced Coenzymes

Y

yeast
8.11: Partial Pressure and Dalton's Law
yield
6.5: Limiting Reagent and Percent Yield

Z

zwitterions
18.4: Acid-Base Properties of Amino Acids

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GLOSSARY

A

Acetyl-CoA | A molecule that participates in many biochemical reactions in protein, carbohydrate and lipid metabolism. Its main function is to deliver the acetyl group to the citric acid cycle (Krebs cycle) to be oxidized for energy production.

addition polymerization | A reaction in which monomers add to one another to produce a polymeric product that contains all the atoms of the starting monomers.

addition reactions | A reaction in which substituent groups join to hydrocarbon molecules at points of unsaturation—the double or triple bonds.

alcohol | An organic compound with an OH functional group on an aliphatic carbon atom.

aldehyde | An organic compound with a carbonyl functional group that has an hydrogen atom attached and either a hydrocarbon group or a second hydrogen atom.

alkaloid | A nitrogen-containing organic compound obtained from plants that has physiological properties.

alkanes (or saturated hydrocarbons) | A hydrocarbon with only carbon-to-carbon single bonds and existing as a continuous chain of carbon atoms also bonded to hydrogen atoms

alkenes | A hydrocarbon with one or more carbon–carbon double bonds.

alkyl group | A hydrocarbon group derived from an alkane by removal of a hydrogen atom.

alkyl halide (or haloalkane) | A compound resulting from the replacement of a hydrogen atom of an alkane with a halogen atom.

Alkynes | A hydrocarbon with a carbon–carbon triple bond.

alloy | A solid solution of a metal with other substances dissolved in it.

alpha particle | A type of radioactive emission that is equivalent to a helium atom nucleus.

amide | An organic compound with a carbonyl group joined to a nitrogen atom from ammonia or an amine.

amine | An organic compound derived from ammonia by the replacement of one, two, or three of the hydrogens atoms by alkyl or aryl groups.

amino group | An NH_2 unit.

amorphous | A solid with no regular structure.

amphiprotic | A substance that can either donate or accept a proton, depending on the circumstances.

amylopectin | A branched polymer of glucose units found in starch.

anabolism | Metabolic reactions in which molecules are synthesized.

anaerobic metabolism | A biochemical process that takes place in the absence of oxygen.

anions | A negatively charged ion.

anomeric carbon | The carbon atom that was the carbonyl carbon atom in the straight-chain form of a monosaccharide.

anticodon | A set of three nucleotides on the tRNA that is complementary to, and pairs with, the codon on the mRNA.

antioxidants | A substance in foods that acts as a reducing agent.

aromatic compound | Any compound that contains a benzene ring or has certain benzene-like properties.

aromatic hydrocarbons | A hydrocarbon with a benzene-like structure.

aryl group | A group derived from an aromatic hydrocarbon by the removal of a hydrogen atom.

atomic bomb | A weapon that depends on a nuclear chain reaction to generate immense forces.

atomic mass | A weighted average of the masses of all the element's naturally occurring isotopes.

atomic mass unit | One-twelfth the mass of a ^{12}C atom.

atomic radius | The approximate size of an atom.

autoionization of water | The process by which water ionizes into hydronium ions and hydroxide ions as it acts as an acid and a base.

Avogadro's number | The value 6.022×10^{23}.

B

balanced | A property of a chemical equation when there are the same number of atoms of each element in the reactants and products.

base | A compound that increases the concentration of hydroxide ion (OH^-) in aqueous solution.

Base (or basic) units | A fundamental unit of SI.

beta particle | A type of radioactive emission that is equivalent to an electron.

Bilayers | A double layer of lipids arranged so that nonpolar tails are found between an inner surface and outer surface consisting of hydrophilic heads.

Bile | The yellowish green liquid produced in the liver.

biochemistry | The chemistry of molecules found in living organisms.

boiling point | The temperature at which a substance goes from a liquid to a gas (or from a gas to a liquid).

boiling point elevation | The raising of the boiling point of a solution versus the pure solvent.

bond length | The distance between two nuclei in a covalent bond.

Boyle's law | The gas law that relates pressure and volume.

Brønsted-Lowry base | A compound that accepts a hydrogen ion (H^+) in a reaction; a proton acceptor.

buffer | A solution that resists dramatic changes in pH.

C

calorie | A unit of energy widely used in the health professions and everyday life.

capacity | The amount of strong acid or base a buffer can counteract.

carbohydrates | A compound composed of carbon, hydrogen, and oxygen atoms that is a polyhydroxy aldehyde or ketone or a compound that can be broken down to form such a compound. It is one of the three main components of the human diet.

carboxyl group | A functional group that contains a carbon–oxygen bond and an OH group also attached to the same carbon atom.

carboxylic acids | An organic compound that has a carboxyl functional group.

cations | A positively charged ion.

cerebrosides | A sphingolipid that contains a fatty acid unit, a sphingosine unit, and galactose or glucose.

chain reaction | An exponential growth in a process.

Charles's law | The gas law that relates volume and absolute temperature.

chemical bond | A very strong attraction between two atoms.

chemical equilibrium (or equilibrium) | The condition in which the extent of a chemical reaction does not change any further.

chemical formula | A concise list of the elements in a compound and the ratios of these elements.

Chemical properties | A characteristic that describes how matter changes its chemical structure or composition.

chemical reaction | A representation of a chemical change.

chemical symbol | A one- or two-letter abbreviation for an element.

chiral carbon | A carbon atom that has four different groups attached to it.

Cholesterol | A steroid that is found in mammals.

cis-trans isomers (or geometric isomers) | Isomers that have different configurations because of the presence of a rigid structure such as a double bond or ring.

citric acid cycle | A cyclic sequence of reactions that brings about the oxidation of a two-C unit to carbon dioxide and water.

codon | A set of three nucleotides on the mRNA that specifies a particular amino acid.

coefficient | A number that gives the number of molecules of a substance in a balanced chemical equation.

coenzymes | A cofactor that is an organic molecule.

colligative properties | A characteristic of solutions that depends only on the number of dissolved particles.

combination (composition) reaction | A chemical reaction that makes a single substance from two or more reactants.

combined gas law | The gas law that relates pressure, volume, and absolute temperature.

combustion reaction | A chemical reaction in which a substance combines with molecular oxygen to make oxygen-containing compounds of other elements in the reaction.

competitive inhibitor | A compound that resembles a particular substrate and competes with the substrate for binding at the active site of an enzyme to slow the rate of the reaction.

complementary bases | Specific base pairings in the DNA double helix.

compound | A substance that can be broken down into chemically simpler components.

concentration | How much solute is dissolved in a certain amount of solvent.

condensed structural formulas | An organic chemical formula that shows the hydrogen atoms (or other atoms or groups) right next to the carbon atoms to which they are attached.

conversion factor | A fraction that has equivalent quantities in the numerator and the denominator but expressed in different units.

core electrons | An electron in a lower-numbered shell of an atom.

covalent network bonding | A type of interaction in which all the atoms in a sample are covalently bonded to other atoms.

curie (Ci) | A unit of radioactivity equal to 3.7×10^{10} decays per second.

cyclic hydrocarbons | A hydrocarbon with a ring of carbon atoms.

cycloalkanes | A cyclic hydrocarbon with only single bonds.

cytochromes | A protein that contains an iron porphyrin in which iron can alternate between Fe(II) and Fe(III).

cytoplasm | Everything between the cell membrane and the nuclear membrane.

D

decomposition reaction | A chemical reaction in which a single substance is converted into two or more products.

Denaturation | Any change in the three-dimensional structure of a macromolecule that renders it incapable of performing its assigned function.

Density | The mass of an object divided by its volume.

Derived units | A combinations of the SI base units.

diatomic molecules | A two-atom grouping that behaves as a single chemical entity.

digestion | The breakdown of food molecules by hydrolysis reactions into the individual monomer units in the mouth, stomach, and small intestine.

dipole-dipole interaction | An attraction between polar molecules.

Dispersion forces | A force caused by the instantaneous imbalance of electrons about a molecule.

dispersion forces (or London forces) | A force caused by the instantaneous imbalance of electrons about a molecule.

dissociation | The process of cations and anions of an ionic solute separating when the solute dissolves.

Disulfide linkages | A covalent bond that forms by the oxidation and linkage of two sulfur atoms from the side chains of two cysteine residues.

double bond | Two pairs of electrons being shared by two atoms in a molecule.

E

electron | A subatomic particle with a negative electric charge.

electron configuration | A shorthand description of the arrangement of electrons in an atom.

electron transport chain (or respiratory chain) | An organized sequence of oxidation-reduction reactions that ultimately transports electrons to oxygen, reducing it to water.

electronegativity | A relative measure of how strongly an atom attracts electrons when it forms a covalent bond.

emulsion | A dispersion of two liquids that do not normally mix.

enantiomers | Stereoisomers that are nonsuperimposable mirror images of each other.

endothermic | A process that absorbs energy.

Energy | The ability to do work.

equivalents (Eq) | One mole of charge (either positive or negative).

essential fatty acids | A fatty acid that must be obtained from the diet because it cannot be synthesized by the human body.

ester | An organic compound derived from a carboxylic acid and an alcohol in which the OH of the acid is replaced by an OR group.

esterification | The formation of an ester from a carboxylic acid and an alcohol.

ether | An organic compound that has an oxygen atom between two hydrocarbon groups.

Exact numbers | A number that is defined or counted.

exothermic | A process that gives off energy.

F

fats | A compound, composed largely of hydrocarbon chains, that supplies energy for the body.

Feedback inhibition | A normal biochemical process that makes use of noncompetitive inhibitors to control some enzymatic activity.

fibrous proteins | A protein that is elongated or fiberlike and insoluble in water.

formula mass | The sum of the masses of the elements in the formula of an ionic compound.

formula unit | A set of oppositely charged ions that compose an ionic compound.

freezing point depression | The lowering of the freezing point of a solution versus the pure solvent.

functional group | A structural arrangement of atoms and/or bonds that imparts a wide range of important properties to organic compounds.

Fusion | A nuclear process in which small nuclei are combined into larger nuclei, releasing energy.

G

galactosemia | A genetic disease caused by the absence of one of the enzymes needed to convert galactose to glucose.

gamma rays | A type of radioactive emission that is a very energetic form of electromagnetic radiation.

gangliosides | A sphingolipid that contains a fatty acid unit, a sphingosine unit, and a complex oligosaccharide.

gas law | A simple mathematical formula that relates two or more properties of a gas.

Gastric juice | A mixture of water, inorganic ions, hydrochloric acid, and various enzymes and proteins found in the stomach.

Geiger counter | An electrical device that detects radioactivity.

genes | The basic unit of heredity.

genetic code | The identification of each group of three nucleotides and its particular amino acid.

genetic diseases | A hereditary condition caused by an altered DNA sequence.

Globular proteins | A protein that is generally spherical in structure and soluble in water.

glycols | An alcohol with two OH functional groups.

glycolysis | The metabolic pathway in which glucose is broken down to two molecules of pyruvate with the corresponding production of ATP.

glycosidic linkage | The carbon–oxygen-carbon linkage between monosaccharide units in more complex carbohydrates, such as disaccharides or polysaccharides.

groups (or families) | A column of elements on the periodic table.

H

half reactions | A chemical reaction that shows only oxidation or reduction.

half-life | The amount of time it takes for one-half of a radioactive isotope to decay.

halogenated hydrocarbons | A hydrocarbon in which one or more hydrogen atoms has been replaced by a halogen atom.

halogenation | A reaction in which a halogen reacts at a carbon-to-carbon double or triple bond to add halogen atoms to carbon atoms.

heat | The transfer of energy from one part of the universe to another due to temperature differences.

heat of vaporization | The amount of heat per gram or per mole required for a phase change that occurs at the boiling point.

heterocyclic compounds | A cyclic compound in which one or more atoms in the ring is an element other than a carbon atom.

homogeneous mixtures | A mixture that acts as a single substance so that it is not obvious that two or more substances are present.

homologous series | Any family of compounds in which adjacent members differ from each other by a definite factor.

hydration | Solvation by water molecules.

Hydrogen bonding | Bonding between a highly electronegative oxygen atom or nitrogen atom and a hydrogen atom attached to another oxygen atom or nitrogen atom.

hydrogenation | A reaction in which hydrogen gas reacts at a carbon-to-carbon double or triple bond or a carbon-to-oxygen double bond to add hydrogen atoms to carbon atoms.

hydrolysis | The reaction of a substance with water.

I

ideal gas law | The gas law that relates volume, pressure, temperature, and amount of a gas.

ideal gas law constant | The constant the appears in the ideal gas law.

immiscible | Liquids that do not dissolve in each other.

induced-fit model | A model that says an enzyme can undergo a conformational change when it binds substrate molecules.

inner transition metals | An element in the two rows beneath the main body on the periodic table. Such metals are also called the lanthanide and actinide elements.

inorganic chemistry | The study of the chemistry of all other elements.

intermolecular interactions | A force of attraction between different molecules.

Ionic bonding | Bonding that results from electrostatic attractions between positively and negatively charged groups.

ionic compounds | A compound formed with an ionic bond.

ionic interactions | An attraction due to ions of opposite charges.

irreversible inhibitor | A substance that inactivates an enzyme by bonding covalently to a specific group at the active site.

isoelectric point | The pH at which a given amino acid exists in solution as a zwitterion.

isomers | Compounds having the same molecular formula but different structural formulas and properties.

isothermal | A process that occurs at constant temperature.

isotopes | Atoms of the same element that have different numbers of neutrons.

IUPAC System of Nomenclature | A systematic way of naming chemical substances so that each has a unique name.

J

joule | The SI unit of energy, work, and heat.

K

ketogenic amino acids | An amino acid that is converted to acetoacetyl-CoA or acetyl-CoA, which can be used for the synthesis of ketone bodies but not glucose.

ketone | An organic compound whose molecules have a carbonyl functional group between two hydrocarbon groups.

ketoses | A monosaccharide that contains a ketone functional group on the second carbon atom.

kinetic theory of gases | The fundamental theory of the behavior of gases.

L

L sugars | A sugar whose Fischer projection terminates in the same configuration as L-glyceraldehyde.

lattice energy | The strength of interactions between atoms that make ionic bonds.

law | A general statement that explains a large number of observations.

law of conservation of matter | In any given system that is closed to the transfer of matter (in and out), the amount of matter in the system stays constant.

Lewis diagrams | A representation that shows valence electrons as dots around the chemical symbol of an atom (also called Lewis electron dot diagrams).

line-angle formula | An organic chemical formula in which carbon atoms are implied at the corners and ends of lines. Each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds.

lipids | A compound isolated from body tissues that is more soluble in organic solvents than in water.

lock-and-key model | A model that portrays an enzyme as conformationally rigid and able to bond only to a substrate or substrates that exactly fit the active site.

M

mass number | The sum of the numbers of protons and neutrons in a nucleus of an atom.

mass-mass calculations | A stoichiometry calculation converting between the mass of one substance and the mass of a different substance in a chemical reaction.

mass/mass percent | A concentration unit that relates the mass of the solute to the mass of the solution.

mass/volume percent | A concentration unit that relates the mass of the solute to the volume of the solution.

Matter | Anything that has mass and takes up space.

metabolic pathway | A series of biochemical reactions by which an organism converts a given reactant to a specific end product.

microscopic | A view of the universe in which one is working with a few atoms or molecules at a time.

mitochondria | Small, oval organelles with double membranes; the “power plants” of a cell.

modern atomic theory | The fundamental concept that all elements are composed of atoms.

molar mass | The mass of 1 mol of atoms or molecules.

Molarity | Number of moles of solute per liter of solution.

mole-mass calculations | A stoichiometry calculation converting between masses and moles of different substances in a chemical reaction.

mole-mass conversion | The conversion from moles of material to the mass of that same material.

molecular formulas | A chemical formula for a covalent compound.

molecular mass | The mass of a molecule, which is the sum of the masses of its atoms.

molecule | A discrete group of atoms connected by covalent bonds.

mutagens | A chemical or physical agent that cause mutations.

mutarotation | The ongoing interconversion between anomeric forms of a monosaccharide to form an equilibrium mixture.

mutation | Any chemical or physical change that alters the nucleotide sequence in DNA.

N

neutralization | The reaction of acid and base to make water and a salt.

neutron | A subatomic particle with no electric charge.

nomenclature | The systematic naming of chemical compounds.

nonbonding pairs (or lone pairs) | Electron pair that does not participate in covalent bonds.

noncompetitive inhibitor | A compound that can combine with either the free enzyme or the enzyme-substrate complex at a site distinct from the active site to slow the rate of the reaction.

nonelectrolytes | A compound that does not ionize at all when it dissolves.

nonpolar covalent bond | A covalent bond with a balanced electron distribution across the bond.

Nuclear energy | The controlled harvesting of energy from fission reactions.

nuclear reactor | An apparatus designed to carefully control the progress of a nuclear reaction and extract the resulting energy for useful purposes.

nucleotides | A monomer unit that is linked together to form nucleic acids.

nucleus | The central part of an atom that contains protons and neutrons.

O

octet rule | The idea that atoms tend to have eight electrons in their valence shell.

oil | A triglyceride that is a liquid at room temperature.

optimum pH | The pH at which a particular enzyme exhibits maximum activity.

Organic chemistry | The study of the chemistry of carbon compounds.

organic compound | A compound containing carbon atoms.

Osmolarity | A way of reporting the total number of particles in a solution to determine the osmotic pressure.

osmotic pressure | The tendency for solvent molecules to move from the more dilute solution to the more concentrated solution until the concentrations of the two solutions are equal.

oxidative deamination | A reaction in which glutamate loses its amino group as an ammonium ion and is oxidized back to α-ketoglutarate.

oxidative phosphorylation | The process that links ATP synthesis to the operation of the electron transport chain.

oxidizing agent | A species that causes oxidation, which is itself reduced.

P

parts per billion (ppb) | The mass of a solute compared to the mass of a solution times 1,000,000,000.

peptide bond | The amide bond joining two amino acid units in a peptide or protein.

period | A row of elements on the periodic table.

periodic table | A chart of elements that groups the elements by some of their properties.

peripheral proteins | A protein that is more loosely associated with the membrane surface.

pH scale | A logarithmic scale that relates the concentration of the hydrogen ion in solution.

phase | A form of matter that has the same physical properties throughout.

phase change | A physical process in which a substance goes from one phase to another.

phases | A certain form of matter that includes a specific set of physical properties.

phenols | An aromatic compound with an OH group attached directly to a benzene ring.

photosynthesis | The process by which plants use solar energy to convert carbon dioxide and water to glucose.

point mutations | A change in which one nucleotide is substituted, added, or deleted.

polar | A molecule with a net unequal distribution of electrons in its covalent bonds.

polyamide | A condensation polymer in which the monomer units are joined by an amide linkage.

polyatomic ions | An ion with more than one atom.

polycyclic aromatic hydrocarbons (PAHs) | An aromatic hydrocarbon consisting of fused benzene rings sharing a common side.

polymers | A giant molecule formed by the combination of monomers in a repeating manner.

polypeptides | A chain of about 50 or more amino acids.

polysaccharides | A carbohydrate containing many monosaccharide units.

polyunsaturated fatty acids | A fatty acid that has two or more carbon-to-carbon double bonds.

power | The exponent in a number expressed in scientific notation.

pressure | Force divided by area.

primary (1°) alcohol | A compound with an OH group on a carbonatom that is attached to only one other carbon atom.

primary structure | The sequence of amino acids in a polypeptide chain or protein.

products | A substance on the right side of the arrow in a chemical equation.

Proteins | A compound of high molar mass consisting largely or entirely of amino acids linked together.

proton | A subatomic particle with a positive charge.

purines | A heterocyclic amine consisting of a pyrimidine ring fused to a five-member ring with two nitrogen atoms.

Q

quantized | Having a fixed value.

quantum mechanics | The modern theory of electron behavior.

quaternary structure | The arrangement of multiple subunits in a protein.

R

rad | A unit of radioactive exposure equal to 0.01 J/g of tissue.

radioactivity | Emanations of particles and radiation from atomic nuclei.

reducing sugar | Any carbohydrate capable of reducing a mild oxidizing agent, such as Tollens' or Benedict's reagents, without first undergoing hydrolysis.

rem | A unit of radioactive exposure that includes a factor to account for the type of radioactivity.

replication | The process in which the DNA in a dividing cell is copied.

respiration | The process by which cells oxidize organic molecules in the presence of gaseous oxygen to produce carbon dioxide, water, and energy in the form of ATP.

retroviruses | An RNA virus that directs the synthesis of a DNA copy in the host cell.

ribonucleic acid | The nucleic acid responsible for using the genetic information encoded in DNA.

ribosomes | A cellular substructure where proteins are synthesized.

round | The process of assessing the final significant figure of a quantity to determine if it should be kept or moved higher.

S

saponification | The hydrolysis of fats and oils in the presence of a base to make soap.

science | The process by which we learn about the natural universe by observing, testing, and then generating models that explain our

observations.

scientific method | An organized procedure for learning answers to questions.

secondary (2°) alcohol | A compound with an OH group on a carbon atom that is attached to two other carbon atoms.

secondary structure | The fixed arrangement of the polypeptide backbone.

semimetals | An element whose properties are intermediate between metals and nonmetals.

shells | A grouping of electrons within an atom.

significant figures | All the digits of a measured quantity known with certainty and the first uncertain, or estimated, digit.

single bond | A covalent bond formed by a single pair of electrons.

solubility | The limit of how much solute can be dissolved in a given amount of solvent.

solute | The minor component of a solution.

solution | Another name for a homogeneous mixture.

specific heat | A proportionality constant that relates heat to a temperature change.

Sphingolipids | A lipid that contains the unsaturated amino alcohol sphingosine.

Sphingomyelins | A sphingolipid that contains a fatty acid unit, a phosphoric acid unit, a sphingosine unit, and a choline unit.

spontaneous fission | The breaking apart of an atomic nucleus into smaller nuclei.

standard temperature and pressure | 273 K (0°C) and 1.00 atm pressure.

steroids | A lipid with a four-fused-ring structure.

Stock system | The system of indicating a cation's charge with roman numerals.

stoichiometry | The study of the numerical relationships between the reactants and the products in a balanced chemical equation.

strong acid | An acid that is 100% ionized in aqueous solution.

strong base | A base that is 100% ionized in aqueous solution.

structural formula | A chemical formula that shows how the atoms of a molecule are attached to one another.

subshells | A grouping of electrons within a shell.

substrate-level phosphorylation | The synthesis of ATP by the direct transfer of a phosphate group from a metabolite to ADP.

substrates | A compound on which an enzyme acts.

T

tertiary (3°) alcohol | A compound with an OH group on a carbon atom that is attached to three other carbon atoms.

tertiary (3°) amine | A compound that has three alkyl or aryl groups on the nitrogen atom.

tertiary structure | The unique three-dimensional shape of a polypeptide chain as a whole.

theory | A general statement that describes a large set of observations and data.

Thiols | A compound with an SH functional group.

torr | Another name for millimeters of mercury.

tracer | A substance that can be used to follow the pathway of that substance through some structure.

transamination | An exchange of functional groups between any amino acid and an α-keto acid.

transcription | The process in which RNA is synthesized from a DNA template.

translation | The process in which the information encoded in mRNA is used to direct the sequencing of amino acids to synthesize a protein.

triglycerides | An ester composed of three fatty acid units linked to glycerol and found in fats and oils.

triple bonds | Three pairs of electrons being shared by two atoms in a molecule.

U

unit | The scale of measurement for a quantity.

unsaturated | A solution whose solute is less than its solubility limit.

unsaturated hydrocarbons | An alkene or alkyne having one or more multiple (double or triple) bonds between carbon atoms.

V

valence shell electron pair repulsion | The general concept that estimates the shape of a simple molecule.

vapor pressure | The pressure of a vapor that is in equilibrium with its liquid phase.

vapor pressure depression | The lowering of the vapor pressure of a solution versus the pure solvent.

Viruses | An infectious agent that is much smaller and simpler than bacteria.

vitamins | An organic compound that is essential in very small amounts for the maintenance of normal metabolism.

volume | The amount of space that a given substance occupies.

volume/volume percent | A concentration unit that relates the volume of the solute to the volume of the solution.

W

weak base | A base that is less than 100% ionized in aqueous solution.

Z

zwitterion | An electrically neutral compound that contains both negatively and positively charged groups.

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