PERSONAL COPY OF CHEMISTRY FOR CHANGING TIMESEDIT



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Personal Copy of Chemistry For Changing Times

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TABLE OF CONTENTS

Licensing

1: Chemistry

1.1: Science and Technology - The Roots of Knowledge

1.2: Science- Reproducible, Testable, Tentative, Predictive, and Explanatory

1.3: Solving Society's Problems - Scientific Research

1.4: Chemistry - A Study of Matter and Its Changes

1.5: Classification of Matter

1.6: The Measurement of Matter

1.7: Density

1.8: Energy - Heat and Temperature

2: Atoms

2.1: Atoms - Ideas from the Ancient Greeks

2.2: Scientific Laws - Conservation of Mass and Definite Proportions

2.3: John Dalton and the Atomic Theory of Matter

2.4: The Mole and Molar Mass

2.5: Mendeleev and Periodic Table

2.6: Atoms and Molecules- Real and Relevant

3: Atomic Structure

3.1: Electricity and the Atom

3.2: Serendipity in Science - X-Rays and Radioactivity

3.3: Three Types of Radioactivity

3.4: Rutherford's Experiment- The Nuclear Model of the Atom

3.5: The Atomic Nucleus

3.6: Electron Arrangement- The Bohr Model (Orbits)

3.7: Electron Arrangement- The Quantum Model

3.8: Electron Configurations and the Periodic Table

4: Chemical Bonds

4.1: The Art of Deduction- Stable Electron Configurations

4.2: Lewis (Electron-Dot) Symbols

4.3: The Reaction of Sodium with Chlorine

4.4: Using Lewis Symbols for Ionic Compounds

4.5: Formulas and Names of Binary Ionic Compounds

4.6: Covalent Bonds- Shared Electron Pairs

4.7: Unequal Sharing- Polar Covalent Bonds

4.8: Polyatomic Molecules- Water, Ammonia, and Methane

4.9: Polyatomic Ions

4.10: Rules for Writing Lewis Formulas
4.11: Molecular Shapes- The VSEPR Theory
4.12: Shapes and Properties- Polar and Nonpolar Molecules

5: Chemical Accounting

5.1: Chemical Sentences- Equations
5.2: Volume Relationships in Chemical Equations
5.3: Avogadro's Number and the Mole
5.4: Molar Mass- Mole-to-Mass and Mass-to-Mole Conversions
5.5: Solutions
5.6: Section 6-

6: Gases, Liquids, Solids, ... and Intermolecular Forces

6.1: Solids, Liquids, and Gases
6.2: Comparing Ionic and Molecular Substances
6.3: Forces between Molecules
6.4: Forces in Solutions
6.5: Gases- The Kinetic-Molecular Theory
6.6: The Simple Gas Laws
6.7: The Ideal Gas Law

7: Acids and Bases

7.1: Acids and Bases - Experimental Definitions
7.2: Acids and Bases
7.3: Acidic and Basic Anhydrides
7.4: Strong and Weak Acids and Bases
7.5: Neutralization
7.6: The pH Scale
7.7: Buffers and Conjugate Acid-Base Pairs
7.8: Acids and Bases in Industry and in Daily Life

8: Oxidation and Reduction

8.1: Oxidation and Reduction - Four Views
8.2: Oxidizing and Reducing Agents
8.3: Electrochemistry- Cells and Batteries
8.4: Corrosion and Explosion
8.5: Oxygen - An Abundant and Essential Oxidizing Agent
8.6: Some Common Reducing Agents
8.7: Oxidation, Reduction, and Living Things

9: Organic Chemistry

9.1: Prelude to Organic Chemistry
9.2: Aliphatic Hydrocarbons
9.3: Aromatic Compounds- Benzene and Its Relatives

9.4: Halogenated Hydrocarbons- Many Uses, Some Hazards
9.5: The Functional Group
9.6: Alcohols, Phenols, and Ethers
9.7: Aldehydes and Ketones
9.8: Carboxylic Acids and Esters
9.9: Nitrogen-Containing Compounds- Amines and Amides

10: Polymers

10.1: Polymerization - Making Big Ones Out of Little Ones
10.2: Polyethylene - From the Battle of Britain to Bread Bags
10.3: Addition Polymerization - One + One + One + ... Gives One!
10.4: Rubber and Other Elastomers
10.5: Condensation Polymers
10.6: Properties of Polymers
10.7: Plastics and the Environment

11: Nuclear Chemistry

11.1: Natural Radioactivity
11.2: Nuclear Equations
11.3: Half-Life and Radioisotopic Dating
11.4: Artificial Transmutation
11.5: Uses of Radioisotopes
11.6: Penetrating Power of Radiation
11.7: Energy from the Nucleus
11.8: Nuclear Bombs
11.9: Uses and Consequences of Nuclear Energy

12: Chemistry of Earth

12.1: Spaceship Earth- Structure and Composition
12.2: Silicates and the Shapes of Things
12.3: Metals and Ores
12.4: Earth's Dwindling Resources

13: Air

13.1: Earth's Atmosphere- Divisions and Composition
13.2: Chemistry of the Atmosphere
13.3: Outdoor Air Pollution
13.4: Automobile Emissions
13.5: Photochemical Smog- Making Haze While the Sun Shines
13.6: Acid Rain- Air Pollution Water Pollution
13.7: Indoor Air Pollution
13.8: Stratospheric Ozone- Earth's Vital Shield
13.9: Carbon Dioxide and Climate Change

13.10: Who Pollutes? Who Pays?

14: Water

14.1: Water - Some Unique Properties
14.2: Water in Nature
14.3: Chemical and Biological Contamination
14.4: Groundwater Contamination to Tainted Tap Water
14.5: Water Who Uses It and How Much?
14.6: Making Water Fit to Drink
14.7: 14.7?- Making Water Fit to Drink
14.8: Wastewater and Sewage Treatment

15: Energy

15.1: Our Sun, a Giant Nuclear Power Plant
15.2: Energy and Chemical Reactions
15.3: Reaction Rates
15.4: The Laws of Thermodynamics
15.5: Power- People, Horses, and Fossils
15.6: Coal - The Carbon Rock of Ages
15.7: Natural Gas and Petroleum
15.8: Convenient Energy
15.9: Nuclear Energy
15.10: Renewable Energy Sources

16: Biochemistry

16.1: Energy and the Living Cell
16.2: Carbohydrates- A Storehouse of Energy
16.3: Fats and Other Lipids
16.4: Proteins- Polymers of Amino Acids
16.5: Structure and Function of Proteins
16.6: Nucleic Acids- Parts, Structure, and Function
16.7: The Human Genome
16.8: RNA Protein Synthesis and the Genetic Code

17: Food

17.1: Carbohydrates in the Diet
17.2: Fats and Cholesterol
17.3: Proteins- Muscle and Much More
17.4: Minerals, Vitamins, and Other Essentials
17.5: Starvation, Fasting, and Malnutrition
17.6: Flavorings- Spicy and Sweet
17.7: Other Food Additives- Beneficial or Dangerous
17.8: Problems with our Food

18: Drugs

18.1: Pain Relievers- From Aspirin to Oxycodone

18.2: Cold and Allergy Medicines

18.3: Drugs and Infectious Diseases

18.4: Chemicals Against Cancer

18.5: Hormones - The Regulators

18.6: Drugs for the Heart

18.7: Drugs and the Mind

18.8: Drugs and Society

19: Fitness and Health

19.1: Calories - Quantity and Quality

19.2: Vitamins, Minerals, Fluids, and Electrolytes

19.3: Weight Loss - Diets and Exercise

19.4: Measuring Fitness

19.5: Some Muscular Chemistry

19.6: Drugs, Athletic Performance, and the Brain

20: Chemistry Down on the Farm

20.1: Farming and Chemicals- Fertilizers

20.2: The War against Pests

20.3: Herbicides and Defoliants

20.4: Sustainable Agriculture

21: Household Chemicals

21.1: Cleaning with Soap

21.2: Synthetic Detergents

21.3: Laundry Auxiliaries- Softeners and Bleaches

21.4: All-Purpose and Special Purpose Cleaning Products

21.5: Solvents, Paints, and Waxes

21.6: Cosmetics - Personal Care Chemicals

22: Poisons

22.1: Natural Poisons and Food Poisoning

22.2: Poisons and How They Act

22.3: More Chemistry of the Nervous System

22.4: The Lethal Dose

22.5: The Liver as a Detox Facility

22.6: Carcinogens and Teratogens

22.7: Hazardous Wastes

Index
Glossary
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1: CHEMISTRY

1.1: Science and Technology - The Roots of Knowledge

1.2: Science- Reproducible, Testable, Tentative, Predictive, and Explanatory

1.3: Solving Society's Problems - Scientific Research

1.4: Chemistry - A Study of Matter and Its Changes

1.5: Classification of Matter

1.6: The Measurement of Matter

1.7: Density

1.8: Energy - Heat and Temperature

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1.1: Science and Technology - The Roots of Knowledge

Learning Objectives

- Learn the definitions of science, chemistry, and technology.
- Know the principles of green chemistry.

Science is a practice of learning about the natural world. Natural sciences include physics, chemistry, biology, geology and astronomy. Science uses mathematics and logic, which are sometimes called "formal sciences". Natural science makes observations and experiments. Science produces accurate facts, scientific laws and theories. 'Science' also refers to the large amount of knowledge that has been found using this process.

People who study and research science are scientists. Scientists study things by looking at them very carefully, by measuring, and by doing experiments and tests. Scientists try to explain why things act the way that they do, and predict what will happen.

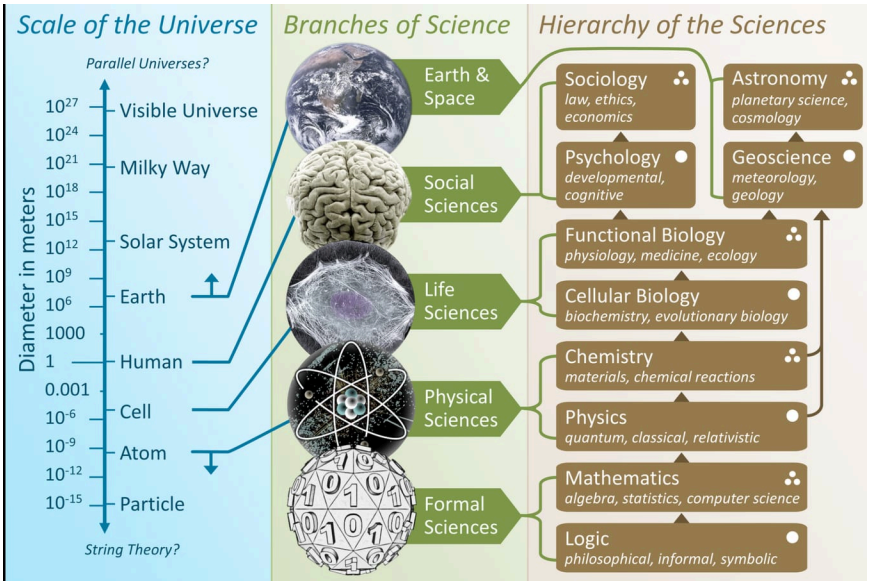


Figure 1.1.1: The scale of the universe mapped to the branches of science. (Source: Wikipedia)

Chemistry is the scientific discipline that involves the properties and behavior of matter, and the changes matter undergoes during a reaction with other substances.

In the scope of its subject, chemistry occupies an intermediate position between physics and biology. It is sometimes called *the central science*, because it provides a foundation for understanding both basic and applied scientific disciplines at a fundamental level (Figure 1.1.1). For example, chemistry explains aspects of plant chemistry (botany), the formation of igneous rocks (geology), how atmospheric ozone is formed and how environmental pollutants are degraded (ecology), the properties of the soil on the moon (astrophysics), how medications work (pharmacology), and how to collect DNA evidence at a crime scene (forensics).

Science is human understanding of how the universe and the things in it work. On the other hand, **technology** is the use of resources to solve a problem (such as knowledge, skills, processes, techniques, tools, and raw materials). Paleolithic technology is the oldest known, but people likely used technology long before then. The Paleolithic age began when hominids (early humans) started to use stones as tools for bashing, cutting, and scraping. The age ended when humans began to make small, fine tools (Mesolithic); it came to a close when they started to plant crops and develop other methods of agriculture (Neolithic).

Technology was once quite simple. It was passed on through word of mouth, until written word was invented. Writing allowed technology to develop much quicker. In the present day, people continue to understand more about the world and the universe. The use of the telescope by Galileo, Einstein's theory of relativity, lasers, and computing are all scientific discoveries. Technology is of great importance to science, medicine, and everyday life.

Green chemistry (also called **sustainable chemistry**) is a type of chemical research and engineering. It supports the design of products and processes that use the smallest amount of dangerous substances possible. In 1990, the Pollution Prevention Act was passed in the United States. This law sought new and original ways to handle pollution. The Pollution Prevention Act aims to avoid problems before they happen.

Green chemistry applies organic chemistry, inorganic chemistry, biochemistry, analytical chemistry, and even physical chemistry. While green chemistry seems to focus on just industrial applications, it does apply to other scientific disciplines. Green chemists aim to reduce the hazards and increase the efficiency of any chemical choice. Green chemistry is distinct from environmental chemistry, which focuses on chemical phenomena in the environment.

The 12 Principles of Green Chemistry

1. **Prevent waste.**
   - Create products without waste, or with minimal wastes, so that the wastes do not need to be taken care of afterwards.
2. **Design safer chemicals and products.**
   - Design chemicals to have little or no toxicity, without altering effectiveness.
3. **Design less hazardous chemical syntheses.**
   - Design a way of synthesizing products, without them being toxic to humans or the environment.
4. **Use renewable raw materials.**
   - Use renewable raw materials, like plant materials; rather than depleting materials, such as fossil fuels.
5. **Use catalysts, not stoichiometric reagents.**
   - Use catalysts, because of their ability to be able to be reused. Catalysts are less harmful than reagents.
6. **Avoid chemical derivatives.**
   - Chemical derivatives generate wastes that can be avoided.
7. **Maximize atom economy.**
   - Maximize the percentage of reactant atoms that convert to usable product atoms in a chemical reaction, so as to minimize or eliminate atomic waste.
8. **Use safer solvents and reaction conditions.**
   - Avoid using harsh solvents; if that cannot be avoided, then use benign chemicals.
9. **Increase energy efficiency.**
   - Use the normal ambient temperature and pressure wherever possible.
10. **Design for degradation.**
    - Design materials to break down into benign substances, by bacterial or other environmentally sound ways.
11. **Analyze in real time to prevent pollution.**
    - Monitor and control the formation of by-products during a reaction.
12. **Minimize the potential for accidents.**
    - Design chemicals to minimize the potential for accidents.

Summary

- Science is the human method to make discoveries about the natural world.
- Chemistry is the branch of science involved with the properties and behavior of matter, and the changes it undergoes during a reaction with other substances.
- Green chemistry applies organic chemistry, inorganic chemistry, biochemistry, analytical chemistry, and physical chemistry to reduce and prevent pollution.
- There are 12 guiding principles in the practice of green chemistry.

Contributors and Attributions

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1.2: Science- Reproducible, Testable, Tentative, Predictive, and Explanatory

Learning Objectives

- Describe the differences between hypothesis and theory as scientific terms.
- Describe the difference between a theory and scientific law.
- Identify the components of the scientific method.

Although many have taken science classes throughout their course of studies, incorrect or misleading ideas about some of the most important and basic principles in science are still commonplace. Most students have heard of *hypotheses*, *theories*, and *laws*, but what do these terms really mean? Before you read this section, consider what you have learned about these terms previously, and what they mean to you. When reading, notice if any of the text contradicts what you previously thought. What do you read that supports what you thought?

What is a Fact?

A **fact** is a basic statement established by experiment or observation. All facts are true under the specific conditions of the observation.

What is a Hypothesis?

One of the most common terms used in science classes is a "**hypothesis**". The word can have many different definitions, dependent on the context in which it is being used:

- An educated guess: a scientific hypothesis provides a suggested solution based on evidence.
- Prediction: if you have ever carried out a science experiment, you probably made this type of hypothesis, in which you predicted the outcome of your experiment.
- Tentative or proposed explanation: hypotheses can be suggestions about why something is observed. In order for a hypothesis to be scientific, a scientist must be able to test the explanation to see if it works, and if it is able to correctly predict what will happen in a situation. For example, "if my hypothesis is correct, I should see _____ result when I perform _____ test."

A hypothesis is tentative; it can be easily changed.

What is a Theory?

The *United States National Academy of Sciences* describes a theory as:

> "Some scientific explanations are so well established that no new evidence is likely to alter them. The explanation becomes a scientific theory. In everyday language a theory means a hunch or speculation. Not so in science. In science, the word **theory** refers to a comprehensive explanation of an important feature of nature supported by facts gathered over time. Theories also allow scientists to make predictions about as yet unobserved phenomena."
>
> "A scientific theory is a well-substantiated explanation of some aspect of the natural world, based on a body of facts that have been repeatedly confirmed through observation and experimentation. Such fact-supported theories are not "guesses," but reliable accounts of the real world. The theory of biological evolution is more than "just a theory." It is as factual an explanation of the universe as the atomic theory of matter (stating that everything is made of atoms) or the germ theory of disease (which states that many diseases are caused by germs). Our understanding of gravity is still a work in progress. But the phenomenon of gravity, like evolution, is an accepted fact."

Note some key features of theories that are important to understand from this description:

- Theories are explanations of natural phenomenon. They aren't predictions (although we may use theories to make predictions). They are explanations of why something is observed.
- Theories aren't likely to change. They have a lot of support and are able to explain many observations satisfactorily. Theories can, indeed, be facts. Theories can change in some instances, but it is a long and difficult process. In order for a theory to change, there must be many observations or evidence that the theory cannot explain.
- Theories are not guesses. The phrase "just a theory" has no room in science. To be a scientific theory carries a lot of weight—it is not just one person's idea about something

Theories aren't likely to change.

What is a Law?

Scientific **laws** are similar to scientific theories in that they are principles that can be used to predict the behavior of the natural world. Both scientific laws and scientific theories are typically well-supported by observations and/or experimental evidence. Usually, scientific laws refer to rules for how nature will behave under certain conditions, frequently written as an equation. Scientific theories are overarching explanations of how nature works, and why it exhibits certain characteristics. As a comparison, theories explain why we observe what we do, and laws describe what happens.

For example, around the year 1800, Jacques Charles and other scientists were working with gases to, among other reasons, improve the design of the hot air balloon. These scientists found, after numerous tests, that certain patterns existed in their observations of gas behavior. If the temperature of the gas increased, the volume of the gas increased. This is known as a natural law. A law is a relationship that exists between variables in a group of data. Laws describe the patterns we see in large amounts of data, but do not describe why the patterns exist.

Laws vs Theories

A common misconception is that scientific theories are rudimentary ideas that will eventually graduate into scientific laws when enough data and evidence has been accumulated. A theory does not change into a scientific law with the accumulation of new or better evidence. Remember, theories are explanations; laws are patterns seen in large amounts of data, frequently written as an equation. A theory will always remain a theory, a law will always remain a law.

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Video 1.2.1 *What is the difference between scientific law and theory?*

The Scientific Method

Scientists search for answers to questions and solutions to problems by using a procedure called the **scientific method**. This procedure consists of making observations, formulating hypotheses, and designing experiments, which in turn lead to additional observations, hypotheses, and experiments in repeated cycles (Figure 1.2.1).

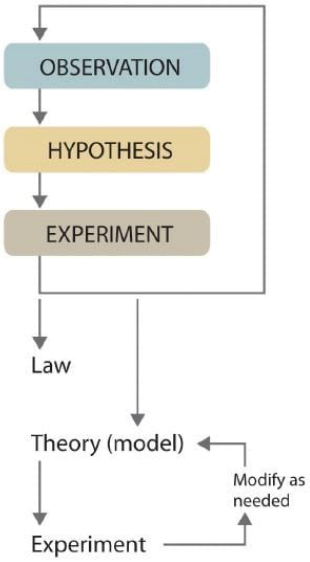


Figure 1.2.1 *The steps in the scientific method.*

Step 1: Make observations.

Observations can be qualitative or quantitative. **Qualitative observations** describe properties or occurrences in ways that do not rely on numbers. Examples of qualitative observations include the following: "the outside air temperature is cooler during the winter season," "table salt is a crystalline solid," "sulfur crystals are yellow," and "dissolving a penny in dilute nitric acid forms a blue solution and a brown gas." **Quantitative observations** are measurements, which by definition consist of both a number and a unit. Examples of quantitative observations include the following: "the melting point of crystalline sulfur is 115.21° Celsius," and "35.9 grams of table salt—the chemical name of which is sodium chloride—dissolve in 100 grams of water at 20° Celsius." For the question of the dinosaurs' extinction, the initial observation was quantitative: iridium concentrations in sediments dating to 66 million years ago were 20–160 times higher than normal.

Step 2: Formulate a hypothesis.

After deciding to learn more about an observation or a set of observations, scientists generally begin an investigation by forming a hypothesis, a tentative explanation for the observation(s). The hypothesis may not be correct, but it puts the scientist's understanding of the system being studied into a form that can be tested. For example, the observation that we experience alternating periods of light and darkness which correspond to observed movements of the sun, moon, clouds, and shadows, is consistent with either of two hypotheses:

1. Earth rotates on its axis every 24 hours, alternately exposing one side to the sun.
2. The sun revolves around Earth every 24 hours.

Suitable experiments can be designed to choose between these two alternatives. In the case of disappearance of the dinosaurs, the hypothesis was that the impact of a large extraterrestrial object caused their extinction. Unfortunately (or perhaps fortunately), this hypothesis does not lend itself to direct testing by any obvious experiment, but scientists can collect additional data that either supports or refutes it.

Step 3: Design and perform experiments.

After a hypothesis has been formed, scientists conduct experiments to test its validity. Experiments are systematic observations or measurements, preferably made under controlled conditions—that is, under conditions in which a single variable changes.

Step 4: Accept or modify the hypothesis.

A properly designed and executed experiment enables a scientist to determine whether the original hypothesis is valid. In the case of validity, the scientist can proceed to step 5. In other cases, experiments may demonstrate that the hypothesis is incorrect or that it must be modified, thus requiring further experimentation.

Step 5: Development of a law and/or theory.

More experimental data are then collected and analyzed, at which point a scientist may begin to think that the results are sufficiently reproducible (i.e., dependable) to merit being summarized in a law—a verbal or mathematical description of a phenomenon that allows for general predictions. A law simply states what happens; it does not address the question of why.

One example of a law, the law of definite proportions (discovered by the French scientist Joseph Proust [1754–1826]), states that a chemical substance always contains the same proportions of elements by mass. Thus, sodium chloride (table salt) always contains the same proportion by mass of sodium to chlorine—in this case, 39.34% sodium and 60.66% chlorine by mass. Sucrose (table sugar) is always 42.11% carbon, 6.48% hydrogen, and 51.41% oxygen by mass.

Whereas a law states only what happens, a theory attempts to explain why nature behaves as it does. Laws are unlikely to change greatly over time, unless a major experimental error is discovered. A theory, in contrast, is incomplete and imperfect; it evolves with time to explain new facts as they are discovered.

Because scientists can enter the cycle shown in Figure 1.2.1 at any point, the actual application of the scientific method to different topics can take many different forms. For example, a scientist may start with a hypothesis formed by reading about work done by others in the field, rather than by making direct observations.

Example 1.2.1

Classify each statement as a law, theory, experiment, hypothesis, or observation.

1. Ice always floats on liquid water.
2. Birds evolved from dinosaurs.
3. Hot air is less dense than cold air, probably because the components of hot air are moving more rapidly.
4. When 10 g of ice was added to 100 mL of water at 25°C, the temperature of the water decreased to 15.5°C after the ice melted.
5. The ingredients of Ivory soap were analyzed to see whether it really is 99.44% pure, as advertised.

Solution

1. This is a general statement of a relationship between the properties of liquid and solid water, so it is a law.
2. This is a possible explanation for the origin of birds, so it is a hypothesis.
3. This is a statement that tries to explain the relationship between the temperature and the density of air based on fundamental principles, so it is a theory.
4. The temperature is measured before and after a change is made in a system, so these are observations.
5. This is an analysis designed to test a hypothesis (in this case, the manufacturer's claim of purity), so it is an experiment.

Exercise 1.2.1

Classify each statement as a law, theory, experiment, hypothesis, qualitative observation, or quantitative observation.

1. Measured amounts of acid were added to a Rolaids tablet to see whether it really "consumes 47 times its weight in excess stomach acid."
2. Heat always flows from hot objects to cooler ones, not in the opposite direction.
3. The universe was formed by a massive explosion that propelled matter into a vacuum.
4. Michael Jordan is the greatest pure shooter ever to play professional basketball.
5. Limestone is relatively insoluble in water, but dissolves readily in dilute acid with the evolution of a gas.

Answer 1: available at the end of this section.

Summary

- A hypothesis is a tentative explanation that can be tested by further investigation.
- A theory is a well-supported explanation of observations.
- A scientific law is a statement that summarizes the relationship between variables.
- An experiment is a controlled method of testing a hypothesis.
- The scientific method is a method of investigation involving experimentation and observation to acquire new knowledge, solve problems, and answer questions. The key steps in the scientific method are:
  - Step 1: Make observations.
  - Step 2: Formulate a hypothesis.
  - Step 3: Test the hypothesis through experimentation.
  - Step 4: Accept or modify the hypothesis.
  - Step 5: Development of a law and/or theory.

Contributors and Attributions

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- Henry Agnew (UC Davis)

Answers

Exercise 1.2.1

experiment
law
theory
hypothesis
observation

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1.3: Solving Society's Problems - Scientific Research

Learning Objective

- Know the meaning and examples of pure and applied research.

How did chemistry develop? What is happening in the field of chemistry today? What career can a chemistry degree apply to? These are all good questions that should be asked by students interested in chemistry. Research in chemistry (or any other field, for that matter) is interesting and challenging. But there are different directions a person can take as they explore research opportunities.

Types of Research

In science, two types of research are generally discussed: pure and applied. **Pure research** focuses on answering basic questions such as, "how do gases behave?" **Applied research** is involved in the process of developing specific preparations for a gas, in order for it to be produced and delivered efficiently and economically. This division sounds like it would be easy to make, but sometimes we cannot draw a clear line between what is "pure" and what is "applied".

Examples of "Pure" Research

A lot of "pure" research is of the "what is this?" or "how does it work?" variety. The early history of chemistry contains many examples. The ancient Greek philosophers debated the composition of matter (E*arth? Air? Fire? Water? All of the above?*). They weren't going to do anything with their knowledge—they just wanted to know.



Figure 1.3.1 *Ancient Greek philosophers.*

Studies on the elements (especially after Mendeleev's periodic table was published) were primarily "pure" research types of experiments. Does this element exist? What are its properties? The scientists did not have any practical application in mind, but were curious about the world around them.

Examples of "Applied" Research

There is a great deal of "applied" research taking place today. In general, no new science principles are discovered, but existing

knowledge is used to develop new products. Research on laundry detergents will probably not offer any new concepts of soap, but will help us develop materials that get our clothes cleaner, use less water, and create lower amounts of pollution.

A lot of research is done by petroleum companies. They want to find better ways to power vehicles, better lubricants to cut down on engine wear, and better ways to lower air pollution. These companies will use information that is readily available to come up with new products.



Figure 1.3.2 A *Gasoline pump*.

Some "In-Between" Examples

Sometimes it is hard to differentiate between pure and applied research. What may start out as simply asking a question may result in some very useful information. If scientists are studying the biochemistry of a microorganism that causes a disease, they may soon find information that would suggest a way to make a chemical that will inactivate the microorganism. The compound could be used to learn more about the biochemistry, but could also be used to cure the disease.

Hemoglobin is a protein in red blood cells that transports oxygen in the bloodstream. Scientists studied hemoglobin simply to learn how it worked. Out of this research came an understanding of how the protein changes shape when oxygen attaches to it. This information was then applied to help patients with sickle cell anemia, a disorder caused by an abnormal hemoglobin structure that makes hemoglobin molecules clump up when oxygen leaves the protein. Basic knowledge of protein structure led to an improved understanding of a wide-spread disease and opened the door for the development of treatments.

Summary

- Pure research focuses on understanding basic properties and processes.
- Applied research focuses on the use of information to create useful materials.
- Sometimes there is no clear line between pure and applied research.

Contributors and Attributions

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1.4: Chemistry - A Study of Matter and Its Changes

Learning Objectives

- Separate physical from chemical properties.
- Label a change as chemical or physical.

Chemistry is the study of matter—what it consists of, what its properties are, and how it changes. Matter is anything that has mass and takes up space—that is, anything that is physically real. Some things are easily identified as matter—the screen on which you are reading this book, for example. Others are not so obvious. Because we move so easily through air, we sometimes forget that it, too, is matter. Because of this, chemistry is a science that has its fingers in just about everything. Even a description of the ingredients in a cake, and how those ingredients change when the cake is baked, is chemistry!

Physical and Chemical Properties

All matter has physical and chemical properties. Physical properties are characteristics that scientists can measure without changing the composition of the sample under study, such as mass, color, and volume (the amount of space occupied by a sample). Chemical properties describe the characteristic ability of a substance to react to form new substances; they include its flammability and susceptibility to corrosion. All samples of a pure substance have the same chemical and physical properties. For example, pure copper is always a reddish-brown solid (a physical property) and always dissolves in dilute nitric acid to produce a blue solution and a brown gas (a chemical property).

Physical Property

A **physical property** is a characteristic of a substance that can be observed or measured without changing the identity of the substance. Silver is a shiny metal that conducts electricity very well. It can be molded into thin sheets—a property called malleability. Salt is dull and brittle and conducts electricity when it has been dissolved into water, which it does quite easily. Physical properties of matter include color, hardness, malleability, solubility, electrical conductivity, density, melting point, and boiling point. In Table 1.4.1, notice that corn oil has a lower mass to volume ratio than water. This means that when added to water, corn oil will “float.”

Table 1.4.1 Densities of Common Substances

Substance	Density at 25°C (g/cm3)
blood	1.035
body fat	0.918
whole milk	1.030
corn oil	0.922
mayonnaise	0.910
honey	1.420

Hardness helps determine how an element (especially a metal) might be used. Many elements are fairly soft (silver and gold, for example) while others (such as titanium, tungsten, and chromium) are much harder. Carbon is an interesting example of hardness. In graphite, (the "lead" found in pencils) the carbon is very soft, while the carbon in a diamond is roughly seven times as hard.



Figure 1.4.1 A pencil (top) and a diamond ring (bottom). Both are a form of carbon, but exhibit very different physical properties.

Melting and boiling points are somewhat unique identifiers, especially of compounds. In addition to giving some idea of the compound's identity, important information can be obtained about the purity of the material.

Chemical Property

A chemical property of matter describes its "potential" to undergo some chemical change or reaction by virtue of its composition; as well as what elements, electrons, and bonding are present to give the potential for chemical change. It is quite difficult to define a chemical property without using the word "change". Eventually, students of chemistry should be able to look at the formula of a compound and state a chemical property. For example, hydrogen has the potential to ignite and explode, given the right conditions—this is a chemical property. Metals in general have the chemical property of reacting with acids. Zinc reacts with hydrochloric acid to produce hydrogen gas—this is a chemical property.



Figure 1.4.2 Heavy rust on the links of a chain near the Golden Gate Bridge in San Francisco; it was continuously exposed to moisture and salt spray, causing surface breakdown, cracking, and flaking of the metal. (CC BY-SA 3.0;).

A chemical property of iron is that it is capable of combining with oxygen to form iron oxide, the chemical name of rust (Figure 1.4.2). The more general term for rusting and other similar processes is corrosion. Other terms that are commonly used

in descriptions of chemical changes are *burn*, *rot*, *explode*, *decompose*, and *ferment*. Chemical properties are very useful in identifying substances. However, unlike physical properties, chemical properties can only be observed as the substance is in the process of being changed into a different substance.

Table 1.4.2: Contrasting Physical and Chemical Properties

Physical Properties	Chemical Properties
Gallium metal melts at 30 °C	Iron metal rusts.
Mercury is a very dense liquid.	A green banana turns yellow when it ripens.
Gold is shiny.	A dry piece of paper burns.

Example 1.4.1

Which of the following is a chemical property of iron?

1. Iron corrodes in moist air.
2. Density = 7.874 g/cm^3
3. Iron is soft when pure.
4. Iron melts at 1808 K.

Solution

"Iron corrodes in air" is the only chemical property of iron from the list.

Exercise 1.4.1A

Which of the following is a physical property of matter?

1. corrosiveness
2. pH (acidity)
3. density
4. flammability

Answer available at the end of this section.

Exercise 1.4.1B

Which of the following is a chemical property?

1. flammability
2. melting point
3. boiling point
4. density

Answer available at the end of this section.

Physical and Chemical Changes

Change is happening all around us all of the time. Just as chemists have classified elements and compounds, they have also classified types of changes. Changes are either classified as physical or chemical changes. Chemists learn a lot about the nature of matter by studying the changes that matter can undergo. Chemists make a distinction between two different types of changes that they study—physical changes and chemical changes.

Physical Change

Physical changes are changes in which no bonds are broken or formed. This means that the same types of compounds or elements that were there at the beginning of the change are there at the end of the change. Because the ending materials are the same as the beginning materials, the properties (such as color, boiling point, etc) will also be the same. Physical changes involve moving molecules around, but not changing them. Some types of physical changes include:

- Changes of state (changes from a solid to a liquid or a gas and vice versa).
- Separation of a mixture.
- Physical deformation (cutting, denting, stretching).
- Making solutions (special kinds of mixtures).

As an ice cube melts, its shape changes as it acquires the ability to flow. However, its composition does not change. Melting is an example of a physical change. A physical change is a change to a sample of matter in which some properties of the material change, but the identity of the matter does not. When liquid water is heated, it changes to water vapor. However, even though the physical properties have changed, the molecules are exactly the same as before. Each water molecule still contains two hydrogen atoms covalently bonded to one oxygen atom. When you have a jar containing a mixture of pennies and nickels, and you sort the mixture so that you have one pile of pennies and another pile of nickels, you have not altered the identity of either the pennies or the nickels—you've merely separated them into two groups. This would be an example of a physical change. Similarly, if you have a piece of paper, you don't change it into something other than a piece of paper by ripping it up. What was paper before you started tearing is still paper when you're done. Again, this is an example of a physical change.



Figure 1.4.3: 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 composition of the constituent molecules is the same: 11.19% hydrogen and 88.81% oxygen by mass. (Public Domain; Moussa).

Physical changes can further be classified as reversible or irreversible. The melted ice cube may be refrozen, so melting is a reversible physical change. Physical changes that involve a change of state are all reversible. Other changes of state include **vaporization** (liquid to gas), **freezing** (liquid to solid), and **condensation** (gas to liquid). Dissolution is also a reversible physical change. When salt is dissolved into water, the salt is said to have entered the aqueous state. The salt may be regained by boiling off the water, leaving the salt behind.

Chemical Change

Chemical changes occur when bonds are broken and/or formed between molecules or atoms. This means that one substance with a certain set of properties (such as melting point, color, taste, etc.) is turned into a different substance with different properties. Chemical changes are frequently harder to reverse than physical changes.

One good example of a chemical change is burning a candle. The act of burning paper actually results in the formation of new

chemicals (carbon dioxide and water, to be exact) from the burning of the wax. Another example of a chemical change is what occurs when natural gas is burned in a furnace. This time, on the left there is a molecule of methane, $\mathrm{CH_4}$, and two molecules of oxygen, $\mathrm{O_2}$; on the right are two molecules of water, $\mathrm{H_2O}$, and one molecule of carbon dioxide, $\mathrm{CO_2}$. In this case, not only has the appearance changed, but the structure of the molecules has also changed. The new substances do not have the same chemical properties as the original ones. Therefore, this is a chemical change.



Figure 1.4.4: The burning of wax to generate water and carbon dioxide is a chemical reaction. (CC-SA-BY-3.0; Andrikkos)

We can't actually see molecules breaking and forming bonds, although that's what defines chemical changes. We have to make other observations to indicate that a chemical change has happened. Some of the evidence for chemical change will involve the energy changes that occur in chemical changes, but some evidence involves the fact that new substances with different properties are formed in a chemical change.

Observations that help to indicate chemical change include:

- Temperature changes (temperature increase or decrease).
- Light given off.
- Unexpected color changes (a substance with a different color is made, rather than just mixing the original colors together).
- Bubbles are formed (but the substance is not boiling—you made a substance that is a gas at the temperature of the beginning materials, instead of a liquid).
- Different smell or taste (do not taste your chemistry experiments, though!).
- A solid forms if two clear liquids are mixed (look for *floaties*—technically called a precipitate).

Example 1.4.2

Label each of the following changes as a physical or chemical change. Give evidence to support your answer.

1. Boiling water.
2. A nail rusting.
3. A green solution and colorless solution are mixed. The resulting mixture is a solution with a pale green color.
4. Two colorless solutions are mixed. The resulting mixture has a yellow precipitate.

Solution

1. Physical: boiling and melting are physical changes. When water boils, no bonds are broken or formed. The change could be written as: $\mathrm{H_2O}\,(l) \rightarrow \mathrm{H_2O}\,(g)$
2. Chemical: The dark grey nail changes color to form an orange flaky substance (the rust); this must be a chemical change. Color changes indicate chemical change. The following reaction occurs: $\mathrm{Fe} + \mathrm{O_2} \rightarrow \mathrm{Fe_2O_3}$

3. Physical: because none of the properties changed, this is a physical change. The green mixture is still green and the colorless solution is still colorless. They have just been combined. No color *change,* or other evidence of chemical change, occurred.
4. Chemical: the formation of a precipitate and the color change from colorless to yellow indicates a chemical change.

Exercise 1.4.2

Label each of the following changes as a physical or chemical change.

1. A mirror is broken.
2. An iron nail corroded in moist air.
3. Copper metal is melted.
4. A catalytic converter changes nitrogen dioxide to nitrogen gas and oxygen gas.

Answer 1: available at the end of this section.

Answer 2: available at the end of this section.

Answer 3: available at the end of this section.

Answer 4: available at the end of this section.

Summary

- A physical property is a characteristic of a substance that can be observed or measured without changing the identity of the substance. Physical properties include color, density, hardness, and melting and boiling points.
- A chemical property describes the ability of a substance to undergo a specific chemical change. To identify a chemical property, we look for a chemical change.
- Physical changes are changes that do not alter the identity of a substance.
- Chemical changes are changes that occur when one substance is turned into another substance.
- Chemical changes are frequently harder to reverse than physical changes. Observations that indicate a chemical change occurred include color change, temperature change, light given off, formation of bubbles, and formation of a precipitate.

Contributors and Attributions

-

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Answers

Exercise 1.4.1A
3.

Exercise 1.4.1B
1.

Exercise 1.4.2
physical change

Exercise 1.4.2
chemical change

Exercise 1.4.2
physical change

Exercise 1.4.2
chemical change

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1.5: Classification of Matter

Learning Objectives

- Describe the solid, liquid and gas phases.
- Explain the difference between a pure substance and a mixture.
- Explain the difference between an element and a compound.
- Explain the difference between a homogeneous mixture and a heterogeneous mixture.

The States of Matter

Matter typically exists in one of three states: **solid**, **liquid**, or **gas**. The state that a given substance exhibits is also a physical property. Some substances exist as gases at room temperature (oxygen and carbon dioxide); 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 1.5.1: Matter is usually classified into one of three states, with plasma sometimes added as a fourth state. (From top to bottom:) Quartz (solid), water (liquid), nitrogen dioxide (gas).

Note

Technically speaking, a fourth state of matter called plasma exists—but it does not naturally occur on earth, so we will omit it from our study here.

Solid

Solids are defined by the following characteristics:

- Definite shape (rigid).
- Definite volume.
- Particles vibrate around fixed axes.

If we were to cool liquid mercury to its freezing point of $-39^{\circ}\mathrm{C}$, we would notice all of the liquid particles go into the solid state, under the right pressure conditions. Mercury can be solidified when its temperature is brought to its freezing point. However, when returned to room temperature conditions, mercury does not exist in a solid state for long, and returns back to its more common liquid form.

Liquid

Liquids have the following characteristics:

- No definite shape (takes the shape of its container).
- Has definite volume.
- Particles are free to move over each other, but are still attracted to each other.

Mercury

Liquid mercury metal is an anomaly. It is the only known metal that is liquid at room temperature. Mercury also has an ability to stick to itself (surface tension)—a property all liquids exhibit. Mercury has a relatively high surface tension, which makes it very unique. In the video below, you see mercury in its common liquid form.

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 $1.5.1$*: Mercury boiling to become a gas.*

If we heat liquid mercury to its boiling point of $357^{\circ}\mathrm{C}$, under the right pressure conditions, all of the particles in the liquid state would go into the gas state.

Gas

Gases have the following characteristics:

- No definite shape (takes the shape of its container).
- No definite volume.
- Particles move in random motion with little or no attraction to each other.
- Highly compressible.

The characteristics of the three states of matter are listed in Table $1.5.1$ and an animation of the movement and position of the individual particles is shown in Figure $1.5.2$

Table $1.5.1$ *Characteristics of the Three States of Matter*

Characteristics	Solids	Liquids	Gases
shape	definite	indefinite	indefinite
volume	definite	definite	indefinite
relative intermolecular interaction strength	strong	moderate	weak

Characteristics	Solids	Liquids	Gases
relative particle positions	in contact and fixed in place	in contact, but not fixed	not in contact, random positions

Table 1.5.2 *images of the states of matter.*

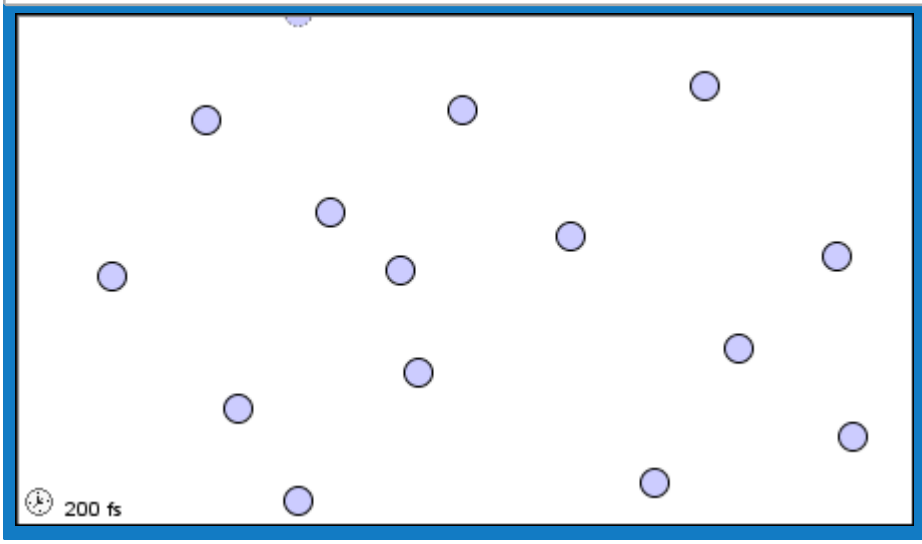
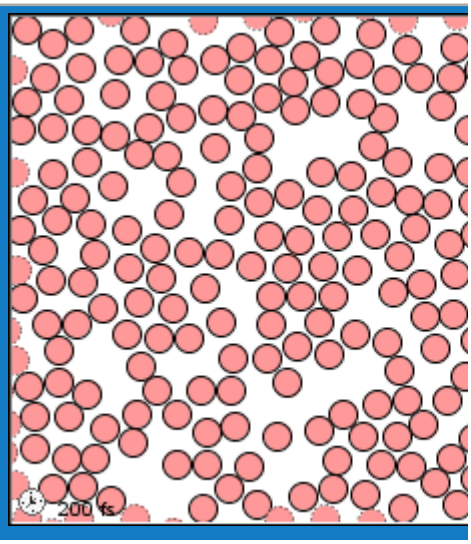
Imag	
The gaseous state	*The liqui*
	

Figure 1.5.2 *A microscopic model showing particles (atoms or molecules) in the gaseous, liquid, and solid states.*

Example 1.5.1

What state(s) of matter does each statement describe?

a. This state has a definite volume, but no definite shape.
b. This state has no definite volume.
c. This state allows the individual particles to move about while remaining in contact.

Solution

a. This statement describes the liquid state.
b. This statement describes the gas state.
c. This statement describes the liquid state.

Exercise 1.5.1

What state or states of matter does each statement describe?

a. This state has individual particles in a fixed position with regard to one another.
b. This state has individual particles far apart from each other in space.
c. This state has a definite shape.

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.

Substances and Mixtures

One useful way of organizing our understanding of matter is to think of a hierarchy that extends down from the most general and complex, to the simplest and most fundamental (Figure 1.5.1). 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 (meaning it's the same everywhere) and properties that are constant throughout the sample (meaning there is only one set of properties such as melting point, color, boiling point, etc. throughout the matter). A material composed of two or more substances is a **mixture**.

Ordinary table salt is called sodium chloride. It is considered a **substance** because it has a uniform and definite composition. All samples of sodium chloride are chemically identical. Water is also a pure substance. Salt easily dissolves in water, but salt water cannot be classified as a substance because its composition can vary. You may dissolve a small or large amount of salt into a given amount of water. A mixture is a physical blend of two or more components, each of which retains its own identity and properties in the **mixture**. Only the form of the salt is changed when it is dissolved into water. It retains its composition and properties.

A **homogeneous** mixture is a mixture in which the composition is uniform throughout the mixture. The salt water described above is homogeneous because the dissolved salt is evenly distributed throughout the entire salt water sample. Often it is easy to confuse a homogeneous mixture with a pure substance, because they are both uniform. The difference is that the composition of the substance is always the same. The amount of salt in the salt water can vary from one sample to another. All solutions would be considered homogeneous because the dissolved material is present in the same amount throughout the solution.

A **heterogeneous mixture** is a mixture in which the composition is not uniform throughout the mixture. Vegetable soup is a heterogeneous mixture. Any given spoonful of soup will contain varying amounts of the different vegetables and other components of the soup.

Elements and Compounds

Elements and compounds are both examples of pure substances. A substance that cannot be broken down into chemically simpler components is an **element**. Aluminum, which is used in soda cans, is an element. A substance that can be broken down into chemically simpler components (because it has more than one element) is a **compound**. For example, water is a compound composed of the elements hydrogen and oxygen. Today, there are about 118 elements in the known universe. In contrast, scientists have identified tens of millions of different compounds to date.

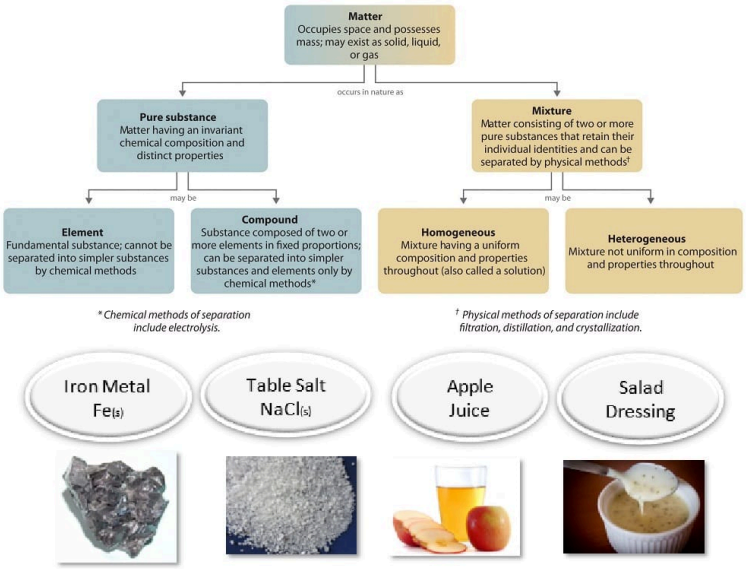


Figure 1.5.3: Relationships between the types of matter and the methods used to separate mixtures.

Atoms, Elements, and Compounds

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 1.5.2 *Atoms, elements, and compounds (first five minutes of video)*

Phase

A **phase** is any part of a sample that has a uniform composition and properties. By definition, a pure substance or a homogeneous mixture consists of a single phase. A heterogeneous mixture consists of two or more phases. When oil and water are combined, they do not mix evenly, but instead form two separate layers. Each of the layers is called a phase.

Example 1.5.2

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:

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

Exercise 1.5.2

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 1.5.3

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 materials, so it is a heterogeneous mixture.
c. Water is a substance; more specifically, because water is composed of hydrogen and oxygen, it is a compound.
d. Oxygen, a substance, is an element.

Exercise 1.5.3

How would a chemist categorize each example of matter?

a. filtered coffee
b. hydrogen
c. an egg

Answer a: available at the end of this section.

Summary

- Three states of matter exist: solid, liquid, and gas.
- Solids have a definite shape and volume.
- Liquids have a definite volume, but take the shape of the container.
- Gases have no definite shape or volume
- 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 1.5.1
solid

Exercise 1.5.1
gas

Exercise 1.5.1
solid

Exercise 1.5.2
homogeneous mixture (solution)
element
heterogeneous mixture
compound

Exercise 1.5.3
a homogeneous mixture (solution)
element
heterogeneous mixture.

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1.6: The Measurement of Matter

Learning Objectives

- Express quantities properly, using a number and a unit.
- State the different measurement systems used in chemistry.
- Express a large number or a small number in scientific notation.
- Learn how to use SI prefixes.
- Perform unit conversions using conversion factors.

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: A nurse or a doctor measuring a patient's blood pressure is taking a measurement. Figure used with permission (GFDL; Pia von Lützau).

Chemists measure the properties of matter and express these measurements as quantities. A quantity is an amount of something, and consists of a number and a unit. The number tells us how many (or how much), and the unit tells us what the scale of measurement is. For example, when a distance is reported as "5 kilometers," we know that the quantity has been expressed in units of kilometers and that the number of kilometers is 5. If you ask a friend how far he or she walks from home to school, and the friend answers "12" without specifying a unit, you do not know whether your friend walks 12 miles, 12 kilometers, 12 furlongs, or 12 yards...etc. *Both a number and a unit must be included to express a quantity properly.*

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

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 the seven base units shown 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.

Exponential Numbers: Powers of Ten

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. Furthermore, use of prefixes is another way to express measurements involving large and small numbers.

Scientific Notation

In scientific notation, numbers are expressed in the form

$$N \times 10^n$$

where N is 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. 12,378
d. 0.00032

Solution

Example 1.6.1 *Solution and Explanation*

	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	Because the decimal point was moved **four places to the left, n = 4**.	1.2378×10^{4}
d	Because the decimal point was moved **four places to the right, n = –4**.	3.2×10^{-4}

Exercise 1.6.1

Convert each ordinary number to scientific notation, or vice versa.

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

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.

Exercise 1.6.2

Convert each ordinary number to scientific notation, or vice versa.

a. 0.000006567
b. 6.22×10^{-2}
c. 9.9×10^{-9}

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.

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*

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 kilometer $(\mathrm{km}) = 1,000\ \mathrm{m}$
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 decimeter $(\mathrm{dm}) = 0.1\ \mathrm{m}$
centi	c	1/100	1 centimeter $(\mathrm{cm}) = 0.01\ \mathrm{m}$
milli	m	1/1,000	1 millimeter $(\mathrm{mm}) = 0.001\ \mathrm{m}$
micro	μ	1/1,000,000	1 micrometer $(\mu\mathrm{m}) = 10^{-6}\ \mathrm{m}$
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 $(\mathrm{pm}) = 10^{-12}\ \mathrm{m}$

There are a couple of odd little practices with the use of metric abbreviations. Most abbreviations are lowercase. We use "m" for meter and not "M". However, when it comes to volume, the base unit "liter" is abbreviated as "L" and not "l". So, 3.5 milliliters is written 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 $6.5\ \mathrm{kg}$, this is easier than saying it weighs $6500\ \mathrm{g}$ or $0.65\ \mathrm{dag}$. 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

Example 1.6.2 *Solution and Explanation*

	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 1.6.3

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.

Mass and Weight

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 1.6.2 (From left to right:) Triple beam balance (source(opens in new window)), digital top-loading balance (source(opens in new window)), and an analytical balance (source).

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 $1\ \mathrm{g}$.

Mass is often confused with the term weight. **Weight** is a measure of force that is equal to the gravitational pull on an object. The weight of an object is dependent on its location. On the moon, the force due to **gravity** is about one sixth that of the gravitational force on Earth. Therefore, a given object will weigh six times more on Earth than it does on the moon. Since mass is dependent only on the amount of matter present in an object, mass does not change with location. Weight measurements are often made with a spring scale, by reading the distance that a certain object pulls down and stretches a spring.

Length and Volume

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 $(\mu\mathrm{m})$.

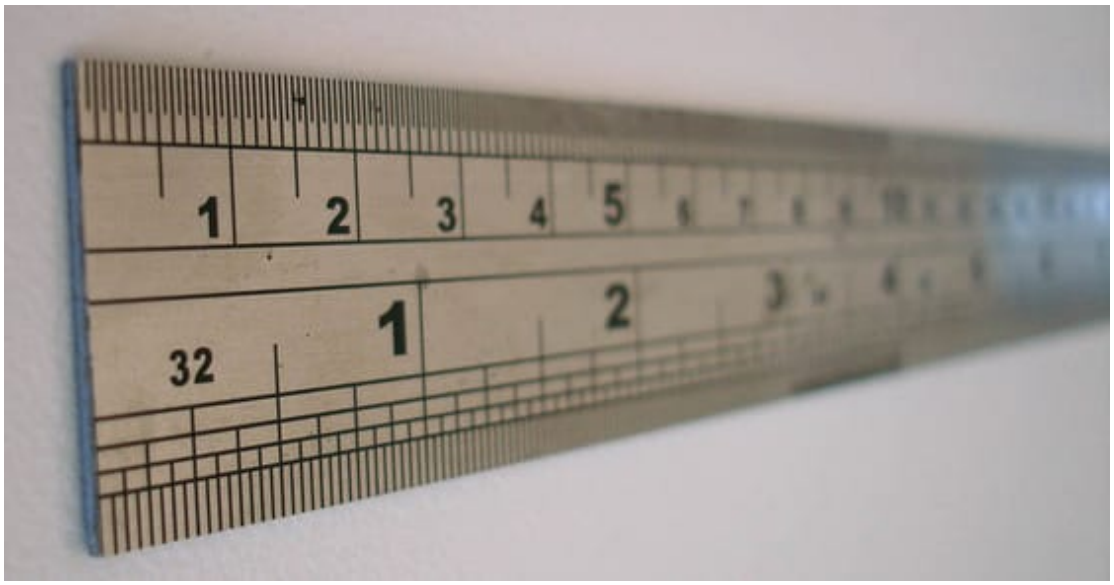


Figure 1.6.3: Metric and English measuring devices. (CC BY-SA 4.0; Ejay)

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. The SI 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 $1\ \mathrm{dm}^3$.

$$1\mathrm{L} = 1000\ \mathrm{cm}^3\ (10\ \mathrm{cm} \times 10\ \mathrm{cm} \times 10\ \mathrm{cm}) = 1\ \mathrm{dm}^3$$

A smaller unit of volume that is commonly used is the milliliter (mL). 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).

$$1\ \mathrm{mL}\ (\mathrm{cm}^3)$$

There are $1000\ \mathrm{mL}$ in $1\ \mathrm{L}$, which is the same as saying that there are $1000\ \mathrm{cm}^3$ in $1\ \mathrm{dm}^3$.



Figure 1.6.4 A typical water bottle is 1 liter in volume.

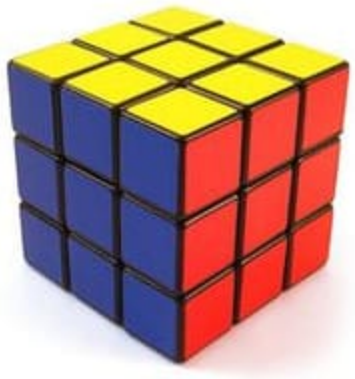


Figure 1.6.5 This Rubik's cube is $5.7\ \text{cm}$ on each side and has a volume of $185.2\ \text{cm}^3$ or $185.2\ \text{mL}$.

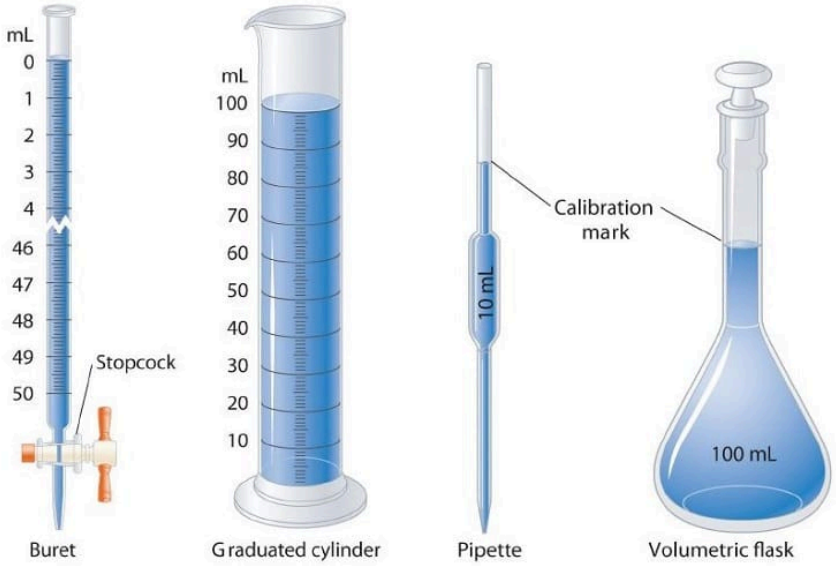


Figure 1.6.6: Buret & graduated cylinder: graduated glassware is used to deliver variable volumes of liquid. Pipette & volumetric flask: volumetric glassware is used to deliver (pipette) or contain (volumetric flask) a single volume accurately when filled to the mark. (CC BY-SA-NC; anonymous).

During your studies of chemistry (and physics also), you will note that mathematical equations are used in many different applications. Many of these equations have a number of different variables with which you will need to work. You should also note that these equations will often require you to use measurements with their units. Algebra skills become very important here!

Converting Between Units with Conversion Factors

A **conversion factor** is a factor used to convert one unit of measurement into another. A simple conversion factor can be used to convert meters into centimeters, or a more complex one can be used to convert miles per hour into meters per second. Since most calculations require measurements to be in certain units, you will find many uses for conversion factors. Always remember that a conversion factor has to represent a fact; this fact can either be simple or much more complex. For instance, you already know that 12 eggs equal one dozen. A more complex fact is that the speed of light is 1.86×10^5 miles/sec. Either one of these can be used as a conversion factor, depending on what type of calculation you might be working with (Table 1.6.1).

Table 1.6.3 Conversion Factors from SI units to English Units

English Units	Metric Units	Quantity
1 ounce (oz)	28.35 grams (g)	*mass
1 fluid once (oz)	2.96 mL	volume
2.205 pounds (lb)	1 kilogram (kg)	*mass

English Units	Metric Units	Quantity
1 inch (in)	2.54 centimeters (cm)	length
0.6214 miles (mi)	1 kilometer (km)	length
1 quarter (qt)	0.95 liters (L)	volume

*Pounds and ounces are technically units of force, not mass, but this fact is often ignored by the non-scientific community.

Of course, there are other ratios which are not listed in Table 1.6.1. They may include:

- Ratios embedded in the text of the problem (using words such as *per* or *in each*, or using symbols such as / or %).
- Conversions in the metric system, as covered earlier in this chapter.
- Common knowledge ratios (such as 60 seconds = 1 minute).

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

$$1\text{ cm} = \frac{1}{100}\text{ m} = 10^{-2}\text{m}$$

or

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

Suppose we divide both sides of the equation by 1m (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:

$$\frac{100\text{ cm}}{1\text{ m}} = \frac{1000\text{ mm}}{1\text{ m}} = \frac{1\times 10^{6}\mu\text{m}}{1\text{ m}} = 1$$

We know that 100 cm *is* 1 m, so we have the same quantity on the top and the bottom of our fraction, although it is expressed in different units.

Performing Dimensional Analysis

Dimensional analysis is amongst the most valuable tools used by physical scientists. Simply put, it is the conversion between an amount in one unit to the corresponding amount in a desired unit, using various conversion factors. This is valuable because certain measurements are more accurate or easier to find than others. The use of units in a calculation to ensure that we obtain the final proper units is called *dimensional analysis*.

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:

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

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:

quantity (in old units) × conversion factor = 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, 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 1.6.1 shows a concept map for constructing a proper conversion.

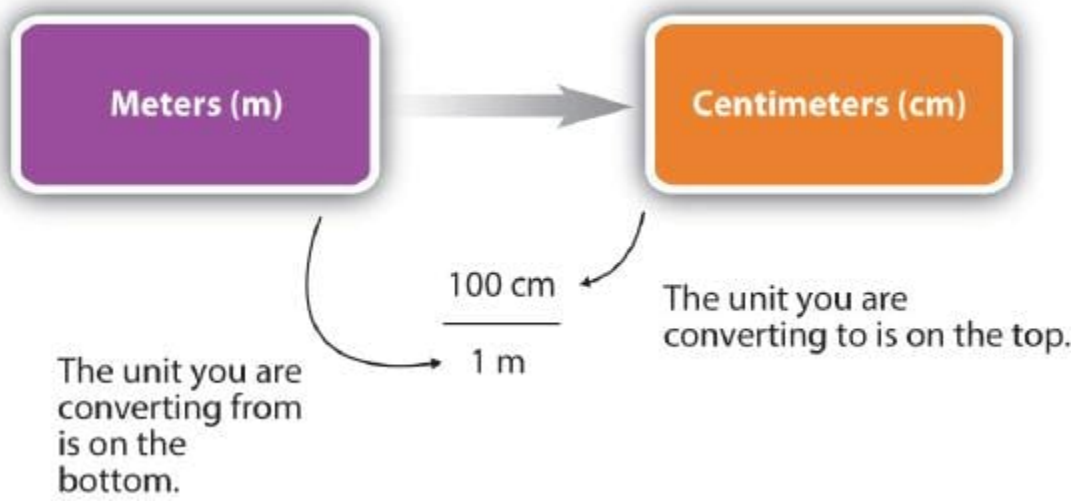


Figure 1.6.7: A Concept Map for Conversions. This is how you construct a conversion factor to convert from one unit to another.

The General Steps in Performing Dimensional Analysis

1. Identify the "**given**" information in the problem. Look for a number with units to start this problem with.
2. What is the problem asking you to "**find**"? In other words, what unit will your answer have?
3. Use **ratios** and conversion factors to cancel out the units that aren't part of your answer, and leave you with units that are part of your answer.
4. When your units cancel out correctly, you are ready to do the **math**. You are multiplying fractions, so you multiply the top numbers and divide by the bottom numbers in the fractions.

Steps for Performing Dimensional Analysis and Examples

Example 1.6.2		
Steps for Problem Solving	The average volume of blood in an adult male is 4.7 L. What is this volume in gallons?	A hummin

Example 1.6.2		
Identify the "given" information and what the problem is asking you to "find."	Given: 4.7 L Find: gal	
List other known quantities.	$1\ L = 3.785 gal$	
Prepare a concept map and use the proper conversion factor.	 $\frac{1\ gal}{3.785\ L}$	
Cancel units and calculate.	$4.7 \not{L} \times \frac{1\ \text{gal}}{3.785\ \not{L}} = 1.2\ \text{gal}$	
Think about your result.	The amount in gal should be slightly less than 4 times smaller than the given amount in L.	The amount in s shoul

Exercise 1.6.4

Perform each conversion.

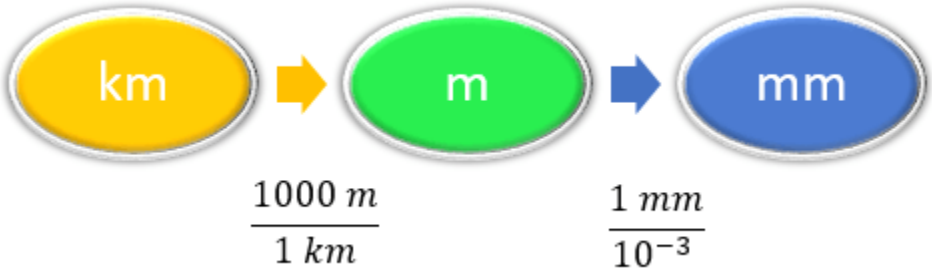
a. 101,000 ns to seconds
b. 32.08 kg to grams
c. 1.53 grams to cg

Answer a: available at the end of this section.

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. We will set up a series of conversion factors so that each conversion factor produces the next unit in the sequence. We first convert the given amount in km to the base unit, which is meters. We know that 1,000 m =1 km. Then we convert meters to mm, remembering that $1\ \text{mm} = 10^{-3}\ \text{m}$.

Concept Map



Convert kilometers to meters to millimeters: use conversion factors 1000 meters per 1 kilometer and 1 millimeter per 0.001 meter

Calculation

$$54.7\ \cancel{\text{km}} \times \frac{1{,}000\ \cancel{\text{m}}}{1\ \cancel{\text{km}}} \times \frac{1\ \cancel{\text{mm}}}{10^{-3}\ \cancel{\text{m}}} = 54{,}700{,}000\ \text{mm} \tag{1.6.1}$$

$$= 5.47 \times 10^{7}\ \text{mm} \tag{1.6.2}$$

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

Example 1.6.4: Unit Conversion

Convert 58.2 ms to megaseconds in one multi-step calculation.

Solution

Example 1.6.4 *Steps for Problem Solving Unit Conversion*

Steps for Problem Solving	Unit Conversion
Identify the "given" information and what the problem is asking you to "find."	Given: 58.2 ms Find: Ms
List other known quantities.	$1ms = 10^{-3}s$ $1Ms = 10^{6}s$

Steps for Problem Solving	Unit Conversion
Prepare a concept map.	 $\frac{10^{-3}s}{1\ ms}$ $\frac{1\ Ms}{10^{6}\ s}$ Convert milliseconds to seconds to microseconds: use conversion factors 0.001 second per millisecond and 1 microsecond per 1 million seconds
Calculate.	$58.2\ \cancel{\text{ms}} \times \frac{10^{-3}\ \cancel{s}}{1\ \cancel{\text{ms}}} \times \frac{1\ \text{Ms}}{1,000,000\ \cancel{s}} = 0.0000000582\ \text{Ms}$ $= 5.82 \times 10^{-8}\ \text{Ms}$ Neither conversion factor affects the number of significant figures in the final answer.

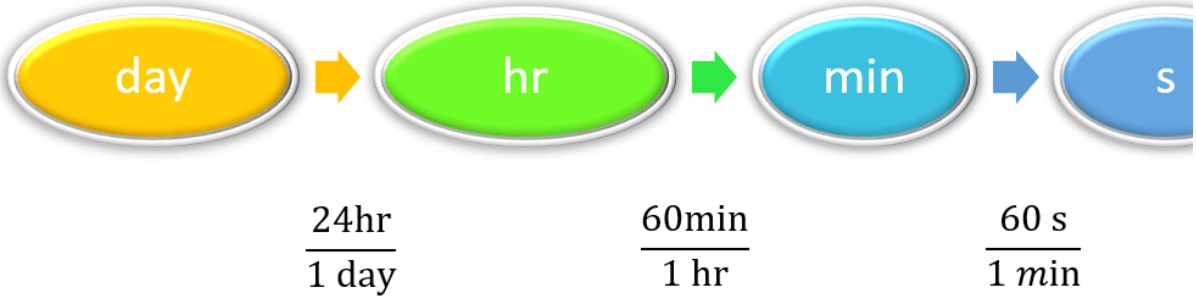
Example 1.6.5: Unit Conversion

How many seconds are in a day?

Solution

Example 1.6.5: Steps for Problem Solving Unit Conversions

Steps for Problem Solving	Unit Conversion
Identify the "given" information and what the problem is asking you to "find."	Given: 1 day Find: s
List other known quantities.	1 day = 24 hours 1 hour = 60 minutes 1 minute = 60 seconds

Steps for Problem Solving	Unit Conversion
Prepare a concept map.	 $\frac{24\text{hr}}{1\text{ day}}$ $\frac{60\text{min}}{1\text{ hr}}$ $\frac{60\text{ s}}{1\ min}$ Convert day to hour to minute to second: use conversion factors 24 hours per day, 60 minutes per hour, and 60 seconds per
Calculate.	$1\text{ d} \times \frac{24\text{ hr}}{1\text{ d}} \times \frac{60\text{ min}}{1\text{ hr}} \times \frac{60\text{ s}}{1\text{ min}} = 86,400\text{ s}$

Exercise 1.6.5

Perform each conversion in one multistep calculation.

a. 43.007 ng to kg
b. 1005 in to ft
c. 12 mi to km

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.

Summary

- 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.
- Mass is a measure of the amount of matter that an object contains.
- Weight is a measure of force that is equal to the gravitational pull on an object.
- Mass is independent of location, while weight depends on location.
- Length is the measurement of the extent of something along its greatest dimension.
- Volume is the amount of space occupied by a sample of matter.
- Volume can be determined by knowing the length of each side of the item.
- Conversion factors are used to convert one unit of measurement into another.
- Dimensional analysis (unit conversions) involves the use of conversion factors that will cancel unwanted units and produce desired units.

Contributors and Attributions

-

- Marisa Alviar-Agnew (Sacramento City College)

- Henry Agnew (UC Davis)
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Answers

Exercise 1.6.1

6.7×10^{10}

Exercise 1.6.1

1.689×10^{3}

Exercise 1.6.1

1.26×10^{1}

Exercise 1.6.2

6.567×10^{-6}

Exercise 1.6.2

0.0622

Exercise 1.6.2

0.0000000099

Exercise 1.6.3

km

Exercise 1.6.3

mg

Exercise 1.6.3

ns

Exercise 1.6.3

cL

Exercise 1.6.4

$1.01000x10^{-4}s$

$3.208x10^{4}g$

$1.53x10^{2}g$

Exercise 1.6.5

$4.3007x10^{-14}kg$

Exercise 1.6.5

83.75 ft

Exercise 1.6.5

19 km

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1.7: Density

Learning Objectives

- Define density.
- Determine the density of various substances.

Density (ρ) is a physical property found by dividing the mass of an object by its volume. Regardless of the sample size, density is always constant. For example, the density of a pure sample of tungsten is always 19.25 grams per cubic centimeter. This means that whether you have one gram or one kilogram of the sample, the density will never vary. The equation, as we already know, is as follows:

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

or just

$$\rho = \frac{m}{V}$$

Table 1.7.1 *Densities of Common Substances*

Substance	Density at 25°C (g/cm3)
blood	1.035
body fat	0.918
whole milk	1.030
corn oil	0.922
mayonnaise	0.910
honey	1.420

Notice in Table 1.7.1 that corn oil has a lower mass to volume ratio than water. This means that when added to water, corn oil will "float."

Density can be measured for all substances, solids, liquids and gases. For solids and liquids, density is often reported using the units of g/cm^3. Densities of gases, which are significantly lower than the densities of solids and liquids, are often given using units of g/L.

Example 1.7.1: Ethyl Alcohol

Calculate the density of a 30.2 mL sample of ethyl alcohol with a mass of 23.71002 g

Solution

$$\rho = \frac{23.71002\,g}{30.2\,mL} = 0.785\,g/mL$$

Exercise 1.7.1

a. Find the density (in kg/L) of a sample that has a volume of 36.5 L and a mass of 10.0 kg.
b. If you have a 2.130 mL sample of acetic acid with mass 2.234 g, what is the density in g/mL?

Answer a available at the end of this section.

Summary

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

Contributors and Attributions

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

Answers

Exercise 1.7.1

$0.274\ kg/L$

$1.049\ g/mL$

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1.8: Energy - Heat and Temperature

Learning Objectives

- Identify the difference between temperature and heat.
- Recognize the different scales used to measure temperature.
- Perform temperature conversions from one unit to another.

The concept of temperature may seem familiar to you, but many people confuse temperature with heat. **Temperature** is a measure of how hot or cold an object is relative to another object (its thermal energy content), whereas **heat** is the flow of thermal energy between objects with different temperatures. 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 1.8.1: 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 $1.8.2$ Daniel Gabriel Fahrenheit (top), Anders Celsius (center), and Lord Kelvin (bottom).

The Fahrenheit 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 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 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 kelvins.

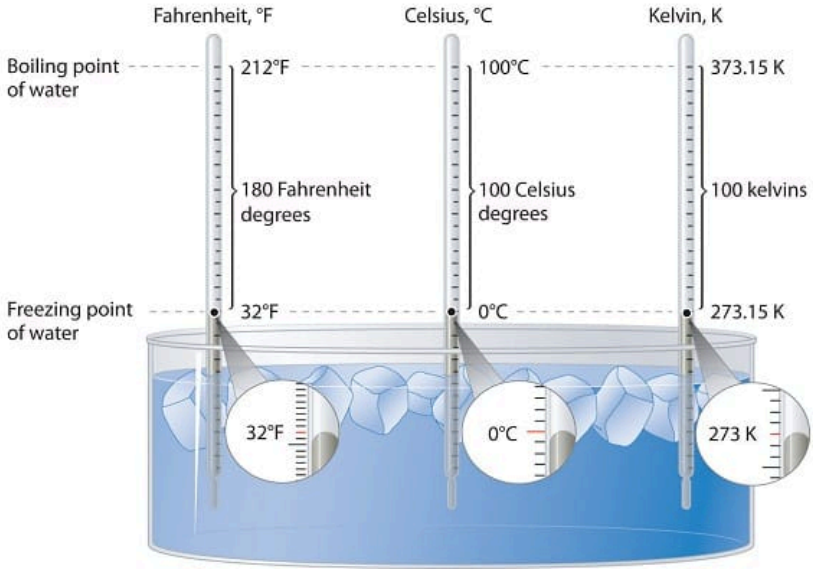


Figure 1.8.1: A Comparison of the Fahrenheit, Celsius, and Kelvin Temperature Scales. Because the difference between the freezing point of water and the boiling point of water is 100° on both the Celsius and Kelvin scales, the size of a degree Celsius (°C) and a kelvin (K) are precisely the same. In contrast, both a degree Celsius and a kelvin are 9/5 the size of a degree Fahrenheit (°F).

Converting between Scales

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:

$$T\,(\text{in °C}) + 273.15 = T\,(\text{in K}) \tag{1.8.1}$$

$$T\ \ (\text{in K}) - 273.15 = T\ (\text{in °C}) \tag{1.8.2}$$

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:

$$°C = \frac{5}{9} \times (°F - 32) \tag{1.8.3}$$

$$°F = \frac{9}{5} \times (°C) + 32 \tag{1.8.4}$$

There is only one temperature for which the numerical value is the same on both the Fahrenheit and Celsius scales: −40°C = −40°F.

Example 1.8.1: 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 1.8.3:

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

Converting from Celsius to Kelvin requires the use of Equation 1.8.1:

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

Exercise 1.8.1

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.

Summary

- Three different scales are commonly used to measure temperature: Fahrenheit (expressed as °F), Celsius (°C), and Kelvin (K).
- The freezing point of water is 0°C = 273.15 K; the boiling point of water is 100°C = 373.15 K.
- Both a degree Celsius and a kelvin are 9/5 the size of a degree Fahrenheit.

Contributors and Attributions

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Answers

Exercise 1.8.1
5527 °C, 9980 °F

Exercise 1.8.1
2807 °C, 5084 °F

Exercise 1.8.1
-195.8 °C, -320.4 °F

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2: ATOMS

2.1: Atoms - Ideas from the Ancient Greeks
2.2: Scientific Laws - Conservation of Mass and Definite Proportions
2.3: John Dalton and the Atomic Theory of Matter
2.4: The Mole and Molar Mass
2.5: Mendeleev and Periodic Table
2.6: Atoms and Molecules- Real and Relevant

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2.1: Atoms - Ideas from the Ancient Greeks

Learning Objectives

- Give a short history of the concept of the atom.
- Describe the contributions of Democritus to atomic theory.

You learned earlier that all matter in the universe is made out of tiny building blocks called atoms; all modern scientists accept the concept of the atom. However, when the concept of the atom was first proposed about 2,500 years ago, ancient philosophers laughed at the idea. It has always been difficult to convince people of the existence of things that are too small to see. We will spend some time considering the evidence (observations) that convince scientists of the existence of atoms.

Democritus and the Greek Philosophers

About 2,500 years ago, early Greek philosophers believed the entire universe was a single, huge entity. In other words, "everything was one." They believed that all objects, all matter, and all substances were connected as a single, unchangeable "thing." One of the first people to propose "atoms" was a man known as Democritus. As an alternative to the beliefs of the Greek philosophers, he suggested that **atomos**, or atomon—tiny, indivisible, solid objects—make up all matter in the universe.



Figure 2.1.1 (Top) Democritus by Hendrick ter Brugghen, 1628. Democritus was known as the "laughing philosopher." It was a good thing he liked to laugh, because most other philosophers were laughing at his theories. (Bottom) British physicist and chemist John Dalton (1766-1844). Unlike the Greek philosophers, John Dalton believed in both logical thinking and experimentation.

Democritus then reasoned that changes occur when the many atomos in an object were reconnected or recombined in different ways. Democritus even extended this theory, suggesting that there were different varieties of atomos with different shapes, sizes, and masses. He thought, however, that shape, size, and mass were the only properties differentiating the different types of atomos. According to Democritus, other characteristics, like color and taste, did not reflect properties of the atomos themselves, but rather, resulted from the different ways in which the atomos were combined and connected to one another.

The early Greek philosophers tried to understand the nature of the world through reason and logic, but not through experiment and observation. As a result, they had some very interesting ideas, but they felt no need to justify their ideas based on life experiences. In a lot of ways, you can think of the Greek philosophers as being "all thought and no action." It's truly amazing how much they achieved using their minds, but because they never performed any experiments, they missed or rejected a lot of discoveries that they could have made otherwise. Greek philosophers dismissed Democritus' theory entirely. Sadly, it took over

two millennia before the theory of atomos (or "atoms," as they're known today) was fully appreciated.

Summary

- 2,500 years ago, Democritus suggested that all matter in the universe was made up of tiny, indivisible, solid objects he called "atomos." However, other Greek philosophers disliked Democritus' "atomos" theory because they felt it was illogical.

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2.2: Scientific Laws - Conservation of Mass and Definite Proportions

Learning Objectives

- Explain the law of conservation of mass.
- Explain the law of definite proportions.

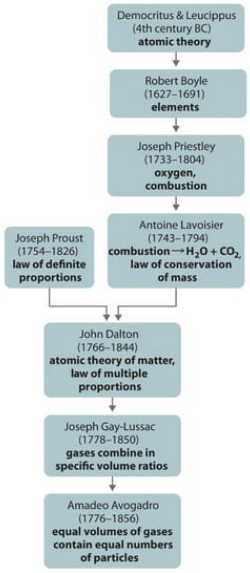


Figure 2.2.1: A summary of the historical development of the concept of the atom.

The Law of Conservation of Mass

It may seem as though burning destroys matter, but the same amount, or mass, of matter still exists after a campfire as before. Figure 2.2.2 (below) shows that when wood burns, it combines with oxygen and changes not only to ashes, but also to carbon dioxide and water vapor. The gases float off into the air, leaving behind just the ashes. Suppose you had measured the mass of the wood before it burned and the mass of the ashes after it burned. Also assume that you had been able to measure the oxygen used by the fire and the gases produced by the fire. What would you find? The total mass of matter after the fire would be the same as the total mass of matter before the fire.

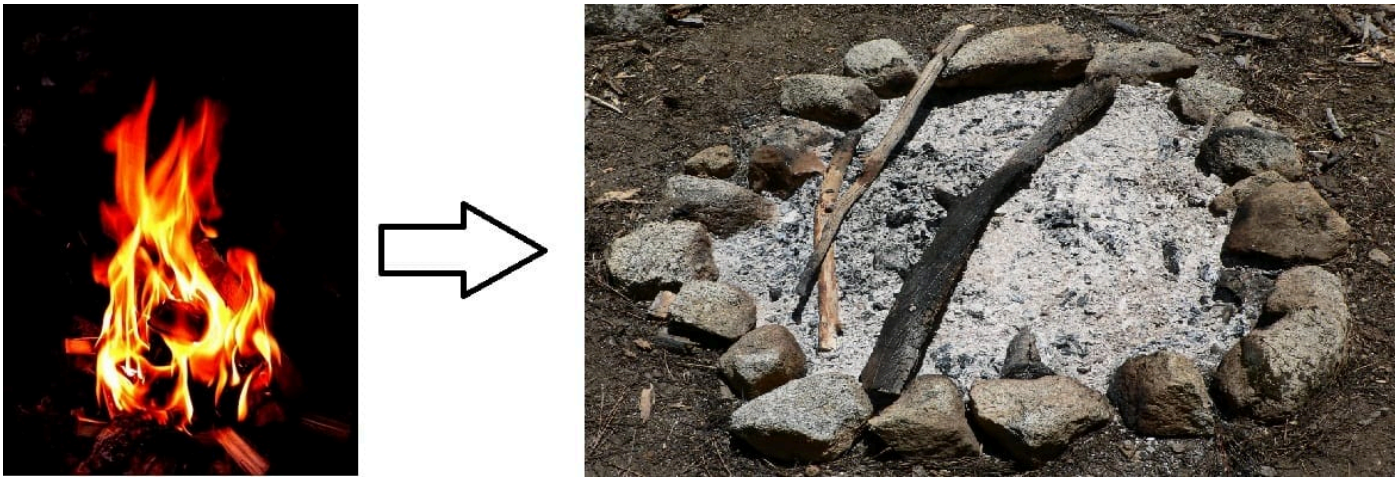


Figure 2.2.2: Burning is a chemical process. The flames are caused as a result of a fuel undergoing combustion (burning). Images used with permission (CC BY-SA 2.5; Einar Helland Berger for fire and for ash).

The law of conservation of mass was created in 1789 by French chemist Antoine Lavoisier. The **law of conservation of mass** states that matter cannot be created or destroyed in a chemical reaction. For example—in Figure 2.2.3—when wood burns, the mass of the soot, ashes, and gases equals the original mass of the wood and the oxygen when it first reacted.

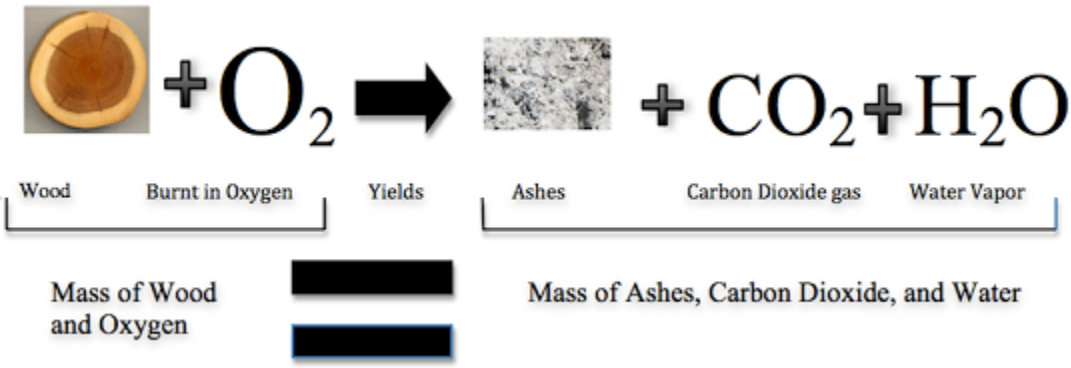


Figure 2.2.3: Image of the wood courtesy of Ehamberg and Stannered on Wikimedia Commons, available under Creative Commons Attribution 2.5 Generic license. Image of ashes courtesy of Walter Siegmund. Image as a whole constructed by Jessica Thornton (UCD).

So, the mass of the product(s) equals the mass of the reactants. Reactants are two or more elements chemically interacting to make a new substance; product is the substance(s) formed as the result of a chemical reaction (Video 2.2.1). Matter (and mass) may not be able to be created or destroyed, but can change forms to other substances like liquids, gases, solids, etc.

YouTube Video

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Video 2.2.1 This is a nice little demonstration showing the conservation of mass in action.

It's important to know the law well. If a 300 kg tree is burning down—when the process is complete—there are only ashes left, and all of them together weigh 10 kg. You may wonder where the other 290 kg went. The missing 290 kg was released into the

atmosphere as smoke, so the only visible matter left is the 10 kg of ash. If you understand the law of conservation of mass, then you know that the other 290 kg had to go somewhere, because it had to equal the mass of the tree before it burnt down.

Example 2.2.1

If heating 10.0 grams of calcium carbonate ($CaCO_3$) produces 4.4 g of carbon dioxide (CO_2) and 5.6 g of calcium oxide (CaO), show that these observations are in agreement with the law of conservation of mass.

Solution

$$\text{Mass of the reactants} = \text{Mass of the products}$$
$$10.0\,\text{g of } CaCO_3 = 4.4\,\text{g of } CO_2 + 5.6\,\text{g of CaO}$$
$$10.0\,\text{g of reactant} = 10.0\,\text{g of products}$$

Because the mass of the reactant is equal to the mass of the products, the observations are in agreement with the law of conservation of mass.

Exercise 2.2.1

Potassium hydroxide (KOH) readily reacts with carbon dioxide (CO_2) to produce Potassium carbonate (K_2CO_3) and water (H_2O). How many grams of potassium carbonate are produced if 224.4 g of KOH react with 88.0 g of CO_2? The reaction also produces 36.0 g of water.

Answer available at the end of this section.

The Law of Definite Proportions

Joseph Proust (1754-1826) formulated the ***law of definite proportions*** (also called the **Law of Constant *Composition*** or **Proust's Law**). This law states that if a compound is broken down into its constituent elements, the masses of the constituents will always have the same proportions, regardless of the quantity or source of the original substance. Joseph Proust based this law primarily on his experiments with basic copper carbonate. The illustration below depicts this law in action.

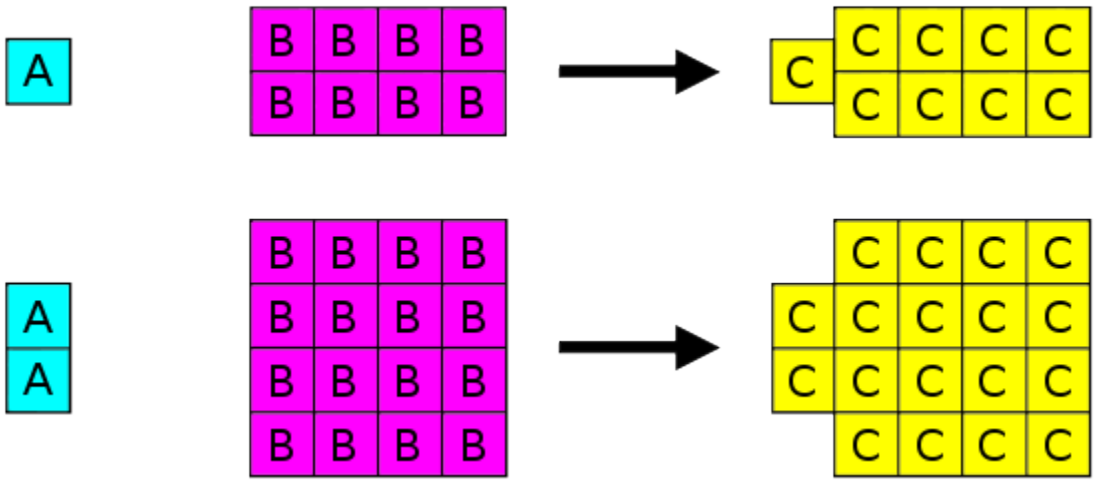


Figure 2.2.4: If 1 gram of A reacts with 8 grams of B, then by the Law of Definite Proportions, 2 grams of A must react with 16 grams of B. If 1 gram of A reacts with 8 grams of B, then by the Law of Conservation of Mass, they must produce 9 grams of C. Similarly, when 2 grams of A react with 16 grams of B, they must produce 18 grams of C.

> Law of Definite Proportions states that in a given type of chemical substance, the elements are always combined in the same proportions by mass.

The Law of Definite Proportions applies when elements are reacted together to form *the same* product. Therefore, while the Law of Definite Proportions can be used to compare two experiments in which hydrogen and oxygen react to form water, the Law of Definite Proportions can *not* be used to compare one experiment in which hydrogen and oxygen react to form water, and another experiment in which hydrogen and oxygen react to form hydrogen peroxide (peroxide is another material that can be made from hydrogen and oxygen).

Example 2.2.2: water

Oxygen makes up 88.8% of the mass of any sample of pure water, while hydrogen makes up the remaining 11.2% of the mass. You can get water by melting ice or snow; or by condensing steam from a river, sea, pond, etc. It can be from different places: USA, UK, Australia, or anywhere. Water can be made by chemical reactions, such as burning hydrogen in oxygen.

However, if the water is **pure**, it will **always** consist of 88.8 % oxygen by mass and 11.2 % hydrogen by mass, irrespective of its source or method of preparation.

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Video 2.2.2 Law of definite proportions.

Summary

- Burning and other changes in matter do not destroy matter.
- The mass of matter is always the same before and after the changes occur.
- The law of conservation of mass states that matter cannot be created or destroyed.
- The law of definite proportions states that a given chemical compound always contains the same elements in the exact same proportions by mass.

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Contributors and Attributions

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Answers

Exercise 2.2.1

276.4 g of potassium carbonate

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2.3: John Dalton and the Atomic Theory of Matter

Learning Objective

- Summarize Dalton's atomic theory.
- Explain the Law of multiple proportions.

While it must be assumed that many more scientists, philosophers, and others studied composition of matter after Democritus, a major leap forward in our understanding of the composition of matter took place in the 1800s with the work of the British scientist John Dalton. He started teaching school at age twelve, and was primarily known as a teacher. In his twenties, he moved to the growing city of Manchester, where he was able to pursue some scientific studies. His work in several areas of science brought him a number of honors. When he died, over 40,000 people in Manchester marched at his funeral.

Dalton's modern atomic theory, proposed around 1803, 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. At that size, it takes over 18 million of these atoms, lined up side by side, to equal the width of a human pinky finger (about 1 cm).

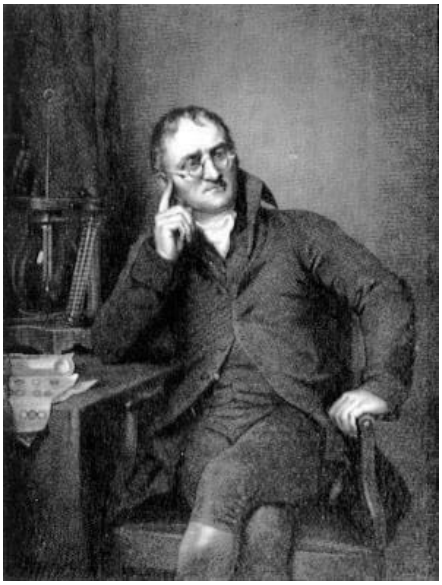


Figure 2.3.1: John Dalton was an English scientist who enunciated the modern atomic theory.

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 his 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 (Figure 2.3.2). Atoms of different elements differ in size, mass, and other properties.

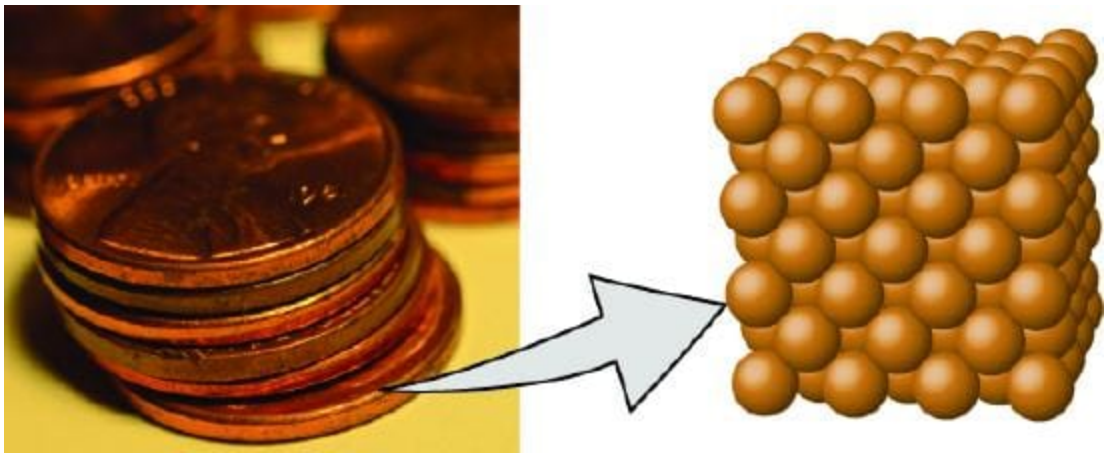


Figure 2.3.2: A pre-1982 copper penny (left) contains approximately 3×10^{22} copper atoms (several dozen are represented as brown spheres at the right), each of which has the same chemical properties. (Credit: modification of work by "slgckgc"/Flickr.)

- Atoms cannot be subdivided, created, or destroyed.
- Atoms of different elements can combine in simple whole number ratios to form chemical compounds (Figure 2.3.3).
- In chemical reactions, atoms are combined, separated, or rearranged.

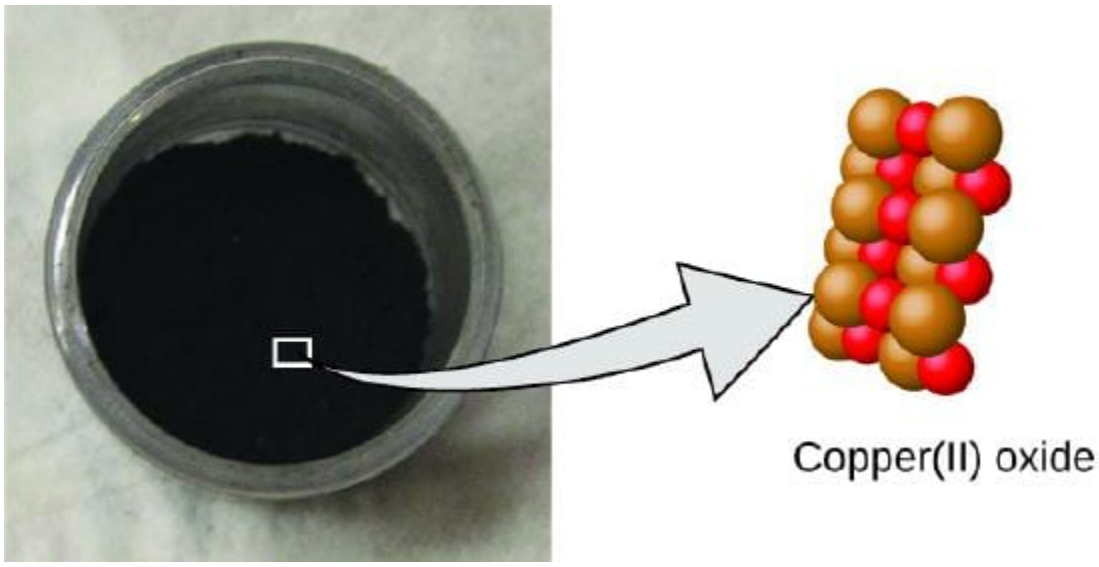


Figure 2.3.3: Copper(II) oxide, a powdery, black compound, results from the combination of two types of atoms—copper (brown spheres) and oxygen (red spheres)—in a 1:1 ratio. (Credit: modification of work by "Chemicalinterest"/Wikimedia Commons.)

Note

Dalton's atomic theory has been largely accepted by the scientific community, with the exception of three changes. Present-day science acknowledges that:

(1) An atom can be further subdivided.

(2) All atoms of an element are *not* identical in mass.

(3) Using nuclear fission and fusion techniques, we can create or destroy atoms by changing them into other atoms.

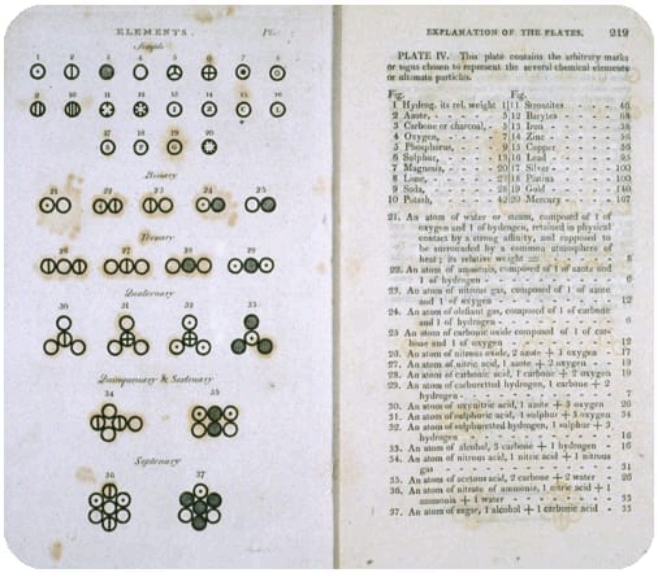


Figure 2.3.5 Dalton's symbols from his text "A New System of Chemical Philosophy."

Example 2.3.1

In the following drawing, the green spheres represent atoms of a certain element. The purple spheres represent atoms of another element. If the spheres touch, they are part of a single unit of a compound. Does the following chemical change represented by these symbols violate any of the ideas of Dalton's atomic theory? If so, which one?



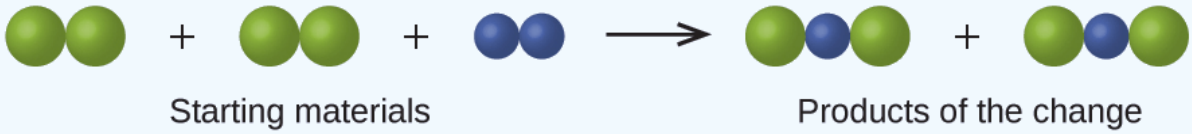
This equation shows that the starting materials of the reaction are two bonded, green spheres, which are being combined with two smaller, bonded purple spheres. The product of the change is one purple sphere that is bonded to one green sphere.

Solution

The starting materials consist of two green spheres and two purple spheres. The products consist of only one green sphere and one purple sphere. This violates Dalton's postulate that atoms are neither created nor destroyed during a chemical change, but are merely redistributed. (In this case, atoms appear to have been destroyed.)

Exercise 2.3.1

In the following drawing, the green spheres represent atoms of a certain element. The purple spheres represent atoms of another element. If the spheres touch, they are part of a single unit of a compound. Does the following chemical change represented by these symbols violate any of the ideas of Dalton's atomic theory? If so, which one?



This equation shows that the starting materials of the reaction are two sets of bonded, green spheres which are each being combined with two smaller, bonded purple spheres. The products of the change are two molecules that each contain one purple sphere bonded between two green spheres.

Answer available at the end of this section.

Law of Multiple Proportions

Many combinations of elements can react to form more than one compound. In such cases, the masses of a particular element that combine with a fixed mass of a second element are demonstrable in ratios of small whole numbers. It's easy to say this, but please make sure that you understand how it works. Nitrogen forms a very large number of oxides, five of which are shown here.

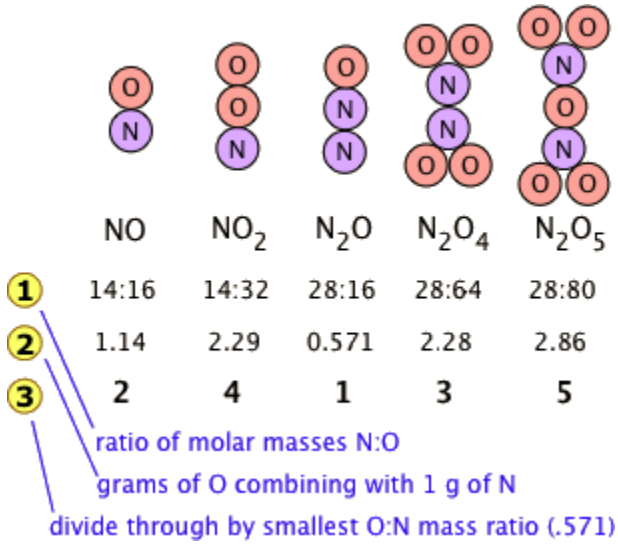


Figure 2.3.6: Law of Multiple Proportions applied to nitrogen oxides (NO_x) compounds. (CC-BY; Stephen Lower.)

- Line 1 shows the ratio of the relative weights of the two elements in each compound. These ratios were calculated by simply taking the molar mass of each element, and multiplying by the number of atoms of that element per mole of the compound. Thus for NO_2, we have (1 × 14) : (2 × 16) = 14:32. (These numbers were not known in the early days of Chemistry because atomic weights [i.e., molar masses] of most elements were not reliably known.)
- The numbers in Line 2 are just the mass ratios of O:N, found by dividing the corresponding ratios in line 1. But someone who depends solely on experiment would work these out by finding the mass of O that combines with unit mass (1 g) of nitrogen.
- Line 3 is obtained by dividing the figures of the Line 2 by the smallest O:N ratio in Line 2 (which is the ratio for N_2O). Note that just as the law of multiple proportions says, the weight of oxygen that combines with unit weight of nitrogen work out to small integers; there is a typo in Line 3—where there is a *3*, there should be a *4*.
- Of course, we just as easily could have illustrated the law by considering the mass of nitrogen that combines with one gram of oxygen; it works both ways!

> The law of multiple proportions states that if two elements form more than one compound between them, the masses of one element combined with a fixed mass of the second element form in ratios of small integers.

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Video 2.3.1 *The law of multiple proportions*

Example 2.3.1: Law Multiple Proportions

A sample of compound A (a clear, colorless gas) is analyzed and found to contain 4.27 g carbon and 5.69 g oxygen. A sample of compound B (also a clear, colorless gas) is analyzed and found to contain 5.19 g carbon and 13.84 g oxygen. Are these data an example of the law of definite proportions, the law of multiple proportions, or neither? What do these data tell you about substances A and B?

Solution

In compound A, the mass ratio of carbon to oxygen is:

$$\frac{1.33\ \text{g O}}{1\ \text{g C}}$$

In compound B, the mass ratio of carbon to oxygen is:

$$\frac{2.67\ \text{g O}}{1\ \text{g C}}$$

The ratio of these ratios is:

$$\frac{\frac{1.33\ \text{g O}}{1\ \text{g C}}}{\frac{2.67\ \text{g O}}{1\ \text{g C}}} = \frac{1}{2}$$

This supports the law of multiple proportions. This means that A and B are different compounds, with A having one-half as much carbon per amount of oxygen (or twice as much oxygen per amount of carbon) as B. A possible pair of compounds that would fit this relationship would be A = CO_2 and B = CO.

Exercise 2.3.1

A sample of compound X (a clear, colorless, combustible liquid with a noticeable odor) is analyzed and found to contain 14.13 g carbon and 2.96 g hydrogen. A sample of compound Y (a clear, colorless, combustible liquid with a noticeable odor that is slightly different from X's odor) is analyzed and found to contain 19.91 g carbon and 3.34 g hydrogen. Are these data an example of the law of definite proportions, the law of multiple proportions, or neither? What do these data tell you about substances X and Y?

Answer available at the end of this section.

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 demonstrates in Video 2.3.1, control of individual atoms can be used to create animations.

YouTube Video

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Video 2.3.1: 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.

Summary

- Dalton's Atomic Theory is the first scientific theory to relate chemical changes to the structure, properties, and behavior of the atom. 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.
- The law of multiple proportions states that whenever the same two elements form more than one compound, the different masses of one element that combine with the same mass of the other element are in the ratio of small whole numbers.

Contributors and Attributions

-

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- Henry Agnew (UC Davis)

- TextMap: Chemistry - The Central Science (Brown et al.)

- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

Answers

Exercise 2.3.1

The starting materials consist of four green spheres and two purple spheres. The products consist of four green spheres and two purple spheres. This does not violate any of Dalton's postulates—atoms are neither created nor destroyed, but are redistributed in small, whole-number ratios.

Exercise 2.3.1

In compound X, the mass ratio of carbon to hydrogen is $\frac{14.13\text{ g C}}{2.96\text{ g H}}$.

In compound Y, the mass ratio of carbon to hydrogen is $\frac{19.91\text{ g C}}{3.34\text{ g H}}$.

The ratio of these ratios is

$$\frac{\frac{14.13\text{ g C}}{2.96\text{ g H}}}{\frac{19.91\text{ g C}}{3.34\text{ g H}}} = \frac{4.77\text{ g C/g H}}{5.96\text{ g C/g H}} = 0.800 = \frac{4}{5}.$$

This small, whole-number ratio supports the law of multiple proportions. This means that X and Y are different compounds.

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2.4: The Mole and Molar Mass

Learning Objectives

- Define mole and molar mass.
- Perform calculations to convert between moles and mass of a substance.
- Perform calculations to convert between mass of a substance and number of particles.

The Mole and Avogadro's Number

It certainly is easy to count bananas or to count elephants (as long as you stay out of their way). However, you would be counting grains of sugar from your sugar canister for a long, long time. Atoms and molecules are extremely small—far, far smaller than a grain of sugar. Counting atoms or molecules is not only unwise, it is absolutely impossible. One drop of water contains about 10^{22} molecules of water. If you counted 10 molecules every second for 50 years without stopping, you would have counted only 1.6×10^{10} molecules. Put another way, at that counting rate, it would take you over 30 trillion years to count the water molecules in one tiny drop.

Chemists of the past needed a name that stood for a very large number of items. Amadeo Avogadro (1776-1856), an Italian scientist, provided such a number. He is responsible for the counting unit of measure called the mole. A **mole** (mol) is the amount of a substance that contains 6.02×10^{23} representative particles of that substance. The mole is the SI unit for amount of a substance. Just like the dozen and the gross, it is a name that stands for a number. There are therefore 6.02×10^{23} water molecules in a mole of water molecules. There also would be 6.02×10^{23} bananas in a mole of bananas—if such a huge number of bananas ever existed.



Figure 2.4.1: Italian scientist Amadeo Avogadro, whose work led to the concept of the mole as a counting unit in chemistry.

The number 6.02×10^{23} is called **Avogadro's number**, the number of representative particles in a mole. It is an experimentally determined number. A **representative particle** is the smallest unit in which a substance naturally exists. For the majority of elements, the representative particle is the atom. Iron, carbon, and helium consist of iron atoms, carbon atoms, and helium atoms, respectively. Seven elements exist in nature as diatomic molecules and they are $\mathrm{H_2}$, $\mathrm{N_2}$, $\mathrm{O_2}$, $\mathrm{F_2}$, $\mathrm{Cl_2}$, $\mathrm{Br_2}$, and $\mathrm{I_2}$. The representative particle for these elements is the molecule. Likewise, all molecular compounds such as $\mathrm{H_2O}$ and $\mathrm{CO_2}$ exist as molecules, and so the molecule is their representative particle. For ionic compounds such as NaCl and $\mathrm{Ca(NO_3)_2}$, the representative particle is the formula unit. A mole of any substance contains Avogadro's number $\left(6.02 \times 10^{23}\right)$ of representative particles.



Figure 2.4.2: The animal mole is very different than the counting unit of the mole. Chemists nonetheless have adopted the mole as their unofficial mascot. National Mole Day is a celebration of chemistry that occurs on October 23 (10/23) of each year.

Converting Between Number of Atoms to Moles and Vice Versa

We can use Avogadro's number as a conversion factor, or ratio, in dimensional analysis problems. If we are given the number of atoms of an element X, we can convert it into moles by using the relationship

$$1 \text{ mol X} = 6.022 \times 10^{23} \text{ X atoms}$$

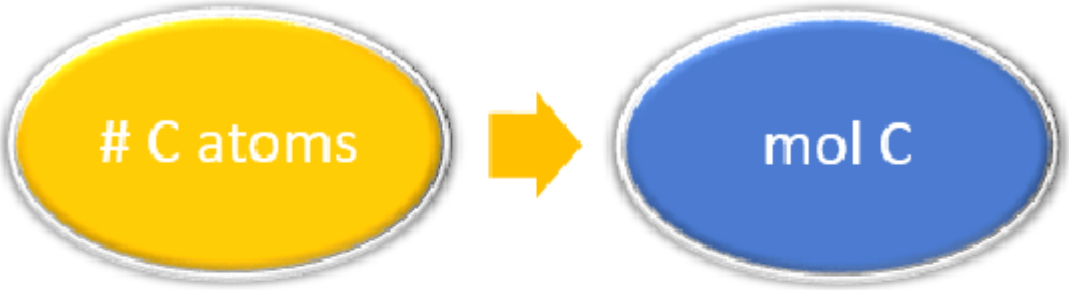
Example 2.4.1: Moles of Carbon

The element carbon exists in two primary forms: graphite and diamond. How many moles of carbon atoms is 4.72×10^{24} atoms of carbon?

Solution

Example 2.4.1: Steps for Problem Solving; Molar Conversion of Carbon

Steps for Problem Solving	The element carbon exists in two primary forms: graphite and diamond. How many moles of carbon atom $\times 10^{24}$ atoms of carbon?
Identify the "given" information and what the problem is asking you to "find."	Given: 4.72×10^{24} C atoms Find: mol C
List other known quantities.	$1\ mol = 6.022 \times 10^{23}$ C atoms

Steps for Problem Solving	The element carbon exists in two primary forms: graphite and diamond. How many moles of carbon atom $\times 10^{24}$ atoms of carbon?
Prepare a concept map and use the proper conversion factor.	 $\frac{1\ mol\ C}{6.022\ \times 10^{23} C\ atoms}$
Cancel units and calculate.	$4.72 \times 10^{24}\ \cancel{\text{C atoms}} \times \frac{1\ \text{mol C}}{6.02 \times 10^{23}\ \cancel{\text{C atoms}}} = 7.84\ \text{mol C}$
Think about your result.	The given number of carbon atoms was greater than Avogadro's number, so the number of moles of C atoms is gr 1 mole. Since Avogadro's number is a measured quantity with three significant figures, the result of the calcula rounded to three significant figures.

Molar Mass

The molar mass of a substance is defined as the mass in grams of 1 mole of that substance. One mole of isotopically pure carbon-12 has a mass of 12 g. For an element, the molar mass is the mass of 1 mol of atoms of that element; for a covalent molecular compound, it is the mass of 1 mol of molecules of that compound; for an ionic compound, it is the mass of 1 mol of formula units. That is, the molar mass of a substance is the mass (in grams per mole) of 6.022 × 10^{23} atoms, molecules, or formula units of that substance. In each case, the number of grams in 1 mol is the same as the number of atomic mass units that describe the atomic mass, the molecular mass, or the formula mass, respectively.

The molar mass of any substance is its atomic mass, molecular mass, or formula mass in grams per mole.

The periodic table lists the atomic mass of carbon as 12.011 amu; the average molar mass of carbon—the mass of 6.022 × 10^{23} carbon atoms—is therefore 12.011 g/mol:

Table 2.4.1 *Molar Mass of Select Substances*

Substance (formula)	Basic Unit	Atomic, Molecular, or Formula Mass (amu)	Molar Mass (g/mol)
carbon (C)	atom	12.011 (atomic mass)	12.011
ethanol (C_2H_5OH)	molecule	46.069 (molecular mass)	46.069
calcium phosphate [$Ca_3(PO_4)_2$]	formula unit	310.177 (formula mass)	310.177

Converting Between Grams and Moles

The molar mass of any substance is the mass in grams of one mole of representative particles of that substance. The

representative particles can be atoms, molecules, or formula units of ionic compounds. This relationship is frequently used in the laboratory. Suppose that for a certain experiment you need 3.00 moles of calcium chloride $(CaCl_2)$. Since calcium chloride is a solid, it would be convenient to use a balance to measure the mass that is needed. Dimensional analysis will allow you to calculate the mass of $CaCl_2$ that you should measure, as shown in Example 2.4.2.

Example 2.4.2: Calcium Chloride

Calculate the mass of 3.00 moles of calcium chloride ($CaCl_2$).

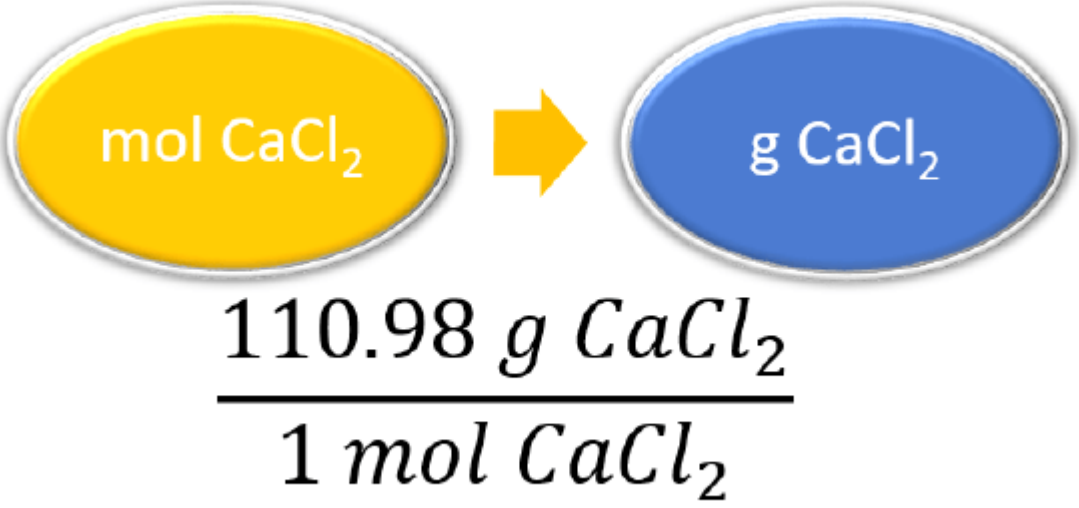


Figure 2.4.3: Calcium chloride is used as a drying agent and as a road deicer.

Solution

Example 2.4.2:Steps for Problem Solving; Calculate the mass of 3.00 moles of calcium chloride ($CaCl_2$).

Steps for Problem Solving	Calculate the mass of 3.00 moles of calcium chloride ($CaCl_2$).
Identify the "given" information and what the problem is asking you to "find."	Given: 3.00 moles of $CaCl_2$ Find: g $CaCl_2$
List other known quantities.	1 ml $CaCl_2$ = 110.98 g $CaCl_2$

Steps for Problem Solving	Calculate the mass of 3.00 moles of calcium chloride ($CaCl_2$).
Prepare a concept map and use the proper conversion factor.	 $$\frac{110.98\ g\ CaCl_2}{1\ mol\ CaCl_2}$$
Cancel units and calculate.	$3.00\ \cancel{\text{mol CaCl}_2} \times \frac{110.98\ \text{g CaCl}_2}{1\ \cancel{\text{mol CaCl}_2}} = 333\ \text{g CaCl}_2$
Think about your result.	

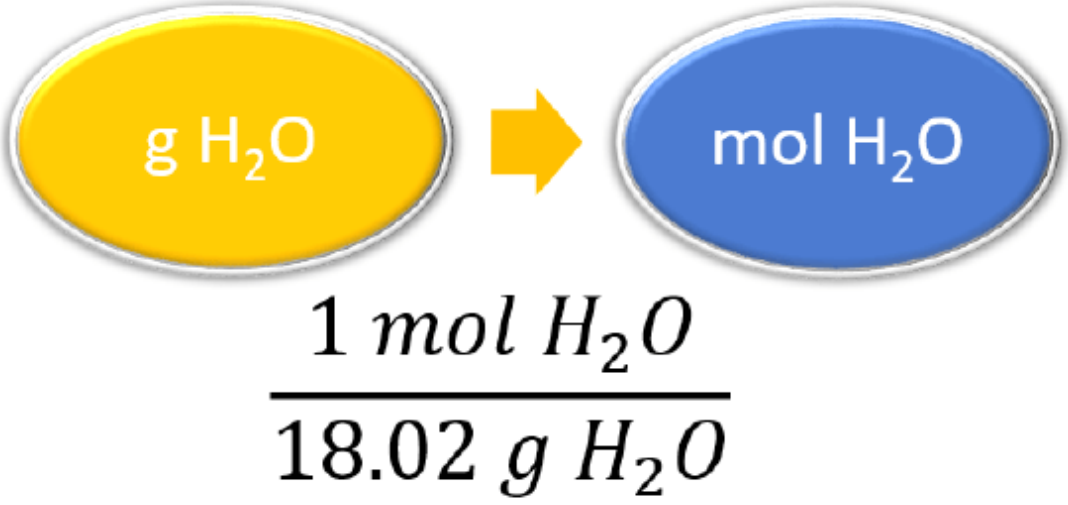
Example 2.4.3: Water

How many moles are present in 108 grams of water?

Solution

Example 2.4.3: Steps for Problem Solving; how many moles are present in 108 grams of water

Steps for Problem Solving	How many moles are present in 108 grams of water?
Identify the "given" information and what the problem is asking you to "find."	Given: 108 g H_2O Find: mol H_2O
List other known quantities.	$1\ \text{mol}\ H_2O = 18.02\ \text{g}\ H_2O$

Steps for Problem Solving	How many moles are present in 108 grams of water?
Prepare a concept map and use the proper conversion factor.	 $\frac{1\ mol\ H_2O}{18.02\ g\ H_2O}$
Cancel units and calculate.	$108\ \cancel{\text{g H}_2\text{O}} \times \frac{1\ \text{mol H}_2\text{O}}{18.02\ \cancel{\text{g H}_2\text{O}}} = 5.99\ \text{mol H}_2\text{O}$
Think about your result.	

Exercise 2.4.1: Nitrogen Gas

What is the mass of $7.50\ \text{mol}$ of Nitrogen gas N_2?

Answer: available at the end of this section.

Conversions Between Mass and Number of Particles

In "Conversions Between Moles and Mass", you learned how to convert back and forth between moles and the number of representative particles. Now you have seen how to convert back and forth between moles and mass of a substance in grams. We can combine the two types of problems into one. Mass and number of particles are both related to moles. To convert from mass to number of particles or vice-versa, it will first require a conversion to moles, as shown in Figure 2.4.1 and Example 2.4.4.



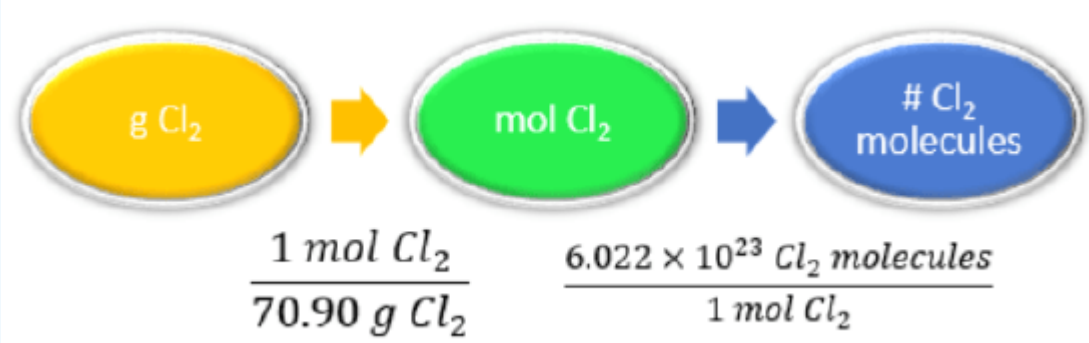
Figure 2.4.4: Conversion from number of particles to mass, or from mass to number of particles, requires two steps. To convert from number of particles to moles, use mol/Avogrado's #, and to convert from moles to mass, use g/mol.

Example 2.4.4: Chlorine

How many molecules is $20.0\ \text{g}$ of chlorine gas, Cl_2?

Solution

Example 2.4.4:Steps for Problem Solving how many molecules is $20.0\ \text{g}$ of chlorine gas, Cl_2?

Steps for Problem Solving	How many molecules is $20.0\ \text{g}$ of chlorine gas, Cl_2?
Identify the "given" information and what the problem is asking you to "find."	Given: 20.0 g Cl_2 Find: # Cl_2 molecules
List other known quantities.	1 mol Cl_2 = 70.90 g Cl_2, 1mol Cl_2 = 6.022 x 10^{23} Cl_2 molecules
Prepare a concept map and use the proper conversion factor.	 The conversion factors are 1 mole Cl2 over 70.90 grams Cl2, and 6.022 times 10^23 Cl2 molecules over 1 mole Cl2.
Cancel units and calculate.	$20.0\ \cancel{\text{g Cl}_2} \times \frac{1\ \cancel{\text{mol Cl}_2}}{70.90\ \cancel{\text{g Cl}_2}} \times \frac{6.02 \times 10^{23}\ \text{molecules Cl}_2}{1\ \cancel{\text{mol Cl}_2}} = 1.70 \times 10^{23}\ \text{molecules Cl}_2$
Think about your result.	Since the given mass is less than half of the molar mass of chlorine, the resulting number of molecules is less than half of Avogadro's number.

Exercise 2.4.2: Calcium Chloride

How many formula units are in 25.0 g of $CaCl_2$?

Answer: available at the end of this section.

Summary

- A mole of any substance contains Avogadro's number $\left(6.02 \times 10^{23}\right)$ of representative particles.
- The molar mass of a substance is defined as the mass in grams of 1 mole of that substance.
- Calculations involving conversions between moles of a material and the mass of that material are described.
- Calculations are illustrated for conversions between mass and number of particles.

Contributors and Attributions

-

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

Answers

Exercise 2.4.1: Nitrogen Gas

210 g

Exercise 2.4.2: Calcium Chloride

1.36 x 10^{23} $CaCl_2$ formula units

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2.5: Mendeleev and 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.

The Periodic Table is the symbol of Chemistry for many. It is a single image that contains all of the known elements in the universe combined into an easily legible table. There are many patterns present in the table as well. All of the elements seem to fit together, connecting to form the "image of chemistry". The idea of elements first came about in 3000 B.C. The great Greek philosopher Aristotle conceived an idea that everything on earth was made up of these elements. In ancient times, elements like gold and silver were readily accessible, however, the elements that Aristotle chose were Earth, Water, Fire, and Air.

Emerging Patterns and Periodicity within the Known Elements

The modern periodic table has evolved through a long history of attempts by chemists to arrange the elements according to their properties, as an aid in predicting chemical behavior. One of the first to suggest such an arrangement was the German chemist Johannes Dobereiner (1780–1849), who noticed that many of the known elements could be grouped into triads. A triad is a set of three elements that have similar properties—for example, chlorine, bromine, and iodine; copper, silver, and gold. Dobereiner proposed that all elements could be grouped in such triads, but subsequent attempts to expand his concept were unsuccessful.

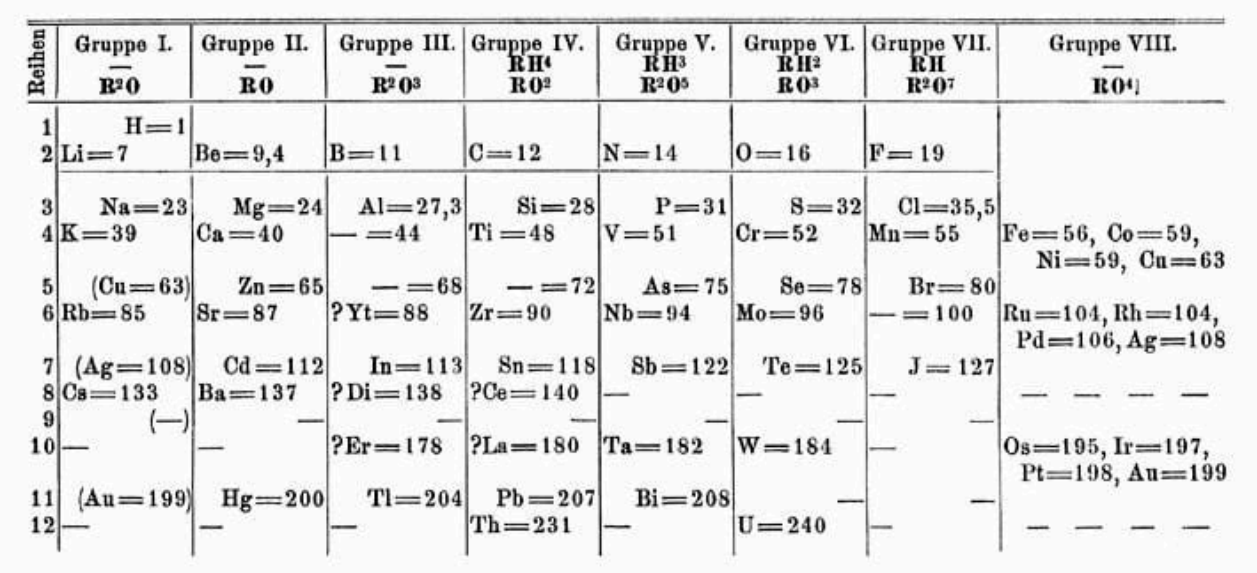
By the mid-19th century, the atomic masses of many of the elements had been determined. Scientists like John Newlands and Alexandre-Emile Béguyer de Chancourtois formed their own versions of periodic tables. The English chemist John Newlands (1838–1898), who hypothesized that the chemistry of the elements might be related to their masses, arranged the known elements in order of increasing atomic mass and discovered that every seventh element had similar properties. Newlands therefore suggested that the elements could be classified into octaves. He described octaves as a group of seven elements, which correspond to the horizontal rows in the main groups of today's periodic table. There were seven elements, because the noble gases were not known at the time. Unfortunately, Newlands's "law of octaves" did not seem to work for elements heavier than calcium, and his idea was publicly ridiculed.

The Periodic Table: Mendeleev and Meyer

The periodic table achieved its modern form through the work of the German chemist Julius Lothar Meyer (1830–1895) and the Russian chemist Dimitri Mendeleev (1834–1907), both of whom focused on the relationships between atomic mass and various physical and chemical properties. In 1869, they independently proposed essentially identical arrangements of the elements. Meyer aligned the elements in his table according to periodic variations in simple atomic properties, such as "atomic volume", which he obtained by dividing the atomic mass (molar mass) in grams per mole by the density of the element in grams per cubic centimeter. This property is equivalent to what is today defined as molar volume—the molar mass of an element divided by its density (measured in cubic centimeters per mole):

$$\frac{molar\ mass\ \left(\not{g}/mol\right)}{density\ \left(\not{g}/cm^3\right)} = molar\ volume\ \left(cm^3/mol\right) \tag{3.1.1}$$

Mendeleev, who first published his periodic table in 1869 (Figure $2.5.1$), is usually credited with the origin of the modern periodic table. The key difference between his arrangement of the elements, and that of Meyer and others, is that Mendeleev did not assume that all the elements had been discovered (in fact, only about two-thirds of the naturally occurring elements were known at the time). Instead, he deliberately left blanks in his table at atomic masses 44, 68, 72, and 100—in the expectation that elements with those atomic masses would be discovered. Those blanks correspond to the elements we now know as scandium, gallium, germanium, and technetium.



Reihen	Gruppe I. — R^2O	Gruppe II. — RO	Gruppe III. — R^2O^3	Gruppe IV. RH^4 RO^2	Gruppe V. RH^3 R^2O^5	Gruppe VI. RH^2 RO^3	Gruppe VII. RH R^2O^7	Gruppe VIII. — RO^4
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — — —

Figure 2.5.1: **Mendeleev's Periodic Table, as Published in the German Journal *Annalen der Chemie und Pharmacie* in 1872.** The column headings "Reihen" and "Gruppe" are German for "row" and "group." Formulas indicate the type of compounds formed by each group, with "R" standing for "any element" and superscripts used where we now use subscripts. Atomic masses are shown after equal signs and increase across each row from left to right.

The groups in Mendeleev's table are determined by how many oxygen or hydrogen atoms are needed to form compounds with each element. For example, in Group I, two atoms of hydrogen (H), lithium (Li), sodium (Na), and potassium (K) form compounds with one atom of oxygen. In Group VII, one atom of fluorine (F), chlorine (Cl), and bromine (Br), react with one atom of hydrogen. Notice how this approach has trouble with the transition metals. Until roughly 1960, a rectangular table based on reactivity—and developed from Mendeleev's table—was standard at the front of chemistry lecture halls.

The most convincing evidence in support of Mendeleev's arrangement of the elements was the discovery of two previously unknown elements whose properties closely corresponded with his predictions (Table 2.5.1). Two of the blanks Mendeleev had left in his original table were below aluminum and silicon, awaiting the discovery of two as-yet-unknown elements, *eka*-aluminum and *eka*-silicon (from the Sanskrit *eka*, meaning "one," as in "one beyond aluminum"). The observed properties of gallium and germanium matched those of *eka*-aluminum and *eka*-silicon so well that once they were discovered, Mendeleev's periodic table rapidly gained acceptance.

YouTube Video

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

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Video 2.5.1: The genius of Mendeleev's periodic table.

Table 2.5.1: Comparison of the Properties Predicted by Mendeleev in 1869 for eka-Aluminum and eka-Silicon with the Properties of Gallium (discovered in 1875) and Germanium (discovered in 1886).

Property	*eka*-Aluminum (predicted)	Gallium (observed)	*eka*-Silicon (predicted)	Germanium (observed)
atomic mass	68	69.723	72	72.64
element	metal	metal	dirty-gray metal	gray-white metal
***mp = melting point; bp = boiling point.**				

Property	*eka*-Aluminum (predicted)	Gallium (observed)	*eka*-Silicon (predicted)	Germanium (observed)
	low mp*	mp = 29.8°C	high mp	mp = 938°C
	d = 5.9 g/cm^3	d = 5.91 g/cm^3	d = 5.5 g/cm^3	d = 5.323 g/cm^3
oxide	E_2O_3	Ga_2O_3	EO_2	GeO_2
	d = 5.5 g/cm^3	d = 6.0 g/cm^3	d = 4.7 g/cm^3	d = 4.25 g/cm^3
chloride	ECl_3	$GaCl_3$	ECl_4	$GeCl_4$
	volatile	mp = 78°C bp* = 201°C	bp < 100°C	bp = 87°C
***mp = melting point; bp = boiling point.**				

When the chemical properties of an element suggested that it might have been assigned the wrong place in earlier tables, Mendeleev carefully reexamined its atomic mass. He discovered, for example, that the atomic masses previously reported for beryllium, indium, and uranium were incorrect. The atomic mass of indium had originally been reported as 75.6, based on an assumed stoichiometry of InO for its oxide. If this atomic mass were correct, then indium would have to be placed in the middle of the nonmetals, between arsenic (atomic mass 75) and selenium (atomic mass 78). Because elemental indium is a silvery-white *metal*, however, Mendeleev postulated that the stoichiometry of its oxide was really In_2O_3 rather than InO. This would mean that indium's atomic mass was actually 113, placing the element between two other metals, cadmium and tin.

One group of elements that was absent from Mendeleev's table is the noble gases, all of which were discovered more than 20 years later—between 1894 and 1898—by Sir William Ramsay (1852–1916; Nobel Prize in Chemistry 1904). Initially, Ramsay did not know where to place these elements in the periodic table. Argon, the first to be discovered, had an atomic mass of 40. This was greater than chlorine's and comparable to that of potassium; so Ramsay, using the same kind of reasoning as Mendeleev, decided to place the noble gases between the halogens and the alkali metals. In 1913, however, young British physicist H. G. J. Moseley (1887–1915) analyzed the frequencies of x-rays emitted by the elements, and discovered that the underlying foundation of the order of the elements was by the *atomic number*—not the atomic mass. Moseley hypothesized that the placement of each element in his series corresponded to its atomic number Z, which is the number of positive charges (protons) in its nucleus. Moseley left his research work at the University of Oxford to join the British army as a telecommunications officer during World War I. He was killed during the Battle of Gallipoli in Turkey. Finally, in 1945, the Manhattan Project yielded the discovery of many new radioactive elements. Glenn T. Seaborg suggested an addition of the actinide and lanthanide series at the bottom of the table. This idea came with the discovery of Americium and Curium, and their unique properties. The change was not accepted at first, but is now included in all periodic tables. Figure 2.5.2 shows the time period for the discovery of the different elements.

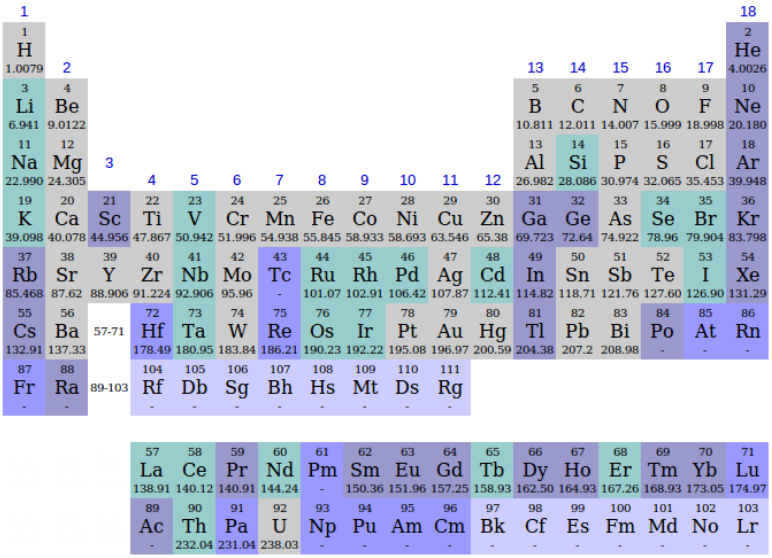


Figure 2.5.2 *Periodic table showing when each element was discovered*

- Before 1800 (36 elements): Discoveries during and before the Age of Enlightenment.
- 1800-1849 (+22 elements): Impulse from Scientific Revolution and Atomic theory and Industrial Revolution.
- 1850-1899 (+23 elements): The age of Classifying Elements received an impulse from the Spectrum analysis.
- 1900-1949 (+13 elements): Impulse from the old quantum theory, the Refinements to the periodic table, and quantum mechanics.
- 1950-1999 (+15 elements): Manhattan Project and Particle physics issues, for atomic numbers 97 and above.

Each element on the modern periodic table is represented by its atomic number and atomic mass (Figure 2.5.3). The **atomic mass** of each element is found under the element symbol in the **periodic table.** Examples are shown below. The atomic mass of tin (Sn) is 118.71 u while the atomic mass of carbon (C) is 12.011 u. On the other hand, the **atomic number (Z)** of each element is found **above** the atomic symbol.

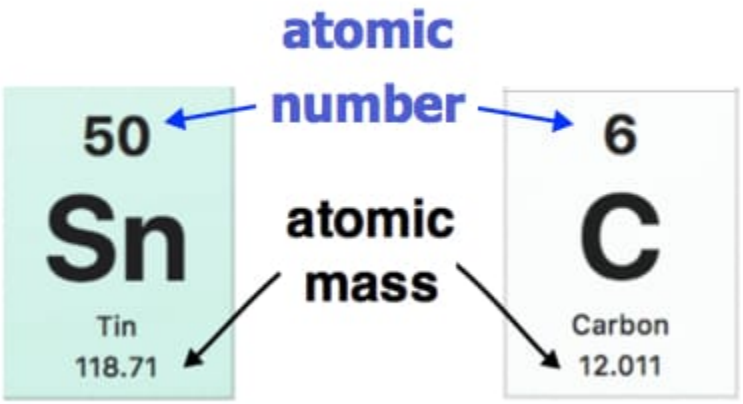


Figure 2.5.3: Key information of an element indicated on entries of the Periodic Table. (public Domain; Pubchem)

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

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

Summary

- The modern periodic table was based on empirical correlations of properties such as atomic mass; early models using limited data noted the existence of **triads** and **octaves** of elements with similar properties.

- The periodic table achieved its current form through the work of Dimitri Mendeleev and Julius Lothar Meyer, both of whom focused on the relationship between atomic mass and chemical properties.
- The correlation with the electronic structure of atoms was discovered when H. G. J. Moseley showed that the periodic arrangement of the elements was determined by atomic number, not atomic mass.

Contributors and Attributions

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- Marisa Alviar-Agnew (Sacramento City College)

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2.6: Atoms and Molecules- Real and Relevant

Learning Objective

- Know the difference between an atom and a molecule.

An **atom** is the smallest unit of ordinary matter that has the properties of a chemical element. Every solid, liquid, gas, and plasma is composed of either neutral (un-ionized), or ionized atoms. Atoms are extremely small; typical sizes are around 100 picometers (1×10^{-10} m, a ten-millionth of a millimeter, or 1/254,000,000 of an inch). They are small enough that attempting to predict their behavior using classical physics—as if they were billiard balls, for example—gives noticeably incorrect predictions due to quantum effects. Current atomic models have incorporated quantum mechanics to better explain and predict this behavior.

Every atom is composed of a nucleus and one or more electrons bound to the nucleus. The nucleus is made of one or more protons and a number of neutrons; only the most common variety (isotope) of hydrogen has no neutrons.

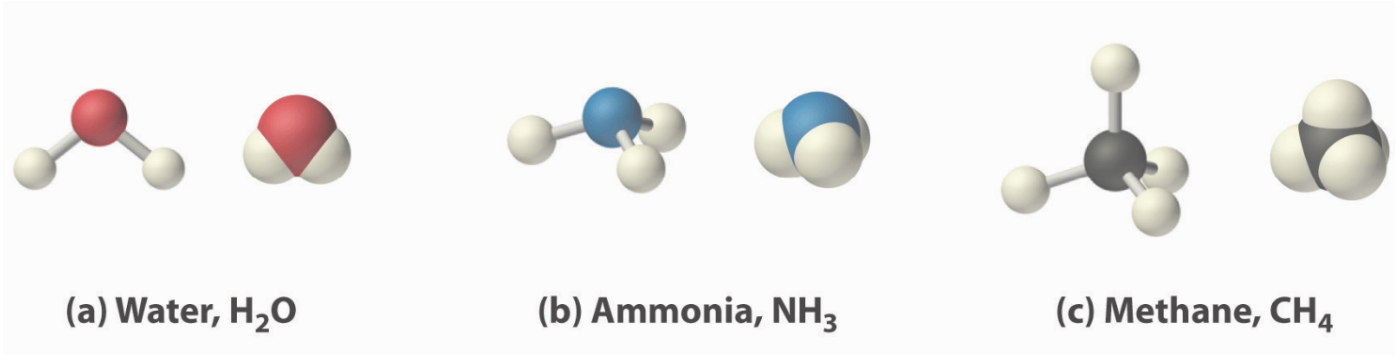
A **molecule** is an electrically neutral group of two or more atoms held together by chemical bonds. Molecules are distinguished from ions by their lack of electrical charge. However, in quantum physics, organic chemistry, and biochemistry, the term *molecule* is often used less strictly—as it is also applied to polyatomic ions.

In the kinetic theory of gases, the term *molecule* is often used for any gas, regardless of its composition. According to this definition, noble gas atoms are considered molecules because they are monatomic molecules.

A molecule may be homonuclear—that is, it consists of atoms of one chemical element, as with oxygen (O_2). A heteronuclear molecule is a chemical compound composed of more than one element, as with water (H_2O). Atoms and complexes connected by non-covalent interactions, such as hydrogen bonds or ionic bonds, are typically not considered single molecules.

Molecules as components of matter are common in organic substances (and therefore biochemistry). They also make up most of the oceans and atmosphere. However, the majority of familiar solid substances on Earth—including most of the minerals that make up the crust, mantle, and core of the Earth—contain many chemical bonds, but are *not* made of identifiable molecules. Also, no typical molecule can be defined for ionic crystals (salts) and covalent crystals (network solids), although these are often composed of repeating unit cells that extend either in a plane (such as in graphene) or three-dimensionally (such as in diamond, quartz, or sodium chloride). The theme of repeated unit-cellular-structure also holds for most condensed phases with metallic bonding, which means that solid metals are also not made of molecules. In glasses (solids that exist in a vitreous disordered state), atoms may also be held together by chemical bonds with no presence of any definable molecule, nor any of the regularity of repeating units that characterizes crystals.

Three common molecules shown below.



From left to right: 3D model of water molecule, 3D model of ammonia molecule, and 3D model of methane molecule

YouTube Video

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Video 2.6.1: The difference between an atom and a molecule.

Summary

- An atom is the smallest unit of matter that has the properties of a chemical element
- A molecule is an electrically neutral group of two or more atoms held together by chemical bonds.

Contributors and Attributions

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3: ATOMIC STRUCTURE

3.1: Electricity and the Atom

3.2: Serendipity in Science - X-Rays and Radioactivity

3.3: Three Types of Radioactivity

3.4: Rutherford's Experiment- The Nuclear Model of the Atom

3.5: The Atomic Nucleus

3.6: Electron Arrangement- The Bohr Model (Orbits)

3.7: Electron Arrangement- The Quantum Model

3.8: Electron Configurations and the Periodic Table

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3.1: Electricity and the Atom

Learning Objectives

- Understand the significance of the experiments performed by Thomson and Millikan.

Alessandro Giuseppe Antonio Anastasio Volta (1745–1827) was an Italian physicist, chemist, and pioneer of electricity and power; who is credited as the inventor of the electric battery and the discoverer of methane. He invented the Voltaic pile in 1799; with this invention, Volta proved that electricity could be generated chemically, and debunked the prevalent theory that electricity was generated solely by living beings. Volta's invention sparked a great amount of scientific excitement and led others to conduct similar experiments, which eventually led to the development of the field of electrochemistry.

Electrolysis

Sir Humphry Davy, 1st Baronet (1778–1829) was a Cornish chemist and inventor. He was a pioneer in the field of electrolysis, which uses the voltaic pile to split common compounds and thus prepare many new elements. He went on to electrolyse molten salts and discovered several new metals, including sodium and potassium in 1807. The following year, he discovered calcium, strontium, barium, magnesium and boron, as well as the elemental nature of chlorine and iodine. He also studied the forces involved in these separations, inventing the new field of electrochemistry.

Davy's laboratory assistant, Michael Faraday, went on to enhance Davy's work and would become the more famous and influential scientist. Davy is supposed to have even claimed Faraday as his greatest discovery. Faraday (1791–1867) was an English scientist who contributed to the study of electromagnetism and electrochemistry. His main discoveries include the principles underlying electromagnetic induction, diamagnetism and electrolysis.

As a chemist, Faraday discovered benzene, investigated the clathrate hydrate of chlorine, invented an early form of the Bunsen burner and the system of oxidation numbers, and popularized terminology such as "anode", "cathode", "electrode" and "ion". Faraday ultimately became the first and foremost Fullerian Professor of Chemistry at the Royal Institution, a lifetime position. His work on electrolysis paved the way for subsequent experiments performed using cathode ray tubes.

Cathode Ray Tubes

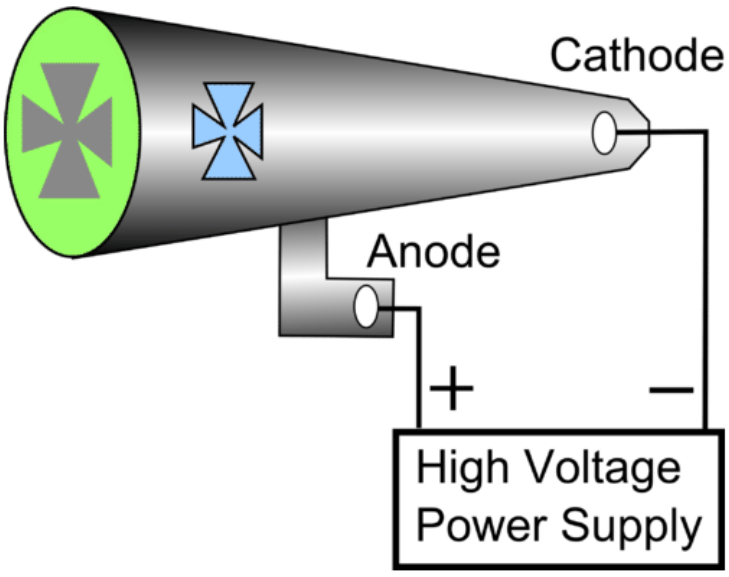
The TV set seen below is becoming harder and harder to find these days. The main reason is because they are older and based on outdated technology. The new TV sets are flat screen technology that take up less space and give better picture quality, especially with the advent of high-definition broadcasting. The technology used in the older TV sets used cathode ray tubes. A beam of electrons was sprayed to a picture tube which was treated to react with the electrons to produce an image. Similar CRT (cathode ray tube) devices were used in computer monitors, now also replaced by flat screen monitors.



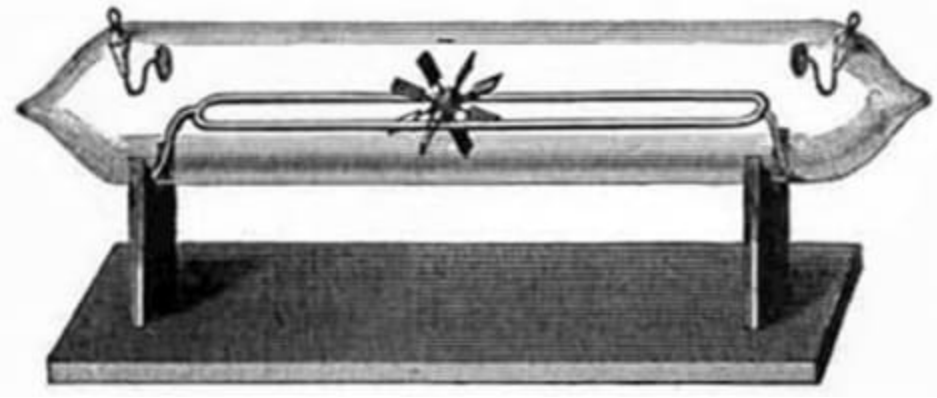
Picture of cathode ray tube monitor

The first cathode ray tube prototype was developed by Heinrich Geissler, a German glassblower and physicist. He used a mercury pump to create a vacuum in a tube. Geissler explored a number of techniques to remove air from the tube and to prevent leaks, as well as ways to get good connections of the wires in the tubes. In 1878, Sir William Crookes, a British scientist, displayed the first cathode rays using a modification of the Geissler apparatus. His major contribution to construction of the tube was to develop ways to evacuate almost all the air from the tube. Crookes also carried out many experiments using more reliable equipment to confirm earlier finding about the properties of cathode rays. He discovered two things which supported the hypothesis that the cathode ray consisted of a stream of particles.

- When an object was placed between the cathode and the opposite end of the tube, it cast a shadow on the glass. The shadow caused by the object indicates that particles were being blocked on their way from the cathode to the anode.



- A cathode ray tube was constructed with a small metal rail between the two electrodes. Attached to the rail was a paddle wheel capable of rotating along the rail. Upon starting up the cathode ray tube, the wheel rotated from the cathode towards the anode. Notice that the cathode and anode are positioned so that the rays will strike the top of the paddle wheel. Crookes concluded that the cathode ray was made of particles which must have mass.



The cathode ray tube was first invented by Sir William Crookes.

Further Research with the Crookes Tube

Crookes' work opened the door to a number of important discoveries. Other scientists were able to demonstrate that the "cathode ray" was actually a stream of **electrons**. In 1897, Karl Ferdinand Braun developed the first oscilloscope, using a cathode ray tube to see an electrical pulse as it passed through the instrument. The invention of television would not have been possible without the cathode ray tube. Work with a modified system led to the discovery of x-rays in 1895 by the German physicist Wilhelm Roentgen. This simple device has led to major advances in science and technology.

Thomson's Experiment: Mass to Charge Ratio

In 1897, the British physicist J. J. Thomson (1856–1940) proved that atoms were not the most basic form of matter. He demonstrated that cathode rays could be deflected, or bent, by magnetic or electric fields, which indicated that cathode rays consist of charged particles (Figure 1.17c). More important, by measuring the extent of the deflection of the cathode rays in magnetic or electric fields of various strengths, Thomson was able to calculate the mass-to-charge ratio of the particles. These particles were emitted by the negatively charged cathode and repelled by the negative terminal of an electric field. Because like charges repel each other and opposite charges attract, Thomson concluded that the particles had a net negative charge; these particles are now called electrons. Most relevant to the field of chemistry, Thomson found that the mass-to-charge ratio of cathode rays is independent of the nature of the metal electrodes or the gas, which suggested that electrons were fundamental components of all atoms.

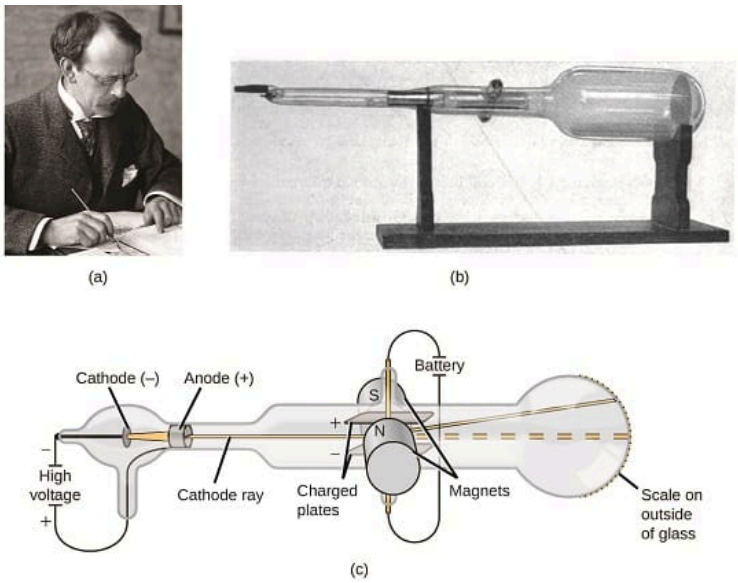


Figure 3.1.1 (a) J. J. Thomson produced a visible beam in a cathode ray tube. (b) This is an early cathode ray tube, invented in 1897 by Ferdinand Braun. (c) In the cathode ray, the beam (shown in yellow) comes from the cathode and is accelerated past the anode toward a fluorescent scale at the end of the tube. Simultaneous deflections by applied electric and magnetic fields permitted Thomson to calculate the mass-to-charge ratio of the particles composing the cathode ray. (credit a: modification of work by Nobel Foundation; credit b: modification of work by Eugen Nesper; credit c: modification of work by "Kurzon"/Wikimedia Commons).

Cathode ray tube

YouTube Video

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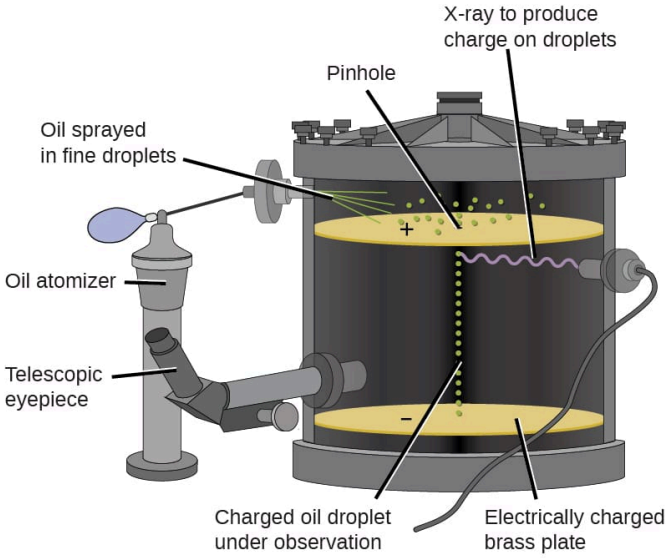
Video 3.1.1 *A cathode ray tube.*

Thomson's experiment

Video 3.1.2*Video from Davidson College demonstrating Thompson's e/m experiment. You can also use an applet from the Google Group Physics Flash to simulate the experiment and here is another applet, from Kings Center for Visual Exploration in Alberta (KCVE) with a detailed explanation*

Millikan's Oil-Drop Experiment: Electron Charge

In 1909, more information about the electron was uncovered by American physicist Robert A. Millikan via his "oil drop" experiments. Millikan created microscopic oil droplets, which could be electrically charged by friction as they formed or by using X-rays. These droplets initially fell due to gravity, but their downward progress could be slowed or even reversed by an electric field lower in the apparatus. By adjusting the electric field strength and making careful measurements and appropriate calculations, Millikan was able to determine the charge on individual drops (Figure 3.1.2) .



Oil drop	Charge in coulombs (C)
A	4.8×10^{-19} C
B	3.2×10^{-19} C
C	6.4×10^{-19} C
D	1.6×10^{-19} C
E	4.8×10^{-19} C

Figure 3.1.2 *Millikan's experiment measured the charge of individual oil drops. The tabulated data are examples of a few possible values. (The experimental apparatus consists of an oil atomizer which sprays fine oil droplets into a large, sealed container. The sprayed oil lands on a positively charged brass plate with a pinhole at the center. As the drops fall through the pinhole, they travel through X-rays that are emitted within the container. This gives the oil droplets an electrical charge. The oil droplets land on a brass plate that is negatively charged. A telescopic eyepiece penetrates the inside of the container so that the user can observe how the charged oil droplets respond to the negatively charged brass plate. The table that accompanies this figure gives the charge, in coulombs or C, for 5 oil drops. Oil drop A has a charge of 4.8 times 10 to the negative 19 power. Oil drop B has a charge of 3.2 times 10 to the negative 19 power. Oil drop C has a charge of 6.4 times 10 to the negative 19 power. Oil drop D has a charge of 1.6 times 10 to the negative 19 power. Oil drop E has a charge of 4.8 times 10 to the negative 19 power.)*

He then concluded that the charge of a single electron is 1.6×10^{-19} C. With this information and Thomson's mass-to-charge ratio (1.759×10^{11} C/kg)., Millikan determined the mass of an electron:

$$Mass\ of\ electron = charge \times \frac{mass}{charge}$$

$$= 1.602 \times 10^{-19}\ \cancel{C} \times \frac{1\ \text{kg}}{1.759 \times 10^{11}\ \cancel{C}} = 9.107 \times 10^{-31}\ \text{kg} \tag{3.1.2}$$

Scientists had now established that the atom was not indivisible as Dalton had believed, and due to the work of Thomson, Millikan, and others, the charge and mass of the negative, subatomic particles—the electrons—were known. However, the positively charged part of an atom was not yet well understood.

Summary

- The cathode ray tube was first invented by Sir William Crookes.
- Experiments showed that the rays had mass.
- Thomson's cathode ray tube showed that atoms contain small, negatively charged particles called electrons.
- Millikan discovered that there is a fundamental electric charge—the charge of an electron.

Contributors and Attributions

-

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- Wikipedia

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3.2: Serendipity in Science - X-Rays and Radioactivity

Learning Objective

- Understand the significance of the discovery of X-rays and radioactivity to the modern view of the structure of the atom.

The discovery of radioactivity took place over several years beginning with the discovery of x-rays in 1895 by Wilhelm Conrad Roentgen and continuing with such people as Henri Becquerel and the Curie family. The application of x-rays and radioactive materials is far reaching in medicine and industry. Radioactive material is used in everything from nuclear reactors to isotope infused saline solutions. These technologies allow us to utilize great amounts of energy and observe biological systems in ways which were unthinkable less than a century ago. As will be discussed in section3.4, the British physicist Ernest Rutherford (1871-1937) conducted experiments (based on the Curies' work) that led to the modern view of the structure of the atom.

Roentgen: The Discovery of X-Rays

From Section 3.1, we saw how J. J. Thomson discovered the electronundefined by using cathode ray tubes (CRT). In November of 1895, a German physicist named Wilhelm Roentgen (Röntgen) used this same technology to discover the x-ray. Roentgen's ray originated from the CRT and reacted with a barium platinocyanide screen to fluoresce. After seeing this, Roentgen placed objects between this ray and the screen. He noted that the ray would still penetrate substances and leave an image on photographic film.

When naming this type of radiation, Roentgen reflected back to his experiments. He could not confidently explain his observations. For this reason, he decided to call this new type of radiation the x-ray. Throughout his lifetime, he continue to explore this technology and even used his wife as a test subject (refer to chapter 1 for her x-ray image). By never patenting this invention, Roentgen freely shared the x-ray with other researchers and medical professionals. In 1901, he was awarded the Nobel Prize in physics for his work with the x-ray.

As with any new technology, people looked for ways to apply the x-ray to day to day life. Thomas Edison, the inventor of the light bulb, thought the average person should have an x-ray machine in their home. He designed x-ray machines to be smaller and portable. Unfortunately, many of his technicians died from radiation poisoning.



Figure 3.2.1

Hand mit Ringen (Hand with Rings): print of Wilhelm Röntgen's first "medical" X-ray, of his wife's hand, taken on 22 December 1895.

Figure 3.2.2***:*** *(left) Photo of Wilhelm Conrad Roengten, the discoverer of x-rays. (right) Surgical operation during World War I using a fluoroscope that used x-rays to find embedded bullets*

During Edison's time, people would host x-ray parties in their homes. The host of these gatherings would allow guests to x-ray different parts of their body. People would leave these events with their framed souvenirs. X-rays were even used to measure foot size. Devices like the fluoroscope were placed in shoe stores. Technicians, consumers, and observers could look in oculars while the foot was being x-rayed. Unnecessary exposure to radiation was not considered as a hazard during these times. In this era, most believed this was the most accurate way to measure the foot.

The harmful effects and different uses of X-rays

In November 1896, an article entitled "the harmful effects of X-rays" was published in Nature. The witness was an X-ray demonstrator during the summer in London. He therefore paid for himself throughout the summer at the rate of several hours per day of exposure. He testified: "In the first two or three weeks I felt no inconvenience, but after a while appeared on the fingers of my right hand many dark spots which pierced under the skin, and gradually they became very painful; the rest of the skin was red and strongly inflamed My hand was so bad that I was constantly forced to bathe it in very cold water An ointment momentarily calm the pain but the epidermis had dried up had become hard and yellow like parchment and completely insensible, so I was not surprised when my hand began to peel. "

"Soon the skin and nails fall off and the fingers swelled, the pain remaining constant. I lost the skin of my right and left hands, and four of my nails have disappeared from the right hand and two left and three others were ready to fall off. During more than six weeks I was unable to hold anything in my right hand and I can not hold a pen since the loss of my nails ..."

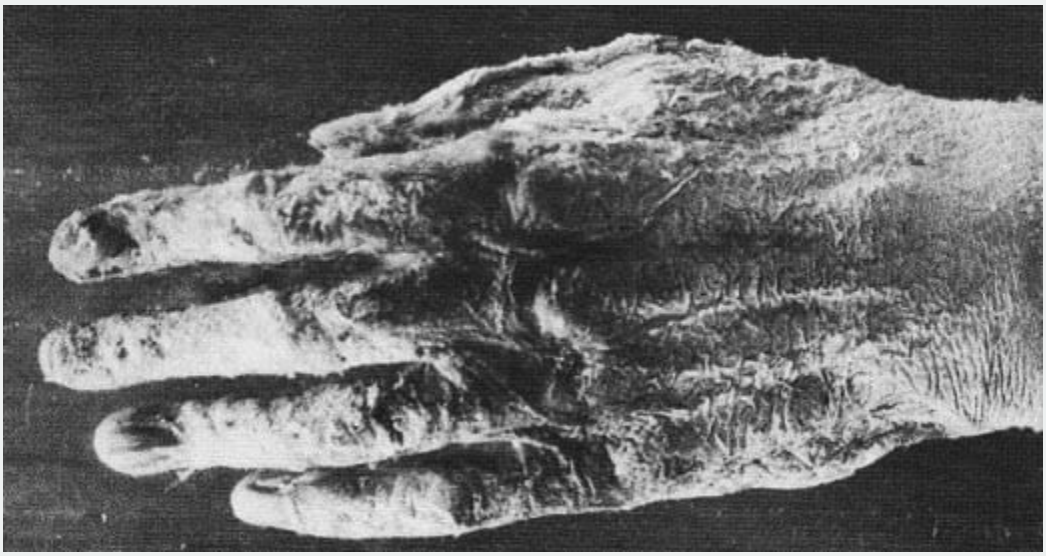


Figure 3.2.3: Radiation poisoning due to over exposure of x-rays.

Different applications use different parts of the X-ray spectrum.

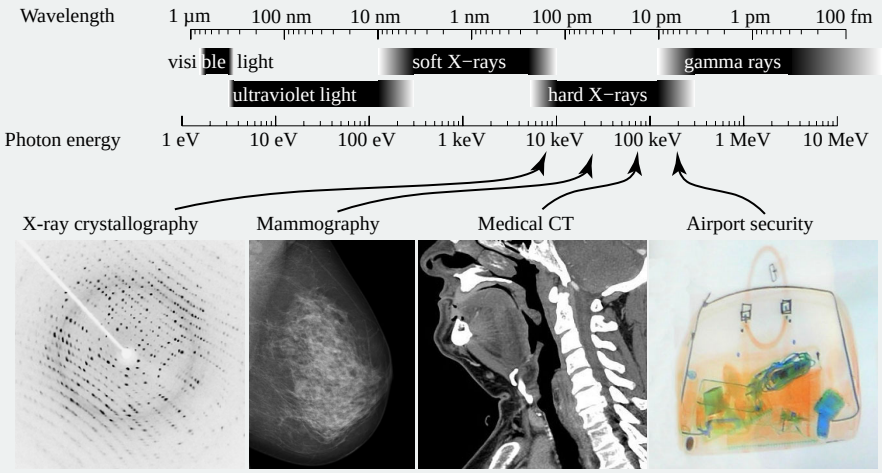
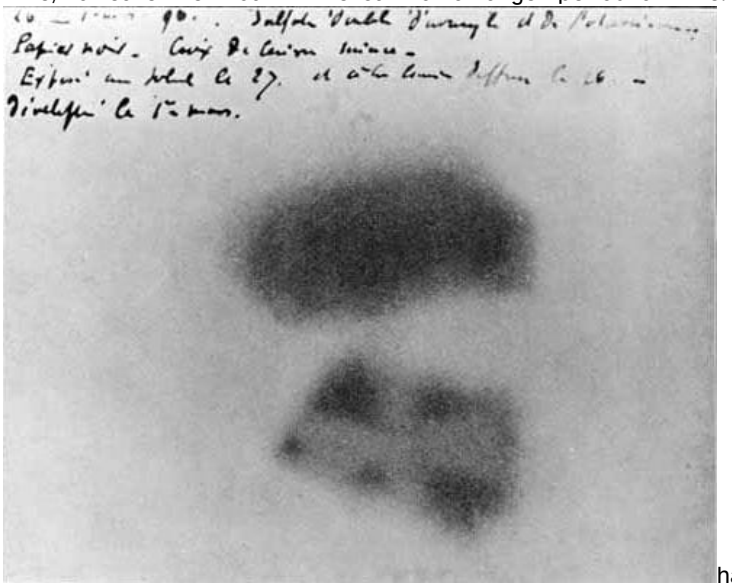


Figure 3.2.4: X-rays are part of the electromagnetic spectrum, with wavelengths shorter than visible light.

The Discovery of Radioactivity

When Becquerel heard about Roentgen's discovery, he wondered if his fluorescent minerals would give the same x-rays. Becquerel placed some of his rock crystals on top of a well-covered photographic plate and sat them in the sunlight. The sunlight made the crystals glow with a bright fluorescent light, but when Becquerel developed the film he was very disappointed. He found that only one of his minerals, a uranium salt, had fogged the photographic plate. He decided to try again, and this time, to leave them out in the sun for a longer period of time. Fortunately, the weather did not cooperate and Becquerel



had to leave the crystals and film stored in a drawer for several cloudy days. Before continuing his experiments, Becquerel decided to check one of the photographic plates to make sure the chemicals were still good. To his amazement, he found that the plate had been exposed in spots where it had been near the uranium containing rocks and some of these rocks had not been exposed to sunlight at all. In later experiments, Becquerel confirmed that the radiation from the uranium had no connection with light or fluorescence, but the amount of radiation was directly proportional to the concentration of uranium in the rock. Becquerel had discovered **radioactivity**.

Figure $3.2.5$***:*** *Image of Becquerel's photographic plate which has been fogged by exposure to radiation from a uranium salt. The shadow of a metal Maltese Cross placed between the plate and the uranium salt is clearly visible (Public Domain).*

The Curies and Radium

One of Becquerel's assistants, a young Polish scientist named Maria Sklowdowska (to become Marie Curie after she married Pierre Curie), became interested in the phenomenon of radioactivity. With her husband, she decided to find out if chemicals other than uranium were radioactive. The Austrian government was happy to send the Curies a ton of pitchblende from the mining region of Joachimstahl because it was waste material that had to be disposed of anyway. The Curies wanted the pitchblende because it was the residue of uranium mining. From the ton of pitchblende, the Curies separated $0.10\ \text{g}$ of a previously unknown element, radium, in the form of the compound radium chloride. This radium was many times more radioactive than uranium.

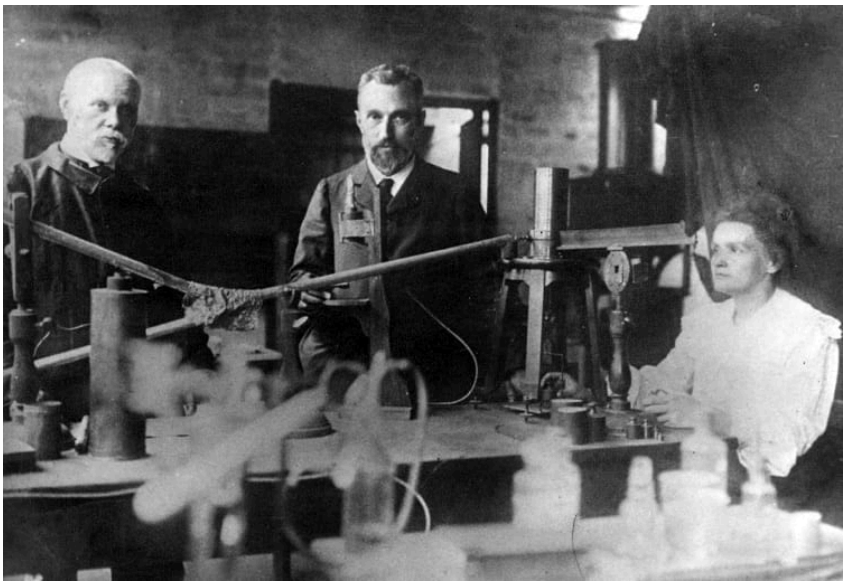


Figure 3.2.6: Marie (left) and Pierre Curie (middle) with Henri Becquerel (right) shared the 1903 Nobel Prize

By 1902, the world was aware of a new phenomenon called radioactivity and of new elements which exhibited natural radioactivity. For this work, Becquerel and the Curies shared the 1903 Nobel Prize in Physics. These three researchers continued to work with hazardous radioactive materials. They experienced various ailments included burns and weakness by touching these substances. In 1906, Pierre Curie accidently fell under a horse drawn cart. He immediately died from his wounds and left Marie with two small children (Irene, 9 years old and Eve, 2 years old). After his death, Marie continued her research by identifying a new element, Polonium. In 1911, she was awarded the Nobel Prize in chemistry for the discoveries of radium and polonium. As of today, Marie Curie is the only person ever to have received two Nobel Prizes in the sciences.

YouTube Video

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Video3.2.2: Everyone knows that winning the Nobel Prize is a big deal, but why do we even have a Nobel Prize? And why does it matter?

Summary

- Henri Becquerel, Marie Curie, and Pierre Curie shared the discovery of radioactivity.
- Wilhelm Roengtgen used cathode ray tubes to discover the x-ray.

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3.3: Three Types of Radioactivity

Learning Objective

Differentiate between alpha particles, beta particles and gamma rays.

Ernest Rutherford, (30 August 1871 – 19 October 1937), was a New Zealand who came to be known as the father of . While working in Thomson's laboratory shortly after Thomson discovered the electron, Rutherford showed that compounds of uranium and other elements emitted at least two distinct types of radiation. One was readily absorbed by matter and seemed to consist of particles that had a positive charge and were massive compared to electrons. Because it was the first kind of radiation to be discovered, Rutherford called these substances **alpha (α) particles**. Rutherford also showed that the particles in the second type of radiation, **beta (β) particles**, had the same charge and mass-to-charge ratio as Thomson's electrons; they are now known to be high-speed electrons. In 1908 was awarded the "for his investigations into the disintegration of the elements, and the chemistry of radioactive substances", for which he was the first Canadian and Oceanian Nobel laureate. A third type of radiation, **gamma (γ) rays**, was discovered somewhat later and found to be similar to the lower-energy form of radiation called x-rays, now used to produce images of bones and teeth.

Table 3.3.1: Names, Symbols, Representations, and Descriptions of the most common types of radioactivity.

Name	Symbol(s)	Representation	Description
Alpha particle	^4_2He or $^4_2\alpha$		(High-energy) helium nuclei consisting of two protons and two neutrons
Beta particle	$^0_{-1}\text{e}$ or $^0_{-1}\beta$		(High-energy) electrons
Gamma ray	γ		Very high-energy electromagnetic radiation

Summary

An alpha particle is a high energy helium nucleus.

A beta particle is a high energy electron.

A gamma ray is a very high energy electromagnetic radiation

Contributors and Attributions

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- TextMap: Chemistry-The Central Science (Brown et al.)

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3.4: Rutherford's Experiment- The Nuclear Model of the Atom

Learning Objectives

- Describe Thomson's "plum pudding" model of the atom and the evidence for it.
- Describe Rutherford's gold foil experiment and explain how this experiment altered the "plum pudding" model.

The electron was discovered by J.J. Thomson in 1897. The existence of protons was also known, as was the fact that atoms were neutral in charge. Since the intact atom had no net charge and the electron and proton had opposite charges, the next step after the discovery of subatomic particles was to figure out how these particles were arranged in the atom. This is a difficult task because of the incredibly small size of the atom. Therefore, scientists set out to design a model of what they believed the atom could look like. The goal of each **atomic model** was to accurately represent all of the experimental evidence about atoms in the simplest way possible.

Following the discovery of the electron, J.J. Thomson developed what became known as the "**plum pudding**" model (Figure 3.4.1) in 1904. Plum pudding is an English dessert similar to a blueberry muffin. In Thomson's plum pudding model of the atom, the electrons were embedded in a uniform sphere of positive charge like blueberries stuck into a muffin. The positive matter was thought to be jelly-like or a thick soup. The electrons were somewhat mobile. As they got closer to the outer portion of the atom, the positive charge in the region was greater than the neighboring negative charges and the electron would be pulled back more toward the center region of the atom.

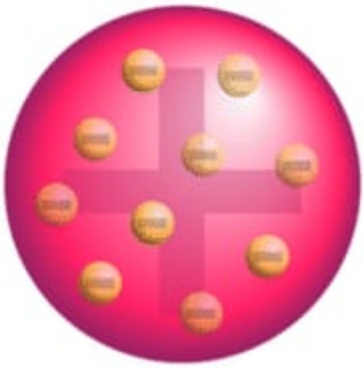


Figure 3.4.1 The "plum pudding" model.

However, this model of the atom soon gave way to a new model developed by New Zealander Ernest Rutherford (1871 - 1937) about five years later. Thomson did still receive many honors during his lifetime, including being awarded the Nobel Prize in Physics in 1906 and a knighthood in 1908.

Atoms and Gold

In 1911, Rutherford and coworkers Hans Geiger and Ernest Marsden initiated a series of groundbreaking experiments that would completely change the accepted model of the atom. They bombarded very thin sheets of gold foil with fast moving alpha particles.

Figure 3.4.2 (a) The experimental setup for Rutherford's gold foil experiment: A radioactive element that emitted alpha particles was directed toward a thin sheet of gold foil that was surrounded by a screen which would allow detection of the deflected particles. (b) According to the plum pudding model (top) all of the alpha particles should have passed through the gold foil with little or no deflection. Rutherford found that a small percentage of alpha particles were deflected at large angles, which could be explained by an atom with a very small, dense, positively-charged nucleus at its center (bottom).

According to the accepted atomic model, in which an atom's mass and charge are uniformly distributed throughout the atom, the scientists expected that all of the alpha particles would pass through the gold foil with only a slight deflection or none at all. Surprisingly, as shown in Figure 3.4.2 *(*while most of the alpha particles were indeed undeflected, a very small percentage (about 1 in 8000 particles) bounced off the gold foil at very large angles. Some were even redirected back toward the source. No prior

knowledge had prepared them for this discovery. In a famous quote, Rutherford exclaimed that it was "as if you had fired a 15-inch [artillery] shell at a piece of tissue and it came back and hit you."

Rutherford needed to come up with an entirely new model of the atom in order to explain his results. Because the vast majority of the alpha particles had passed through the gold, he reasoned that most of the atom was empty space. In contrast, the particles that were highly deflected must have experienced a tremendously powerful force within the atom. He concluded that all of the positive charge and the majority of the mass of the atom must be concentrated in a very small space in the atom's interior, which he called the nucleus. The **nucleus** is the tiny, dense, central core of the atom and is composed of protons and neutrons.

Rutherford's atomic model became known as the **nuclear model**. In the nuclear atom, the protons and neutrons, which comprise nearly all of the mass of the atom, are located in the nucleus at the center of the atom. The electrons are distributed around the nucleus and occupy most of the volume of the atom. It is worth emphasizing just how small the nucleus is compared to the rest of the atom. If we could blow up an atom to be the size of a large professional football stadium, the nucleus would be about the size of a marble.

Rutherford's model proved to be an important step towards a full understanding of the atom. However, it did not completely address the nature of the electrons and the way in which they occupied the vast space around the nucleus. For this and other insights, Rutherford was awarded the Nobel Prize in Chemistry in 1908. Unfortunately, Rutherford would have preferred to receive the Nobel Prize in Physics because he considered physics superior to chemistry. In his opinion, “All science is either physics or stamp collecting.”

Summary

- The plum pudding model is an early attempt to show what an atom looks like.
- Bombardment of gold foil with alpha particles showed that some particles were deflected.
- The nuclear model of the atom consists of a small and dense positively charged interior surrounded by a cloud of electrons.

Contributors and Attributions

-

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- Henry Agnew (UC Davis)

- TextMap: Chemistry - The Central Science

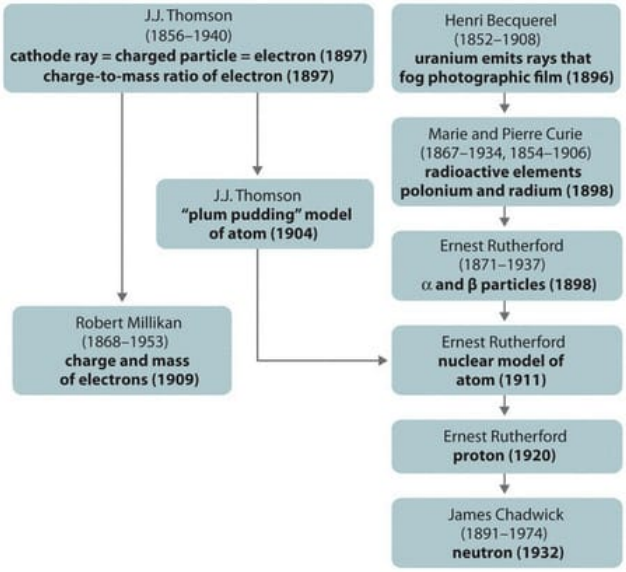
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3.5: The Atomic Nucleus

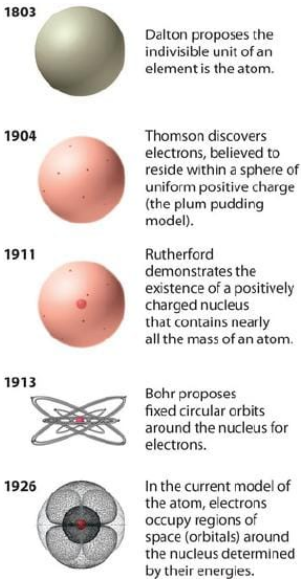
Learning Objectives

- List the properties of the three main subatomic particles.
- Define atomic mass unit (amu).
- Define atomic number and mass number.
- Define isotopes.
- Determine the number of protons, neutrons, and electrons in an atom with a given mass number.



The historical development of the different models of the atom's structure is summarized in Figure 3.5.1. J.J. Thomson and Robert Millikan conducted experiments to study the properties of **electrons**. Rutherford established that the nucleus of the hydrogen atom was a positively charged particle, for which he coined the name **proton** in 1920. He also suggested that the nuclei of elements other than hydrogen must contain electrically neutral particles with approximately the same mass as the proton. The **neutron**, however, was not discovered until 1932, when James Chadwick (1891–1974, a student of Rutherford; Nobel Prize in Physics, 1935) discovered it. As a result of Rutherford's work, it became clear that an α particle contains two protons and neutrons, and is therefore the nucleus of a helium atom.

Figure 3.5.1 *A summary of the historical development of models of the components and structure of the atom. The dates in parentheses are the years in which the key experiments were performed. (CC BY-SA-NC).*



Rutherford's model of the atom is essentially the same as the modern model, except that it is now known that electrons are not uniformly distributed throughout an atom's volume. Instead, they are distributed according to a set of principles described by Quantum Mechanics.

Figure \(\
PageIndex
{2}\) shows how the model of the atom has evolved over time from the indivisible unit of Dalton to the modern view taught today.

Figure 3.5.2*The Evolution of Atomic Theory, as Illustrated by Models of the Oxygen Atom. Bohr's model and the current model are described in Chapter 6, "The Structure of Atoms." Image used with Permission (CC BY-SA-NC).*

The **nucleus** (plural, nuclei) is a positively charged region at the center of the atom. It consists of two types of subatomic particles packed tightly together. The particles are protons, which have a positive electric charge, and neutrons, which are neutral in electric charge. Outside of the nucleus, an atom is mostly empty space, with orbiting negative particles called electrons whizzing through it. Figure 3.5.3 below shows these parts of the atom.

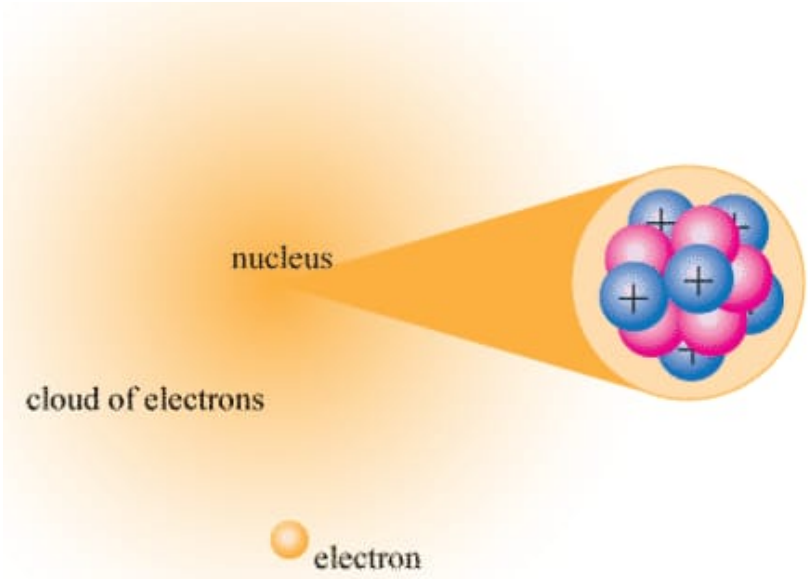


Figure 3.5.3 The nuclear atom

The nucleus of the atom is extremely small. Its radius is only about 1/100,000 of the total radius of the atom. If an atom were the size of a football stadium, the nucleus would be about the size of a pea! Electrons have virtually no mass, but protons and neutrons have a lot of mass for their size. As a result, the nucleus has virtually all the mass of an atom. Given its great mass and tiny size, the nucleus is very dense. If an object the size of a penny had the same density as the nucleus of an atom, its mass

would be greater than 30 million tons!

Holding It All Together

Particles with opposite electric charges attract each other. This explains why negative electrons orbit the positive nucleus. Particles with the same electric charge repel each other. This means that the positive protons in the nucleus push apart from one another. So why doesn't the nucleus fly apart? An even stronger force - called the **strong nuclear force** - holds protons and neutrons together in the nucleus.

*Table 3.5.1 gives the properties and locations of electrons, protons, and neutrons. The third column shows the masses of the three subatomic particles in "atomic mass units." An **atomic mass unit (**amu**)** is defined as one-twelfth the mass of a carbon-12 atom. Atomic mass units (amu) are useful, because, as you can see, the mass of a proton and the mass of a neutron are almost exactly 1 in this unit system.*

Table 3.5.1: Properties of Subatomic Particles

Particle	Symbol	Mass (amu)	Relative Mass (proton = 1)	Relative Charge	Location
proton	p^+	1	1	+1	inside the nucleus
electron	e^-	5.45×10^{-4}	0.00055	–1	outside nucleus
neutron	n^0	1	1	0	inside the nucleus

amu in gram and kilogram

1 amu = 1.6605×10^{-24} g = 1.6605×10^{-27} kg

Atomic Number

Negative and positive charges of equal magnitude cancel each other out. This means that the negative charge on an electron perfectly balances the positive charge on the proton. In other words, a neutral atom must have exactly one electron for every proton. If a neutral atom has 1 proton, it must have 1 electron. If a neutral atom has 2 protons, it must have 2 electrons. If a neutral atom has 10 protons, it must have 10 electrons. You get the idea. In order to be neutral, an atom must have the same number of electrons and protons.

Scientists distinguish between different elements by counting the number of protons in the nucleus (Table 3.5.2). If an atom has only one proton, we know it's a hydrogen atom. An atom with two protons is always a helium atom. If scientists count four protons in an atom, they know it's a beryllium atom. An atom with three protons is a lithium atom, an atom with five protons is a boron atom, an atom with six protons is a carbon atom . . . the list goes on.

Since an atom of one element can be distinguished from an atom of another element by the number of protons in its nucleus, scientists are always interested in this number, and how this number differs between different elements. The number of protons in an atom is called its **atomic number** (Z). This number is very important because it is unique for atoms of a given element. All atoms of an element have the same number of protons, and every element has a different number of protons in its atoms. For example, all helium atoms have two protons, and no other elements have atoms with two protons.

Table 3.5.2: Atoms of the First Six Elements

Name	Protons	Neutrons	Electrons	Atomic Number (Z)	Mass Number (A)
Hydrogen	1	0	1	1	1
Helium	2	2	2	2	4
Lithium	3	4	3	3	7
Beryllium	4	5	4	4	9

Name	Protons	Neutrons	Electrons	Atomic Number (Z)	Mass Number (A)
Boron	5	6	5	5	11
Carbon	6	6	6	6	12

Of course, since neutral atoms have to have one electron for every proton, an element's atomic number also tells you how many electrons are in a neutral atom of that element. For example, hydrogen has an atomic number of 1. This means that an atom of hydrogen has one proton, and, if it's neutral, one electron as well. Gold, on the other hand, has an atomic number of 79, which means that an atom of gold has 79 protons, and, if it's neutral, 79 electrons as well.

Neutral Atoms

Atoms are neutral in electrical charge because they have the same number of negative electrons as positive protons (Table $3.5.2$). Therefore, the atomic number of an atom also tells you how many electrons the atom has. This, in turn, determines many of the atom's chemical properties.

Mass Number

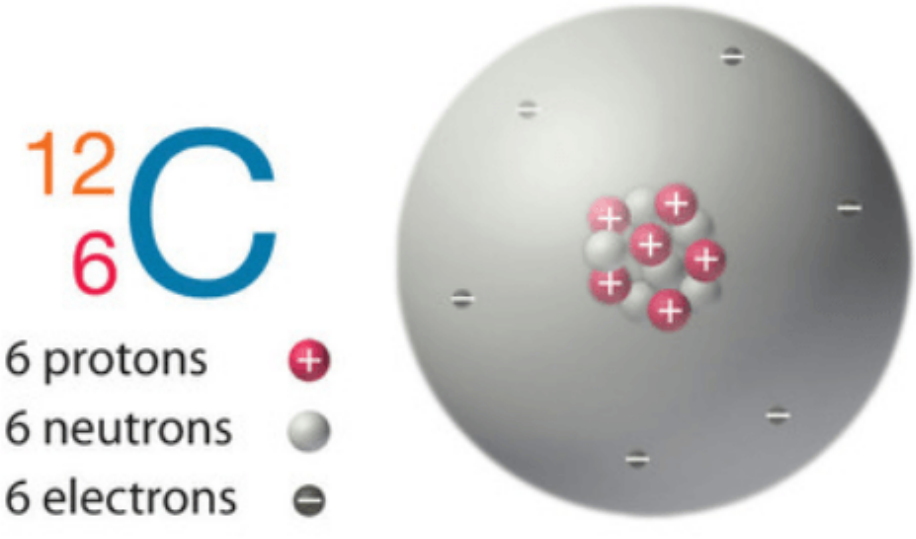
The **mass number** (A) of an atom is the total number of protons and neutrons in its nucleus. The mass of the atom is a unit called the atomic mass unit (amu). One atomic mass unit is the mass of a proton, or about 1.67×10^{-27} kilograms, which is an extremely small mass. A neutron has just a tiny bit more mass than a proton, but its mass is often assumed to be one atomic mass unit as well. Because electrons have virtually no mass, just about all the mass of an atom is in its protons and neutrons. Therefore, the total number of protons and neutrons in an atom determines its mass in atomic mass units (Table $3.5.2$).

Consider helium again. Most helium atoms have two neutrons in addition to two protons. Therefore the mass of most helium atoms is 4 atomic mass units ($2\ \text{amu}$ for the protons + $2\ \text{amu}$ for the neutrons). However, some helium atoms have more or less than two neutrons. Atoms with the same number of protons but different numbers of neutrons are called isotopes. Because the number of neutrons can vary for a given element, the mass numbers of different atoms of an element may also vary. For example, some helium atoms have three neutrons instead of two (these are called isotopes and are discussed in detail later on)

Why do you think that the "mass number" includes protons and neutrons, but not electrons? You know that most of the mass of an atom is concentrated in its nucleus. The mass of an atom depends on the number of protons and neutrons. You have already learned that the mass of an electron is very, very small compared to the mass of either a proton or a neutron (like the mass of a penny compared to the mass of a bowling ball). Counting the number of protons and neutrons tells scientists about the total mass of an atom. An atom's mass number is very easy to calculate provided you know the number of protons and neutrons in an atom. The mass number of a carbon atom with 6 protons and 7 neutrons is calculated and shown as follows:

$$\text{mass number } A = (\text{number of protons}) + (\text{number of neutrons})$$

$$\text{mass number} = 6 + 6 = 12$$



Example 3.5.1

What is the mass number of an atom of helium that contains 2 neutrons?

Solution

$(\text{number of protons}) = 2$ (Remember that an atom of helium always has 2 protons.)

$(\text{number of neutrons}) = 2$

$\text{mass number} = (\text{number of protons}) + (\text{number of neutrons})$

$\text{mass number} = 2 + 2 = 4$

Isotopes

All atoms of the same element have the same number of protons, but some may have different numbers of neutrons. For example, all carbon atoms have six protons, and most have six neutrons as well. But some carbon atoms have seven or eight neutrons instead of the usual six. Atoms of the same element that differ in their numbers of neutrons are called **isotopes**. Many isotopes occur naturally. Usually one or two isotopes of an element are the most stable and common. Different isotopes of an element generally have the same physical and chemical properties. That's because they have the same numbers of protons and electrons.

An Example: Hydrogen Isotopes

Hydrogen is an example of an element that has isotopes. Three isotopes of hydrogen are modeled in Figure 3.5.4. Most hydrogen atoms have just one proton and one electron and lack a neutron. These atoms are just called hydrogen. Some hydrogen atoms have one neutron as well. These atoms are the isotope named deuterium. Other hydrogen atoms have two neutrons. These atoms are the isotope named tritium.

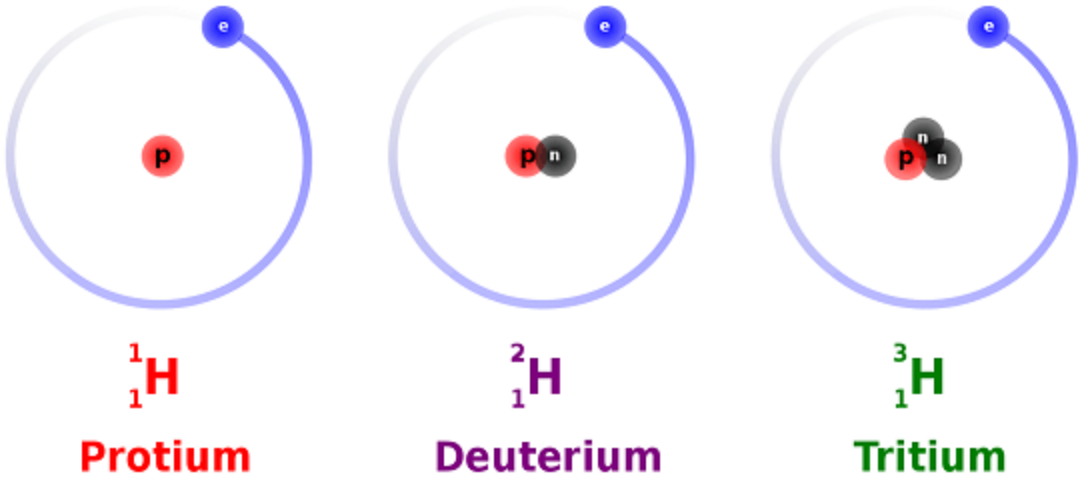


Figure 3.5.4: The three most stable isotopes of hydrogen: protium (A = 1), deuterium (A = 2), and tritium (A = 3). (CC SA-BY 3.0; Balajijagadesh).

For most elements other than hydrogen, isotopes are named for their mass number. For example, carbon atoms with the usual 6 neutrons have a mass number of 12 (6 protons + 6 neutrons = 12), so they are called carbon-12. Carbon atoms with 7 neutrons have atomic mass of 13 (6 protons + 7 neutrons = 13). These atoms are the isotope called carbon-13.

Example 3.5.2: Lithium Isotopes

a. What is the atomic number and the mass number of an isotope of lithium containing 3 neutrons.
b. What is the atomic number and the mass number of an isotope of lithium containing 4 neutrons?

Solution

A lithium atom contains 3 protons in its nucleus irrespective of the number of neutrons or electrons.

a.

$$\begin{aligned} \text{atomic number} &= (\text{number of protons}) = 3 \\ &\quad (\text{number of neutrons}) = 3 \end{aligned}$$

$$\begin{aligned} \text{mass number} &= (\text{number of protons}) + (\text{number of neutrons}) \\ \text{mass number} &= 3 + 3 \\ &= 6 \end{aligned}$$

b.

$$\begin{aligned} \text{atomic number} &= (\text{number of protons}) = 3 \\ &\quad (\text{number of neutrons}) = 4 \end{aligned}$$

$$\begin{aligned} \text{mass number} &= (\text{number of protons}) + (\text{number of neutrons}) \\ \text{mass number} &= 3 + 4 \\ &= 7 \end{aligned}$$

Notice that because the lithium atom always has 3 protons, the atomic number for lithium is always 3. The mass number, however, is 6 in the isotope with 3 neutrons, and 7 in the isotope with 4 neutrons. In nature, only certain isotopes exist. For instance, lithium exists as an isotope with 3 neutrons, and as an isotope with 4 neutrons, but it doesn't exist as an isotope with 2 neutrons or as an isotope with 5 neutrons.

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$$
\begin{array}{lll}
[x \mapsto s]x & = s & \\
[x \mapsto s]y & = y & \text{als } y \neq x \\
[x \mapsto s](\lambda(y)t_1) & = \lambda(y)[x \mapsto s]t_1 & \text{als } y \neq x \text{ en } y \notin FV(s) \\
[x \mapsto s](t_1\ t_2) & = ([x \mapsto s]t_1)\ ([x \mapsto s]t_2) &
\end{array}
$$

Exercise 3.5.1

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.

Symbols for Isotopes

There are two main ways in which scientists frequently show the mass number of an atom they are interested in. It is important to note that the mass number is *not* given on the periodic table. These two ways include writing a nuclear symbol or by giving the name of the element with the mass number written.

To write a **nuclear symbol**, the mass number is placed at the upper left (superscript) of the chemical symbol and the atomic number is placed at the lower left (subscript) of the symbol. The complete nuclear symbol for helium-4 is drawn below:



Nuclear symbol for helium-4: The element symbol is He, the mass number to the top left is 4, and the atomic number to the bottom left is 2

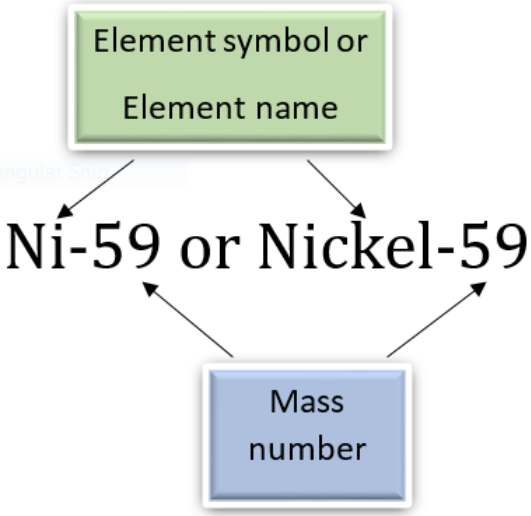
The following nuclear symbols are for a nickel nucleus with 31 neutrons and a uranium nucleus with 146 neutrons.

$$^{59}_{28}\text{Ni}$$

$$^{238}_{92}\text{U}$$

In the nickel nucleus represented above, the atomic number 28 indicates the nucleus contains 28 protons, and therefore, it must contain 31 neutrons in order to have a mass number of 59. The uranium nucleus has 92 protons as do all uranium nuclei and this particular uranium nucleus has 146 neutrons.

Another way of representing isotopes is by adding a hyphen and the mass number to the chemical name or symbol. Thus the two nuclei would be Nickel-59 or Ni-59 and Uranium-238 or U-238, where 59 and 238 are the mass numbers of the two atoms, respectively. Note that the mass numbers (not the number of neutrons) are given to the side of the name.



One way to represent isotopes: The element symbol or name comes first, then a hyphen, then the mass number

Example 3.5.3: POTASSIUM-40

How many protons, electrons, and neutrons are in an atom of $^{40}_{19}\mathrm{K}$?

Solution

$$\text{atomic number} = (\text{number of protons}) = 19$$

For all atoms with no charge, the number of electrons is equal to the number of protons.

$$\text{number of electrons} = 19$$

The mass number, 40 is the sum of the protons and the neutrons.

To find the number of neutrons, subtract the number of protons from the mass number.

$$\text{number of neutrons} = 40 - 19 = 21.$$

Example 3.5.4: Zinc-65

How many protons, electrons, and neutrons are in an atom of zinc-65?

Solution

$$\text{number of protons} = 30$$

For all atoms with no charge, the number of electrons is equal to the number of protons.

$$\text{number of electrons} = 30$$

The mass number, 65 is the sum of the protons and the neutrons.

To find the number of neutrons, subtract the number of protons from the mass number.

$$\text{number of neutrons} = 65 - 30 = 35$$

Exercise 3.5.2

How many protons, electrons, and neutrons are in each atom?

a. $^{60}_{27}\text{Co}$
b. Na-24
c. $^{45}_{20}\text{Ca}$
d. Sr-90

Answer a: available at the end of this section.

Table 3.5.3: Properties of Isotopes of the First Six Elements.

Element	Symbol	Atomic Number	Number of Protons	Number of Neutrons	Mass (amu)	% Natural Abundance
hydrogen	$^{1}_{1}\text{H}$ (protium)	1	1	0	1.0078	99.989
	$^{2}_{1}\text{H}$ (deuterium)	1	1	1	2.0141	0.0115
	$^{3}_{1}\text{H}$ (tritium)	1	1	2	3.01605	— (trace)
helium	$^{3}_{2}\text{He}$	2	2	1	3.01603	0.00013
	$^{4}_{2}\text{He}$	2	2	2	4.0026	100
lithium	$^{6}_{3}\text{Li}$	3	3	3	6.0151	7.59
	$^{7}_{3}\text{Li}$	3	3	4	7.0160	92.41
beryllium	$^{9}_{4}\text{Be}$	4	4	5	9.0122	100
boron	$^{10}_{5}\text{B}$	5	5	5	10.0129	19.9
	$^{11}_{5}\text{B}$	5	5	6	11.0093	80.1
carbon	$^{12}_{6}\text{C}$	6	6	6	12.0000	98.89
	$^{13}_{6}\text{C}$	6	6	7	13.0034	1.11
	$^{14}_{6}\text{C}$	6	6	8	14.0032	— (trace)

Summary

- The atom consists of discrete particles that govern its chemical and physical behavior.
- Each atom of an element contains the same number of protons, which is the atomic number (*Z*).
- Neutral atoms have the same number of electrons and protons.
- Atoms of an element that contain different numbers of neutrons are called isotopes.
- Each isotope of a given element has the same atomic number but a different mass number (*A*), which is the sum of the numbers of protons and neutrons.
- The relative masses of atoms are reported using the atomic mass unit (amu) which is defined as one-twelfth of the mass of one atom of carbon-12, with 6 protons, 6 neutrons, and 6 electrons. The nuclear model of the atom consists of a small and dense positively charged interior surrounded by a cloud of electrons.

Contributors and Attributions

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- TextMap: Chemistry-The Central Science (Brown et al.)
- TextMap: Fundamentals of General, Organicn, and Biological Chemistry (McMurry et al.)

- Marisa Alviar-Agnew (Sacramento City College)

- Henry Agnew (UC Davis)

Answers

Exercise 3.5.1

Atomic number = 50, mass number = 118

Exercise 3.5.2

27 protons, 27 electrons, 33 neutrons
11 protons, 11 electrons, 13 neutrons
20 protons, 20 electrons, 25 neutrons
38 protons, 38 electrons, 52 neutrons

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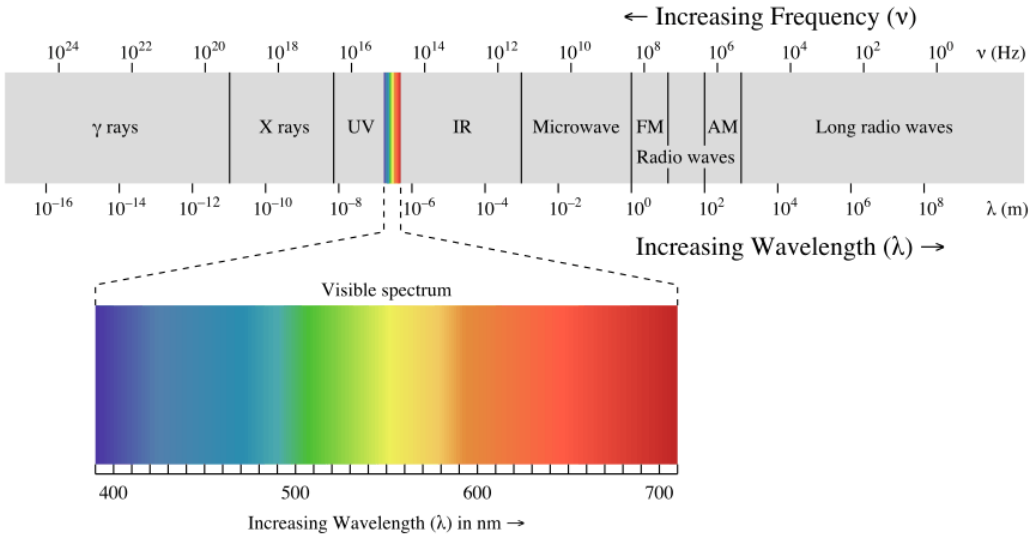
3.6: Electron Arrangement- The Bohr Model (Orbits)

Learning Objectives

- Know the properties of different types of electromagnetic radiation.
- Define an energy level in terms of the Bohr model.
- Discuss how the Bohr model can be used to explain atomic spectra.
- Describe the arrangement of electrons using the shell model.

Electromagnetic waves have an extremely wide range of wavelengths, frequencies, and energies. The highest energy form of electromagnetic waves are gamma (γ) rays and the lowest energy form are radio waves.

The figure below shows the **electromagnetic spectrum**, which is all forms of electromagnetic radiation. On the far left of Figure 3.6.1 are the highest energy electromagnetic waves. These are called **gamma rays** and can be quite dangerous, in large numbers, to living systems. The next lower energy form of electromagnetic waves are called **x-rays**. Most of you are familiar with the penetration abilities of these waves. They can also be dangerous to living systems. Humans are advised to limit as much as possible the number of medical x-rays they have per year. Next lower, in energy, are **ultraviolet rays**. These rays are part of sunlight and the upper end of the ultraviolet range can cause sunburn and perhaps skin cancer. The tiny section next in the spectrum is the **visible range of light** ... this section has been greatly expanded in the bottom half of the figure so it can be discussed in more detail. The visible range of electromagnetic radiation are the frequencies to which the human eye responds. Lower in the spectrum are infrared rays and radio waves.



The electromagnetic spectrum, with its various regions labeled. The borders of each region are approximate. As frequency increases wavelength decreases. Gamma rays: frequency between 1020 and 1024, wavelength between 10-16 and 10-12; X-Rays: frequency between 1016 and 1020, wavelength between 10-12 and 10-8; UV: frequencies between 1015 and 1017, wavelengths between 10-8 and 10-6; visible spectrum of light: wavelength to between 400 and 700 nm; IR: frequencies between 1011 and 1015, wavelengths between 10-6 and 10 -3; Microwave: frequencies between 108 and 1011, wavelengths between 103 and 100; radio waves: frequencies between 105 and 108, , wavelengths between 100 and 103; long radio waves: the frequencies between 100 and 105.

The light energies that are in the visible range are electromagnetic waves that cause the human eye to respond when those frequencies enter the eye. The eye sends a signal to the brain and the individual "sees" various colors. The highest energy waves in the visible region cause the brain to see violet and as the energy decreases, the colors change to blue, green, yellow, orange, and red. When the energy of the wave is above or below the visible range, the eye does not respond to them. When the eye receives several different frequencies at the same time, the colors are blended by the brain. If all frequencies of light strike the eye together, the brain sees white and if there are no visible frequencies striking the eye, the brain sees black. The objects that you see around you are light absorbers - that is, the chemicals on the surface of the object will absorb certain frequencies and

not others. Your eyes detect the frequencies that strike your eye. Therefore, if your friend is wearing a red shirt, it means the dye in that shirt absorbs every frequency except red and the red frequencies are reflected. If your only light source was one exact frequency of blue light and you shined it on a shirt that was red in sunlight, the shirt would appear black because no light would be reflected. The light from fluorescent types of lights do not contain all the frequencies of sunlight and so clothes inside a store may appear to be a slightly different color than when you get them home.

Continuous and Line Spectra

Electric light bulbs contain a very thin wire in them that emits light when heated. The wire is called a filament. The particular wire used in light bulbs is made of tungsten. A wire made of any metal would emit light under these circumstances but tungsten was chosen because the light it emits contains virtually every frequency and therefore, the light emitted by tungsten appears white. A wire made of some other element would emit light of some color that was not convenient for our uses. Every element emits light when energized by heating or passing electric current through it. Elements in solid form begin to glow when they are heated sufficiently and elements in gaseous form emit light when electricity passes through them. This is the source of light emitted by neon signs and is also the source of light in a fire.



Figure 3.6.2 Human/Need/Desire. Neon sculpture by Bruce Nauman (1983), who has been characterized as a conceptual artist.

Each Element Has a Unique Spectrum

The light frequencies emitted by atoms are mixed together by our eyes so that we see a blended color. Several physicists, including Angstrom in 1868 and Balmer in 1875, passed the light from energized atoms through glass prisms in such a way that the light was spread out so they could see the individual frequencies that made up the light. The **emission spectrum** (or **atomic spectrum**) of a chemical element is the unique pattern of light obtained when the element is subjected to heat or electricity.



Figure 3.6.3 Atomic Emission Spectrum of Hydrogen.

When hydrogen gas is placed into a tube and electric current passed through it, the color of emitted light is pink. But when the color is spread out, we see that the hydrogen spectrum is composed of four individual frequencies. The pink color of the tube is the result of our eyes blending the four colors. Every atom has its own characteristic spectrum; no two atomic spectra are alike. The image below shows the emission spectrum of iron. Because each element has a unique emission spectrum, elements can be defined using them.

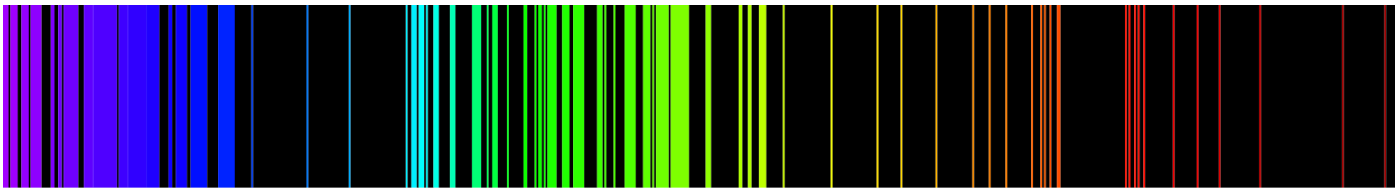


Figure 3.6.4 Atomic Emission Spectrum of Iron.

You may have heard or read about scientists discussing what elements are present in the sun or some more distant star, and after hearing that, wondered how scientists could know what elements were present in a place no one has ever been. Scientists determine what elements are present in distant stars by analyzing the light that comes from stars and finding the atomic spectrum of elements in that light. If the exact four lines that compose hydrogen's atomic spectrum are present in the light emitted from the star, that element contains hydrogen.

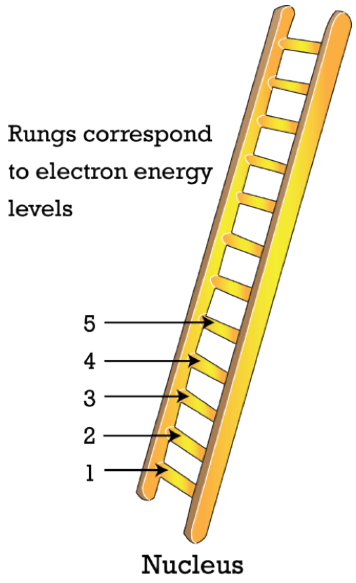
Bohr's Explanation of Line Spectra

In 1913, the Danish physicist Niels Bohr proposed a model of the electron cloud of an atom in which electrons orbit the nucleus and were able to produce atomic spectra. Understanding Bohr's model requires some knowledge of electromagnetic radiation (or light). Bohr's key idea in his model of the atom is that electrons occupy definite orbitals that require the electron to have a specific amount of energy. In order for an electron to be in the electron cloud of an atom, it must be in



one of the allowable orbitals and it must have the precise energy required for that orbit. Orbits closer to the nucleus would require smaller amounts of energy for an electron and orbits farther from the nucleus would require the electrons to have a greater amount of energy. The possible orbits are known as **energy levels (n)**. One of the weaknesses of Bohr's model was that he could not offer a reason why only certain energy levels or orbits were allowed.

***Figure** 3.6.5**:** Niels Bohr with Albert Einstein at Paul Ehrenfest's home in Leiden (December 1925).*



Bohr hypothesized that the only way electrons could gain or lose energy would be to move from one energy level to another, thus gaining or losing precise amounts of energy. The energy levels are **quantized**, meaning that only specific amounts are possible. It would be like a ladder that had rungs only at certain heights. The only way you can be on that ladder is to be on one of the rungs and the only way you could move up or down would be to move to one of the other rungs. Suppose we had such a ladder with 10 rungs. Other rules for the ladder are that only one person can be on a rung in normal state and the ladder occupants must be on the lowest rung available. If the ladder had five people on it, they would be on the lowest five rungs. In this situation, no person could move down because all the lower rungs are full. Bohr worked out rules for the maximum number of electrons that could be in each energy level in his model and required that an atom in its normal state (ground state) had all electrons in the lowest energy levels available. Under these circumstances, no electron could lose energy because no electron could move down to a lower energy level. In this way, Bohr's model explained why electrons circling the nucleus did not emit energy and spiral into the nucleus.

Figure 3.6.6 *The energy levels (n= 1,2,3...) of the electrons can be viewed as rungs on a ladder.*

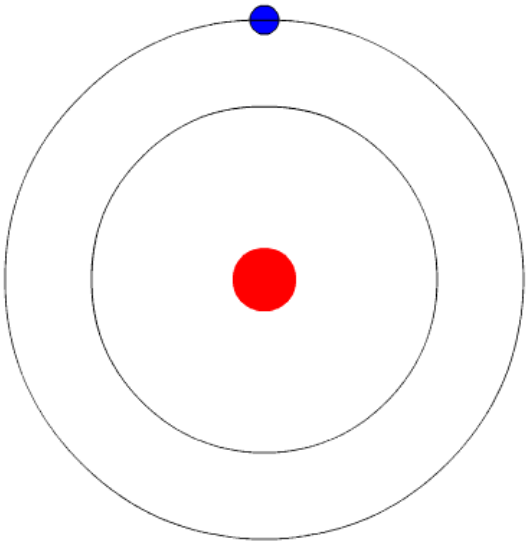


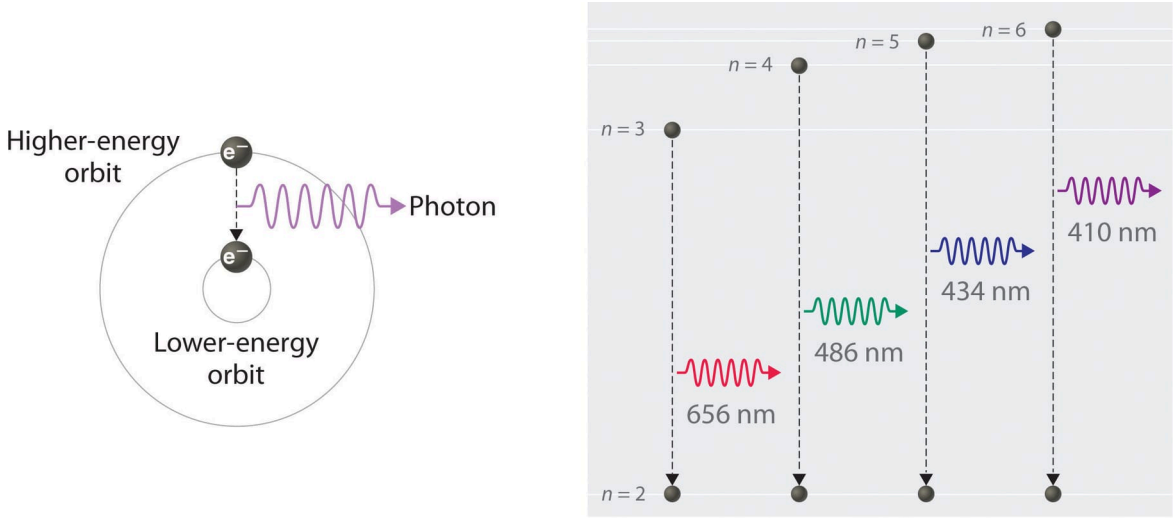
Figure 3.6.7 In Bohr's Model of the atom, electrons absorb energy to move to a higher level and release energy to move to lower levels. (CC BY-SA 3.0; Kurzon).

The evidence used to support Bohr's model came from the atomic spectra. He suggested that an atomic spectrum is made by the electrons in an atom moving energy levels.

Ground States and Excited States

The electrons typically have the lowest energy possible, called the **ground state**. If the electrons are given energy (through heat, electricity, light, etc.) the electrons in an atom could absorb energy by jumping to a higher energy level, or **excited state**. The electrons then give off the energy in the form of a piece of light, called a **photon**, they had absorbed to fall back to a lower energy level. The energy emitted by electrons dropping back to lower energy levels would always be precise amounts of energy because the differences in energy levels were precise. This explains why you see specific lines of light when looking at an atomic spectrum - each line of light matches a specific "step down" that an electron can take in that atom. This also explains why each element produces a different atomic spectrum. Because each element has different acceptable energy levels for their electrons, the possible steps each element's electrons can take differ from all other elements.

Based on the wavelengths of the spectral lines, Bohr was able to calculate the energies that the hydrogen electron would have in each of its allowed energy levels. He then mathematically showed which energy level transitions correspond to the spectral lines in the atomic emission spectrum (see below).



(a) Electronic emission transition **(b) Balmer series transitions**

The emission of light by a hydrogen atom in an excited state. (a) Light is emitted when the electron undergoes a transition from an orbit with a higher value of n (at a higher energy) to an orbit with a lower value of n (at lower energy). (b) The Balmer series of emission lines is due to transitions from orbits with n ≥ 3 to the orbit with n = 2. The differences in energy between these levels corresponds to light in the visible portion of the electromagnetic spectrum. (CC BY-SA-NC; anonymous by request).

He found that the four visible spectral lines corresponded to transitions from higher energy levels down to the second energy level $(n = 2)$. This is called the Balmer series (Figure $3.6.8$). Transitions ending in the ground state $(n = 1)$ are called the Lyman series, but the energies released are so large that the spectral lines are all in the ultraviolet region of the spectrum. The transitions called the Paschen series and the Brackett series both result in spectral lines in the infrared region because the energies are too small.

Bohr's model was a tremendous success in explaining the spectrum of the hydrogen atom. Unfortunately, when the mathematics of the model was applied to atoms with more than one electron, it was not able to correctly predict the frequencies of the spectral lines. While Bohr's model represented a great advancement in the atomic model and the concept of **electron transitions** between energy levels is valid, improvements were needed in order to fully understand all atoms and their chemical behavior.

Different metal electrons emit different wavelengths of light to return to their respective ground states, so the flame colors are varied. These flames can be used to produce atomic emmision spectra of the elements combusted. Using known values of emission spectra, one can perform a flame test on un unknown substance, gather an emmision spectrum from it, and determine which elements are in the unknown substance.

For example, in the case of copper ion, there are multiple different "paths" that the excited electrons can follow to emit photon of certain discrete energy. This produces multiple spectra lines because each discrete energy level difference will yield a specific wavelength of light, which determines the color.

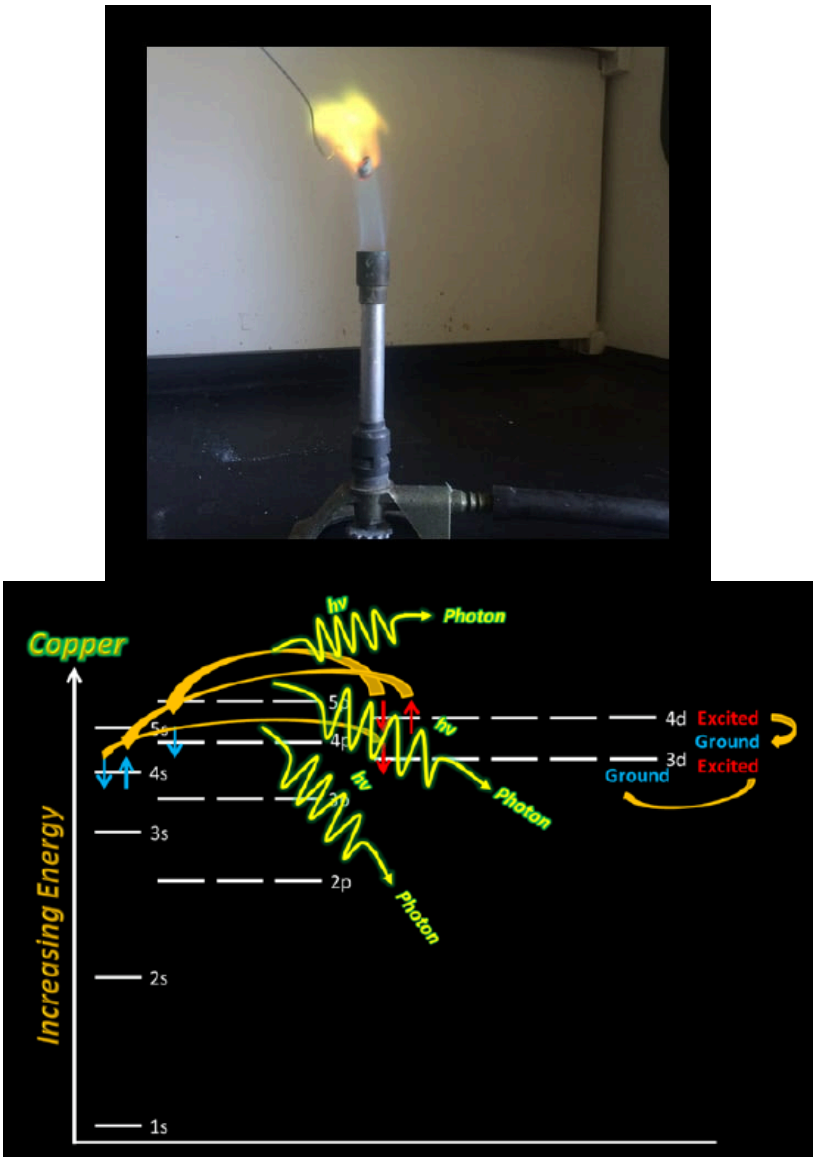


Figure 3.6.9 *(left): Copper is heated and as the electrons fall back, certain color of light is emitted. (right): Submicroscopic view of the electron movement, as electrons fall.*

Building Atoms: Main Shells

An electron shell is the outside part of an atom around the atomic nucleus. It is a group of atomic orbitals with the same value of the principal quantum number n. Electron shells have one or more electron subshells, or sublevels. The name for electron shells comes from the Bohr model, in which groups of electrons were believed to go around the nucleus at certain distances, so that their orbits formed "shells".

An electron shell may be thought of as an orbit followed by electrons around an atom nucleus. Because each shell can contain only a fixed number of electrons, each shell is associated with a particular range of electron energy, and thus each shell must fill completely before electrons can be added to an outer shell. The electrons in the outermost shell determine the chemical properties of the atom (see Valence shell). For an explanation of why electrons exist in these shells see electron configuration.

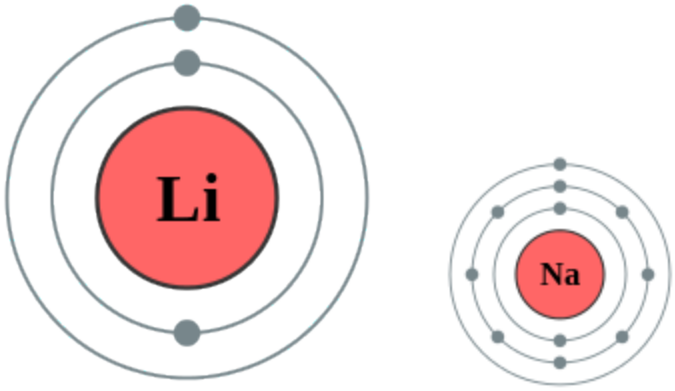


Figure 3.6.10 *A shell diagram of lithium (left) and Sodium (right)*

The electron shells are labeled K, L, M, N, O, P, and Q; or 1, 2, 3, 4, 5, 6, and 7; going from innermost shell outwards. Electrons in outer shells have higher average energy and travel farther from the nucleus than those in inner shells. This makes them more important in determining how the atom reacts chemically and behaves as a conductor, because the pull of the atom's nucleus upon them is weaker and more easily broken. In this way, a given element's reactivity is highly dependent upon its electronic configuration.

Drawing Shell Models

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 3.6.1 *How to draw the shell model for sulfur.*

Note: The number of electrons that can occupy each energy level are 2 (first level), 8 (2nd level), 18 (3rd level), and 32 (4th level) based on the formula: # of electrons = $2(n)^2$, wherein n = principle energy level.

Table 3.6.1 shows the number of electrons that fill each shell for neutral atoms of several elements. As mentioned earlier, the innermost shell (corresponding to lowest energy) is filled first and only a fixed number of electrons is allowed in each shell. The only electron in hydrogen (Z=1) goes to the first shell. In lithium atom (Z=3), the two electrons fill the first shell, and the third electron goes to the second shell. An argon atom (Z=18) has 18 electrons. The 10 electrons fill the first and second shells, and the remaining 8 electrons go to the third shell. The electron configuration for elements pass argon are covered in more detail in section 3.7.

Table 3.6.1 Electron Configuraion (Arrangement) of Several Elements.

Element Symbol	Atomic Number* (Z)	First Shell n=1 (2 electrons allowed)	Second Shell n=2 (8 electrons allowed)	Third Shell n=3 (18 electrons allowed)
H	1	1		
He	2	2		
C	6	2	4	
N	7	2	5	
Na	11	2	8	1
Mg	12	2	8	2
Cl	17	2	8	7
Ar	18	2	8	8

Note:* In a neutral atom he number of protons is equal to the number of electrons.

Summary

- Electromagnetic radiation has a wide spectrum, including gamma rays, X-rays, UV rays, visible light, IR radiation, microwaves, and radio waves.
- The different colors of light differ in their frequencies (or wavelengths).

- Bohr's model suggests each atom has a set of unchangeable energy levels and electrons in the electron cloud of that atom must be in one of those energy levels.
- Bohr's model suggests that the atomic spectra of atoms is produced by electrons gaining energy from some source, jumping up to a higher energy level, then immediately dropping back to a lower energy level and emitting the energy different between the two energy levels.
- The existence of the atomic spectra is support for Bohr's model of the atom.
- Bohr's model was only successful in calculating energy levels for the hydrogen atom.
- The shell model is a good representation of electron arrangement only for elements 1-18.

Contributors and Attributions

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3.7: Electron Arrangement- The Quantum Model

Learning Objectives

- Represent the organization of electrons by an electron configuration based on the quantum mechanical model of an atom.

Quantum mechanics is the study of the motion of objects that are atomic or subatomic in size and thus demonstrate wave-particle duality. One of the fundamental (and hardest to understand) principles of quantum mechanics is that the electron is both a particles and a wave. In the everyday macroscopic world of things we can see, something cannot be both. But this duality can exist in the quantum world of the submicroscopic at the atomic scale.



At the heart of quantum mechanics is the idea that we cannot specify accurately the location of an electron. All we can say is that there is a probability that it exists within this certain volume of space. The scientist Erwin Schrödinger developed an equation that deals with these calculations, which we will not pursue at this time. Recall that in the Bohr model, the exact path of the electron was restricted to very well-defined circular **orbits** around the nucleus. An **orbital** is the quantum mechanical refinement of Bohr's orbit. In contrast to his concept of a simple circular orbit with a fixed radius, orbitals are mathematically derived regions of space with different *probabilities* of having an electron.

Figure 3.7.1 *The Erwin Schrödinger.*

Building Atoms by Orbital Filling

In the quantum-mechanical model of an atom, electrons in the same atom that have the same principal quantum number (n) or principal energy level are said to occupy an electron **shell** of the atom. Orbitals define regions in space where you are likely to find electrons. As shown in Figure 3.7.2 *s* orbitals are spherical shaped, and *p* orbitals are dumb-bell shaped. Orbitals within a shell are divided into **subshells (sublevels)**. There are two subshells in the second shell namely the 2s subshell (with one orbital) and the 2p subshell (with three orbitals), see Table 3.7.1. It should be noted that the diagrams in Figure 3.7.2 are estimates of the electron distribution in space, not surfaces electrons are fixed on.

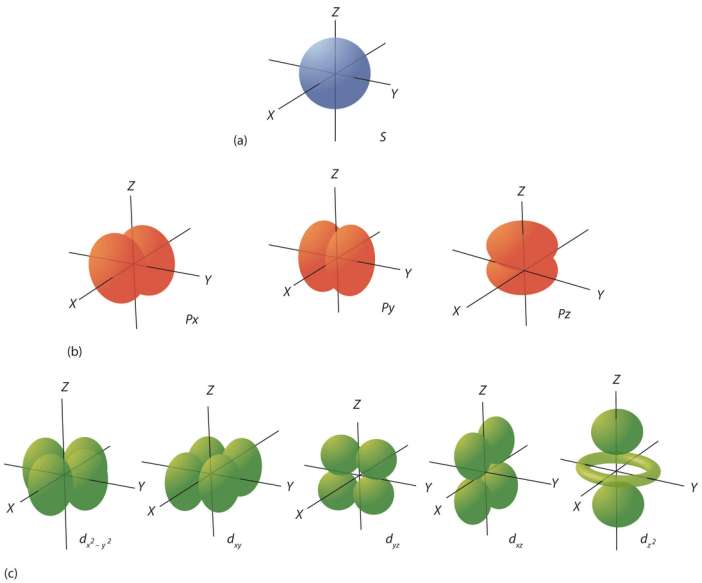


Figure 3.7.2: Electron Orbitals. (a) The lone s orbital is spherical in distribution. (b) The three *p* orbitals are shaped like dumbbells, and each one points in a different direction. (c) The five *d* orbitals are rosette in shape, except for the *orbital, which is a "dumbbell + torus" combination. They are all oriented in different directions.*

Table 3.7.1 summarizes the number and type orbitals that can be found within each principal energy level as well as the number of electrons allowed.

Table 3.7.1 Electron Arrangement Within Energy Levels

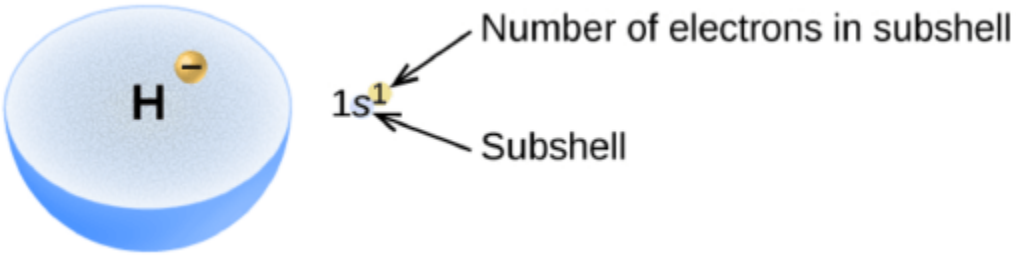
Principal Quantum Number (n) (Principal Shell)	Sublevels (Subshell)	Number of Orbitals per Sublevel	Number of Electrons per Sublevel (Maximum of 2 electrons/orbital)
1	1s	1 (1s)	2
2	2s	1 (2s)	2
	2p	3 (2px 2py 2pz)	6
3	3s	1 (3s)	2

Principal Quantum Number (n) (Principal Shell)	Sublevels (Subshell)	Number of Orbitals per Sublevel	Number of Electrons per Sublevel (Maximum of 2 electrons/orbital)
	3p	3 (3px 3py 3pz)	6
	3d	5 (refer to Figure $3.7.2c$)	10

In contrast to the shell model discussed in section 3.6, chemists more often use a more detailed electron configuration to represent the organization of electrons in shells and subshells in an atom. An atom's electron configuration includes the shell and subshell labels, with a right superscript giving the number of electrons in that subshell. The shells and subshells are listed in the order of filling. Electrons are typically organized around an atom by starting at the lowest possible quantum numbers first, which are the shells-subshells with lower energies.

For example, an H atom has a single electron in the 1s subshell. Its electron configuration is **H: $1s^1$**

He has two electrons in the 1s subshell. Its electron configuration is **He: $1s^2$**



The three electrons for Li are arranged in the 1s subshell (two electrons) and the 2s subshell (one electron). The electron configuration of Li is

Li: $1s^2 2s^1$

Figure $3.7.3$ *The diagram of an electron configuration of hydrogen right*

specifies the subshell and superscript number of electrons.

Table $3.7.2$*: Electron Configurations of First and Second-Period Elements*

Element Name	Symbol	Atomic Number	Electron Configuration
Hydrogen	H	1	$1s^1$
Helium	He	2	$1s^2$
Lithium	Li	3	$1s^2 2s^1$
Beryllium	Be	4	$1s^2 2s^2$
Boron	B	5	$1s^2 2s^2 2p^1$

Element Name	Symbol	Atomic Number	Electron Configuration
Carbon	C	6	$1s^2 2s^2 2p^2$
Nitrogen	N	7	$1s^2 2s^2 2p^3$
Oxygen	O	8	$1s^2 2s^2 2p^4$
Fluorine	F	9	$1s^2 2s^2 2p^5$
Neon	Ne	10	$1s^2 2s^2 2p^6$

In order to create ground state electron configurations for any element, it is necessary to know the way in which the atomic sublevels are organized in order of increasing energy. Figure 3.7.4 shows the order of increasing energy of the sublevels.

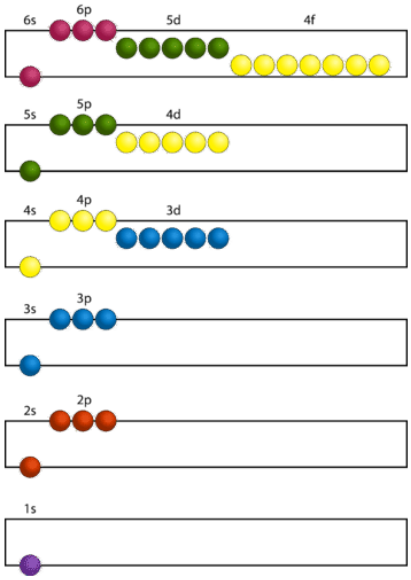


Figure 3.7.4: Electrons are added to atomic orbitals in order from low energy (bottom of the graph) to high (top of the graph) according to the Aufbau principle. Principle energy levels are color coded, while sublevels are grouped together and each circle represents an orbital capable of holding two electrons.

Figure 3.7.5 illustrates the traditional way to remember the filling order for atomic orbitals.

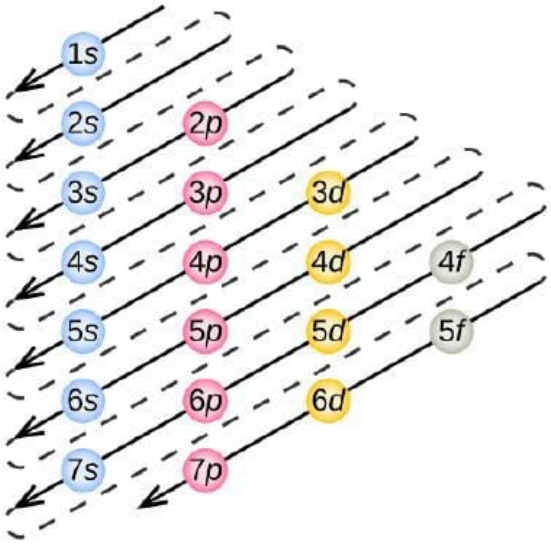


Figure 3.7.5 *The arrow leads through each subshell in the appropriate filling order for electron configurations. This chart is straightforward to construct. Simply make a column for all the s orbitals with each n shell on a separate row. Repeat for p, d, and f. Be sure to only include orbitals allowed by the quantum numbers (no 1p or 2d, and so forth). Finally, draw diagonal lines from top to bottom as shown.*

Example 3.7.1: Nitrogen Atoms

Nitrogen has 7 electrons. Write the electron configuration for nitrogen.

Solution:

Take a close look at Figure 9.6.5, and use it to figure out how many electrons go into each sublevel, and also the order in which the different sublevels get filled.

1. Begin by filling up the 1s sublevel. **This gives $1s^2$**. Now all of the orbitals in the red n = 1 block are filled.

Answer available at the end of this section.

2. Next, fill the 2s sublevel. This gives **$1s^2 2s^2$**. Now all of the orbitals in the s sublevel of the orange n = 2 block are filled.

Answer available at the end of this section.

3. Notice that we haven't filled the entire n = 2 block yet... there are still the p orbitals!

Answer available at the end of this section.

The overall electron configuration is: **$1s^2 2s^2 2p^3$**.

Example 3.7.2: Potassium Atoms

Potassium has 19 electrons. Write the electron configuration code for potassium.

Solution

This time, take a close look at Figure 9.6.5.

1. Begin by filling up the 1s sublevel. **This gives $1s^2$**. Now the n = 1 level is filled.

Answer available at the end of this section.

2. Next, fill the 2*s* sublevel. **This gives $1s^2 2s^2$**

Answer available at the end of this section.

3. Next, fill the 2*p* sublevel. T**his gives $1s^2 2s^2 2p^6$.** Now the $n = 2$ level is filled.

Answer available at the end of this section.

4. Next, fill the 3*s* sublevel. **This gives $1s^2 2s^2 2p^6 3s^2$**

Answer available at the end of this section.

5. Next, fill the 3*p* sublevel. **This gives $1s^2 2s^2 2p^6 3s^2 3p^6$**

Answer available at the end of this section.

Here's where we have to be careful – right after $3p^6$!!

Answer available at the end of this section.

6. The final electron goes into the 4*s* sublevel. **This gives $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$**

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

Exercise 3.7.1: Magnesium and Sodium Atoms

What is the electron configuration for Mg and Na?

Answer Mg available at the end of this section.

Answer Na available at the end of this section.

Summary

- Orbitals define regions in space where you are likely to find electrons. *s* orbitals are spherical shaped. *p* orbitals are dumb-bell shaped. The three possible *p* orbitals are always perpendicular to each other.
- Electron configuration notation simplifies the indication of where electrons are located in a specific atom. Superscripts are used to indicate the number of electrons in a given sublevel.
- Electrons are added to atomic orbitals in order from low energy to high energy.

Contributors and Attributions

-
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- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

- TextMap: Beginning Chemistry (Ball et al.)

Answers

Example 3.7.1**: Nitrogen Atoms**

Since we used 2 electrons, there are 7 – 2 = **5 electrons left**

Example 3.7.1**: Nitrogen Atoms**

Since we used another 2 electrons, there are 5 – 2 = **3 electrons left**

Example 3.7.1**: Nitrogen Atoms**

The final 3 electrons go into the 2*p* sublevel. This gives $\mathbf{1s^2 2s^2 2p^3}$

Example 3.7.2**: Potassium Atoms**

Since we used 2 electrons, there are 19 – 2 = **17 electrons left**

Example 3.7.2**: Potassium Atoms**

Since we used another 2 electrons, there are 17 – 2 = **15 electrons left**

Example 3.7.2**: Potassium Atoms**

Since we used another 6 electrons, there are 15 – 6 = **9 electrons left**

Example 3.7.2**: Potassium Atoms**

Since we used another 2 electrons, there are 9 – 2 = **7 electrons left**

Example 3.7.2**: Potassium Atoms**

Since we used another 6 electrons, there are 7 – 6 = **1 electron left**

Example 3.7.2**: Potassium Atoms**

Remember, 4s comes before 3*d*!

Exercise 3.7.1**: Magnesium and Sodium Atoms**

Mg: $1s^2 2s^2 2p^6 3s^2$

Exercise 3.7.1**: Magnesium and Sodium Atoms**

Na: $1s^2 2s^2 2p^6 3s^1$

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3.8: Electron Configurations and the Periodic Table

Interactive periodic table of the elements, in pictures and words

https://elements.wlonk.com/ElementsTable.htm

Interactive Periodic Table of the Elements, in Pictures and Words © 2005-2016 Keith Enevoldsen elements.wlonk.com

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elements.wlonk.com

Learning Objectives

- Know the classification of the different elements.
- Define valence electrons.
- Describe how the number of valence electrons are related the arrangement of the main group elements and its chemical behavior.

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). In and atomic , the **main group** is the group of elements whose lightest members are represented by , , , , , , , and as arranged in the of the elements. The main group includes the elements (except , which is sometimes not included) in groups 1 and 2, and groups 13 to 18. Main-group elements (with some of the lighter) are the most abundant elements on , in the , and in the . They are sometimes also called the **representative elements**. In older nomenclature the main-group elements are groups IA and IIA, and groups IIIB to 0 (CAS groups IIIA to VIIIA). Group 12 is labelled as group IIB in both systems. Group 3 is labelled as group IIIA in the older nomenclature (CAS group IIIB).

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.

One way to categorize the elements of the periodic table is shown in Figure 3.8.1. The first two columns on the left and the last six columns on the right as mentioned earlier are the main group elements. The ten-column block between these columns contains the **transition metals**. The two rows beneath the main body of the periodic table contain the **inner transition metals**. The elements in these two rows are also referred to as, respectively, the **lanthanide metals** and the **actinide metals**.

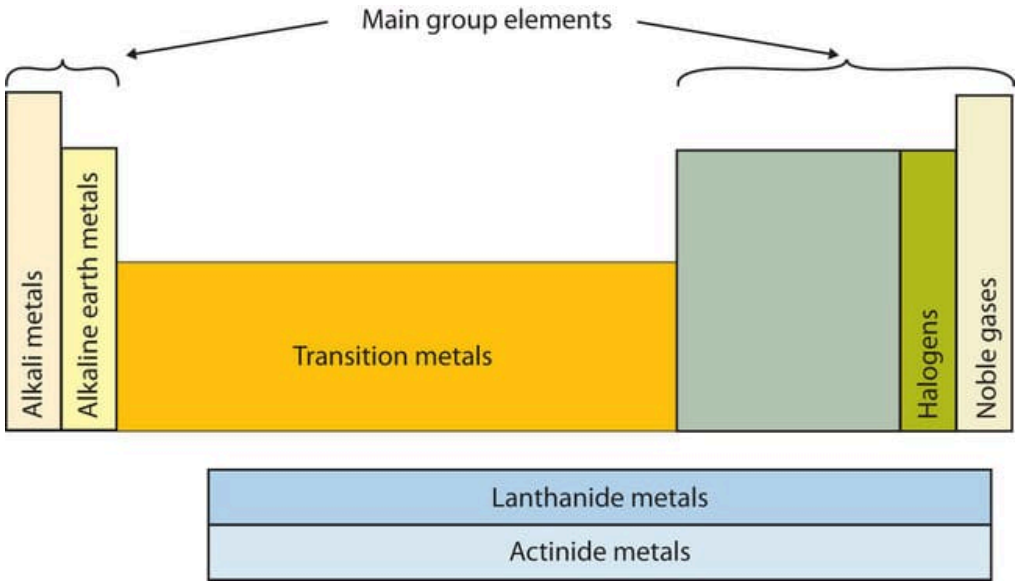


Figure 3.8.1: Special names for sections of the periodic table.

Family Features: Outer Electron Configurations

Valence Electrons

The valence shell is the outermost shell of an atom in its uncombined state, which contains the electrons most likely to account for the nature of any reactions involving the atom and of the bonding interactions it has with other atoms. **Valence electrons** are the outer-shell electrons of an atom. These are electrons that can participate in the formation of a chemical bond. The presence of valence electrons can determine the element's chemical properties and whether it may bond with other elements.

An atom with a closed shell of valence electrons tends to be chemically inert. An atom with one or two valence electrons more than a closed shell is highly reactive, because the extra valence electrons are easily removed to form a positive ion. An atom with one or two valence electrons fewer than a closed shell is also highly reactive, because of a tendency either to gain the missing valence electrons (thereby forming a negative ion), or to share valence electrons (thereby forming a covalent bond).

The number of valence electrons of an element can be determined by the periodic table group (vertical column) in which the element is categorized (Table 3.8.1). With the exception of groups 3–12 (the transition metals), the units digit of the group number identifies how many valence electrons are associated with a neutral atom of an element listed under that particular column.

Table 3.8.1: Number of Valence Electrons for Main Periodic Table Groups.

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

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

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

Valence Electrons and the Periodic Table

YouTube Video

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

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Video 3.8.1 *Finding the valence electron for an element.*

Family Groups

As previously noted, the periodic table is arranged so that elements with similar chemical behaviors are in the same group. Chemists often make general statements about the properties of the elements in a group using descriptive names with historical origins.

Group 1: The Alkali Metals

The alkali metals are lithium, sodium, potassium, rubidium, cesium, and francium. Hydrogen is unique in that it is generally placed in Group 1, but it is not a metal.

The compounds of the alkali metals are common in nature and daily life. One example is table salt (sodium chloride); lithium compounds are used in greases, in batteries, and as drugs to treat patients who exhibit manic-depressive, or bipolar, behavior. Although lithium, rubidium, and cesium are relatively rare in nature, and francium is so unstable and highly radioactive that it exists in only trace amounts, sodium and potassium are the seventh and eighth most abundant elements in Earth's crust, respectively.

Group 2: The Alkaline Earth Metals

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

Group 17: The Halogens

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

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

Group 18: The Noble Gases

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

Example 3.8.1: Groups

Provide the family or group name of each element.

a. Li
b. Ar
c. Cl

Solution

a. Lithium is an alkali metal (Group 1)
b. Argon is a noble gas (Group 18)
c. Chlorine is a halogen (Group 17)

Exercise 3.8.1: Groups

Provide the family or group name of each element.

a. F
b. Ca
c. Kr

Answer a: available at the end of this section.

Metals and Nonmetals

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 metalloid (or semi metal), as shown in Figure 3.8.2. A **metal** is a substance that is shiny, typically (but not always) silvery in color, and an excellent conductor of electricity and heat. Metals are also malleable (they can be beaten into thin sheets) and ductile (they can be drawn into thin wires). A **nonmetal** is typically dull and a poor conductor of electricity and heat. Solid nonmetals are also very brittle. As shown in Figure 3.8.2, metals occupy the left three-fourths of the periodic table, while nonmetals (except for hydrogen) are clustered in the upper right-hand corner of the periodic table. The elements with properties intermediate between those of metals and nonmetals are called **metalloids** (or **semi-metals**). Elements adjacent to the bold line in the right-hand portion of the periodic table have semimetal properties.

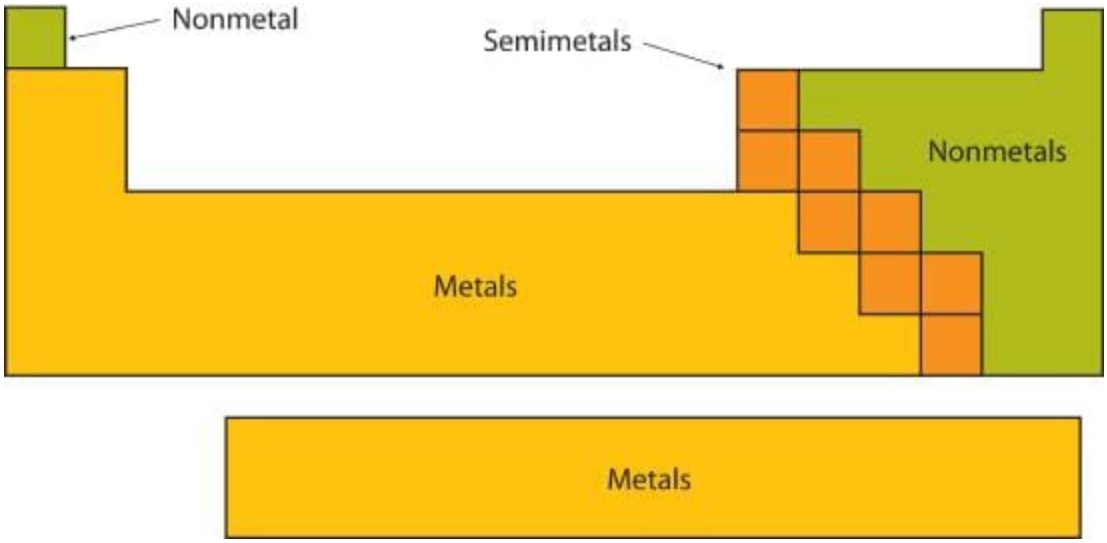


Figure 3.8.2: Types of Elements. Elements are either metals, nonmetals, or metalloids (or semi metals). Each group is located in a different part of the periodic table.

Example 3.8.2

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. In Figure 3.8.1, selenium lies above and to the right of the diagonal line marking the boundary between metals and nonmetals, so it should be a nonmetal.
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 3.8.2

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

Answer available at the end of this section.

Example 3.8.3: Classification of Elements

Classify each element as metal, non metal, transition metal or inner transition metal.

a. Li
b. Ar
c. Am
d. Fe

Solution

a. Lithium is a metal.
b. Argon is a non metal
c. Americium is an inner transition metal
d. Iron is a transition metal.

Exercise 3.8.3: Classification of Elements

Classify each element as metal, non metal, transition metal or inner transition metal.

a. F
b. U
c. Cu

Answer a: available at the end of this section.

Alkali Metals

YouTube Video

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Video 3.8.2 *Alkali metals in water.*

Summary

- Valence electrons are the outer-shell electrons of an atom. These are electrons that can participate in the formation of a chemical bond.
- Elements that exhibit similar chemistry appear in vertical columns called groups (numbered 1–18 from left to right).
- The seven horizontal rows are called periods. Some of the groups have widely-used common names, including the alkali metals (Group 1) and the alkaline earth metals (Group 2) on the far left, and the halogens (Group 17) and the noble gases (Group 18) on the far right.
- An important grouping of elements in the periodic table are the main group elements, the transition metals, and the inner transition metals (the lanthanides, and the actinides).
- The elements can be broadly divided into metals, nonmetals, and semi metals. Semi metals exhibit properties intermediate between those of metals and nonmetals. Metals are located on the left of the periodic table, and nonmetals are located on the upper right. They are separated by a diagonal band of semi metals.
- Metals are lustrous, good conductors of electricity, and readily shaped (they are ductile and malleable). Solid nonmetals are generally brittle and poor electrical conductors.

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Contributors and Attributions

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Answers

Exercise 3.8.1**: Groups**

Fluorine is a halogen (Group 17)
Calcium is a alkaline earth metal (Group 2)
Krypton is a noble gas (Group 18)

Exercise 3.8.2

Indium is a metal.

Exercise 3.8.3**: Classification of Elements**

Fluorine is a nonmetal.
Uranium is a metal (and a inner transition metal too)
Copper is a metal (and a transition metal too)

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4: CHEMICAL BONDS

4.1: The Art of Deduction- Stable Electron Configurations

4.2: Lewis (Electron-Dot) Symbols

4.3: The Reaction of Sodium with Chlorine

4.4: Using Lewis Symbols for Ionic Compounds

4.5: Formulas and Names of Binary Ionic Compounds

4.6: Covalent Bonds- Shared Electron Pairs

4.7: Unequal Sharing- Polar Covalent Bonds

4.8: Polyatomic Molecules- Water, Ammonia, and Methane

4.9: Polyatomic Ions

4.10: Rules for Writing Lewis Formulas

4.11: Molecular Shapes- The VSEPR Theory

4.12: Shapes and Properties- Polar and Nonpolar Molecules

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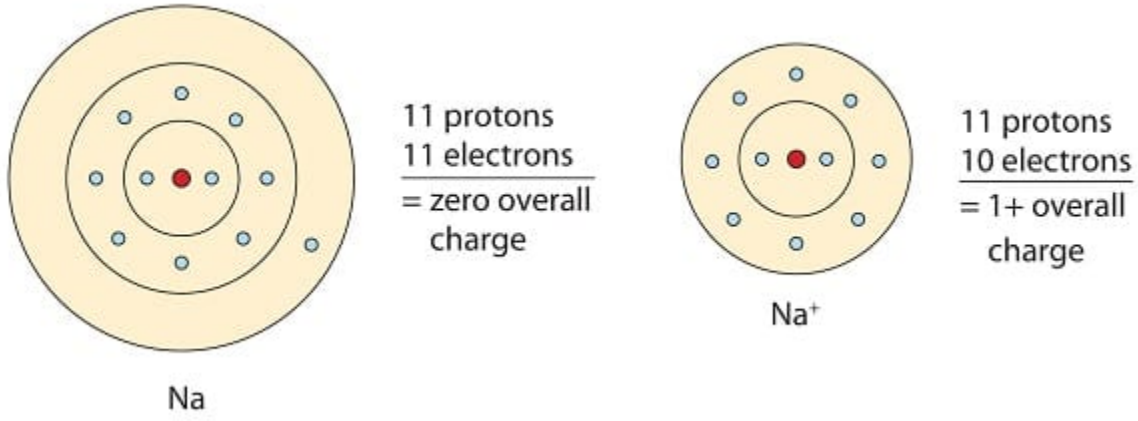
4.1: The Art of Deduction- Stable Electron Configurations

Learning Objective

- Define the octet rule.

The **octet rule** is a chemical rule of thumb that reflects observation that elements tend to bond in such a way that each atom has eight electrons in its valence shell, giving it the same electronic configuration as a noble gas.

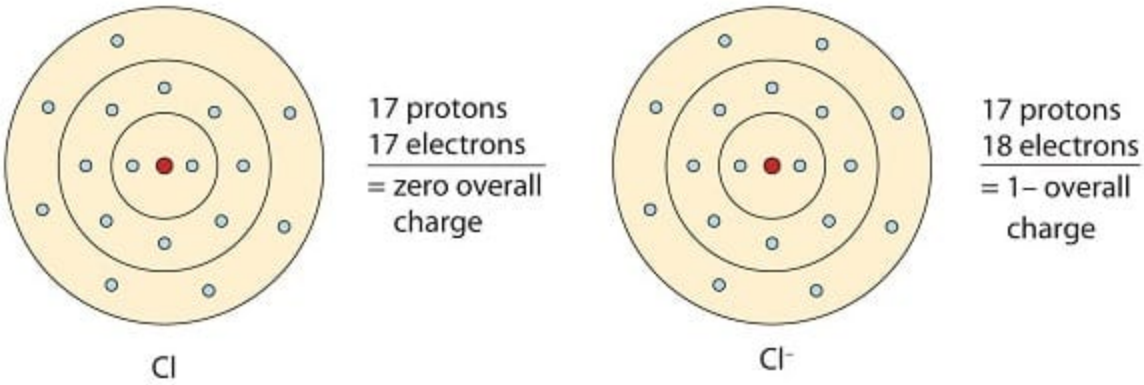
Referring to the octet rule, atoms attempt to get a noble gas electron configuration, which is eight valence electrons. Metals have few electrons in their outer-most orbitals. By losing those electrons, these metals can achieve noble gas configuration and satisfy the octet rule. Sodium has one valence electron, so giving it up would result in the same electron configuration as **neon**. Due to the loss of electron, a positively charged cation (Na^+) called sodium ion is formed.



Sodium (Na) neutral (left): 11 protons and 11 electrons equal zero overall charge; Sodium (Na) positive (right): 11 protons and 10 electrons equals one plus overall charge

Similarly, nonmetals that have close to 8 electrons in their valence shells tend to readily accept electrons to achieve noble gas configuration. Chlorine has seven valence electrons, so if it takes one it will have eight (an octet). Chlorine has the electron configuration of **argon** when it gains an electron. The resulting ion (Cl^-) is called chloride ion.

The octet rule could have been satisfied if chlorine gave up all seven of its valence electrons and sodium took them. In that case, both would have the electron configurations of noble gasses, with a full valence shell. However, their charges would be much higher. It would be Na^{7-} and Cl^{7+}, which is much less stable than Na^+ and Cl^-. Atoms are more stable when they have no charge, or a small charge.



Chlorine (Cl) neutral (left): 17 protons and 17 electrons equal zero overall charge; chlorine (Cl) negative (right): 11 protons and 10 electrons equals one minus overall charge

Summary

The octet rule refers to the tendency of atoms to prefer to have eight electrons in the valence shell.

Contributor

Organic Chemistry Supplemental_Modules_(Organic_Chemistry)/Fundamentals/Ionic_and_Covalent_Bonds

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4.2: Lewis (Electron-Dot) Symbols

Learning Objective

- Draw a Lewis electron dot diagram for an atom.
- Know the importance of Lewis dot in bonding.

At the beginning of the 20th century, an American physical chemist G. N. Lewis (1875–1946) devised a system of symbols—now called *Lewis electron dot symbols* (often shortened to *Lewis dot symbols*) that can be used for predicting the number of bonds formed by most elements in their compounds.

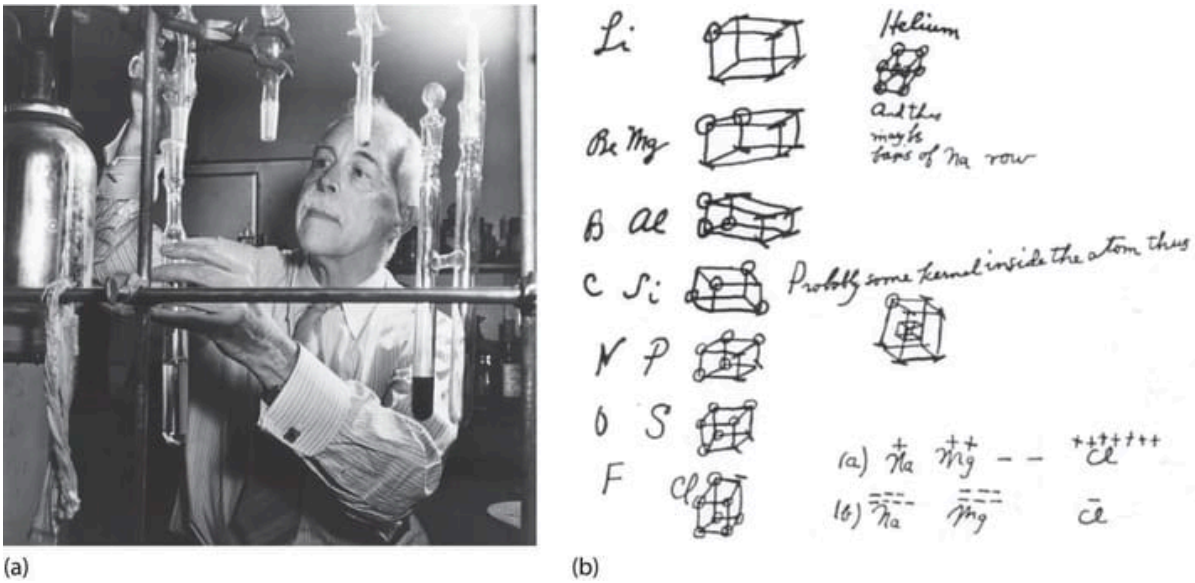
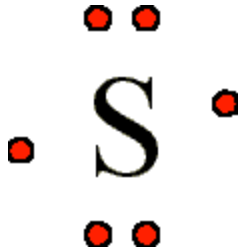


Figure 4.2.1 G. N. Lewis and the Octet Rule. (a) Lewis is working in the laboratory. (b) In Lewis's original sketch for the octet rule, he initially placed the electrons at the corners of a cube rather than placing them as we do now.

Lewis Dot symbols

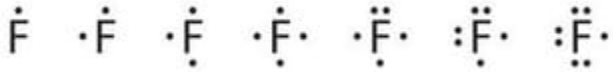
- convenient representation of valence electrons
- allows scientists to keep track of valence electrons during bond formation
- consists of the atomic symbol for the element plus a dot for each **valence** electron

To write an element's Lewis dot symbol, we place dots representing its valence electrons, one at a time, around the element's chemical symbol. Up to four dots are placed above, below, to the left, and to the right of the symbol (in any order, as long as elements with four or fewer valence electrons have no more than one dot in each position). The next dots, for elements with more than four valence electrons, are again distributed one at a time, each paired with one of the first four. For example, the element sulfur has six valence electrons (note roman numeral above group on the periodic table) and its Lewis symbol would be:



S two dots above two dots below and 1 dot left and right

Fluorine, for example, has seven valence electrons, so its Lewis dot symbol is constructed as follows:



Dot symbols for fluorine

Lewis eventually published his theory of chemical bonding in 1916. Formation of chemical bonds to complete the requirement of eight electrons for the atom becomes a natural tendency. Lewis dot symbols of the first two periods are given here to illustrate this point. In fact, the entire group (column) of elements have the same Lewis dot symbols, because they have the same number of valence electrons.

By going through the periodic table, we see that the Lewis electron dot symbols of atoms will never have more than eight dots around the atomic symbo see Table 4.2.1.

Table 4.2.1 *Lewis Dot Symbols of the Main Group Elements*

H·							He:
Li·	·Be ·	**\(\ce{ \cdot \underset{\:}{\overset{\Large{\cdot}}{B}} \cdot}\)**	·Ċ ·	:Ṅ·	:Ȯ·	:F̈·	:N̈e:
Na K Rb Cs	Mg Ca Sr Ba	Al Ga In Tl	Si Ge Sn Pb	P As Sb Bi	S Se Te Po	Cl Br I At	Ar Kr At Rn

Example 4.2.1: Lewis Dot Diagrams

What is the Lewis electron dot diagram 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:

$$\cdot\dot{\underset{\cdot\cdot}{Se}}:$$

Exercise 4.2.1

What is the Lewis electron dot diagram for each element?

a. phosphorus
b. argon

Answer a available at the end of this section.

Summary

- Lewis electron dot diagrams use dots to represent valence electrons around an atomic symbol.
- Lewis dot symbols can be used to predict the number of bonds formed by elements in a compound.

Contributors and Attributions

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Answers

Exercise 4.2.1



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4.3: The Reaction of Sodium with Chlorine

Learning Objectives

- Explain the bonding nature of ionic compounds.
- Relate microscopic bonding properties to macroscopic solid properties.

Neutral atoms and their associated ions have very different physical and chemical properties. Sodium *atoms* form sodium metal, a soft, silvery-white metal that burns vigorously in air and reacts explosively with water. Chlorine *atoms* form chlorine gas, Cl_2, a yellow-green gas that is extremely corrosive to most metals and very poisonous to animals and plants. The vigorous reaction between the elements sodium and chlorine forms the white, crystalline compound sodium chloride, common table salt, which contains sodium *cations* and chloride *anions* (Figure 4.3.1). The compound composed of these ions exhibits properties entirely different from the properties of the elements sodium and chlorine. Chlorine is poisonous, but sodium chloride is essential to life; sodium atoms react vigorously with water, but sodium chloride simply dissolves in water.



Figure 4.3.1 (a) Sodium is a soft metal that must be stored in mineral oil to prevent reaction with air or water. (b) Chlorine is a pale yellow-green gas. (c) When combined, they form white crystals of sodium chloride (table salt). (credit a: modification of work by "Jurii"/Wikimedia Commons) Commons)

Ionic Bonds

When two atoms approach each other, they have the potential to bond (or connect). If a metal and a nonmetal interact, then an ionic bond will result. These types of bonds involve the metal donating it(s) valence electron(s) to a nonmetal. As the electronic transfer occurs, both atoms will achieve more stable confirmations. The end result will be a less reactive compound. These type of species are composed of both cations and anions. In addition, they are crystalline and solid in nature (Figure 4.3.2). A few examples of real-world ionic compounds would be NaCl (table salt) and NaF (active ingredient in toothpaste).

The formula for table salt is NaCl. It is the result of Na^+ ions and Cl^- ions bonding together (Figure 4.3.3). If sodium metal and chlorine gas mix under the right conditions, they will form salt. The sodium loses an electron, and the chlorine gains that electron. This reaction is highly favorable because of the electrostatic attraction between the particles. In the process, a great amount of light and heat is released. The resulting salt is mostly unreactive — it is stable. It will not undergo any explosive reactions, unlike



the sodium and chlorine that it is made of.

Figure 4.3.2 *NaCl crystals.*

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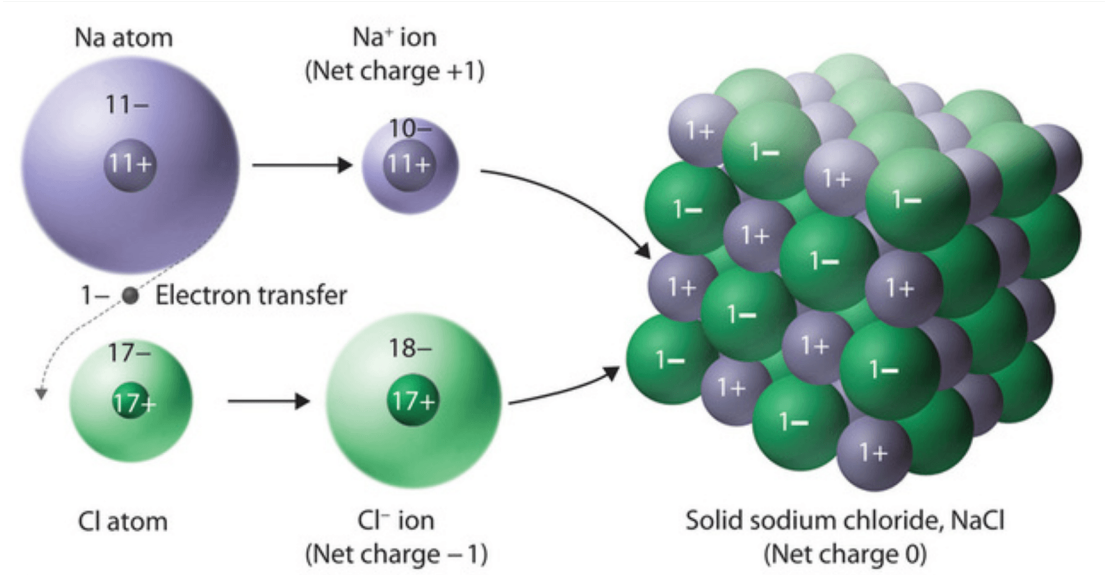
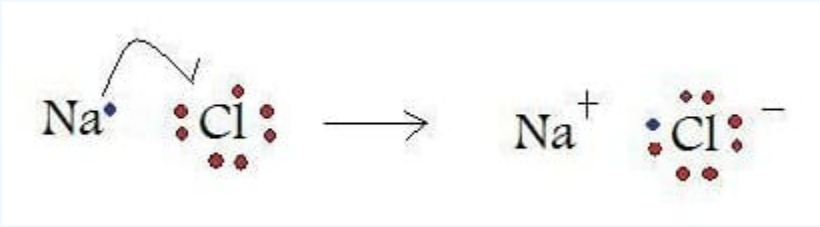


Figure 4.3.3 The formation of sodium chloride from the attraction of sodium and chloride ions.

The reaction is represented with Lewis dot symbols below.

Chloride Salts



The sodium atom is donating its 1 valence electron to the chlorine atom. This creates a sodium cation and a chlorine anion. Notice that the net charge of the resulting compound is 0.

Summary

- An ionic bond is formed when a metal donates it(s) valence electron(s) to a nonmetal.
- The resulting ionic compound is more stable and less reactive.

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- TextMap: Chemistry a Central Science (Brown et al.)

- Marisa Alviar-Agnew (Sacramento City College)

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4.4: Using Lewis Symbols for Ionic Compounds

Learning Objectives

- State the octet rule.
- Define cations and anions.
- Define *ionic bond*.
- Draw Lewis structures for ionic compounds.

The Octet Rule: The Drive for Eight

The **octet rule** refers to the tendency of atoms to prefer to have eight electrons in the *valence shell*. When atoms have fewer than eight electrons, they tend to react and form more stable compounds. When discussing the octet rule, we do not consider d or f electrons. Only the s and p electrons are involved in the octet rule, making it useful for the *main group elements* (elements not in the transition metal or inner-transition metal blocks); an octet in these atoms corresponds to an electron configurations ending with s^2p^6.

Note

The noble gases rarely form compounds. They have the most stable configuration (full octet, no charge), so they have no reason to react and change their configuration. All other elements attempt to gain, lose, or share electrons to achieve a noble gas configuration.

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

Cations

A neutral sodium atom is likely to achieve an octet in its outermost shell by losing its one valence electron.

$$\mathrm{Na} \rightarrow \mathrm{Na^+} + \mathrm{e^-}$$

The **cation** produced in this way, Na^+, is called the sodium ion to distinguish it from the element. The outermost shell of the sodium ion is the second electron shell, which has eight electrons in it. The octet rule has been satisfied. F

Anions

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

A neutral chlorine atom has seven electrons in its outermost shell. Only one more electron is needed to achieve an octet in chlorine's valence shell. (In table salt, this electron comes from the sodium atom.)

$$\mathrm{e^-} + \mathrm{Cl} \longrightarrow \mathrm{Cl^-}$$

In this case, the ion has the same outermost shell as the original atom, but now that shell has eight electrons in it. Once again,

the octet rule has been satisfied. The resulting anion, Cl^-, is called the chloride ion; note the slight change in the suffix (*-ide* instead of *-ine*) to create the name of this anion.

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

Note the usefulness of the periodic table in predicting likely ion formation and charge (Figure 4.4.1). Moving from the far left to the right on the periodic table, main-group elements tend to form cations with a charge equal to the group number. That is, group 1 elements form 1+ ions; group 2 elements form 2+ ions, and so on. Moving from the far right to the left on the periodic table, elements often form anions with a negative charge equal to the number of groups moved left from the noble gases. For example, group 17 elements (one group left of the noble gases) form 1– ions; group 16 elements (two groups left) form 2– ions, and so on. This trend can be used as a guide in many cases, but its predictive value decreases when moving toward the center of the periodic table. In fact, transition metals and some other metals often exhibit variable charges that are not predictable by their location in the table. For example, copper can form ions with a 1+ or 2+ charge, and iron can form ions with a 2+ or 3+ charge.

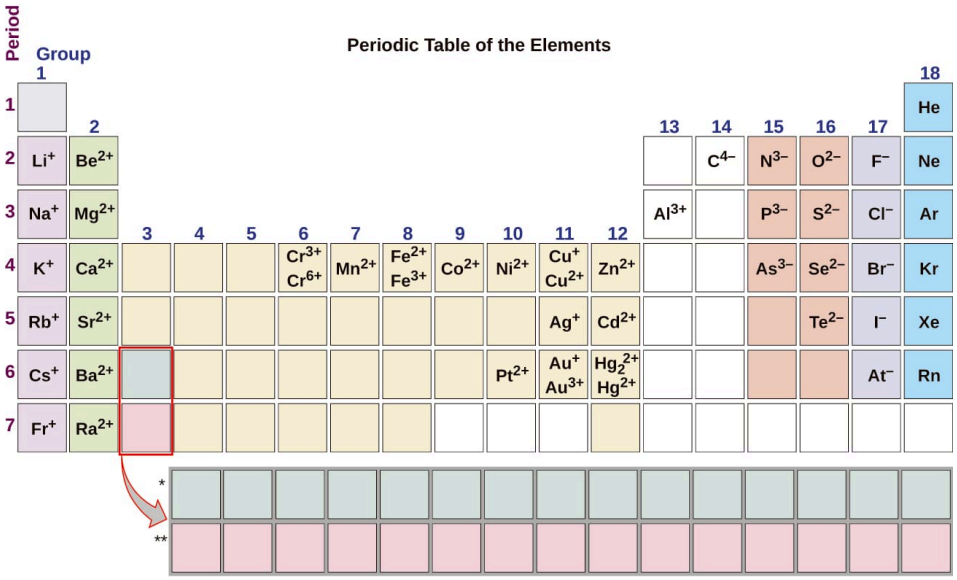


Figure 4.4.1: Some elements exhibit a regular pattern of ionic charge when they form ions.

Group one of the periodic table contains L i superscript plus sign in period 2, N a superscript plus sign in period 3, K superscript plus sign in period 4, R b superscript plus sign in period 5, C s superscript plus sign in period 6, and F r superscript plus sign in period 7. Group two contains B e superscript 2 plus sign in period 2, M g superscript 2 plus sign in period 3, C a superscript 2 plus sign in period 4, S r superscript 2 plus sign in period 5, B a superscript 2 plus sign in period 6, and R a superscript 2 plus sign in period 7. Group six contains C r superscript 3 plus sign and C r superscript 6 plus sign in period 4. Group seven contains M n superscript 2 plus sign in period 4. Group eight contains F e superscript 2 plus sign and F e superscript 3 plus sign in period 4. Group nine contains C o superscript 2 plus sign in period 4. Group ten contains N i superscript 2 plus sign in period 4, and P t superscript 2 plus sign in period 6. Group 11 contains C U superscript plus sign and C U superscript 2 plus sign in period 4, A g superscript plus sign in period 5, and A u superscript plus sign and A u superscript 3 plus sign in period 6. Group 12 contains Z n superscript 2 plus sign in period 4, C d superscript 2 plus sign in period 5, and H g subscript 2 superscript 2 plus sign and H g superscript 2 plus sign in period 6. Group 13 contains A l superscript 3 plus sign in period 3. Group 14 contains C superscript 4 negative sign in period 2. Group 15 contains N superscript 3 negative sign in period 2, P superscript 3 negative sign in period 3, and A s superscript 3 negative sign in period 4. Group 16 contains O superscript 2 negative sign in period 2, S superscript 2 negative sign in period 3, S e superscript 2 negative sign in period 4 and T e superscript 2 negative sign in period 5. Group 17 contains F superscript negative sign in period 2, C l superscript negative sign in period 3, B r superscript negative sign in period 4, I superscript negative sign in period 5, and A t superscript negative sign in period 6. Group 18 contains H e in period 1, N e in period 2, A r in period 3, K r in period 4, X e in period 5 and R n in period 6.

Lewis Symbols for Ionic Compounds

In the section above, we saw how ions are formed by losing electrons to make cations or by gaining electrons to form anions. The astute reader may have noticed something: Many of the ions that form have eight electrons in their valence shell. Either atoms gain enough electrons to have eight electrons in the valence shell and become the appropriately charged anion, or they lose the electrons in their original valence shell; the *lower* shell, now the valence shell, has eight electrons in it, so the atom becomes positively charged. For whatever reason, having eight electrons in a valence shell is a particularly energetically stable arrangement of electrons. When atoms form compounds, the octet rule is not always satisfied for all atoms at all times, but it is a very good

rule of thumb for understanding the kinds of bonding arrangements that atoms can make.

It is not impossible to violate the octet rule. Consider lithium: 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 Li^+ ion. We *could* remove another electron by adding even more energy to the ion, to make the Li^{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 Li^+ 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.

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

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

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

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

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

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

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

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

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:

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

where we have written the final formula (the formula for sodium chloride) as per the convention for ionic compounds, without listing the charges explicitly. The attraction between oppositely charged ions is called an **ionic bond,** and it is one of the main types of chemical bonds in chemistry. Ionic bonds are caused by electrons *transferring* from one atom to another.

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:



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

$$\mathbf{Mg}^{2+} + \left[:\ddot{\mathbf{O}}:\right]^{2-} \qquad Mg^{2+}O^{2-} \; or \; MgO$$

Remember, in the final formula for the ionic compound, we do not write the charges on the ions.

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:

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

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:



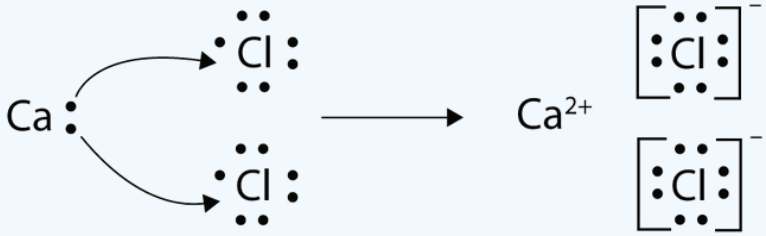
These three ions attract each other to give an overall neutral-charged ionic compound, which we write as Na_2O. The need for the number of electrons lost being equal to the number of electrons gained explains why ionic compounds have the ratio of cations to anions that they do. This is required by the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

Example 4.4.1: Synthesis of calcium chloride from Elements

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. Thus we need two Cl atoms to accept the two electrons from one Ca atom. The transfer process looks as follows:

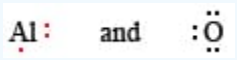


The oppositely charged ions attract each other to make $CaCl_2$.

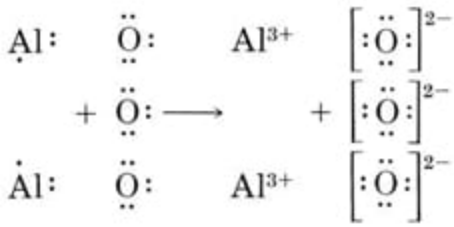
Example 4.4.2: Ionic Formula

Find the formula of the ionic compound formed from O and Al.

Solution: We first write down Lewis diagrams for each atom involved:



We now see that each O atom needs 2 electrons to make up an octet, while each Al atom has 3 electrons to donate. In order that the same number of electrons would be donated as accepted, we need 2 Al atoms ($2 \times 3e^-$ donated) and 3 O atoms ($3 \times 2e^-$ accepted). The whole process is then



The resultant oxide consists of aluminum ions, Al^{3+}, and oxide ions, O^{2-}, in the ratio of 2:3. The formula is Al_2O_3.

Exercise 4.4.1

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.

Summary

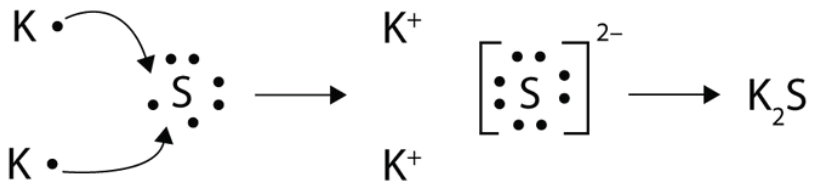
- The tendency to form species that have eight electrons in the valence shell is called the octet rule.
- The attraction of oppositely charged ions caused by electron transfer is called an ionic bond.
- The strength of ionic bonding depends on the magnitude of the charges and the sizes of the ions.

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Answers

Exercise 4.4.1



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4.5: Formulas and Names of Binary Ionic Compounds

Learning Objectives

- Use the rules for naming ionic compounds.
- Write the correct formula for an ionic compound.

Names of Binary ionic Compounds

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

Naming Ions

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

We have seen that some elements lose different numbers of electrons, producing ions of different charges (Figure 4.4.1) . Iron, for example, can form two cations, each of which, when combined with the same anion, makes a different compound with unique physical and chemical properties. Thus, we need a different name for each iron ion to distinguish Fe^{2+} from Fe^{3+}. The same issue arises for other ions with more than one possible charge.

There are two ways to make this distinction. In the simpler, more modern approach, called the **Stock system** (Table 4.5.1), an ion's positive charge is indicated by a roman numeral in parentheses after the element name, followed by the word ion. Thus, Fe^{2+} is called the iron(II) ion, while Fe^{3+} is called the iron(III) ion. This system is used only for elements that form more than one common positive ion. We do not call the Na^+ ion the sodium(I) ion because (I) is unnecessary. Sodium forms only a 1+ ion, so there is no ambiguity about the name *sodium ion*.

Table 4.5.1: The Modern and Common System of Cation Names

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

Element	Stem	Charge	Modern Name (Stock System)	Common Name
		3+	gold(III) ion	auric ion

The second system, called the **common system**, is not conventional but is still prevalent and used in the health sciences. This system recognizes that many metals have two common cations. The common system uses two suffixes (*-ic* and *-ous*) that are appended to the stem of the element name. The *-ic* suffix represents the greater of the two cation charges, and the *-ous* suffix represents the lower one. In many cases, the stem of the element name comes from the Latin name of the element. Table 4.5.1 lists the elements that use the common system, along with their respective cation names.

Table 4.5.2: Some Monatomic Anions

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

The 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 4.5.2 lists the names of some common monatomic ions.

Example 4.5.1

Name each ion.

a. Ca^{2+}
b. S^{2-}
c. Cu^+

Solution

a. the calcium ion
b. the sulfide ion
c. the copper(I) ion or the cuprous ion

Exercise 4.5.1

Name each ion.

a. Fe^{2+}

b. Fe^{3+}
c. Ba^{2+}

Answer a: available at the end of this section.

Example 4.5.2

Write the formula for each ion.

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

Solution

a. Br^{-}
b. Cu^{2+}
c. Mg^{2+}

Exercise 4.5.2

Write the formula for each ion.

a. the fluoride ion
b. the stannous ion
c. the potassium ion

Answer a: available at the end of this section.

Naming Binary Ionic Compounds with a Metal that Forms Only One Type of Cation

Now that we know how to name ions, we are ready to name ionic compounds. A **binary** ionic compound is a compound composed of a **monatomic** metal **cation** and a monatomic nonmetal **anion**. The metal cation is named first, followed by the nonmetal anion as illustrated in Figure 4.5.1 for the compound $BaCl_2$. The word *ion* is dropped from both parts.

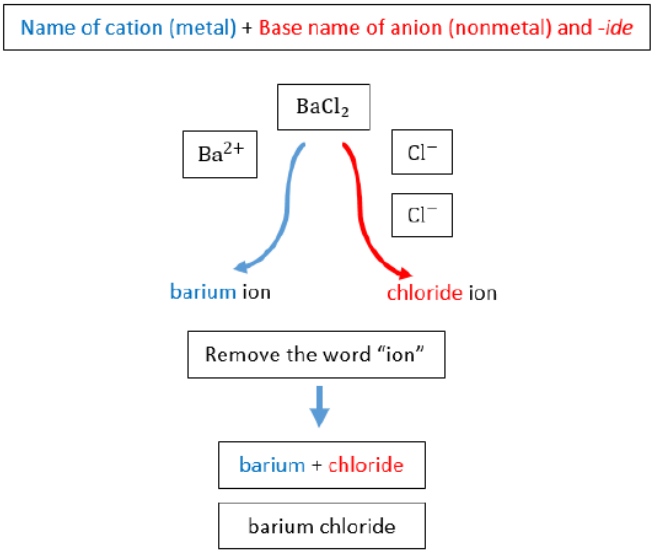


Figure 4.5.1 *Naming* $BaCl_2$

Naming formula: Name of metal cation + base name of nonmetal anion + suffix -ide. BaCl2 is named as barium chloride.

Subscripts in the formula do not affect the name.

Example 4.5.3: Naming Ionic Compounds

Name each ionic compound.

a. $CaCl_2$
b. AlF_3
c. KCl

Solution

a. Using the names of the ions, this ionic compound is named calcium chloride.
b. The name of this ionic compound is aluminum fluoride.
c. The name of this ionic compound is potassium chloride

Exercise 4.5.3

Name each ionic compound.

a. AgI
b. MgO
c. Ca_3P_2

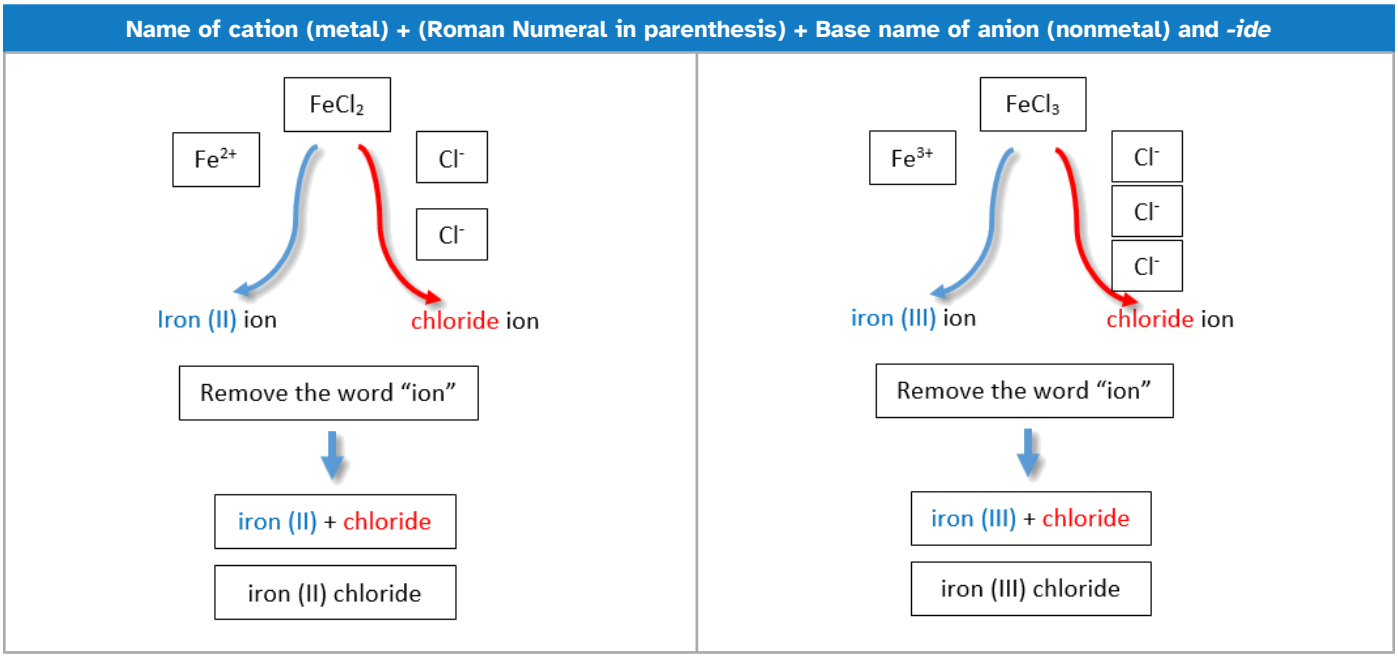
Answer a: available at the end of this section.

Naming Binary Ionic Compounds with a Metal That Forms More Than One Type of Cation

If you are given a formula for an ionic compound whose cation can have more than one possible charge, you must first determine the charge on the cation before identifying its correct name. For example, consider $FeCl_2$ and $FeCl_3$. In the first compound, the iron ion has a 2+ charge because there are two Cl^- ions in the formula (1– charge on each chloride ion). In the second compound,

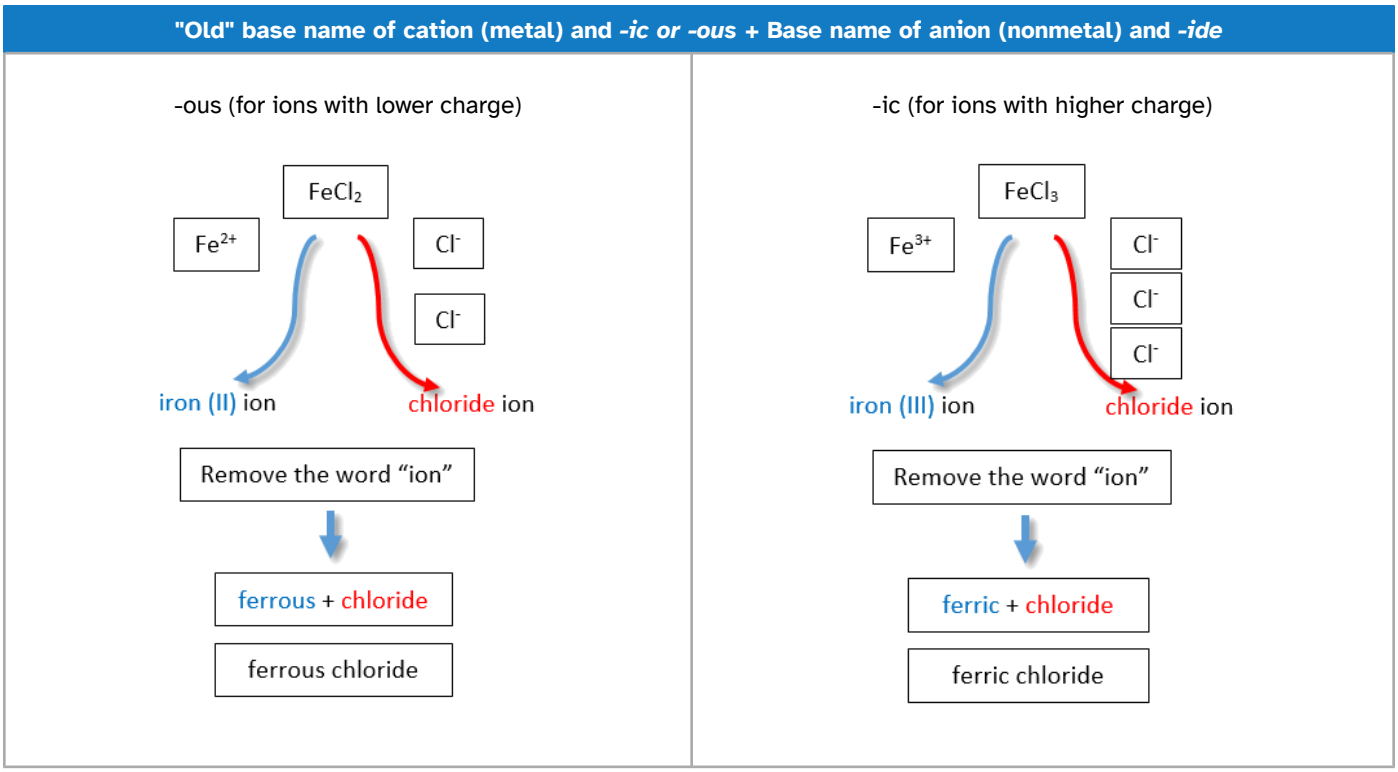
the iron ion has a 3+ charge, as indicated by the three Cl^- ions in the formula. These are two different compounds that need two different names. By the Stock system, the names are iron(II) chloride and iron(III) chloride (Figure 4.5.2).

Figure 4.5.2 Naming the $FeCl_2$ and $FeCl_3$ compounds in the modern/stock system.



If we were to use the stems and suffixes of the common system, the names would be ferrous chloride and ferric chloride, respectively (Figure 4.5.3) .

Figure 4.5.3 Naming the $FeCl_2$ and $FeCl_3$ compounds in the old/common System.



Example 4.5.4:

Name each ionic compound.

a. Co_2O_3
b. $FeCl_2$

Solution

Example 4.5.4: Explanation of the names of ionic compounds

Ionic Compound	Explanation	Answer
Co_2O_3	We know that cobalt can have more than one possible charge; we just need to determine what it is. • Oxide always has a 2– charge, so with three oxide ions, we have a total negative charge of 6–. • This means that the two cobalt ions have to contribute 6+, which for two cobalt ions means that each one is 3+. • Therefore, the proper name for this ionic compound is cobalt(III) oxide.	cobalt(III) oxide
$FeCl_2$	Iron can also have more than one possible charge. • Chloride always has a 1– charge, so with two chloride ions, we have a total negative charge of 2–. • This means that the one iron ion must have a 2+charge. • Therefore, the proper name for this ionic compound is iron(II) chloride.	iron(II) chloride

Exercise 4.5.4

Name each ionic compound.

a. $AuCl_3$
b. PbO_2
c. CuO

Answer a: available at the end of this section.

Figure 4.5.4 is a synopsis of how to name simple ionic compounds.

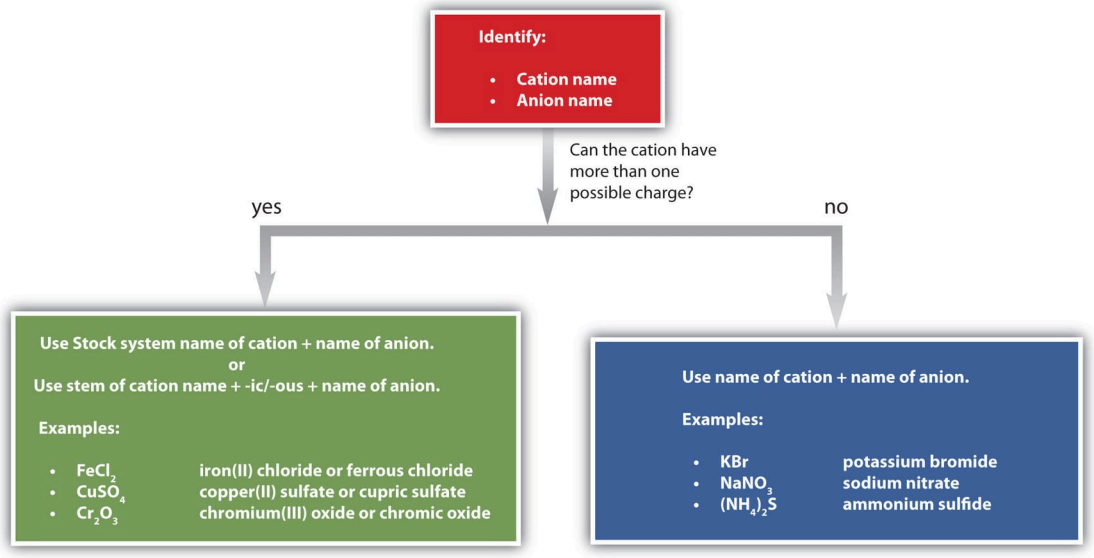


Figure 4.5.4: A Guide to Naming Simple Ionic Compounds.

Exercise 4.5.5

Name each ionic compound.

a. $ZnBr_2$
b. Al_2O_3
c. AuF_3
d. AgF

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.

Writing Formulas of Ionic Compounds

Ionic compounds do not exist as molecules. In the solid state, ionic compounds are in crystal lattice containing many ions each of the cation and anion. An ionic formula, like $NaCl$, is an empirical formula. This formula merely indicates that sodium chloride is made of an equal number of sodium and chloride ions. Sodium sulfide, another ionic compound, has the formula Na_2S. This formula indicates that this compound is made up of twice as many sodium ions as sulfide ions. This section will teach you how to find the correct ratio of ions, so that you can write a correct formula.

If you know the name of a binary ionic compound, you can write its **chemical formula**. Start by writing the metal ion with its charge, followed by the nonmetal ion with its charge. Because the overall compound must be electrically neutral, decide how many of each ion is needed in order for the positive and negative charge to cancel each other out.

Example 4.5.5: Aluminum Nitride and Lithium Oxide

Write the formula for aluminum nitride and lithium oxide.

Solution

Example 4.5.5: Steps for Problem Solving Writing Formulas

Steps for Problem Solving	Write the formula for aluminum nitride	Write the formula for lithium oxide
1. Write the symbol and charge of the cation (metal) first and the anion (nonmetal) second.	[redacted] [redacted]	Li^+ [redacted]
2. Use a multiplier to make the total charge of the cations and anions equal to each other.	total charge of cations = total charge of anions 1(3+) = 1(3-) +3 = -3	total charge of cations = total charge of anions 2(1+) = 1(2-) +2 = -2
3. Use the multipliers as subscript for each ion.	Al_1N_1	Li_2O_1
4. Write the final formula. Leave out all charges and all subscripts that are 1.	AlN	Li_2O

An alternative way to writing a correct formula for an ionic compound is to use the **crisscross method**. In this method, the numerical value of each of the ion charges is crossed over to become the subscript of the other ion. Signs of the charges are dropped.

Example 4.5.6: The Crisscross Method for lead (IV) oxide

Write the formula for lead (IV) oxide.

Solution

Example 4.5.6: Steps For Problem Solving the Crisscross Method for writing formulas.

Crisscross Method	Example: Write the formula for lead (IV) oxide
1. Write the symbol and charge of the cation (metal) first and the anion (nonmetal) second.	[redacted] [redacted]
2. Transpose only the number of the positive charge to become the subscript of the anion and the number only of the negative charge to become the subscript of the cation.	
3. Reduce to the lowest ratio.	Pb_2O_4
4. Write the final formula. Leave out all subscripts that are 1.	PbO_2

Exercise 4.5.6

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

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

Answer a: available at the end of this section.

Be aware that ionic compounds are empirical formulas and so must be written as the lowest ratio of the ions.

Example 4.5.7: Sulfur Compound

Write the formula for sodium combined with sulfur.

Solution

Example 4.5.7: Steps For Problem Solving the Crisscross Method for writing formulas.

Crisscross Method	Write the formula for sodium combined with sulfur
1. Write the symbol and charge of the cation (metal) first and the anion (nonmetal) second.	Na^+ [redacted]
2. Transpose only the number of the positive charge to become the subscript of the anion and the number only of the negative charge to become the subscript of the cation.	
3. Reduce to the lowest ratio.	This step is not necessary.
4. Write the final formula. Leave out all all subscripts that are 1.	Na_2S

Exercise 4.5.7

Write the formula for each ionic compound.

a. sodium bromide
b. lithium chloride
c. magnesium oxide

Answer a: available at the end of this section.

Recognizing Ionic Compounds

There are two ways to recognize ionic compounds. First, compounds between metal and nonmetal elements are usually ionic. For example, $CaBr_2$ contains a metallic element (calcium, a group 2 (or 2A) metal) and a nonmetallic element (bromine, a group 17 (or 7A) nonmetal). Therefore, it is most likely an ionic compound. (In fact, it *is* ionic.) In contrast, the compound NO_2 contains two elements that are both nonmetals (nitrogen, from group 15 (or 5A), and oxygen, from group 16 (or 6A). It is not an ionic compound; it belongs to the category of covalent compounds discussed elsewhere. Also note that this combination of nitrogen and oxygen has no electric charge specified, so it is *not* the nitrite ion.

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

Example 4.5.8

Identify each compound as ionic or not ionic.

a. Na_2O
b. PCl_3
c. OF_2

Solution

Example 4.5.8: Steps For Problem Solving Identifying Ionic Compounds

Explanation	Answer
a. Sodium is a metal, and oxygen is a nonmetal. Therefore, Na_2O is expected to be ionic.	Na_2O, ionic
b. Both phosphorus and chlorine are nonmetals. Therefore, PCl_3 is not ionic.	PCl_3, not ionic
c. Both oxygen and fluorine are nonmetals. Therefore, OF_2 is not ionic.	OF_2, ionic

Exercise 4.5.8

Identify each compound as ionic or not ionic.

a. N_2O
b. $FeCl_3$

Answer a: available at the end of this section.

Summary

- Ionic compounds are named by stating the cation first, followed by the anion.
- Positive and negative charges must balance.
- Some anions have multiple forms and are named accordingly with the use of roman numerals in parenthesis.
- Formulas for ionic compounds contain the symbols and number of each atom present in a compound in the lowest whole number ratio.

Contributors and Attributions

-
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- Henry Agnew (UC Davis)

Answers

Exercise 4.5.1
iron(II) ion
iron(III) ion
barium ion

Exercise 4.5.2
F^-
Sn^{2+}
K^+

Exercise 4.5.3
silver iodide
magnesium oxide
calcium phosphide

Exercise 4.5.4
gold(III) chloride
lead(IV) oxide
copper(II) oxide

Exercise 4.5.5
zinc bromide

Exercise 4.5.5

aluminum oxide

Exercise 4.5.5

gold(III) fluoride or auric fluoride

Exercise 4.5.5

silver fluoride

Exercise 4.5.6

CaO

CuS

Cu_2S

Exercise 4.5.7

NaBr

LiCl

MgO

Exercise 4.5.8

not ionic

ionic

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4.6: Covalent Bonds- Shared Electron Pairs

Learning Objectives

- Define covalent bond.
- Illustrate covalent bond formation with Lewis electron dot diagrams.

Ionic bonding typically occurs when it is easy for one atom to lose one or more electrons and another atom to gain one or more electrons. However, some atoms won't give up or gain electrons easily. Yet they still participate in compound formation. How? There is another mechanism for obtaining a complete valence shell: *sharing* electrons. When electrons are shared between two atoms, they make a bond called a **covalent bond**.

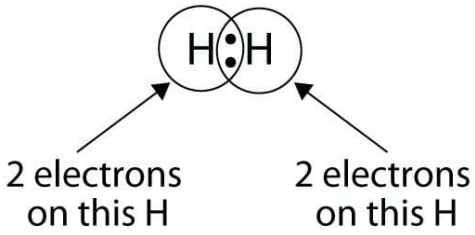
Chemists frequently use Lewis diagrams to represent covalent bonding in molecular substances. For example, the Lewis diagrams of two separate hydrogen atoms are as follows:



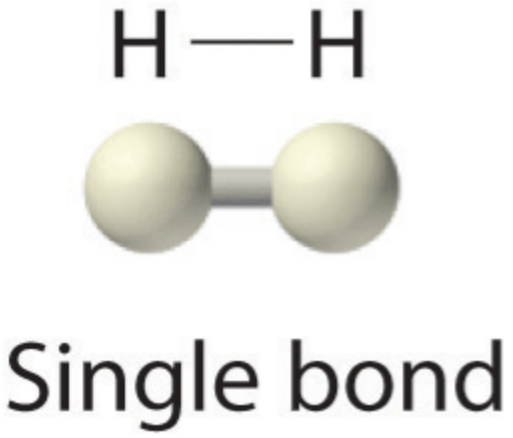
The Lewis diagram of two hydrogen atoms sharing electrons looks like this:



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. (This explains why hydrogen is one of the diatomic elements.) For simplicity's sake, it is not unusual to represent the covalent bond with a dash, instead of with two dots:



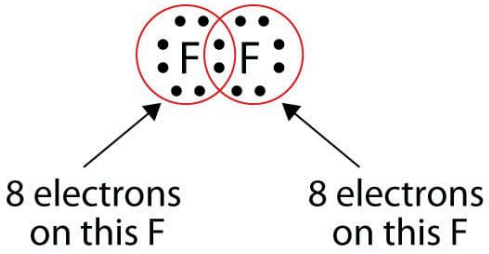
Because two atoms are sharing one pair of electrons, this covalent bond is called a **single bond**. As another example, consider fluorine. F atoms have seven electrons in their valence shell:



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:

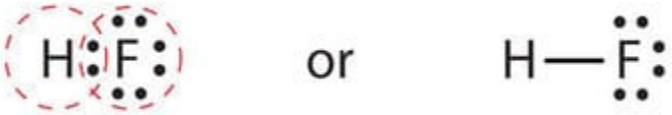


There are two different types of electrons in the fluorine diatomic molecule. The **bonding electron pair** makes the covalent bond. Each F atom has three other pairs of electrons that do not participate in the bonding; they are called **lone pair electrons**. Each F atom has one bonding pair and three lone pairs of electrons.

Covalent bonds can be made between different elements as well. One example is HF. Each atom starts out with an odd number of electrons in its valence shell:



The two atoms can share their unpaired electrons to make a covalent bond:



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

Example 4.6.1:

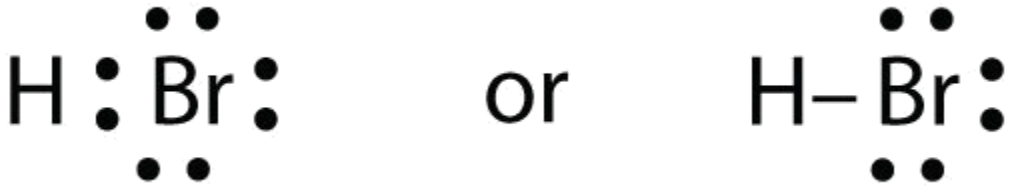
Use Lewis electron dot diagrams to illustrate the covalent bond formation in HBr.

Solution

HBr is very similar to HF, except that it has Br instead of F. The atoms are as follows:



The two atoms can share their unpaired electron:



Exercise 4.6.1

Use Lewis electron dot diagrams to illustrate the covalent bond formation in Cl_2.

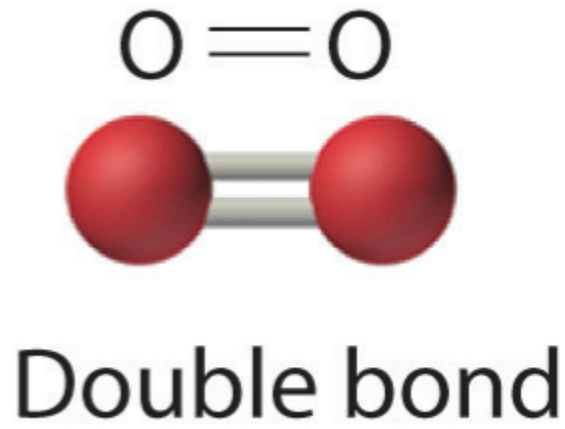
Answer: available at the end of this section.

When working with covalent structures, it sometimes looks like you have leftover electrons. You apply the rules you learned so far and there are still some electrons hanging out there unattached. You can't just leave them there. So where do you put them?

Multiple Covalent Bonds

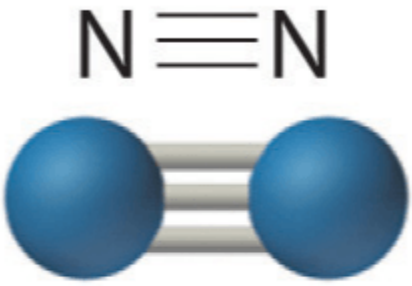
The sharing of a pair of electrons represents a single covalent bond, usually just referred to as a ***single bond***. However, in many molecules atoms attain complete octets by sharing more than one pair of electrons between them:

- Two electron pairs shared a ***double bond***



Double bond

- Three electron pairs shared a ***triple bond***



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.



Summary

- Covalent bonds are formed when atoms share electrons.
- Lewis electron dot diagrams can be drawn to illustrate covalent bond formation.
- Double bonds or triple bonds between atoms may be necessary to properly illustrate the bonding in some molecules.

Contributors and Attributions

-
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Answers

Exercise 4.6.1



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4.7: Unequal Sharing- Polar Covalent Bonds

Learning Objectives

- Define electronegativity
- Determine the polarity of a covalent bond.

Electronegativity

The ability of an atom in a molecule to attract shared electrons is called **electronegativity**. When two atoms combine, the difference between their electronegativities is an indication of the type of bond that will form. If the difference between the electronegativities of the two atoms is small, neither atom can take the shared electrons completely away from the other atom and the bond will be covalent. If the difference between the electronegativities is large, the more electronegative atom will take the bonding electrons completely away from the other atom (electron transfer will occur) and the bond will be ionic. This is why metals (low electronegativities) bonded with nonmetals (high electronegativities) typically produce ionic compounds.

A bond may be so polar that an electron actually transfers from one atom to another, forming a true ionic bond. How do we judge the degree of polarity? Scientists have devised a scale called **electronegativity**, a scale for judging how much atoms of any element attract electrons. Electronegativity is a unitless number; the higher the number, the more an atom attracts electrons. A common scale for electronegativity is shown in Figure 4.7.1.

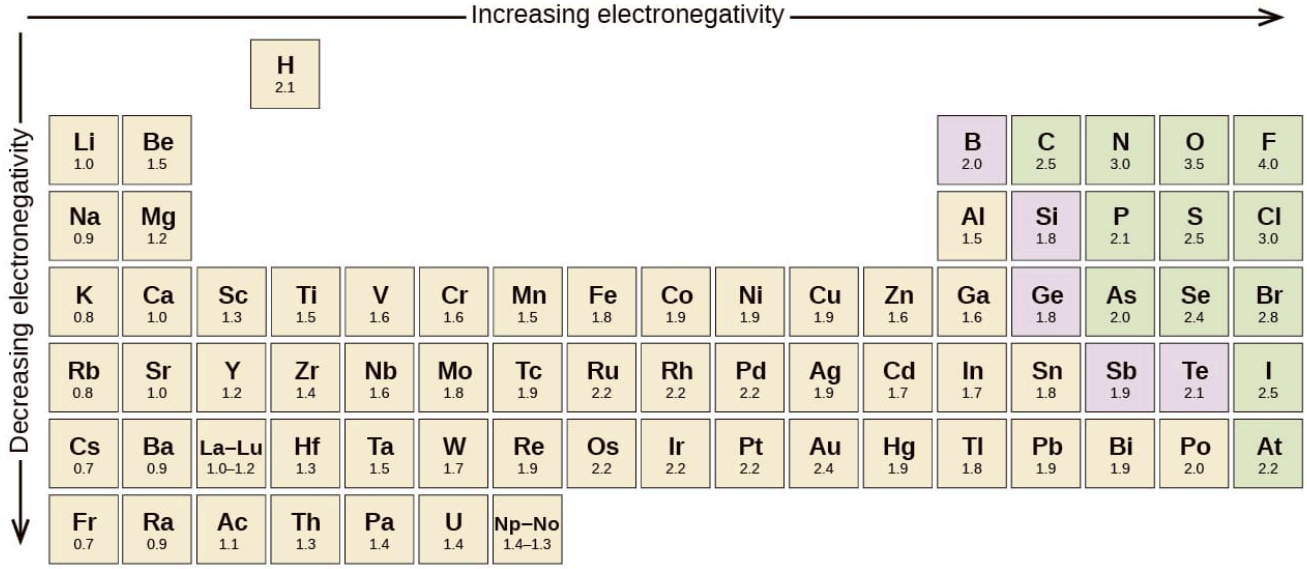


Figure 4.7.1 Electronegativities of the Elements. Electronegativities are used to determine the polarity of covalent bonds.

Bond Polarity

The polarity of a covalent bond can be judged by determining the *difference* of the electronegativities of the two atoms involved in the covalent bond, as summarized in the following table:

Table 4.7.1:Electronegativity differences and bond type

Electronegativity Difference	Bond Type
0	nonpolar covalent
0–0.4	slightly polar covalent

Electronegativity Difference	Bond Type
0.5–2.0	definitely polar covalent
>2.0	likely ionic

Nonpolar Covalent Bonds

A bond in which the electronegativity difference is less than 1.9 is considered to be mostly covalent in character. However, at this point we need to distinguish between two general types of covalent bonds. A **nonpolar covalent bond** is a covalent bond in which the bonding electrons are shared equally between the two atoms. In a nonpolar covalent bond, the distribution of electrical charge is balanced between the two atoms.

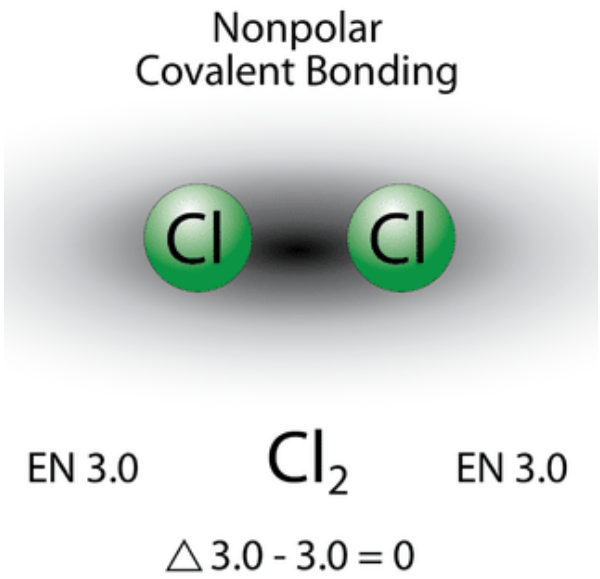


Figure 4.7.2 A nonpolar covalent bond is one in which the distribution of electron density between the two atoms is equal.

The two chlorine atoms share the pair of electrons in the single covalent bond equally, and the electron density surrounding the Cl_2 molecule is symmetrical. Also note that molecules in which the electronegativity difference is very small (<0.5) are also considered nonpolar covalent. An example would be a bond between chlorine and bromine ($\Delta EN = 3.0 - 2.8 = 0.2$).

Polar Covalent Bonds

A bond in which the electronegativity difference between the atoms is between 0.5 and 2.0 is called a polar covalent bond. A **polar covalent bond** is a covalent bond in which the atoms have an unequal attraction for electrons and so the sharing is unequal. In a polar covalent bond, sometimes simply called a polar bond, the distribution of electrons around the molecule is no longer symmetrical.

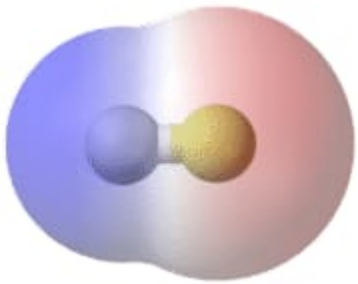


Figure 4.7.3 In the polar covalent bond of HF, the electron density is unevenly distributed. There is a higher density (red) near the fluorine atom, and a lower density (blue) near the hydrogen atom.

An easy way to illustrate the uneven electron distribution in a polar covalent bond is to use the Greek letter delta (δ).

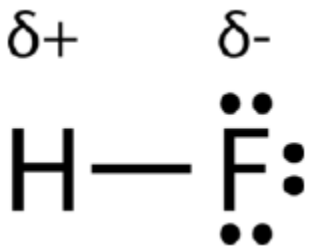


Figure $4.7.4$ Use of δ to indicate partial charge.

The atom with the greater electronegativity acquires a partial negative charge, while the atom with the lesser electronegativity acquires a partial positive charge. The delta symbol is used to indicate that the quantity of charge is less than one. A crossed arrow can also be used to indicate the direction of greater electron density.

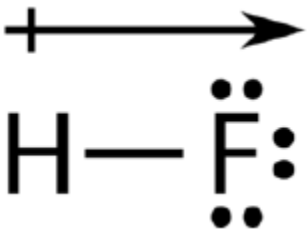


Figure $4.7.5$ Use of crossed arrow to indicate polarity

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

Electronegativity differences in bonding using Pauling scale. Using differences in electronegativity to classify bonds as covalent, polar covalent, or ionic.

Example $4.7.1$: Bond Polarity

What is the polarity of each bond?

a. C–H
b. O–H

Solution

Using Figure $4.7.1$, we can calculate the difference of the electronegativities of the atoms involved in the bond.

a. For the C–H bond, the difference in the electronegativities is 2.5 – 2.1 = 0.4. Thus we predict that this bond will be non polar covalent.
b. For the O–H bond, the difference in electronegativities is 3.5 – 2.1 = 1.4, so we predict that this bond will be definitely polar covalent.

Exercise 4.7.1

What is the polarity of each bond?

a. Rb–F
b. P–Cl

Answer a available at the end of this section.

Summary

- The type of bond (polar covalent,non polar covalent or ionic) between two atoms is determined by the differences in electronegativity.
- For atoms sharing a polar covalent bond, the atom with the greater electronegativity acquires a partial negative charge, while the atom with the lesser electronegativity acquires a partial positive charge.

Contributors and Attributions

-
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Answers

Exercise 4.7.1

likely ionic

polar covalent

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4.8: Polyatomic Molecules- Water, Ammonia, and Methane

Learning Objectives

- Determine the number of bonds formed by common nonmetal elements.
- Illustrate covalent bond formation with Lewis electron dot diagrams.

More than two atoms can participate in covalent bonding, although any given covalent bond will be between two atoms only. Water, ammonia, and methane are common examples that will be discussed in detail below. Carbon is unique in the extent to which it forms single, double, and triple bonds to itself and other elements. The number of bonds formed by an atom in its covalent compounds is not arbitrary. Hydrogen, oxygen, nitrogen, and carbon have very strong tendencies to form substances in which they have one, two, three, and four bonds to other atoms, respectively (Table 4.8.1).

Table 4.8.1 The Number of Bonds That Selected Atoms Commonly Form to Other Atoms

Atom	Number of Bonds
H (group 1)	1
O (group 16)	2
N (group 15)	3
C (group 14)	4

Water

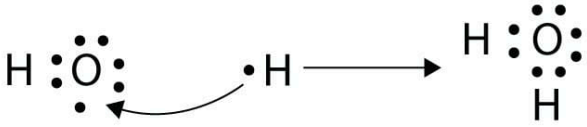
Consider H and O atoms:



The H and O atoms can share an electron to form a covalent bond:



The H atom has a complete valence shell. However, the O atom has only seven electrons around it, which is not a complete octet. We fix this by including a second H atom, whose single electron will make a second covalent bond with the O atom:



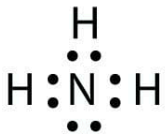
(It does not matter on what side the second H atom is positioned.) Now the O atom has a complete octet around it, and each H atom has two electrons, filling its valence shell. This is how a water molecule, H_2O, is made.

Ammonia

The N atom has the following Lewis electron dot diagram:



It has three unpaired electrons, each of which can make a covalent bond by sharing electrons with an H atom. The electron dot diagram of NH_3 is as follows:

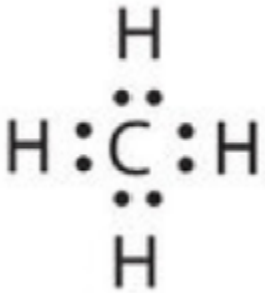


Methane

The C atom has the following Lewis electron dot diagram:

Image result for carbon lewis dot

It has four unpaired electrons, each of which can make a covalent bond by sharing electrons with an H atom. The electron dot diagram of CH_4 is as follows:



Summary

In polyatomic molecules, there is a pattern of covalent bonds that different atoms can form.

Contributors and Attributions

- TextMap: Beginning Chemistry (Ball et al.)
- Marisa Alviar-Agnew (Sacramento City College)

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4.9: Polyatomic Ions

Learning Objectives

- Recognize polyatomic ions in chemical formulas.
- Write the correct formula for ionic compounds with polyatomic ions.
- Use the rules for naming ionic compounds with polyatomic ions.

Polyatomic Ions

Some ions consist of groups of atoms bonded together and have an overall electric charge. Because these ions contain more than one atom, they are called polyatomic ions. Polyatomic ions have characteristic formulas, names, and charges that should be memorized. For example, NO_3^- is the nitrate ion; it has one nitrogen atom and three oxygen atoms and an overall 1– charge. Table 4.9.1 lists the most common polyatomic ions.

Table 4.9.1 Some Polyatomic Ions

Name	Formula
ammonium ion	NH_4^+
acetate ion	$C_2H_3O_2^-$ (also written $CH_3CO_2^-$)
carbonate ion	CO_3^{2-}
chromate ion	CrO_4^{2-}
dichromate ion	$Cr_2O_7^{2-}$
hydrogen carbonate ion (bicarbonate ion)	HCO_3^-
cyanide ion	CN^-
hydroxide ion	OH^-
nitrate ion	NO_3^-
nitrite ion	NO_2^-
permanganate ion	MnO_4^-
phosphate ion	PO_4^{3-}
hydrogen phosphate ion	HPO_4^{2-}
dihydrogen phosphate ion	$H_2PO_4^-$
sulfate ion	SO_4^{2-}
hydrogen sulfate ion (bisulfate ion)	HSO_4^-
sulfite ion	SO_3^{2-}

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

subscript is placed *outside* the parentheses. This is to show that the subscript applies to the entire polyatomic ion. An example is $Ba(NO_3)_2$.

Writing Formulas for Ionic Compounds Containing Polyatomic Ions

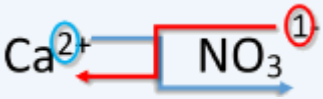
Writing a formula for ionic compounds containing polyatomic ions also involves the same steps as for a binary ionic compound. Write the symbol and charge of the cation followed by the symbol and charge of the anion.

Example 4.9.1: Calcium Nitrate

Write the formula for calcium nitrate.

Solution

Example 4.9.1: Steps For Problem Solving, Write the formula for calcium nitrate

Criss Cross Method	Write the formula for calcium nitrate
1. Write the symbol and charge of the cation (metal) first and the anion (nonmetal) second.	[redacted] NO_3^-
2. Transpose only the number of the positive charge to become the subscript of the anion and the number only of the negative charge to become the subscript of the cation.	 The 2+ charge on Ca becomes the subscript of NO3 and the 1- charge on NO3 becomes the subscript of Ca.
3. Reduce to the lowest ratio.	$Ca_1(NO_3)_2$
4. Write the final formula. Leave out all subscripts that are 1. If there is only 1 of the polyatomic ion, leave off parentheses.	$Ca(NO_3)_2$

Example 4.9.2

Write the chemical formula for an ionic compound composed of the potassium ion and the sulfate ion

Solution

Example 4.9.2: Explanation for Writing the Chemical Formula for an Ionic Compound Composed of the Potassium Ion and the Sulfate Ion

Explanation	Answer
Potassium ions have a charge of 1+, while sulfate ions have a charge of 2–. We will need two potassium ions to balance the charge on the sulfate ion, so the proper chemical formula is K_2SO_4.	K_2SO_4

Exercise 4.9.1

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.

Naming Ionic Compounds with Polyatomic Ions

The process of naming ionic compounds with polyatomic ions is the same as naming binary ionic compounds. The cation is named first, followed by the anion. One example is the ammonium Sulfate compound in Figure 4.9.6.

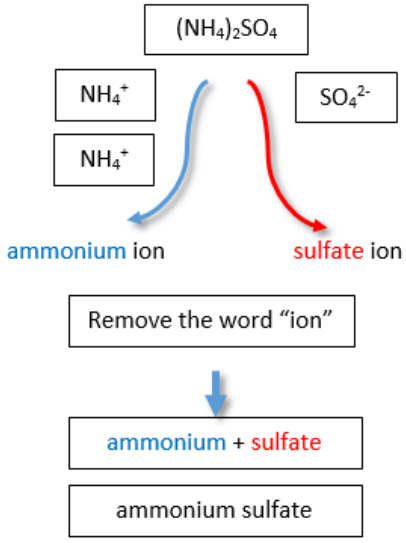


Figure 4.9.2 *Naming Ionic Compounds with Polyatomic Ions*

Example 4.9.3: Naming Ionic Compounds

Write the proper name for each ionic compound.

a. (NH4)2S
b. AlPO4,
c. Fe3(PO4)2

Solution

Example 4.9.3: Explanation for Naming Ionic Compounds

Ionic Compound	Explanation	Answer
a. **(NH4)2S**	a. The ammonium ion has a 1+ charge and the sulfide ion has a 2– charge. Two ammonium ions need to balance the charge on a single sulfide ion. The compound's name is ammonium sulfide.	ammonium sulfide
b. AlPO4,	b. The ions have the same magnitude of charge, one of each (ion) is needed to balance the charges. The name of the compound is aluminum phosphate.	aluminum phosphate

Ionic Compound	Explanation	Answer
c. $Fe_3(PO_4)_2$	c. Neither charge is an exact multiple of the other, so we have to go to the least common multiple of 6. To get 6+, three iron(II) ions are needed, and to get 6–, two phosphate ions are needed . The compound's name is iron(II) phosphate.	iron(II) phosphate

Exercise 4.9.2

Write the proper name for each ionic compound.

a. $(NH_4)_3PO_4$
b. $Co(NO_2)_3$

Answer a: available at the end of this section.

Summary

- Formulas for ionic compounds contain the symbols and number of each atom and/or polyatomic ion present in a compound in the lowest whole number ratio.
- The process of naming ionic compounds with polyatomic ions are the same as binary ionic compounds.

Contributors and Attributions

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

Answers

Exercise 4.9.1

$MgCO_3$

$Al(CH_3COO)_3$

Exercise 4.9.2

ammonium phosphate

cobalt(III) nitrite

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4.10: Rules for Writing Lewis Formulas

Learning Objective

- Write Lewis structures for molecules and ions.
- Know the exceptions to the octet rule.

The following procedure can be used to construct Lewis electron structures for more complex molecules and ions:

How-to: Constructing Lewis electron structures

1. 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.

2. 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.

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.

7. Final check

- Always make sure all valence electrons are accounted for and each atom has an octet of electrons except for hydrogen (with two electrons).

The central atom is usually the least electronegative element in the molecule or ion; hydrogen and the halogens are usually terminal.

Now let's apply this procedure to some particular compounds, beginning with one we have already discussed.

Example 4.10.1: Water

Write the Lewis Structure for H_2O.

Solution

Example 4.10.1: steps for writing the Lewis structure of water

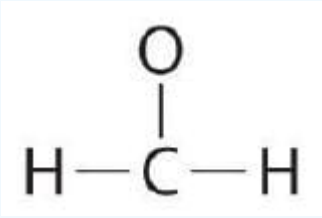
Steps for Writing Lewis Structures	Example 4.10.1:
1. Determine the total number of valence electrons in the molecule or ion.	Each H atom (group 1) has 1 valence electron, and the O atom (group 16) has 6 valence electrons, for a total of 8 valence electrons.
2. Arrange the atoms to show specific connections.	**H O H** Because H atoms are almost always terminal, the arrangement within the molecule must be HOH.
3. Place a bonding pair of electrons between each pair of adjacent atoms to give a single bond. 4. Beginning with the terminal atoms, add enough electrons to each atom to give each atom an octet (two for hydrogen).	Placing one bonding pair of electrons between the O atom and each H atom gives **H -O- H** with 4 electrons left over. Each H atom has a full valence shell of 2 electrons.
5. If any electrons are left over, place them on the central atom.	Adding the remaining 4 electrons to the oxygen (as two lone pairs) gives the following structure: 
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.	Not necessary
7. Final check	The Lewis structure gives oxygen an octet and each hydrogen two electrons,

Example 4.10.2

Write the Lewis structure for the CH_2O molecule

Solution

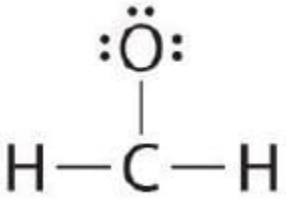
Steps are writing the Lewis structure of the CH_2O molecule

Steps for Writing Lewis Structures	Example 4.10.2
1. Determine the total number of valence electrons in the molecule or ion.	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.
2. Arrange the atoms to show specific connections.	 Because carbon is less electronegative than oxygen and hydrogen is normally terminal, C must be the central atom.
3. Place a bonding pair of electrons between each pair of adjacent atoms to give a single bond.	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. Beginning with the terminal atoms, add enough electrons to each atom to give each atom an octet (two for hydrogen).

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.

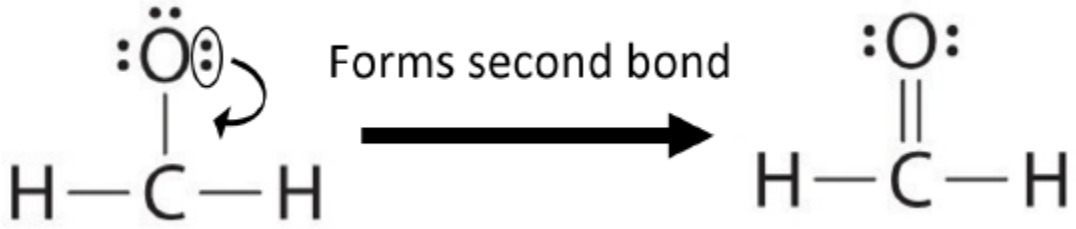
5. If any electrons are left over, place them on the central atom.

Not necessary

There are no electrons left to place on the central atom.

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.

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:



7. Final check 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.

Exercise 4.10.1

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 CO2 available at the end of this section.

The United States Supreme Court has the unenviable task of deciding what the law is. This responsibility can be a major challenge when there is no clear principle involved or where there is a new situation not encountered before. Chemistry faces the same challenge in extending basic concepts to fit a new situation. Drawing of Lewis structures for polyatomic ions uses the same approach, but tweaks the process a little to fit a somewhat different set of circumstances.

Lewis Structures for Polyatomic Ions

Recall that a polyatomic ion is a group of atoms that are covalently bonded together and which carry an overall electrical charge. The ammonium ion, NH_4^+, is formed when a hydrogen ion (H^+) attaches to the lone pair of an ammonia (NH_3) molecule in a coordinate covalent bond.

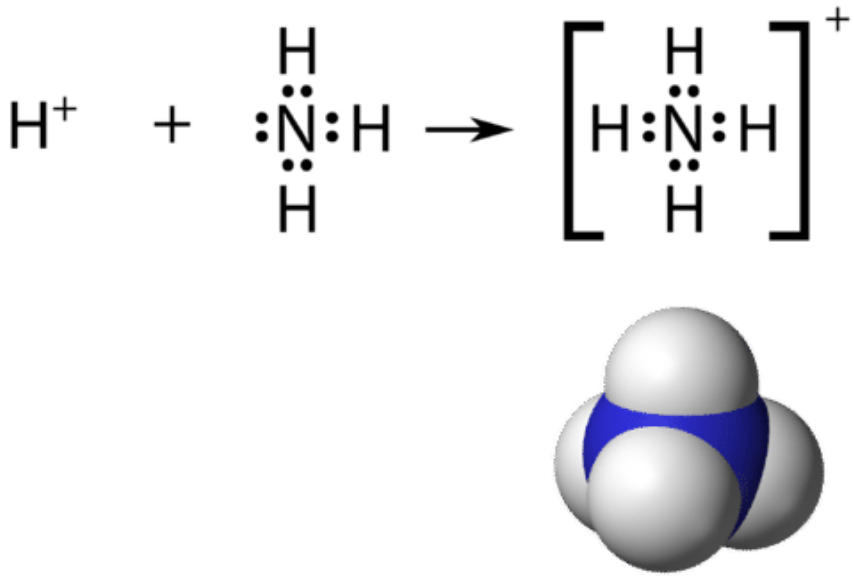


Figure 4.10.3: The ammonium ion.

When drawing the Lewis structure of a polyatomic ion, the charge of the ion is reflected in the number of total valence electrons in the structure. In the case of the ammonium ion:

$$1\ \text{N atom} = 5 \text{ valence electrons}$$

4 H atoms $= 4 \times 1 = 4$ valence electrons

subtract 1 electron for the $1+$charge of the ion

total of 8 valence electrons in the ion

It is customary to put the Lewis structure of a polyatomic ion into a large set of brackets, with the charge of the ion as a superscript outside the brackets.

Exercise 4.10.2

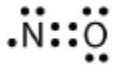
Draw the Lewis electron dot structure for the sulfate ion.

Answer available at the end of this section.

Exceptions to the Octet Rule

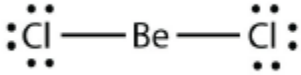
As important and useful as the octet rule is in chemical bonding, there are some well-known violations. This does not mean that the octet rule is useless—quite the contrary. As with many rules, there are exceptions, or violations.

There are three violations to the octet rule. Odd-electron molecules represent the first violation to the octet rule. Although they are few, some stable compounds 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, NO_2, and ClO_2. The Lewis electron dot diagram for NO is as follows:

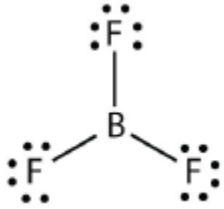


Although the O atom has an octet of electrons, the N atom has only seven electrons in its valence shell. Although NO is a stable compound, it is very chemically reactive, as are most other odd-electron compounds.

Electron-deficient molecules represent the second violation to the octet rule. These stable compounds have less than eight electrons around an atom in the molecule. 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:

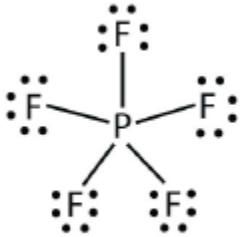


Boron commonly makes only three covalent bonds, resulting in only six valence electrons around the B atom. A well-known example is BF_3:



The third violation to the octet rule is found in those compounds with more than eight electrons assigned to their valence shell. These are called expanded valence shell molecules. Such compounds are formed only by central atoms in the third row of the

periodic table or beyond that have empty *d* orbitals in their valence shells that can participate in covalent bonding. One such compound is PF_5. The only reasonable Lewis electron dot diagram for this compound has the P atom making five covalent bonds:



Formally, the P atom has 10 electrons in its valence shell.

Example 4.10.3: Octet Violations

Identify each violation to the octet rule by drawing a Lewis electron dot diagram.

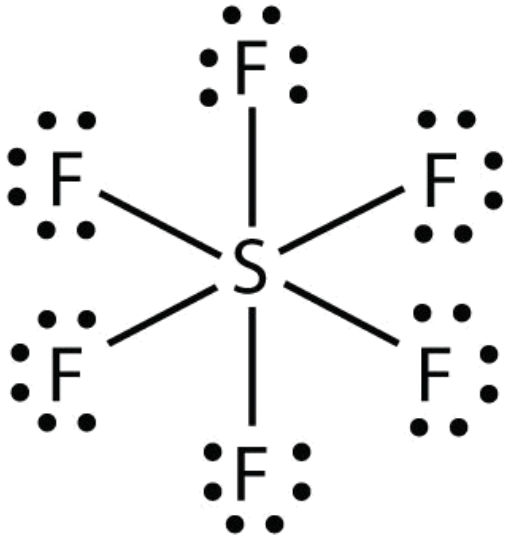
a. ClO
b. SF_6

Solution

a. 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:



b. In 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 4.10.3: Xenon Difluoride

Identify the violation to the octet rule in XeF_2 by drawing a Lewis electron dot diagram.

Answer: available at the end of this section.

The Xe atom has an expanded valence shell with more than eight electrons around it.

Summary

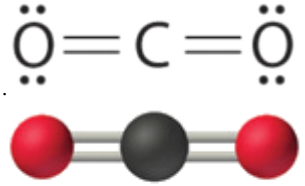
- Lewis dot symbols (Lewis structures) provide a simple rationalization of why elements form compounds with the observed stoichiometries.
- In Lewis electron structures, we encounter **bonding pairs**, which are shared by two atoms, and **lone pairs**, which are not shared between atoms.
- Lewis structures for polyatomic ions follow the same rules as those for other covalent compounds.
- There are three violations to the octet rule: odd-electron molecules, electron-deficient molecules, and expanded valence shell molecules

Contributors and Attributions

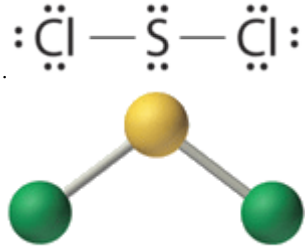
- Modified by Joshua Halpern (Howard University)
-
- Marisa Alviar-Agnew (Sacramento City College)
- Henry Agnew (UC Davis)

Answers

Exercise 4.10.1

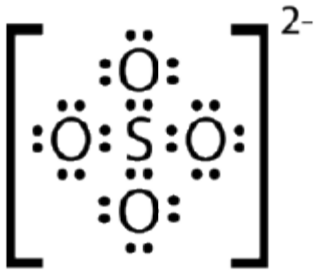


Carbon dioxide



Sulfur dichloride

Exercise 4.10.2



Exercise 4.10.3**: Xenon Difluoride**



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4.11: Molecular Shapes- The VSEPR Theory

Learning Objective

- Determine the shape of simple molecules and polyatomic ions.

Molecules have shapes. There is an abundance of experimental evidence to that effect—from their physical properties to their chemical reactivity. Small molecules—molecules with a single central atom—have shapes that can be easily predicted. The basic idea in molecular shapes is **called valence shell electron pair repulsion (VSEPR).** It basically says that electron pairs, being composed of negatively charged particles, repel each other to get as far away from each other as possible. VSEPR makes a distinction between *electron group geometry*, which expresses how electron groups (bonds and nonbonding electron pairs) are arranged, and *molecular geometry*, which expresses how the atoms in a molecule are arranged. However, the two geometries are related.

There are two types of **electron groups**: any type of bond—single, double, or triple—and lone electron pairs. When applying VSEPR to simple molecules, the first thing to do is to count the number of electron groups around the central atom. Remember that a multiple bond counts as only *one* electron group.

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—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 shape is linear. Examples include BeH_2 and CO_2:



Figure 4.11.1 *Beryllium hydride and carbon dioxide bonding.*

The two molecules, shown in the figure below in a "ball and stick" model.

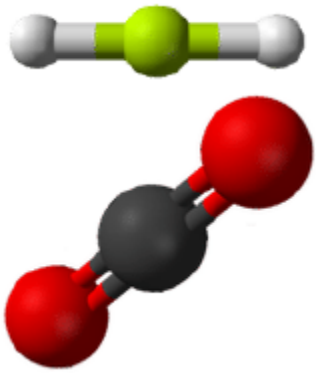


Figure 4.11.2 *Beryllium hydride and carbon dioxide models.*

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:

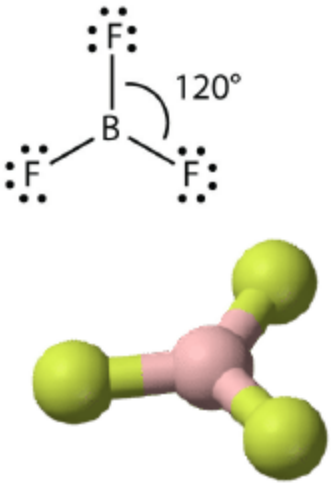


Figure 4.11.3 *Boron trifluoride bonding.*

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:

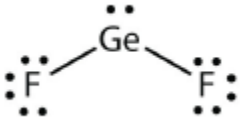


Figure 4.11.4: Germanium *difluoride bonding.*

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 shape is called *bent* or *angular*.

A molecule with four electron groups about the central atom orients the four groups in the direction of a tetrahedron, as shown in Figure 4.11.1 Tetrahedral Geometry. If there are four atoms attached to these electron groups, then the molecular shape is also *tetrahedral*. Methane (CH_4) is an example.

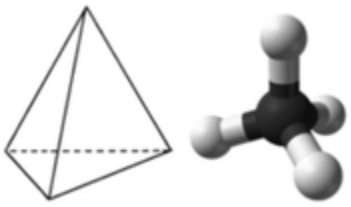


Figure 4.11.5 *Tetrahedral structure of methane.*

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.

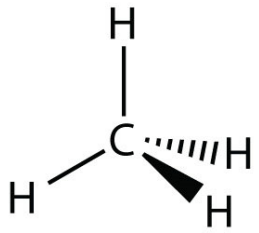


Figure 4.11.6 *Methane bonding.*

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.

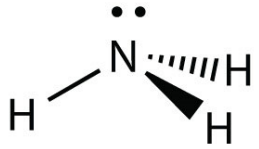


Figure 4.11.7 *Ammonia bonding.*

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 4.11.8 *Water bonding.*

Although the electron groups are oriented in the shape of a tetrahedron, the shape of the molecule is *bent* 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.

Double or triple bonds count as a single electron group. The Lewis electron dot diagram of formaldehyde (CH_2O) is shown in Figure 4.11.9.



Figure 4.11.9 *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.

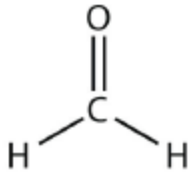


Figure 4.11.10: Formaldehyde bonding.

(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. Figure 4.11.11 illustrates several representations of the water, ammonia, and methane molecules.

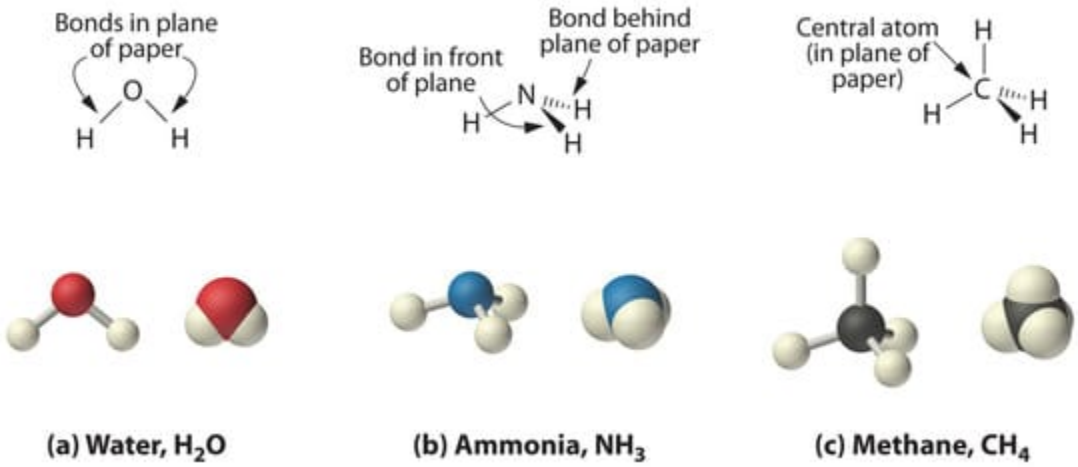


Figure 4.11.11 The three-dimensional structures, ball and stick models,and space filling models of water, ammonia, and methane. *(a) Water is a V-shaped molecule, in which all three atoms lie in a plane. (b) In contrast, ammonia has a pyramidal structure, in which the three hydrogen atoms form the base of the pyramid and the nitrogen atom is at the vertex. (c) The four hydrogen atoms of methane form a tetrahedron; the carbon atom lies in the center.*

Table 4.11.1 summarizes the shapes of molecules based on their number of electron groups and surrounding atoms and the common shapes are shown in figure 4.11.1.

Table 4.11.1: Summary of Molecular Shapes

Number of Electron Groups on Central Atom	Number of Bonding Groups	Number of Lone Pairs	Electron Geometry	Molecular Shape
2	2	0	linear	linear
3	3	0	trigonal planar	trigonal planar
3	2	1	trigonal planar	bent
4	4	0	tetrahedral	tetrahedral
4	3	1	tetrahedral	trigonal pyramidal
4	2	2	tetrahedral	bent

Figure* 4.11.12*: Common structures for molecules and Ppolyatomic ions that consist of a central atom bonded to two or three other atoms.

Example 4.11.1:

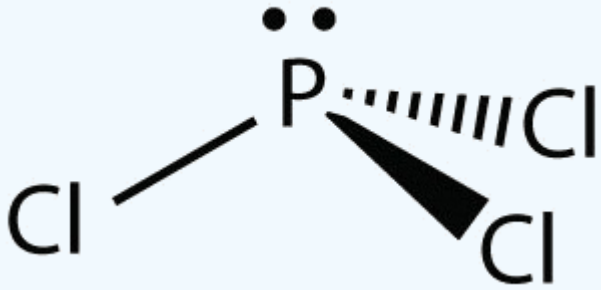
What is the approximate shape of each molecule?

a. PCl_3
b. NOF

Solution

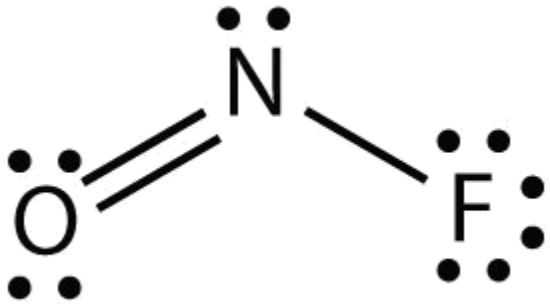
The first step is to draw the Lewis structure of the molecule.

1. 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 4.11.1

What is the approximate molecular shape of CH_2Cl_2?

Answer available at the end of this section.

Exercise 4.11.2

Ethylene (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.

Summary

The approximate shape of a molecule can be predicted from the number of electron groups and the number of surrounding atoms.

Contributors and Attributions

-
- TextMap: Beginning Chemistry (Ball et al.)
- Marisa Alviar-Agnew (Sacramento City College)
- Henry Agnew (UC Davis)

Answers

Exercise 4.11.1

Tetrahedral

Exercise 4.11.2

Trigonal planar about both central C atoms

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4.12: Shapes and Properties- Polar and Nonpolar Molecules

Learning Objective

- Determine if a molecule is polar or nonpolar.

Molecular Polarity

To determine if a molecule is polar or nonpolar, it is frequently useful to look at Lewis structures. **Nonpolar compounds** will be symmetric, meaning all of the sides around the central atom are identical - bonded to the same element with no unshared pairs of electrons. Notice that a tetrahedral molecule such as $\mathrm{CCl_4}$ is nonpolar Figure $(4.12.1$. Another non polar molecule shown below is boron trifluoride, BF_3. BF_3 is a trigonal planar molecule and all three peripheral atoms are the same.

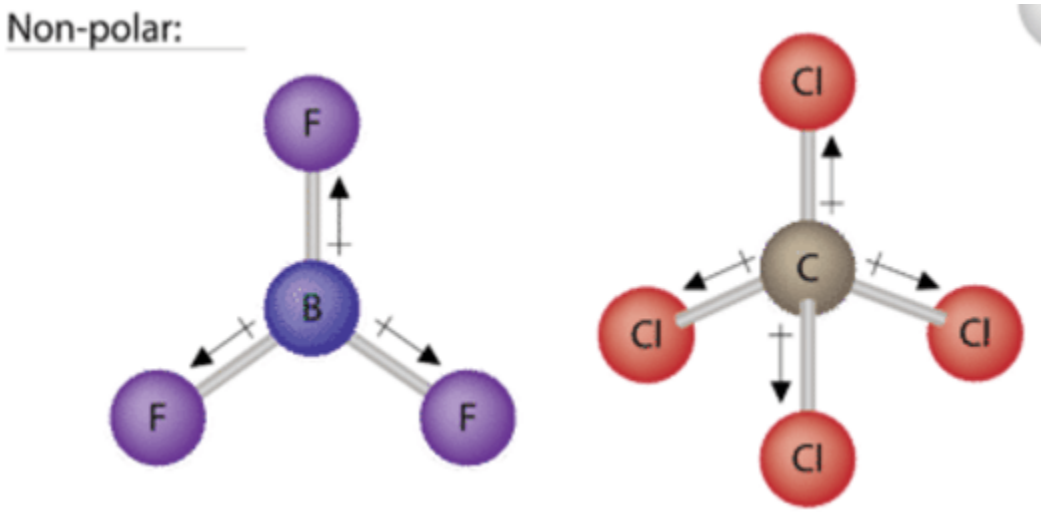
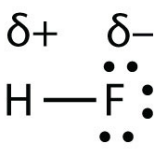


Figure $4.12.1$ Some examples of nonpolar molecules based on molecular geometry (BF_3 and CCl_4).

Polar molecules are asymmetric, either containing lone pairs of electrons on a central atom or having atoms with different electronegativities bonded. This works pretty well - as long as you can visualize the molecular geometry. That's the hard part. To know how the bonds are oriented in space, you have to have a strong grasp of Lewis structures and VSEPR theory. Assuming you do, you can look at the structure of each one and decide if it is polar or not - *whether or not you know the individual atom electronegativity*. This is because you know that all bonds between dissimilar elements are polar, and in these particular examples, it doesn't matter which direction the dipole moment vectors are pointing (out or in).

A **polar molecule** is a molecule in which one end of the molecule is slightly positive, while the other end is slightly negative. A diatomic molecule that consists of a polar covalent bond, such as HF, is a polar molecule.



As mentioned in section 4.7, because the electrons in the bond are nearer to the F atom, this side of the molecule takes on a

partial negative charge, which is represented by δ– (δ is the lowercase Greek letter delta). The other side of the molecule, the H atom, adopts a partial positive charge, which is represented by δ+. 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. A molecule with two poles is called a **dipole** (see figure below). Hydrogen fluoride is a dipole.



Figure 4.12.2 A dipole is any molecule with a positive end and a negative end, resulting from unequal distribution of electron density throughout the molecule.

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 (CO_2) is a linear molecule. The oxygen atoms are more electronegative than the carbon atom, so there are two individual dipoles pointing outward from the C atom to each O atom. However, since the dipoles are of equal strength and are oriented this way, they cancel out and the overall molecular polarity of CO_2 is zero.

Water is a bent molecule because of the two lone pairs on the central oxygen atom. The individual dipoles point from the H atoms toward the O atom. Because of the shape, the dipoles do not cancel each other out and the water molecule is polar. In the figure below, the net dipole is shown in blue and points upward.

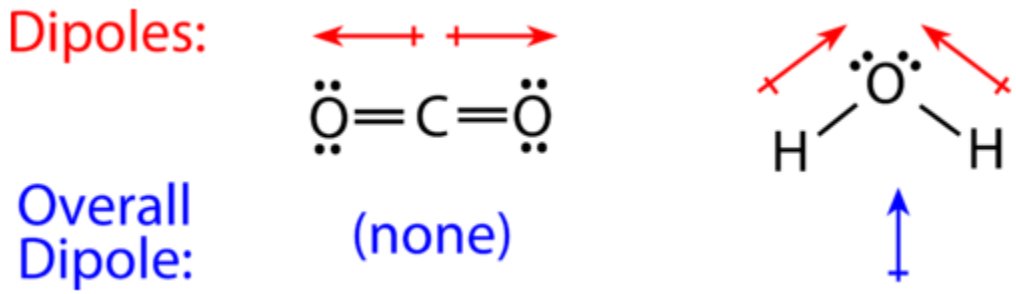


Figure 4.12.3 *The molecular geometry of a molecule affects its polarity. Each CO bond has a dipole moment, but they point in opposite directions so that the net CO2 molecule is nonpolar. In contrast, water is polar because the OH bond moments do not cancel out.*

Three other polar molecules are shown below with the arrows pointing to the more electron dense atoms. Just like the water molecule, none of the bond moments cancel out.

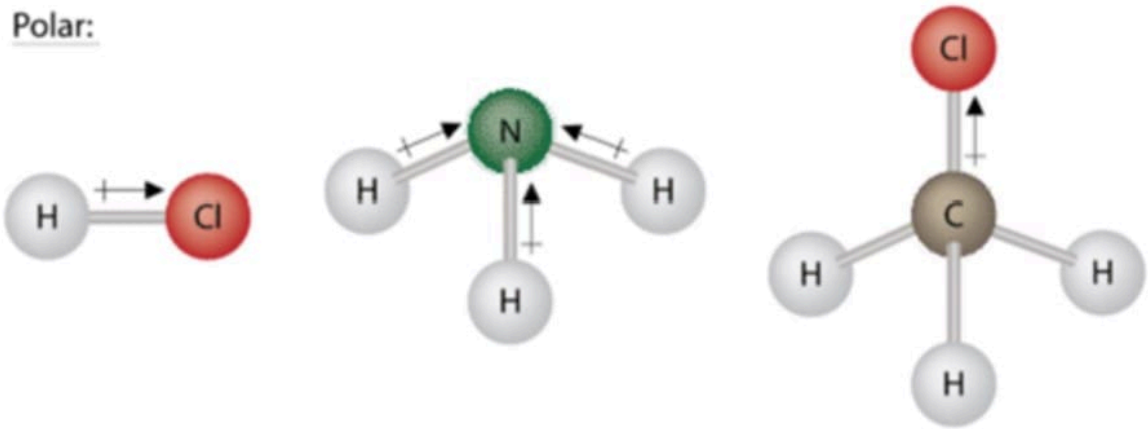


Figure 4.12.4 Some examples of polar molecules based on molecular geometry (HCl, NH3 and CH3Cl).

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 does 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.

Example 4.12.1:

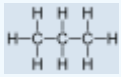
Label each of the following as polar or nonpolar.

a. Water, H_2O: 

b. Methanol, CH_3OH: 

c. Hydrogen Cyanide, HCN: 

d. Oxygen, O_2: 

e. Propane, C_3H_8: 

Solution

a. Water is polar. Any molecule with lone pairs of electrons around the central atom is polar.
b. Methanol is polar. This is not a symmetric molecule. The $-\mathrm{OH}$ side is different from the other 3 $-\mathrm{H}$ sides.
c. Hydrogen cyanide is polar. The molecule is not symmetric. The nitrogen and hydrogen have different electronegativities, creating an uneven pull on the electrons.
d. Oxygen is nonpolar. The molecule is symmetric. The two oxygen atoms pull on the electrons by exactly the same amount.
e. Propane is nonpolar, because it is symmetric, with H atoms bonded to every side around the central atoms and no unshared pairs of electrons.

Exercise 4.12.1

Label each of the following as polar or nonpolar.

a. SO_3

b. NH_3

Answer available at the end of this section.

Summary

- Non polar molecules are symmetric with no unshared electrons.
- Polar molecules are asymmetric, either containing lone pairs of electrons on a central atom or having atoms with different electronegativities bonded.

Contributors and Attributions

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

Answers

Exercise 4.12.1

non polar

polar

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5: CHEMICAL ACCOUNTING

5.1: Chemical Sentences- Equations

5.2: Volume Relationships in Chemical Equations

5.3: Avogadro's Number and the Mole

5.4: Molar Mass- Mole-to-Mass and Mass-to-Mole Conversions

5.5: Solutions

5.6: Section 6-

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5.1: Chemical Sentences- Equations

Learning Objectives

- Identify the reactants and products in any chemical reaction.
- Convert word equations into chemical equations.
- Use the common symbols, (s), (l), (g), (aq), and $\rightarrow$ appropriately when writing a chemical reaction.
- Explain the roles of subscripts and coefficients in chemical equations.
- Balance a chemical equation when given the unbalanced equation.
- Explain the role of the Law of Conservation of Mass in a chemical reaction.

In a chemical change, new substances are formed. In order for this to occur, the chemical bonds of the substances break, and the atoms that compose them separate and rearrange themselves into new substances with new chemical bonds. When this process occurs, we call it a chemical reaction. A **chemical reaction** is the process in which one or more substances are changed into one or more new substances.

Reactants and Products

To describe a chemical reaction, we need to indicate what substances are present at the beginning and what substances are present at the end. The substances that are present at the beginning are called **reactants** and the substances present at the end are called **products**.

Sometimes when reactants are put into a reaction vessel, a reaction will take place to produce products. Reactants are the starting materials, that is, whatever we have as our initial ingredients. The products are just that, wheat is produced or the result of what happens to the reactants when we put them together in the reaction vessel. If we think about baking chocolate chip cookies, our reactants would be flour, butter, sugar, vanilla, some baking soda, salt, egg, and chocolate chips. What would be the products? Cookies! The reaction vessel would be our mixing bowl.

$$\underbrace{\text{Flour} + \text{Butter} + \text{Sugar} + \text{Vanilla} + \text{Baking Soda} + \text{Eggs} + \text{Chocolate Chips}}_{\text{Ingredients = Reactants}} \rightarrow \underbrace{\text{Cookies}}_{\text{Product}}$$

Writing Chemical Equations

When sulfur dioxide is added to oxygen, sulfur trioxide is produced. Sulfur dioxide and oxygen, $\mathrm{SO_2} + \mathrm{O_2}$, are reactants and sulfur trioxide, $\mathrm{SO_3}$, is the product.

$$\underbrace{2\,\mathrm{SO_2\,(g)} + \mathrm{O_2\,(g)}}_{\text{Reactants}} \rightarrow \underbrace{2\,\mathrm{SO_3\,(g)}}_{\text{Products}}$$

In chemical reactions, the reactants are found before the symbol "$\rightarrow$" and the products are found after the symbol "$\rightarrow$". The general equation for a reaction is:

$$\text{Reactants} \rightarrow \text{Products}$$

There are a few special symbols that we need to know in order to "talk" in chemical shorthand. In the table below is the summary of the major symbols used in chemical equations. You will find there are others but these are the main ones that we need to know. Table $5.1.1$ shows a listing of symbols used in chemical equations.

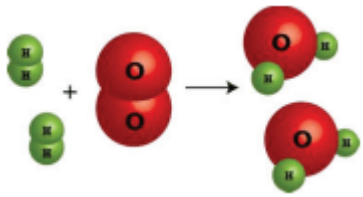
Table $5.1.1$ *Symbols Used in Chemical Equations*

Symbol	Description
$+$	used to separate multiple reactants or products
$\rightarrow$	yield sign; separates reactants from products

Symbol	Description
$\rightleftharpoons$	replaces the yield sign for reversible reactions that reach equilibrium
$\overset{\text{Pt}}{\rightarrow}$	formula written above the arrow is used as a catalyst in the reaction
$\overset{\Delta}{\rightarrow}$	triangle indicates that the reaction is being heated
(s)	reactant or product in the solid state
(l)	reactant or product in the liquid state
(g)	reactant or product in the gas state
(aq)	reactant or product in an aqueous solution (dissolved in water)

Chemists have a choice of methods for describing a chemical reaction.

1. They could draw a picture of the chemical reaction.



2. They could write a word equation for the chemical reaction:
"*Two molecules of hydrogen gas react with one molecule of oxygen gas to produce two molecules of water vapor.*"

3. They could write the equation in chemical shorthand.

$$2\text{H}_2\,(g) + \text{O}_2\,(g) \rightarrow 2\text{H}_2\text{O}\,(g)$$

In the symbolic equation, chemical formulas are used instead of chemical names for reactants and products and symbols are used to indicate the phase of each substance. It should be apparent that the chemical shorthand method is the quickest and clearest method for writing chemical equations.

We could write that an aqueous solution of calcium nitrate is added to an aqueous solution of sodium hydroxide to produce solid calcium hydroxide and an aqueous solution of sodium nitrate. Or in shorthand we could write:

$$\text{Ca}(\text{NO}_3)_2\,(aq) + 2\text{NaOH}\,(aq) \rightarrow \text{Ca}(\text{OH})_2\,(s) + 2\text{NaNO}_3\,(aq)$$

How much easier is that to read? Let's try it in reverse? Look at the following reaction in shorthand and write the word equation for the reaction:

$$\text{Cu}\,(s) + \text{AgNO}_3\,(aq) \rightarrow \text{Cu}(\text{NO}_3)_2\,(aq) + \text{Ag}\,(s)$$

The word equation for this reaction might read something like "solid copper reacts with an aqueous solution of silver nitrate to produce a solution of copper (II) nitrate with solid silver."

To turn word equations into symbolic equations, we need to follow the given steps:

1. Identify the reactants and products. This will help you know what symbols go on each side of the arrow and where the $+$ signs go.
2. Write the correct formulas for all compounds. You will need to use the rules you learned in Chapter 5 (including making all ionic compounds charge balanced).
3. Write the correct formulas for all elements. Usually this is given straight off of the periodic table. However, there are seven elements that are considered diatomic, meaning they are always found in pairs in nature. They include those elements listed in the table.

Table 5.1.2 Diatomic Elements

Element Name	Hydrogen	Nitrogen	Oxygen	Fluorine	Chlorine	Bromine	Iodine
Formula	H_2	N_2	O_2	F_2	Cl_2	Br_2	I_2

Example 5.1.1

Transfer the following symbolic equations into word equations or word equations into symbolic equations.

a. $\mathrm{HCl}\,(aq) + \mathrm{NaOH}\,(aq) \rightarrow \mathrm{NaCl}\,(aq) + \mathrm{H_2O}\,(l)$
b. Gaseous propane, $\mathrm{C_3H_8}$, burns in oxygen gas to produce gaseous carbon dioxide and liquid water.
c. Hydrogen fluoride gas reacts with an aqueous solution of potassium carbonate to produce an aqueous solution of potassium fluoride, liquid water, and gaseous carbon dioxide.

Solution

a. An aqueous solution of hydrochloric acid reacts with an aqueous solution of sodium hydroxide to produce an aqueous solution of sodium chloride and liquid water.

b. Reactants: propane ($\mathrm{C_3H_8}$) and oxygen ($\mathrm{O_2}$)

Product: carbon dioxide ($\mathrm{CO_2}$) and water ($\mathrm{H_2O}$)

$$\mathrm{C_3H_8}\,(g) + \mathrm{O_2}\,(g) \rightarrow \mathrm{CO_2}\,(g) + \mathrm{H_2O}\,(l)$$

c. Reactants: hydrogen fluoride and potassium carbonate

Products: potassium fluoride, water, and carbon dioxide

$$\mathrm{HF}\,(g) + \mathrm{K_2CO_3}\,(aq) \rightarrow \mathrm{KF}\,(aq) + \mathrm{H_2O}\,(l) + \mathrm{CO_2}\,(g)$$

Exercise 5.1.1

Transfer the following symbolic equations into word equations or word equations into symbolic equations.

a. hydrogen gas reacts with nitrogen gas to produce gaseous ammonia
b. $\mathrm{HCl}\,(aq) + \mathrm{LiOH}\,(aq) \rightarrow \mathrm{NaCl}\,(aq) + \mathrm{H_2O}\,(l)$
c. copper metal is heated with oxygen gas to produce solid copper(II) oxide.

Answer a available at the end of this section.

Even though chemical compounds are broken up and new compounds are formed during a chemical reaction, atoms in the reactants do not disappear nor do new atoms appear to form the products. In chemical reactions, atoms are never created or destroyed. The same atoms that were present in the reactants are present in the products - they are merely reorganized into different arrangements. In a complete chemical equation, the two sides of the equation must be present on the reactant and the product sides of the equation.

Coefficients and Subscripts

There are two types of numbers that appear in chemical equations. There are subscripts, which are part of the chemical formulas of the reactants and products and there are coefficients that are placed in front of the formulas to indicate how many molecules of that substance is used or produced.

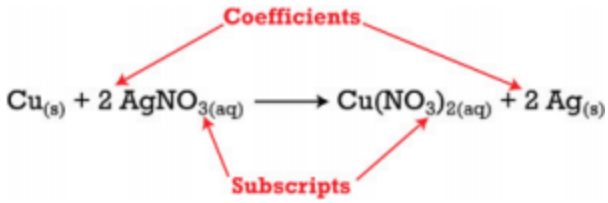


Figure 5.1.1Balancing Equations. You cannot change subscripts in a chemical formula to balance a chemical equation; you can change only the coefficients. Changing subscripts changes the ratios of atoms in the molecule and the resulting chemical properties. For example, water (H_2O) and hydrogen peroxide (H_2O_2) are chemically distinct substances.

The **subscripts** are part of the formulas and once the formulas for the reactants and products are determined, the subscripts may not be changed. The **coefficients** indicate the number of each substance involved in the reaction and may be changed in order to balance the equation. The equation above indicates that one mole of solid copper is reacting with two moles of aqueous silver nitrate to produce one mole of aqueous copper (II) nitrate and two atoms of solid silver.

Balancing a Chemical Equation

Because the identities of the reactants and products are fixed, the equation cannot be balanced by changing the subscripts of the reactants or the products. To do so would change the chemical identity of the species being described, as illustrated in Figure 5.1.2.

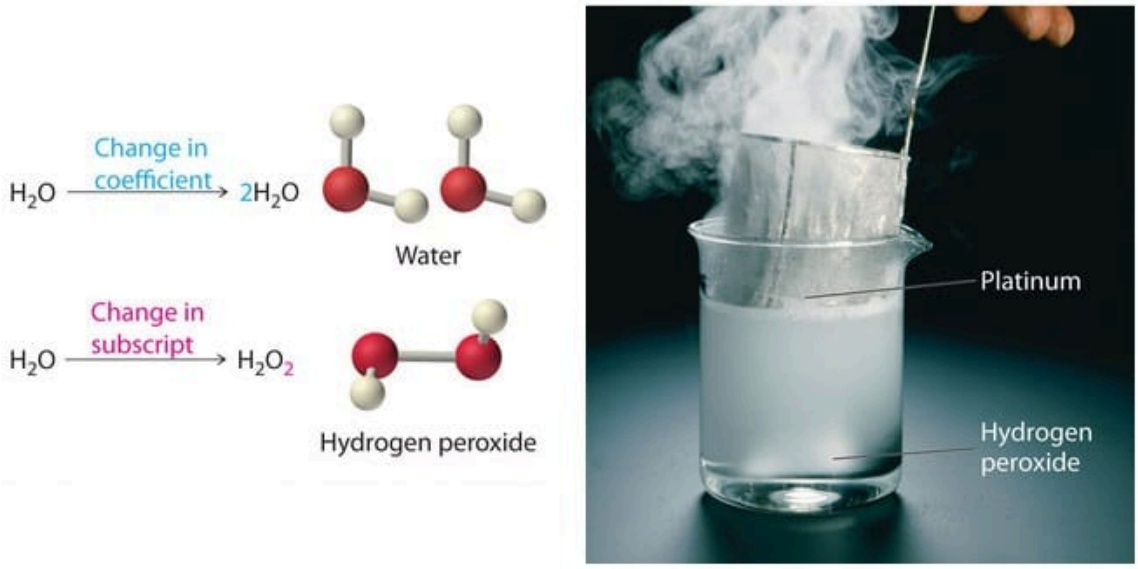


Figure 5.1.2 H_2O_2 decomposes to H_2O and O_2 gas when it comes in contact with the metal platinum (left), whereas no such reaction occurs between water and platinum (right).

The simplest and most generally useful method for balancing chemical equations is “inspection,” better known as trial and error. The following is an efficient approach to balancing a chemical equation using this method.

Steps in Balancing a Chemical Equation

1. Identify the most complex substance.
2. Beginning with that substance, choose an element(s) that appears in only one reactant and one product, if possible. Adjust the coefficients to obtain the same number of atoms of this element(s) on both sides.
3. Balance polyatomic ions (if present on both sides of the chemical equation) as a unit.
4. Balance the remaining atoms, usually ending with the least complex substance and using fractional coefficients if necessary. If a fractional coefficient has been used, multiply both sides of the equation by the denominator to obtain whole numbers for the coefficients.

5. Count the numbers of atoms of each kind on both sides of the equation to be sure that the chemical equation is balanced.

Example 5.1.2: Combustion of Heptane

Balancing the chemical Equation for the combustion of Heptane (C_7H_{16})

$$C_7H_{16}\,(l) + O_2\,(g) \longrightarrow CO_2\,(g) + H_2O\,(g)$$

Solution

Example 5.1.2: Steps for Problem Solving the Combustion Of Heptane

Steps	Explanation
1. **Identify the most complex substance.**	The most complex substance is the one with the largest number of different atoms, which is C_7H_{16}. We will assum that the final balanced chemical equation contains 1 molecule or formula unit of this substance.
2. **Adjust the coefficients.**	a. Because one molecule of n-heptane contains 7 carbon atoms, we need 7 CO_2 molecules, each of which cont carbon atom, on the right side: $$C_7H_{16}\,(l) + O_2\,(g) \longrightarrow \underline{7}CO_2\,(g) + H_2O\,(g)$$ *Reactants and Products of Elements*

Reactants	Element/Polyatomic Ion	Produ
7	C	7

b. Because one molecule of n-heptane contains 16 hydrogen atoms, we need 8 H_2O molecules, each of which hydrogen atoms, on the right side:

$$C_7H_{16}\,(l) + O_2\,(g) \longrightarrow 7\,CO_2\,(g) + \underline{8}H_2O\,(g)$$

Reactants and Products of Elements

Reactants	Element/Polyatomic Ion	Produ
7	C	7
16	H	16

3. **Balance polyatomic ions as a unit.**	There are no polyatomic ions to be considered in this reaction.

4. **Balance the remaining atoms**.	The carbon and hydrogen atoms are now balanced, but we have 22 oxygen atoms on the right side and only 2 atoms on the left. We can balance the oxygen atoms by adjusting the coefficient in front of the least complex s O_2, on the reactant side: $$\mathrm{C_7H_{16}\,(l) + \underline{11}O_2\,(g) \longrightarrow 7\,CO_2\,(g) + 8\,H_2O\,(g)}$$ *Reactants and Products of Elements*

Reactants	Element/Polyatomic Ion	Produ
7	C	7
16	H	16
22	O	22

5. **Check your work.**	The equation is now balanced, and there are no fractional coefficients: there are 7 carbon atoms, 16 hydrogen ato oxygen atoms on each side. Always check to be sure that a chemical equation is balanced.

Example 5.1.3: Combustion of Isooctane

Combustion of Isooctane ($\mathrm{C_8H_{18}}$)

$$\mathrm{C_8H_{18}\,(l) + O_2\,(g) \longrightarrow CO_2\,(g) + H_2O\,(g)}$$

Solution

The assumption that the final balanced chemical equation contains only one molecule or formula unit of the most complex substance is not always valid, but it is a good place to start. The combustion of any hydrocarbon with oxygen produces carbon dioxide and water.

Example 5.1.3: Solution for the combustion of isooctane

steps	examples
1. **Identify the most complex substance.**	The most complex substance is the one with the largest number of different atoms, which is $\mathrm{C_8H_{18}}$. We will assum that the final balanced chemical equation contains 1 molecule or formula unit of this substance.

2. **Adjust the coefficients.**	a. The first element that appears only once in the reactants is carbon: 8 carbon atoms in isooctane means that must be 8 CO_2 molecules in the products: $$C_8H_{18}(l) + O_2(g) \longrightarrow \underline{8}CO_2(g) + H_2O(g)$$ *Reactants and Products of Elements* **Reactants** | **Element/Polyatomic Ion** | **Produ** 8 | C | 8 b. Eighteen hydrogen atoms in isooctane means that there must be 9 H_2O molecules in the products: $$C_8H_{18}(l) + O_2(g) \longrightarrow 8\,CO_2(g) + \underline{9}H_2O(g)$$ *Reactants and Products of Elements* **Reactants** | **Element/Polyatomic Ion** | **Produ** 8 | C | 8 18 | H | 18
3. **Balance polyatomic ions as a unit.**	There are no polyatomic ions to be considered in this reaction.
4. **Balance the remaining atoms.**	The carbon and hydrogen atoms are now balanced, but we have 25 oxygen atoms on the right side and only 2 atoms on the left. We can balance the least complex substance, O_2, but because there are 2 oxygen atoms per molecule, we must use a fractional coefficient ($\frac{25}{2}$) to balance the oxygen atoms: $$C_8H_{18}(l) + \underline{\frac{25}{2}}O_2\ (g) \longrightarrow 8\,CO_2(g) + 9\,H_2O(g)$$ *Reactants and Products of Elements* **Reactants** | **Element/Polyatomic Ion** | **Produ** 8 | C | 8 18 | H | 18 25 | O | 25 The equation is now balanced, but we usually write equations with whole-number coefficients. We can eliminat fractional coefficient by multiplying all coefficients on both sides of the chemical equation by **2**: $$\underline{2}C_8H_{18}(l) + \underline{25}O_2(g) \longrightarrow \underline{16}CO_2(g) + \underline{18}H_2O(g)$$

5. **Check your work.**	The balanced chemical equation has 16 carbon atoms, 36 hydrogen atoms, and 50 oxygen atoms on each side *Reactants and Products of Elements* **Reactants** | **Element/Polyatomic Ion** | **Produ** 16 | C | 16 36 | H | 36 50 | O | 50 Balancing equations requires some practice on your part as well as some common sense. If you find yourself u large coefficients or if you have spent several minutes without success, go back and make sure that you have w formulas of the reactants and products correctly.

Example 5.1.4: Precipitation of Lead (II) Chloride

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

Example 5.1.4: Solution for the combustion of isooctane

Steps for Problem Solving	**Example 5.1.4**
1. **Identify the most complex substance.**	The most complex substance is lead (II) chloride. $$\mathrm{Pb(NO_3)_2\,(aq) + NaCl\,(aq) \longrightarrow NaNO_3\,(aq) + PbCl_2\,(s)}$$
2. **Adjust the coefficients.**	There are twice as many chloride ions in the reactants than in the products. Place a 2 in front of the NaCl in or balance the chloride ions. $$\mathrm{Pb(NO_3)_2\,(aq) + \underline{2}NaCl\,(aq) \longrightarrow NaNO_3\,(aq) + PbCl_2\,(s)}$$ *Reactants and Products of Elements* **Reactants** | **Element/Polyatomic Ion** | **Produ** 1 | Pb | 1 2 | Na | 1 2 | Cl | 2

3. **Balance polyatomic ions as a unit.**	The nitrate ions are still unbalanced. Place a 2 in front of the $NaNO_3$. The result is: $$Pb(NO_3)_2\,(aq) + 2\,NaCl\,(aq) \longrightarrow \underline{2}NaNO_3\,(aq) + PbCl_2\,(s)$$ *Reactants and Products of Elements*

Reactants	Element/Polyatomic Ion	Produ
1	Pb	1
2	Na	2
2	Cl	2
2	NO_3^-	2

4. **Balance the remaining atoms.**	There is no need to balance the remaining atoms because they are already balanced.
5. **Check your work.**	$$Pb(NO_3)_2\,(aq) + 2\,NaCl\,(aq) \longrightarrow 2\,NaNO_3\,(aq) + PbCl_2\,(s)$$ *Reactants and Products of Elements*

Reactants	Element/Polyatomic Ion	Produ
1	Pb	1
2	Na	2
2	Cl	2
2	NO_3^-	2

Exercise 5.1.2

Is each chemical equation balanced?

a. $2\,Hg(\ell)^+\ O_2\,(g) \ \rightarrow Hg_2O_2\,(s)$
b. $C_2H_4\,(g) + 2\,O_2(g) \longrightarrow 2\,CO_2\,(g) + 2\,H_2O\,(g)$
c. $Mg(NO_3)_2\,(s) + 2\,Li\,(s) \ \rightarrow Mg(s)^+\ 2\,LiNO_3\,(s)$

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.

Exercise 5.1.3

Balance the following chemical equations.

a. $N_2\,(g) + O_2\,(g) \longrightarrow NO_2\,(g)$
b. $Pb(NO_3)_2\,(aq) + FeCl_3\,(aq) \longrightarrow Fe(NO_3)_3\,(aq) + PbCl_2\,(s)$
c. $C_6H_{14}\,(l) + O_2(g) \longrightarrow CO_2\,(g) + H_2O\,(g)$

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.

Summary

- A chemical reaction is the process in which one or more substances are changed into one or more new substances.
- Chemical reactions are represented by chemical equations.
- Chemical equations have reactants on the left, an arrow that is read as "yields", and the products on the right.
- To be useful, chemical equations must always be balanced. Balanced chemical equations have the same number and type of each atom on both sides of the equation.
- The coefficients in a balanced equation must be the simplest whole number ratio. Mass is always conserved in chemical reactions.

Contributors and Attributions

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- Henry Agnew (UC Davis)

Answers

Exercise 5.1.1

$H_2(g) + N_2(g) \rightarrow NH_3(g)$

An aqueous solution of hydrochloric acid reacts with an aqueous solution of lithium hydroxide to produce an aqueous solution of lithium chloride and liquid water.

$Cu(s) + O_2(g) \rightarrow CuO(s)$

Exercise 5.1.2

yes

Exercise 5.1.2

no

Exercise 5.1.2

yes

Exercise 5.1.3

N_2 (g) + $2O_2$ (g) → $2NO_2$ (g)

Exercise 5.1.3

$3Pb(NO_3)_2$(aq) + $2FeCl_3$(aq) → $2Fe(NO_3)_3$(aq) + $3PbCl_2$(s)

Exercise 5.1.3

$2C_6H_{14}$(l) + $19O_2$(g) → $12CO_2$(g) + $14H_2O$(g)

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5.2: Volume Relationships in Chemical Equations

Learning Objectives

- Identify the relative volume of gas consumed or produced based on a balanced chemical equation for a reaction.

The behavior of gases can be represented by gas laws as will be discussed in more detail in Chapter 6. Avogadro's law states that all gases (that show ideal behavior) contain the same number of molecules in the same volume (at the same temperature and pressure). Thus, the ratios of volumes of gases involved in a chemical reaction are given by the coefficients in the equation for the reaction, provided that the gas volumes are measured at the same temperature and pressure.

We can extend Avogadro's law (that the volume of a gas is directly proportional to the number of moles of the gas) to chemical reactions with gases: Gases combine, or react, in definite and simple proportions by volume, provided that all gas volumes are measured at the same temperature and pressure. For example, since nitrogen and hydrogen gases react to produce ammonia gas according to the balanced equation below

$$\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \longrightarrow 2\,\mathrm{NH_3}(g)$$

a given volume of nitrogen gas reacts with three times that volume of hydrogen gas to produce two times that volume of ammonia gas, if pressure and temperature remain constant.

The explanation for this is illustrated in Figure 5.2.1. According to Avogadro's law, equal volumes of gaseous N_2, H_2, and NH_3, at the same temperature and pressure, contain the same number of molecules. Because one molecule of N_2 reacts with three molecules of H_2 to produce two molecules of NH_3, the volume of H_2 required is three times the volume of N_2, and the volume of NH_3 produced is two times the volume of N_2.

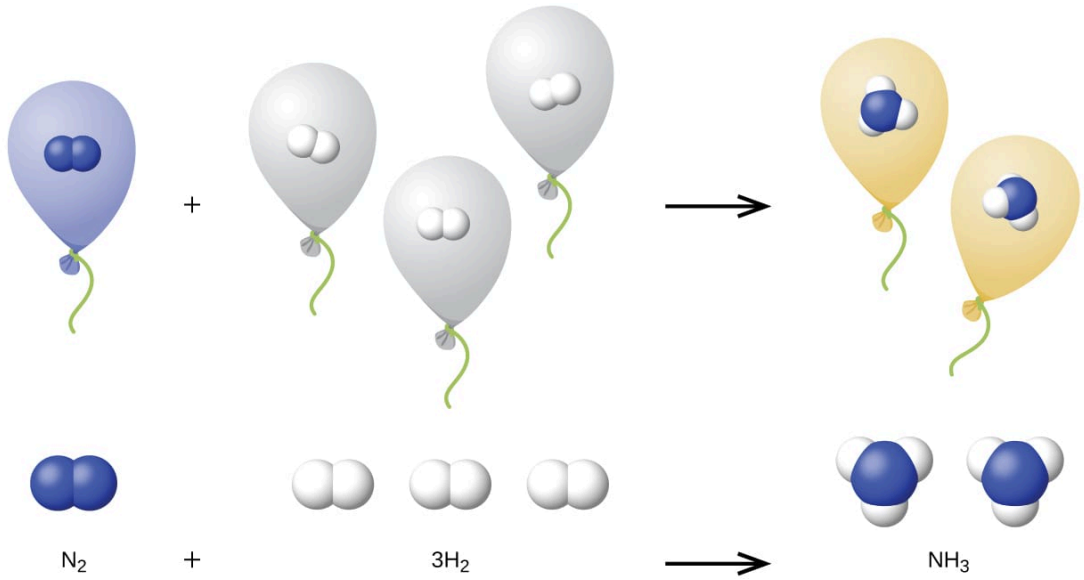


Figure 5.2.1: *One volume of N_2 combines with three volumes of H_2 to form two volumes of NH_3.*

This diagram provided models the chemical reaction written with formulas across the bottom of the figure. The reaction is written; N subscript 2 plus 3 H subscript 2 followed by an arrow pointing right to N H subscript 3. Just above the formulas, space-filling models are provided. Above N H subscript 2, two blue spheres are bonded. Above 3 H subscript 2, three pairs of two slightly smaller white spheres are bonded. Above N H subscript 3, two molecules are shown composed each of a central blue sphere to which three slightly smaller white spheres are bonded. Across the top of the diagram, the reaction is illustrated with balloons. To the left is a light blue balloon which is labeled “N subscript 2”. This balloon contains a single space-filling model composed of two bonded blue spheres. This balloon is followed by a plus sign, then three grey balloons which are each labeled “H subscript 2.” Each of these balloons similarly contain a single space-filling model composed of two bonded white spheres. These white spheres are slightly smaller than the blue spheres. An arrow follows which points right to two light green balloons which are each labeled “N H subscript 3.” Each light green balloon contains a space-filling model composed of a single central blue sphere to which three slightly smaller white spheres are bonded.

Example 5.2.5: Reaction of Gases

Propane, $C_3H_8(g)$, is used in gas grills to provide the heat for cooking. What volume of $O_2(g)$ measured at 25 °C and 760 torr is required to react with 2.7 L of propane measured under the same conditions of temperature and pressure? Assume that the propane undergoes complete combustion.

Solution

The ratio of the volumes of C_3H_8 and O_2 will be equal to the ratio of their coefficients in the balanced equation for the reaction:

$$\begin{aligned} &\mathrm{C_3H_8}(g) + 5\,\mathrm{O_2}(g) \longrightarrow && 3\,\mathrm{CO_2}(g) + 4\,\mathrm{H_2O}(l) && (5.2.1)\\ &1\ \text{volume} + 5\ \text{volumes} && 3\ \text{volumes} + 4\ \text{volumes} && (5.2.2) \end{aligned}$$

From the equation, we see that one volume of C_3H_8 will react with five volumes of O_2:

$$2.7\ \mathrm{L}\ \cancel{\mathrm{C_3H_8}} \times \frac{5\ \mathrm{L\ O_2}}{1\ \mathrm{L}\ \cancel{\mathrm{C_3H_8}}} = 13.5\ \mathrm{L\ O_2}$$

A volume of 13.5 L of O_2 will be required to react with 2.7 L of C_3H_8.

Exercise 5.2.5

An acetylene tank for an oxyacetylene welding torch provides 9340 L of acetylene gas, C_2H_2, at 0 °C and 1 atm. How many tanks of oxygen, each providing 7.00×10^3 L of O_2 at 0 °C and 1 atm, will be required to burn the acetylene?

$$2\,C_2H_2 + 5\,O_2 \longrightarrow 4\,CO_2 + 2\,H_2O$$

Answer available at the end of this section.

Example 5.2.6: Volumes of Reacting Gases

Ammonia is an important fertilizer and industrial chemical. Suppose that a volume of 683 billion cubic feet of gaseous ammonia, measured at 25 °C and 1 atm, was manufactured. What volume of $H_2(g)$, measured under the same conditions, was required to prepare this amount of ammonia by reaction with N_2?

$$N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)$$

Solution

Because equal volumes of H_2 and NH_3 contain equal numbers of molecules and each three molecules of H_2 that react produce two molecules of NH_3, the ratio of the volumes of H_2 and NH_3 will be equal to 3:2. Two volumes of NH_3, in this case in units of billion ft^3, will be formed from three volumes of H_2:

$$683\ \cancel{\text{billion ft}^3\ \text{NH}_3} \times \frac{3\ \text{billion ft}^3\ \text{H}_2}{2\ \cancel{\text{billion ft}^3\ \text{NH}_3}} = 1.02 \times 10^3\ \text{billion ft}^3\ \text{H}_2$$

The manufacture of 683 billion ft^3 of NH_3 required 1020 billion ft^3 of H_2. (At 25 °C and 1 atm, this is the volume of a cube with an edge length of approximately 1.9 miles.)

Exercise 5.2.6

What volume of $O_2(g)$ measured at 25 °C and 760 torr is required to react with 17.0 L of ethylene, $C_2H_4(g)$, measured under the same conditions of temperature and pressure? The products are CO_2 and water vapor.

Answer available at the end of this section.

Summary

Avogadro's law may be used to determine the volume of gaseous reactant(s) or product(s) based on a balanced chemical equation.

Contributors and Attributions

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Answers

Exercise 5.2.5

3.34 tanks (2.34×10^4 L)

Exercise 5.2.6

51.0 L

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5.3: Avogadro's Number and the Mole

Learning Objectives

- Use Avogadro's number to convert to moles and vice versa given the number of particles of an element.
- Know the definition of the mole.
- Determine the formula mass of an ionic or molecular compound.
- Determine the percent composition of each element in a compound from the chemical formula.

When objects are very small, it is often inconvenient or inefficient, or even impossible to deal with the objects one at a time. For these reasons, we often deal with very small objects in groups, and have even invented names for various numbers of objects. The most common of these is "dozen" which refers to 12 objects. We frequently buy objects in groups of 12, like doughnuts or pencils. Even smaller objects such as straight pins or staples are usually sold in boxes of 144, or a dozen dozen. A group of 144 is called a "gross".

This problem of dealing with things that are too small to operate with as single items also occurs in chemistry. Atoms and molecules are too small to see, let alone to count or measure. Chemists needed to select a group of atoms or molecules that would be convenient to operate with.

Avogadro's Number:Counting Atoms

Owing to their tiny size, atoms and molecules cannot be counted by direct observation. But much as we do when "counting" beans in a jar, we can estimate the number of particles in a sample of an element or compound if we have some idea of the volume occupied by each particle and the volume of the container. Once this has been done, we know the number of formula units (to use the most general term for any combination of atoms we wish to define) in any arbitrary weight of the substance. The number will of course depend both on the formula of the substance and on the weight of the sample. However, if we consider a weight of substance that is the same as its formula (molecular) weight expressed in grams, we have only one number to know: **Avogadro's number**.

Avogadro's number

Avogadro's number is known to ten significant digits:

$$N_A = 6.022141527 \times 10^{23}.$$

However, you only need to know it to three significant figures:

$$N_A \approx 6.02 \times 10^{23}. \tag{5.3.1}$$

So 6.02×10^{23} of *what*? Well, of anything you like: apples, stars in the sky, burritos. However, the only *practical* use for N_A is to have a more convenient way of expressing the huge numbers of the tiny particles such as atoms or molecules that we deal with in chemistry. Avogadro's number is a *collective number*, just like a dozen. Students can think of 6.02×10^{23} as the "chemist's dozen".

Before getting into the use of Avogadro's number in problems, take a moment to convince yourself of the reasoning embodied in the following examples.

Things to understand about Avogadro's number

- It is a *number*, just as is "dozen", and thus is *dimensionless*.
- It is a *huge* number, far greater in magnitude than we can visualize
- Its practical use is limited to counting tiny things like atoms, molecules, "formula units", electrons, or photons.

- The value of N_A can be known only to the precision that the number of atoms in a measurable weight of a substance can be estimated. Because large numbers of atoms cannot be counted directly, a variety of ingenious indirect measurements have been made involving such things as Brownian motion and X-ray scattering.

The Mole: "A Dozen Eggs and a Mole of Sugar, Please"

The **mole** (symbol: **mol**) is the base unit of amount of substance ("number of substance") in the International System of Units or System International (SI), defined as exactly $6.02214076 \times 10^{23}$ particles, e.g., atoms, molecules, ions or electrons. The current definition was adopted in November 2018, revising its old definition based on the number of atoms in 12 grams of carbon-12 (^{12}C) (the isotope of carbon with relative atomic mass 12 Daltons by definition).

It is not obvious why eggs come in dozens rather than 10s or 14s, or why a ream of paper contains 500 sheets rather than 400 or 600. The definition of a mole—that is, the decision to base it on 12 g of carbon-12—is also arbitrary. The important point is that 1 mole of carbon—or of anything else, whether atoms, compact discs, or houses—always has the same number of objects: 6.02×10^{23}.

The Mole

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 $5.3.1$ *How big is a mole?*

Converting Between Number of Atoms to Moles and Vice Versa

We can use Avogadro's number as a conversion factor, or ratio, in dimensional analysis problems. If we are given the number of atoms of an element X, we can convert it into moles of by using the relationship

$$1 \text{ mol X} = 6.022 \times 10^{23} \text{ X atoms.}$$

An example on the use of Avogadro's number as a conversion factor is given below for carbon.

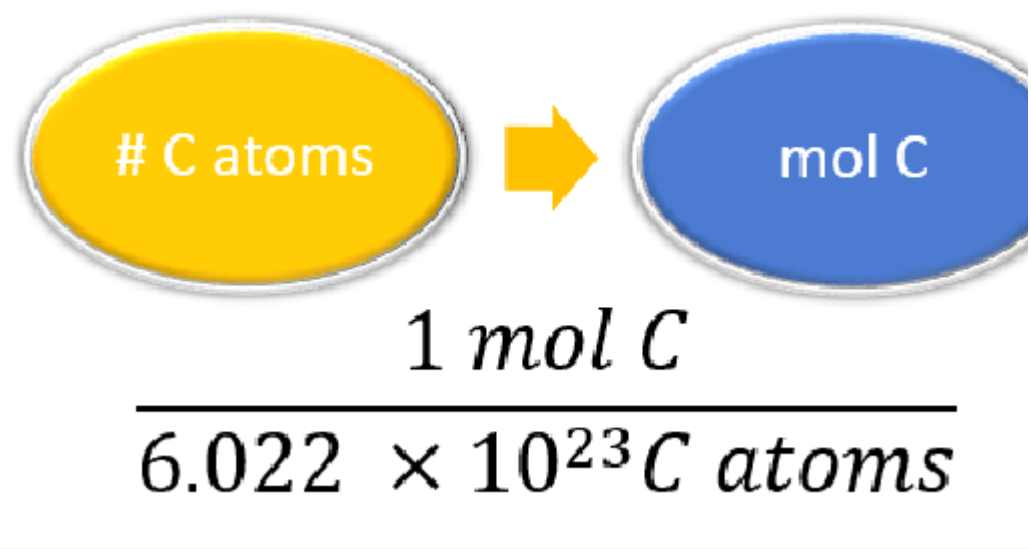
Example $5.3.1$: Moles of Carbon

The element carbon exists in two primary forms: graphite and diamond. How many moles of carbon atoms is 4.72×10^{24} atoms of carbon?

Solution

Example $5.3.1$*:Steps for Problem Solving how many moles of carbon atoms is* 4.72×10^{24} *atoms of carbon?*

Steps for Problem Solving	Example
Identify the "given"information and what the problem is asking you to "find."	Given: 4.72×10^{24} C atoms Find: mol C

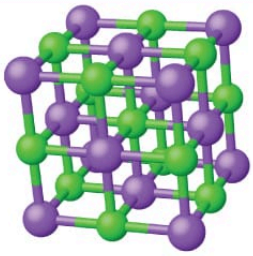
Steps for Problem Solving	Example
List other known quantities	$1\ mol = 6.022 \times 10^{23}$ C atoms
Prepare a concept map and use the proper conversion factor.	 $\frac{1\ mol\ C}{6.022 \times 10^{23} C\ atoms}$
Cancel units and calculate.	$4.72 \times 10^{24}\ \cancel{\text{C atoms}} \times \frac{1\ \text{mol C}}{6.02 \times 10^{23}\ \cancel{\text{C atoms}}} = 7.84\ \text{mol C}$
Think about your result.	The given number of carbon atoms was greater than Avogadro's number,so the number of moles of C atoms mole. Since Avogadro's number is a measured quantity with three significant figures, the result of the calcul to three significant figures

Formula Mass

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

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

Element	Quantity		Average atomic mass (amu)		Subtotal
Na	1	×	22.99	=	22.99
Cl	1	×	35.45	=	35.45
				Formula mass	58.44

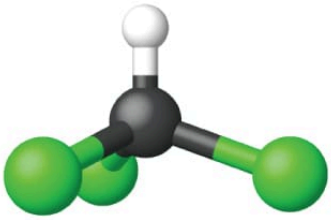


A table and diagram are shown. The table is made up of six columns and four rows. The header row reads: “Element,” “Quantity,” a blank space, “Average atomic mass (a m u),” a blank space and “Subtotal (a m u).” The first column contains the symbols “N a”, “C l,” and a merged cell. The merged cell runs 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.

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

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.

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



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.

To two decimal places, the formula mass of $CHCl_3$ is 119.37 amu.

For ionic compounds with polyatomic ions, the sum must include the number and mass of each atom in the formula for the polyatomic ion. as shown in the example below for aluminum sulfate, $Al_2(SO_4)_3$.

Example 5.3.2 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:

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The formula mass for $Al_2(SO_4)_3$, is 342.14 amu.

Exercise 5.3.1

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

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

Answer

a. 79.87 amu

b. 187.77 amu

c. 383.0 amu

Percent Composition of a Compound from a Chemical Formula

The percent composition of a compound can also be determined from the formula of the compound. The subscripts in the formula are first used to calculate the mass of each element in one mole of the compound. That is divided by the molar mass of the compound and multiplied by 100%.

$$\%\text{ by mass} = \frac{\text{mass of element in 1 mol}}{\text{molar mass of compound}} \times 100\%$$

The percent composition of a given compound is always the same as long as the compound is pure.

Example 5.3.3

Dichlorine heptoxide (Cl_2O_7) is a highly reactive compound used in some organic synthesis reactions. Calculate the percent composition of dichlorine heptoxide.

Solution

Example 5.3.3:*Steps for Problem Solving calculate the percent composition of dichlorine heptoxide* (Cl_2O_7).

Steps for Problem Solving	Example
Identify the "given"information and what the problem is asking you to "find."	Given : Cl_2O_7 Find: % Composition (% Cl and %O)
List other known quantities	Mass of Cl in 1 mol Cl_2O_7 , 2 Cl : 2 x 35.45 g = 70.90 g Mass of O in 1 mol Cl_2O_7 , 7 O: 7 x 16.00 g = 112.00 g Molar mass of Cl_2O_7 = 182.90 g/mol
Cancel units and calculate.	$\%\mathrm{Cl} = \frac{70.90\ \mathrm{g\ Cl}}{182.90\ \mathrm{g}} \times 100\% = 38.76\%\ \mathrm{Cl}$ $\%\ \mathrm{O} = \frac{112.00\ \mathrm{g\ O}}{182.90\ \mathrm{g}} \times 100\% = 61.24\%\ \mathrm{O}$ Calculate the percent by mass of each element by dividing the mass of that element in 1 mole of the co molar mass of the compound and multiplying by 100%.
Think about your result.	The percentages add up to 100%.

Percent composition can also be used to determine the mass of a certain element that is contained in any mass of a compound. In the previous sample problem, it was found that the percent composition of dichlorine heptoxide is $38.76\%\ \mathrm{Cl}$ and $61.24\%\ \mathrm{O}$. Suppose that you needed to know the masses of chlorine and oxygen present in a $12.50\ \mathrm{g}$ sample of dichlorine heptoxide. You can set up a conversion factor based on the percent by mass of each element.

$$12.50\ \mathrm{g\ Cl_2O_7} \times \frac{38.76\ \mathrm{g\ Cl}}{100\ \mathrm{g\ Cl_2O_7}} = 4.845\ \mathrm{g\ Cl}$$

$$12.50\ \mathrm{g\ Cl_2O_7} \times \frac{61.24\ \mathrm{g\ O}}{100\ \mathrm{g\ Cl_2O_7}} = 7.655\ \mathrm{g\ O}$$

The sum of the two masses is $12.50\ \mathrm{g}$, the mass of the sample size.

Exercise 5.3.2

Barium fluoride is a transparent crystal that can be found in nature as the mineral frankdicksonite. Determine the percent composition of barium fluoride.

Answer a: available at the end of this section.

Summary

- The **mole** (symbol: **mol**) is the base unit of amount of substance ("number of substance") in the International System of Units or System International (SI), defined as exactly 6.02214076×10^{23} particles, e.g., atoms, molecules, ions or electrons.
- Avogadro's number is related to moles of any substance X as follows:

$$1 \text{ mol X} = 6.022 \times 10^{23} \text{ X atoms.}$$

- Formula masses of ionic and molecular compounds can be determined from the masses of the atoms in their formulas.
- Processes are described for calculating the percent composition of a compound based on the chemical formula.

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- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook
- Marisa Alviar-Agnew (Sacramento City College)
- Henry Agnew (UC Davis)
- Wikipedia

Answers

Exercise 5.3.2

78.32% Ba and 21.67% F

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5.4: Molar Mass- Mole-to-Mass and Mass-to-Mole Conversions

Learning Objectives

- Perform conversions between mass and moles of a substance.
- Convert from mass or moles of one substance to mass or moles of another substance in a chemical reaction.
- Use a balanced chemical equation to determine molar relationships between substances.

Molar Mass

The **molar mass** of any substance is the mass in grams of one mole of representative particles of that substance. The representative particles can be atoms, molecules, or formula units of ionic compounds. This relationship is frequently used in the laboratory. The simplest type of manipulation using molar mass as a conversion factor is a mole-mass conversion (or its reverse, a mass-mole conversion). In such a conversion, we use the molar mass of a substance as a conversion factor to convert mole units into mass units (or, conversely, mass units into mole units).

We also established that 1 mol of Al has a mass of 26.98 g (Example). Stated mathematically,

$$1 \text{ mol Al} = 26.98 \text{ g Al}$$

We can divide both sides of this expression by either side to get one of two possible conversion factors:

$$\frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \text{ and } \frac{26.98 \text{ g Al}}{1 \text{ mol Al}} \tag{5.4.1}$$

The first conversion factor can be used to convert from mass to moles, and the second converts from moles to mass. Both can be used to solve problems that would be hard to do “by eye.”

Example 5.4.1

What is the mass of 3.987 mol of Al?

Solution

Example 5.4.1: Steps for Problem Solving the mass of 3.987 moles of aluminum (Al).

Steps for Problem Solving	Example
Identify the "given"information and what the problem is asking you to "find."	Given: 3.987 mol of Al Find: g Al
List other known quantities	1 mol Al = 26.98 g Al

Steps for Problem Solving	Example
Prepare a concept map and use the proper conversion factor.	mol Al → g Al $\frac{26.98\ \text{g Al}}{1\ \text{mol Al}}$
Cancel units and calculate.	$3.987\ \cancel{\text{mol Al}} \times \frac{26.98\ \text{g Al}}{1\ \cancel{\text{mol Al}}} = 107.6\ \text{g Al}$
Think about your result.	The calculated value makes sense because it is almost four times times the mass for 1 mole of aluminum. Our final answer is expressed to four significant figures.

Exercise 5.4.1

How many moles are present in 100. g of Al? (Hint: you will have to use the other conversion factor we obtained for aluminum.)

Answer

3.71 g Al

Conversions like this are possible for any substance, as long as the proper atomic mass, formula mass, or molar mass is known (or can be determined) and expressed in grams per mole. Figure 5.4.1 is a chart for determining what conversion factor is needed, and Figure 5.4.2 is a flow diagram for the steps needed to perform a conversion.

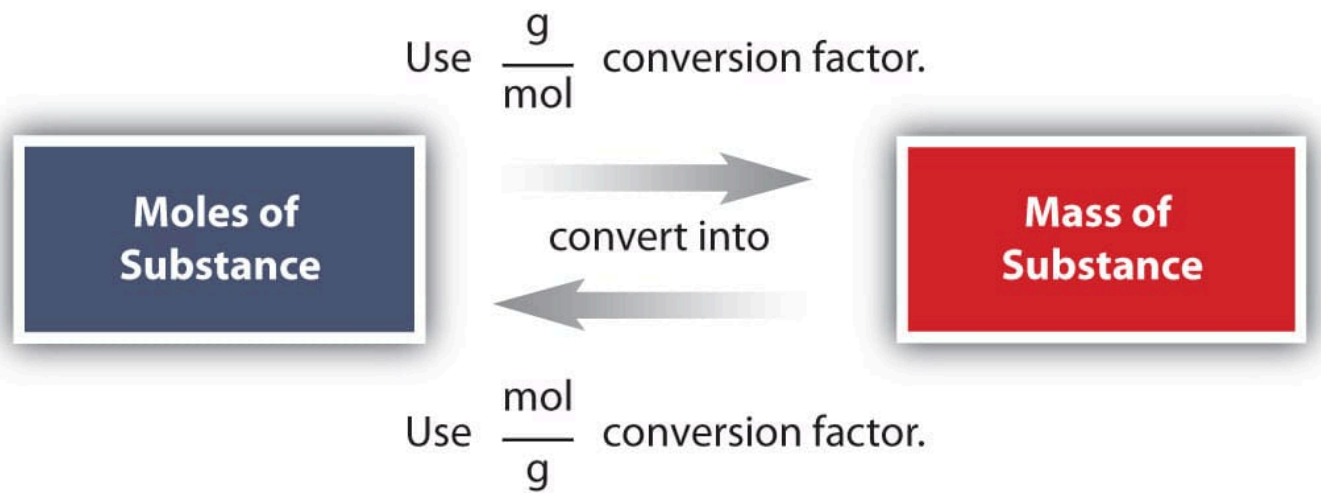


Figure 5.4.1 A Simple Flowchart for Converting between Mass and Moles of a Substance. It takes one mathematical step to convert from moles to mass or from mass to moles.

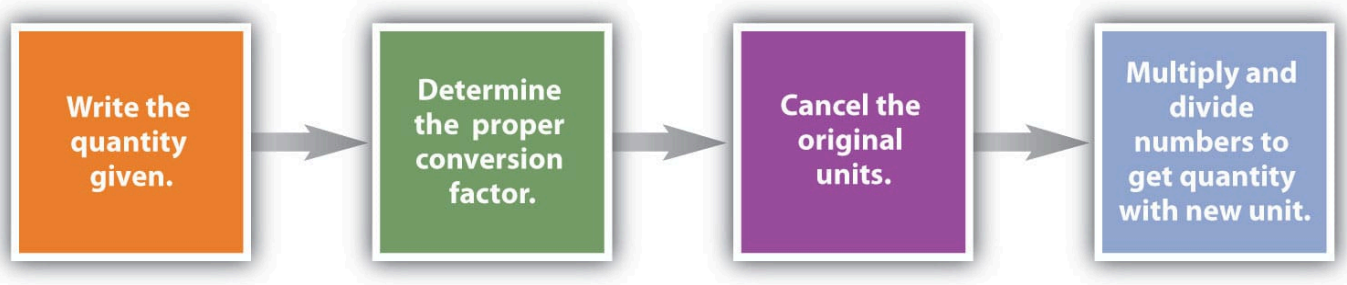


Figure 5.4.2 A Flowchart Illustrating the Steps in Performing a Unit Conversion. When performing many unit conversions, the same logical steps can be taken.

Suppose that for a certain experiment you need 3.00 moles of calcium chloride $(CaCl_2)$. Since calcium chloride is a solid, it would be convenient to use a balance to measure the mass that is needed. Dimensional analysis will allow you to calculate the mass of $CaCl_2$ that you should measure as show in Example 5.4.3.

Example 5.4.2: Calcium Chloride

Calculate the mass of 3.00 moles of calcium chloride ($CaCl_2$).

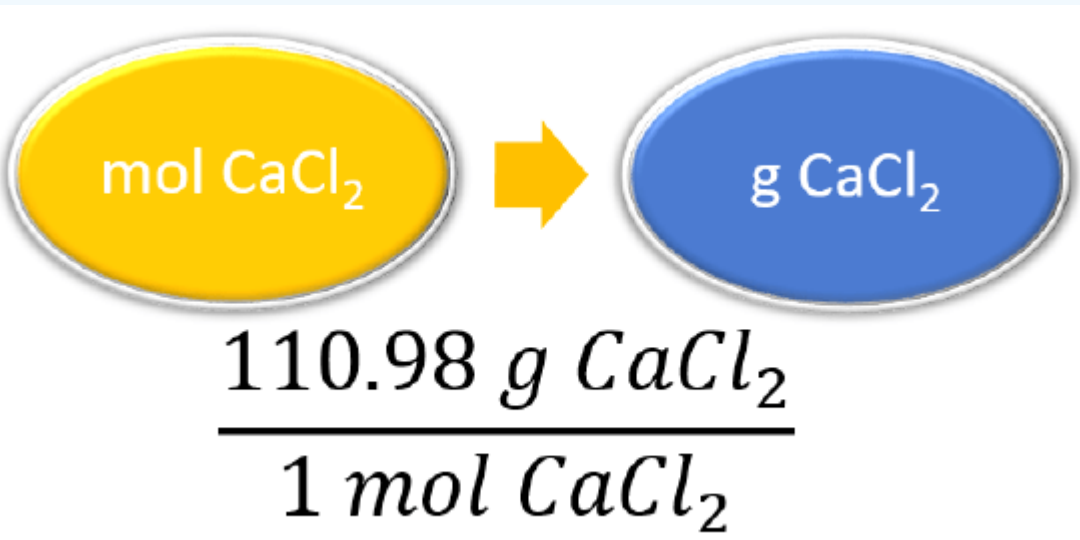


Figure 5.4.1: Calcium chloride is used as a drying agent and as a road deicer.

Solution

Example 5.4.2: Steps for Problem Solving the mass of 3.00 moles of calcium chloride (CaCl2).

Steps for Problem Solving	Example
Identify the "given"information and what the problem is asking you to "find."	Given: 3.00 moles of $CaCl_2$ Find: g $CaCl_2$
List other known quantities	1 ml $CaCl_2$ = 110.98 g $CaCl_2$

Steps for Problem Solving	Example
Prepare a concept map and use the proper conversion factor.	 $\frac{110.98\ g\ CaCl_2}{1\ mol\ CaCl_2}$
Cancel units and calculate.	$3.00\ \cancel{\text{mol CaCl}_2} \times \frac{110.98\ \text{g CaCl}_2}{1\ \cancel{\text{mol CaCl}_2}} = 333\ \text{g CaCl}_2$
Think about your result.	

Exercise 5.4.2: Calcium Oxide

What is the mass of $7.50\ \text{mol}$ of (calcium oxide) CaO?

Answer: available at the end of this section.

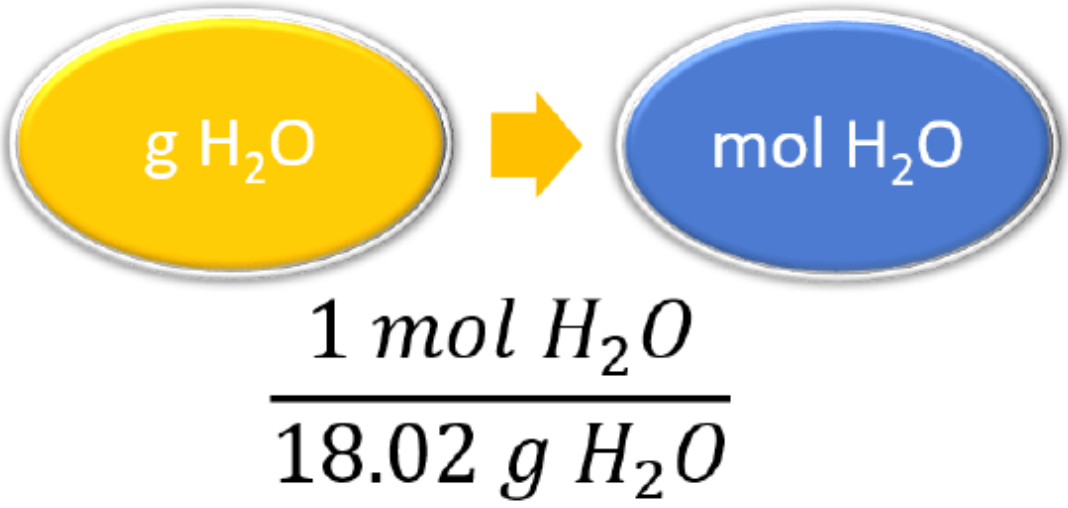
Example 5.4.3: Water

How many moles are present in 108 grams of water?

Solution

Example 5.4.3: Steps for Problem Solving moles in 108 grams of water?

Steps for Problem Solving	Example
Identify the "given"information and what the problem is asking you to "find."	Given: 108 g H_2O Find: mol H_2O
List other known quantities	$1\ \text{mol}\ H_2O = 18.02\ \text{g}\ H_2O$

Steps for Problem Solving	Example
Prepare a concept map and use the proper conversion factor.	 $$\frac{1\ mol\ H_2O}{18.02\ g\ H_2O}$$
Cancel units and calculate.	$108\ \cancel{\text{g H}_2\text{O}} \times \frac{1\ \text{mol H}_2\text{O}}{18.02\ \cancel{\text{g H}_2\text{O}}} = 5.99\ \text{mol H}_2\text{O}$
Think about your result.	

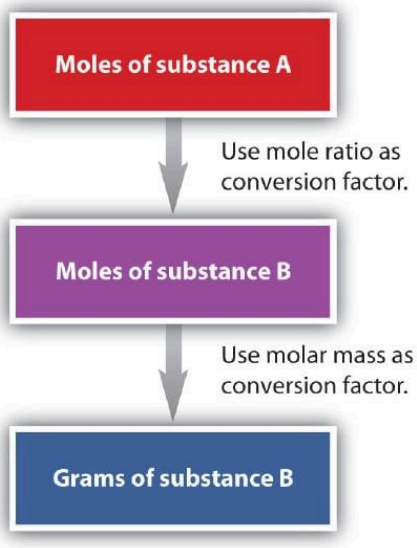
Exercise 5.4.3: Nitrogen Gas

What is the mass of $7.50\ \text{mol}$ of Nitrogen gas N_2?

Answer: available at the end of this section.

Mole and Mass Relationships in Chemical Equations

We have established that a balanced chemical equation is balanced in terms of moles as well as atoms or molecules. We have used balanced equations to set up ratios, now in terms of moles of materials, that we can use as conversion factors to answer stoichiometric questions, such as how many moles of substance A react with so many moles of reactant B. We can extend this technique even further. Recall that we can relate a molar amount to a mass amount using molar mass. We can use that ability to answer stoichiometry questions in terms of the masses of a particular substance, in addition to moles. We do this using the following sequence:



Collectively, these conversions are called mole-mass calculations.

As an example, consider the balanced chemical equation

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

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.

As usual, we start with the quantity we were given:

$$3.59 \ \cancel{\text{mol Fe}_2\text{O}_3} \times \left(\frac{3 \text{ mol SO}_3}{1 \ \cancel{\text{mol Fe}_2\text{O}_3}} \right) = 10.77 \text{ mol SO}_3 \tag{5.4.2}$$

The mol Fe_2O_3 units cancel, leaving mol SO_3 unit. Now, we take this answer and convert it to grams of SO_3, using the molar mass of SO_3 as the conversion factor:

$$10.77 \ \cancel{\text{mol SO}_3} \times \left(\frac{80.06 \text{ g SO}_3}{1 \ \cancel{\text{mol SO}_3}} \right) = 862 \text{ g SO}_3 \tag{5.4.3}$$

Our final answer is expressed to three significant figures. Thus, in a two-step process, we find that 862 g of SO_3 will react with 3.59 mol of Fe_2O_3. Many problems of this type can be answered in this manner.

The same two-step problem can also be worked out in a single line, rather than as two separate steps, as follows:

$$3.59 \ \cancel{mol\ Fe_2O_3} \times \underbrace{\left(\frac{3 \ \cancel{mol\ SO_3}}{1 \ \cancel{mol\ Fe_2O_3}} \right)}_{\text{converts to moles of SO}_3} \times \underbrace{\left(\frac{80.06\ g\ SO_3}{1 \ \cancel{mol\ SO_3}} \right)}_{\text{converts to grams of SO}_3} = 862\ g\ SO_3$$

We get exactly the same answer when combining all the math steps together as we do when we calculate one step at a time.

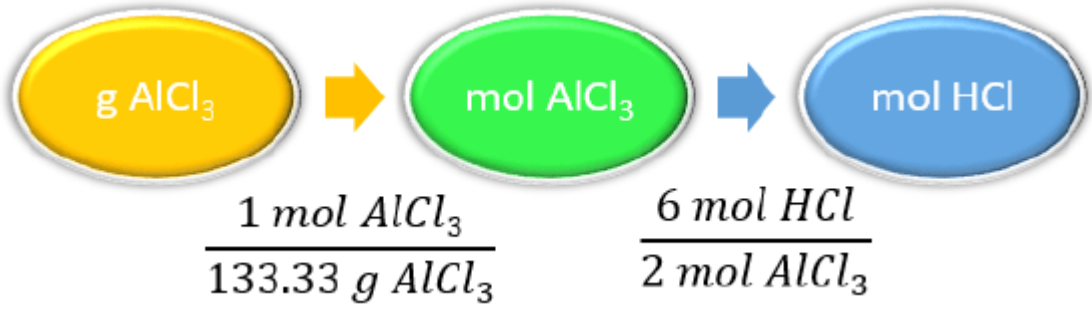
Example 5.4.4: Generation of Aluminum Oxide

How many moles of HCl will be produced when 249 g of AlCl3 are reacted according to this chemical equation?

$$2AlCl_3 + 3H_2O(\ell) \rightarrow Al_2O_3 + 6HCl(g)$$

Solution

Example 5.4.4: Steps for Problem Solving how many moles are in 249 g of AlCl3 ?

Steps for Problem Solving	Example
Identify the "given"information and what the problem is asking you to "find."	Given: 249 g AlCl3 Find: moles HCl
List other known quantities	1 mol AlCl3 = 133.33 g/mol 6 mol of HCl to 2 mol AlCl3
Prepare a concept map and use the proper conversion factor.	
Cancel units and calculate.	$249\ \cancel{g\ AlCl_3} \times \frac{1\ \cancel{mol\ AlCl_3}}{133.33\ \cancel{g\ AlCl_3}} \times \frac{6\ mol\ HCl}{2\ \cancel{mol\ AlCl_3}} = 5.60\ mol\ HCl$
Think about your result.	Since 249 g of $AlCl_3$ is less than 266.66 g, the mass for 2 moles of $AlCl_3$ and the relationship is 6 mol of HCl to 2 mol $AlCl_3$, the answer should be less than 6 moles of HCl.

Exercise 5.4.4: Generation of Aluminum Oxide

How many moles of Al2O3 will be produced when 23.9 g of H2O are reacted according to this chemical equation?

$$2AlCl_3 + 3H_2O(\ell) \rightarrow Al_2O_3 + 6HCl(g)$$

Answer available at the end of this section.

Molar Relationships in Chemical Equations

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

$$2H_2 + O_2 \rightarrow 2H_2O$$

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

$$4H_2 + 2O_2 \rightarrow 4H_2O$$

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

$$22H_2 + 11O_2 \rightarrow 22H_2O$$

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

$$2\ mol\ H_2 + 1\ mol\ O_2 \rightarrow 2\ mol\ H_2O$$

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

$$2H_2 + O_2 \rightarrow 2H_2O$$

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."

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*.

Example 5.4.5

How many moles of oxygen react with hydrogen to produce 27.6 mol of H_2O?

Solution

Example 5.4.5: Steps for Problem Solving how many moles of oxygen react with hydrogen to produce 27.6 mol of H2O?

Steps for Problem Solving	Example
Find a balanced equation that describes the reaction	Unbalanced: $H_2 + O_2 \rightarrow H_2O$ Balanced: $\underline{\mathbf{2}}H_2 + O_2 \rightarrow \underline{\mathbf{2}}H_2O$
Identify the "given"information and what the problem is asking you to "find."	Given: moles H_2O Find: moles oxygen
List other known quantities	1 mol O_2 = 2 mol H_2O
Prepare a concept map and use the proper conversion factor.	 $\frac{1\ mol\ O_2}{2\ mol\ H_2O}$
Cancel units and calculate.	$\cancel{27.6\ \text{mol}\ H_2O} \times \frac{1\ \text{mol}\ O_2}{\cancel{2\ \text{mol}\ H_2O}} = 13.8\ \text{mol}\ O_2$ To produce 27.6 mol of H_2O, 13.8 mol of O_2 react.
Think about your result.	Since each mole of oxygen produces twice as many moles of water, it makes sense that the produced amount is greater than the reactant amount

Example 5.4.6

How many moles of ammonia are produced if 4.20 moles of hydrogen are reacted with an excess of nitrogen?

Solution

Example 5.4.6: *Steps for Problem Solving how many moles of ammonia are produced if 4.20 moles of hydrogen are reacted with an excess of nitrogen*

Steps for Problem Solving	Example
Find a balanced equation that describes the reaction	Unbalanced: $N_2 + H_2 \rightarrow NH_3$ Balanced: $N_2 + \underline{3}H_2 \rightarrow \underline{2}NH_3$
Identify the "given"information and what the problem is asking you to "find."	Given: $H_2 = 4.20\ \text{mol}$ Find: mol of NH_3
List other known quantities	3 mol H_2 = 2 mol NH_3
Prepare a concept map and use the proper conversion factor.	 $\frac{2\ mol\ NH_3}{3\ mol\ H_2}$
Cancel units and calculate.	$\cancel{4.20\ \text{mol}\ H_2} \times \frac{2\ \text{mol}\ NH_3}{\cancel{3\ \text{mol}\ H_2}} = 2.80\ \text{mol}\ NH_3$ The reaction of $4.20\ \text{mol}$ of hydrogen with excess nitrogen produces $2.80\ \text{mol}$ of ammonia
Think about your result.	The result corresponds to the 3:2 ratio of hydrogen to ammonia from the balanced equation.

Exercise 5.4.5

a. Given the following balanced chemical equation,

$$C_5H_{12} + 8\,O_2 \longrightarrow 5\,CO_2 + 6\,H_2O$$

how many moles of H_2O can be formed if 0.0652 mol of C_5H_{12} were to react?

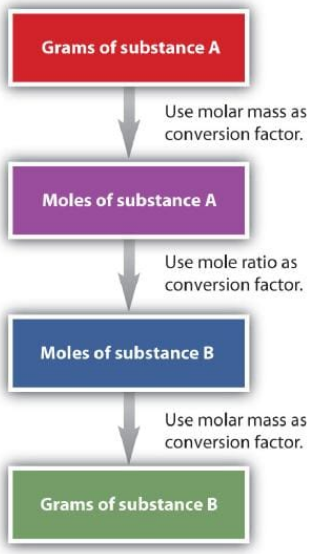
b. Balance the following unbalanced equation and determine how many moles of H_2O are produced when 1.65 mol of NH_3 react.

$$NH_3 + O_2 \longrightarrow N_2 + H_2O$$

Answer a: available at the end of this section.

Mass Relationships in Chemical Equations

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 5.4.7: Decomposition of Ammonium Nitrate

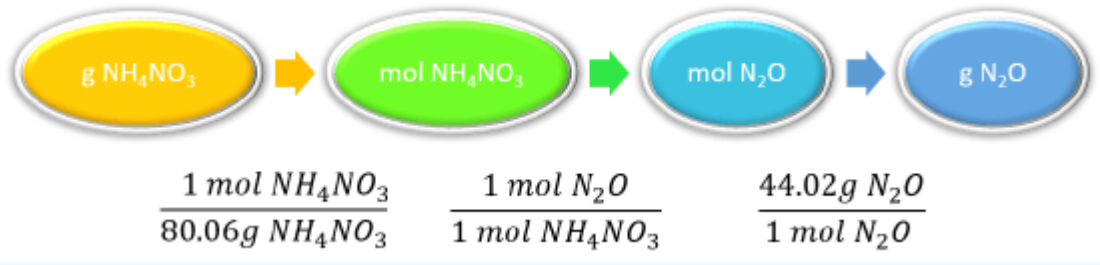
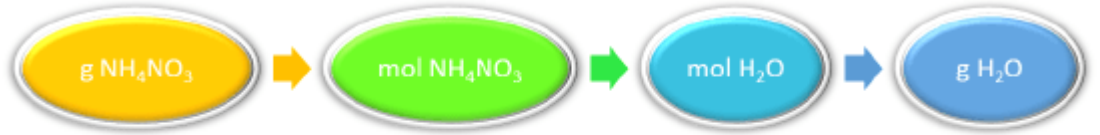
Ammonium nitrate decomposes to dinitrogen monoxide and water according to the following equation.

$$\mathrm{NH_4NO_3}\,(s) \rightarrow \mathrm{N_2O}\,(g) + 2\mathrm{H_2O}\,(l)$$

In a certain experiment, $45.7\ \mathrm{g}$ of ammonium nitrate is decomposed. Find the mass of each of the products formed.

Example 5.4.7: Steps for Problem Solving the Decomposition of Ammonium Nitrate

Steps for Problem Solving	Example 5.4.2
Identify the "given"information and what the problem is asking you to "find."	Given: $45.7\ \mathrm{g}\ \mathrm{NH_4NO_3}$ Find: Mass $\mathrm{N_2O} = ?\ \mathrm{g}$ Mass $\mathrm{H_2O} = ?\ \mathrm{g}$

Steps for Problem Solving	Example 5.4.2
List other known quantities	1 mol $NH_4NO_3 = 80.06\ g/mol$ 1 mol $N_2O = 44.02\ g/mol$ 1 mol $H_2O = 18.02\ g/mol$ 1 mol NH_4NO_3 to 1 mol N_2O to 2 mol H_2O
Prepare two concept maps and use the proper conversion factor.	 $\frac{1\ mol\ NH_4NO_3}{80.06g\ NH_4NO_3}$ $\frac{1\ mol\ N_2O}{1\ mol\ NH_4NO_3}$ $\frac{44.02g\ N_2O}{1\ mol\ N_2O}$  $\frac{1\ mol\ NH_4NO_3}{80.06g\ NH_4NO_3}$ $\frac{2\ mol\ H_2O}{1\ mol\ NH_4NO_3}$ $\frac{18.02g\ H_2O}{1\ mol\ H_2O}$
Cancel units and calculate.	$45.7\ \text{g}\ NH_4NO_3 \times \frac{1\ \text{mol}\ NH_4NO_3}{80.06\ \text{g}\ NH_4NO_3} \times \frac{1\ \text{mol}\ N_2O}{1\ \text{mol}\ NH_4NO_3} \times \frac{44.02\ \text{g}\ N_2O}{1\ \text{mol}\ N_2O} = 25.1\ \text{g}\ N_2O$ $45.7\ \text{g}\ NH_4NO_3 \times \frac{1\ \text{mol}\ NH_4NO_3}{80.06\ \text{g}\ NH_4NO_3} \times \frac{2\ H_2O}{1\ \text{mol}\ NH_4NO_3} \times \frac{18.02\ \text{g}\ H_2O}{1\ \text{mol}\ H_2O} = 20.6\ \text{g}\ H_2O$
Think about your result.	The total mass of the two products is equal to the mass of ammonium nitrate which decomposed, demonstrating the law of conservation of mass. Each answer has three significant figures.

Exercise 5.4.6: Carbon Tetrachloride

Methane can react with elemental chlorine to make carbon tetrachloride (CCl_4). The balanced chemical equation is as follows.

$$CH_4\,(g) + 4\,Cl_2\,(g) \longrightarrow CCl_2\,(l) + 4\,HCl\,(l)$$

How many grams of HCl are produced by the reaction of 100.0g of CH_4?

Answer available at the end of this section.

Summary

- Calculations involving conversions between moles of a substance and the mass of that substance are described.

- The balanced chemical reaction can be used to determine molar and mass relationships between substances.

Contributors and Attributions

- TextMap: The Basics of GOB Chemistry (Ball et al.)
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- Henry Agnew (UC Davis)

Answers

Exercise 5.4.2: Calcium Oxide

420.60 g

Exercise 5.4.3: Nitrogen Gas

210 g

Exercise 5.4.4: Generation of Aluminum Oxide

0.442 mol Al_2O_3

Exercise 5.4.5

3.14 mol H_2O

$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$; 2.48 mol H_2O

Exercise 5.4.6: Carbon Tetrachloride

908.7g HCl

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5.5: Solutions

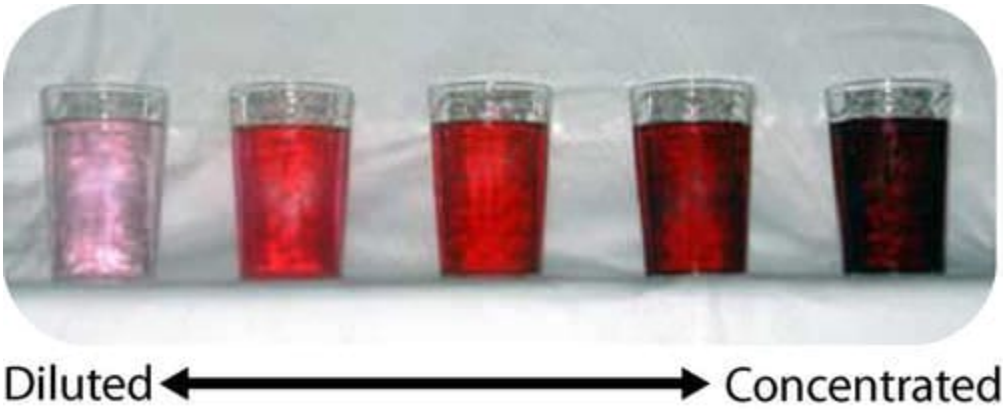
Learning Objectives

- Learn some terminology involving solutions.
- Express the amount of solute in a solution in various concentration units.

When one substance dissolves into another, a solution is formed. A **solution** *is a homogenous mixture consisting of a solute dissolved into a solvent*. The **solute** *is the substance that is being dissolved,* while the **solvent** *is the dissolving medium*. Solutions can be formed with many different types and forms of solutes and solvents. In this chapter, we will focus on solution where the solvent is water. An **aqueous solution** *is water that contains one or more dissolved substance*. The dissolved substances in an aqueous solution may be solids, gases, or other liquids.

In order to be a true solution, a mixture must be stable. When sugar is fully dissolved into water, it can stand for an indefinite amount of time, and the sugar will not settle out of the solution. Further, if the sugar-water solution is passed through a filter, it will remain with the water. This is because the dissolved particles in a solution are very small, usually less than 1 nm in diameter. Solute particles can be atoms, ions, or molecules, depending on the type of substance that has been dissolved. Water typically dissolves most ionic compounds and polar molecules. Nonpolar molecules, such as those found in grease or oil, do not dissolve in water.

Solution Concentrations



Solutions of a red dye in water from the most dilute (on the left) to the most concentrated (on the right).

A **concentrated** solution is one in which there is a large amount of solute in a given amount of solvent. A **dilute** solution is one in which there is a small amount of solute in a given amount of solvent. A dilute solution is a concentrated solution that has been, in essence, watered down. Think of the frozen juice containers you buy in the grocery store. What you have to do is take the frozen juice from inside these containers and usually empty it into 3 or 4 times the container size full of water to mix with the juice concentrate and make your container of juice. Therefore, you are diluting the concentrated juice. When we talk about solute and solvent, the concentrated solution

has a lot of solute versus the dilute solution that would have a smaller amount of solute.

The terms "concentrated" and "dilute" provide qualitative methods of describing concentration. Although qualitative observations are necessary and have their place in every part of science, including chemistry, we have seen throughout our study of science that there is a definite need for quantitative measurements in science. This is particularly true in solution chemistry. In this section, we will explore some quantitative methods of expressing solution concentration.

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. When we say that vinegar is 5% acetic acid in water, we are giving the concentration. If we said the mixture was 10% acetic acid, this would be more concentrated than the vinegar solution and we know exactly by how much.

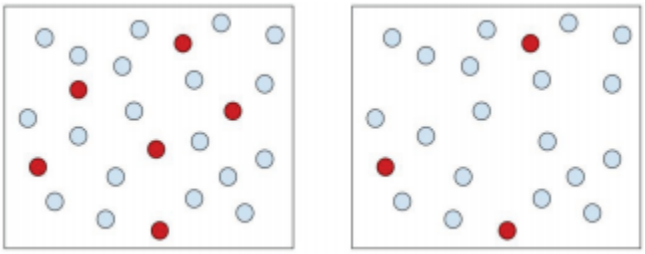


Figure 5.5.2 *The solution on the left is more concentrated than the solution on the right because there is a greater ratio of solute (red balls) to solvent (blue balls) particles. The solution particles are closer together. The solution on the right is more dilute (less concentrated). (CC-SA-BY-3.0 Tracy Poulsen).*

Molarity

One way of expressing concentration is to give the number of moles of solute per unit volume of solution. Of all the quantitative measures of concentration, molarity is the one used most frequently by chemists. **Molarity** is defined as the number of moles of solute per liter of solution.

$$\text{molarity} = \frac{\text{number of moles of solute}}{\text{number of liters of solution}} \tag{5.5.1}$$

The symbol for molarity is M or moles/liter. Chemists also use square brackets to indicate a reference to the molarity of a substance. For example, the expression $[\mathrm{Ag^+}]$ refers to the molarity of the silver ion in solution. Solution concentrations expressed in molarity are the easiest to calculate with but the most difficult to make in the lab. 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.

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

$$\frac{1.5\ \text{mol NaCl}}{0.500\ \text{L solution}} = 3.0\ \text{M NaCl}$$

Sometimes (aq) is added when the solvent is water, as in “3.0 M NaCl (aq).” You would read as "a 3.00 ***molar*** sodium chloride solution," meaning that there are 3.00 moles of NaOH dissolved per one liter of solution.

> Be sure to note that molarity is calculated as the total volume of the **entire** solution, not just volume of solvent! The solute contributes to total volume.

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?

First, convert the mass of solute to moles using the molar mass of HCl (36.5 g/mol):

$$22.4\ \cancel{g HCl} \times \frac{1\ mol\ HCl}{36.5\ \cancel{g HCl}} = 0.614\ mol\ HCl$$

Now we can use the definition of molarity to determine a concentration:

$$M\ =\ \frac{0.614\ mol\ HCl}{1.56 L\ solution} = 0.394\ M HCl$$

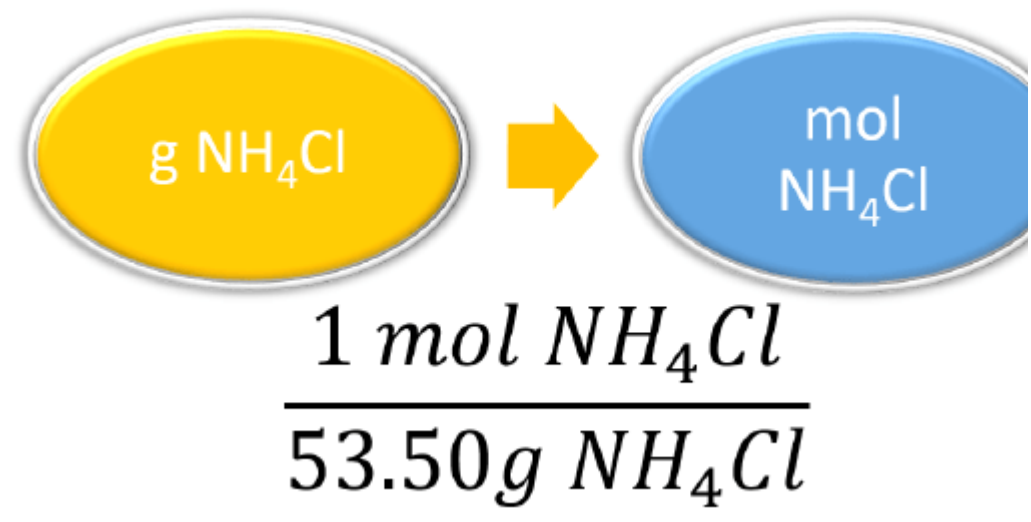
Before a molarity concentration can be calculated, the amount of the solute must be expressed in moles, and the volume of the solution must be expressed in liters, as demonstrated in the following example.

Example 5.5.1

A solution is prepared by dissolving $42.23\ \text{g}$ of NH_4Cl into enough water to make $500.0\ \text{mL}$ of solution. Calculate its molarity.

Solution

Example 5.5.1: Steps for Problem Solving Molarity

Steps for Problem Solving	Example
Identify the "given"information and what the problem is asking you to "find."	Given: Mass $= 42.23\ \text{g}\ \text{NH}_4\text{Cl}$ Volume solution $= 500.0\ \text{mL} = 0.5000\ \text{L}$ Find: Molarity = ? M
List other known quantities.	Molar mass $\text{NH}_4\text{Cl} = 53.50\ \text{g/mol}$
Plan the problem.	1. The mass of the ammonium chloride is first converted to moles.  2. Then the molarity is calculated by dividing by liters. Note the given volume has been converted to liters $\text{M} = \frac{\text{mol NH}_4\text{Cl}}{\text{L solution}}$

Steps for Problem Solving	Example
Cancel units and calculate.	Now substitute the known quantities into the equation and solve. $42.23\ \cancel{\text{g NH}_4\text{Cl}} \times \frac{1\ \text{mol}\ \cancel{\text{NH}_4\text{Cl}}}{53.50\ \text{g NH}_4\text{Cl}} = 0.7893\ \text{mol NH}_4\text{Cl}$ $\frac{0.7893\ \text{mol NH}_4\text{Cl}}{0.5000\ \text{L solution}} = 1.579\ \text{M}$
Think about your result.	The molarity is $1.579\ \text{M}$, meaning that a liter of the solution would contain $1.579\ \text{mol NH}_4\text{Cl}$. Four significant appropriate.

Exercise 5.5.1

What is the molarity of a solution made when 66.2 g of $C_6H_{12}O_6$ are dissolved to make 235 mL of solution?

Answer available at the end of this section.

Exercise 5.5.2

What is the concentration, in mol/L, where $137\ \text{g}$ of NaCl has been dissolved in enough water to make $500\ \text{mL}$ of solution?

Answer available at the end of this section.

Figure 5.5.1 illustrates how a solution is prepared with the measured amount of a solid solute and the desired final volume of the solution.

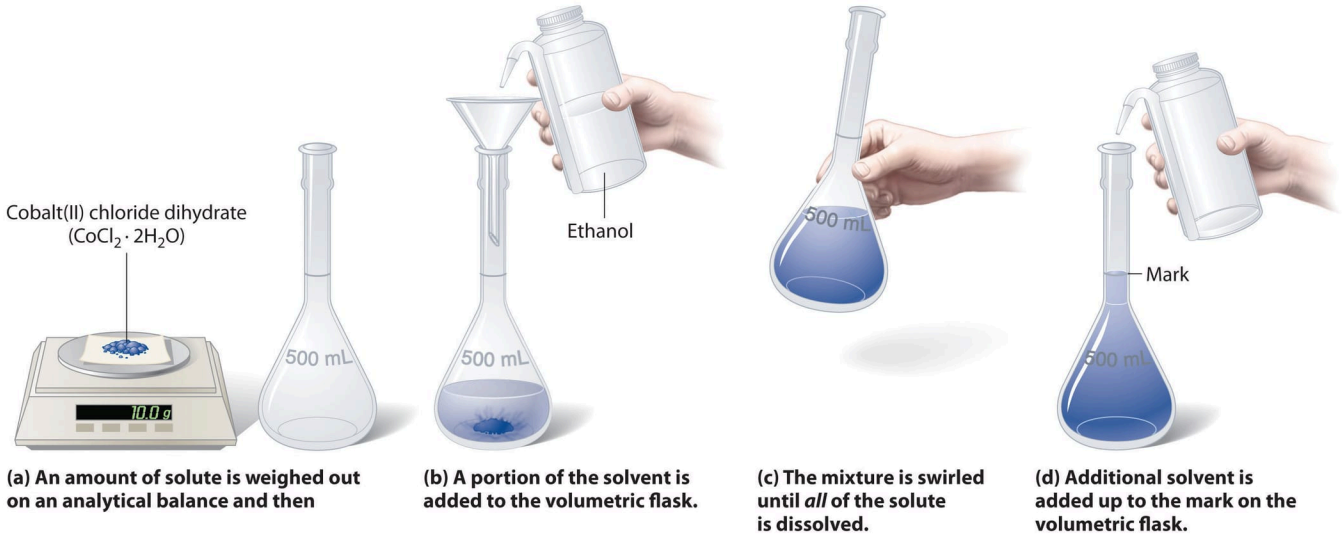


Figure 5.5.3: Preparation of a solution of known concentration using a solid solute.

(a) An amount of solute is weighted out on an analytical balance, (b) a portion of the solvent is added to the volumetric flask. (c) the mixture is swirled until all of the solute is dissolved. (d) additional solvent is added up to the mark on the volumetric flask.

Percent Concentrations

There are several ways of expressing the concentration of a solution by using a percentage. The percent can further be determined in one of two ways: (1) the ratio of the mass of the solute divided by the mass of the solution or (2) the ratio of the volume of the solute divided by the volume of the solution.

Percent by Volume

The percentage of solute in a solution can more easily be determined by volume when the solute and solvent are both liquids. The volume of the solute divided by the volume of the solution expressed as a percent yields the percent by volume $\left(\frac{\text{volume}}{\text{volume}}\right)$ of the solution. If a solution is made by adding $40\ \text{mL}$ of ethanol to $20\ \text{mL}$ of water, the percent by volume is:

$$\text{Percent by volume} = \frac{\text{volume of solute}}{\text{volume of solution}} \times 100\% \tag{5.5.4}$$

$$= \frac{40\ \text{mL ethanol}}{240\ \text{mL solution}} \times 100\% \tag{5.5.5}$$

$$= 16.7\%\ \text{ethanol} \tag{5.5.6}$$

Frequently, ingredient labels on food products and medicines have amounts listed as percentages (see figure below).

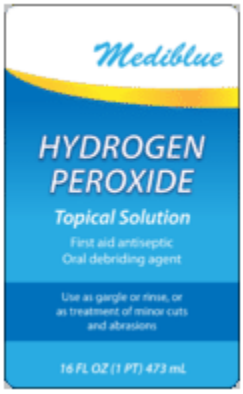


Figure $5.5.4$ Hydrogen peroxide is commonly sold as *a* 3% *by volume solution for use as a disinfectant.*

Percent by Mass

The mass/mass percent (% m/m) is defined as the mass of a solute divided by the mass of a solution times 100:

$$\%\ \text{m/m} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

mass of solution = mass of solute + mass solvent

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.

Suppose that a solution was prepared by dissolving $25.0\ \text{g}$ of sugar into $100.0\ \text{g}$ of water.

The mass of the solution is

mass of solution = 25.0g sugar + 100.0g water = 125.0 g

The percent by mass would be calculated by:

$$\text{Percent by mass} = \frac{25.0\ \text{g sugar}}{125.0\ \text{g solution}} \times 100\% = 20.0\%\ \text{sugar}$$

Example 5.5.2

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 5.5.3

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.

Using Mass Percent in Calculations

Sometimes you may want to make up a particular mass of solution of a given percent by mass and need to calculate what mass of the solute to use. Using mass percent as a conversion can be useful in this type of problem. The mass percent can be expressed as a conversion factor in the form $\frac{g\ \text{solute}}{100\ \text{gsolution}}$ or $\frac{100\ \text{gsolution}}{g\ \text{solute}}$

For example, if you need to make $3000.0\ \mathrm{g}$ of a 5.00% solution of sodium chloride, the mass of solute needs to be determined.

Solution

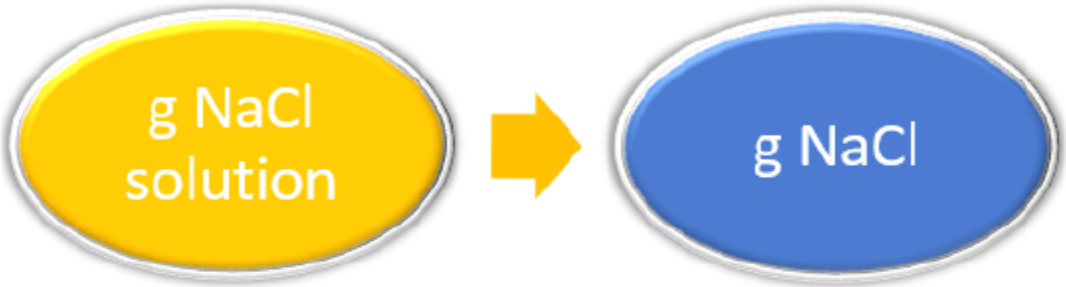
Given: 3000.0 g NaCl solution

5.00% NaCl solution

Find: mass of solute = ? g NaCl

Other known quantities: 5.00 g NaCl is to 100 g solution

The appropriate conversion factor (based on the given mass percent) can be used follows:



$$\frac{5.00\ g\ NaCl}{100\ g\ NaCl\ solution}$$

To solve for the mass of NaCl, the given mass of solution is multiplied by the conversion factor.

$$gNaCl = 3,000.0\ \cancel{g\ NaCl\ solution} \times \frac{5.00\ g\ NaCl}{100\ \cancel{g\ NaCl\ solution}} = 150.0g\ NaCl$$

You would need to weigh out $150\ \text{g}$ of NaCl and add it to $2850\ \text{g}$ of water. Notice that it was necessary to subtract the mass of the $\text{NaCl}\ (150\ \text{g})$ from the mass of solution $(3000\ \text{g})$ to calculate the mass of the water that would need to be added.

Exercise 5.5.4

What is the amount (in g) of hydrogen peroxide (H_2O_2) needed to make a 6.00 kg , 3.00 % (by mass) H_2O_2 solution?

Answer

180. g H_2O_2

Summary

- Solutions are composed of a solvent (major component) and a solute (minor component).
- Concentration of solutions can be more precisely expressed in terms of molarity, percent by volume, and percent by mass.

Contributors and Attributions

-
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Answers

Exercise 5.5.1

1.57 M $C_6H_{12}O_6$

Exercise 5.5.2

4.69 M NaCl

Exercise 5.5.3

7.90 %

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5.6: Section 6-

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6: GASES, LIQUIDS, SOLIDS, ... AND INTERMOLECULAR FORCES

6.1: Solids, Liquids, and Gases

6.2: Comparing Ionic and Molecular Substances

6.3: Forces between Molecules

6.4: Forces in Solutions

6.5: Gases- The Kinetic-Molecular Theory

6.6: The Simple Gas Laws

6.7: The Ideal Gas Law

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6.1: Solids, Liquids, and Gases

Learning Objectives

- Describe the different states of matter.
- Describe the different changes that occur between solid, liquid, and gas.

Matter can exist in one of several different states, including a gas, liquid, or solid state. The amount of energy in molecules of matter determines the **state of matter**.

- A **gas** is a state of matter in which atoms or molecules have enough energy to move freely. The molecules come into contact with one another only when they randomly collide.
- A **liquid** is a state of matter in which atoms or molecules are constantly in contact but have enough energy to keep changing positions relative to one another.
- A **solid** is a state of matter in which atoms or molecules do not have enough energy to move. They are constantly in contact and in fixed positions relative to one another.

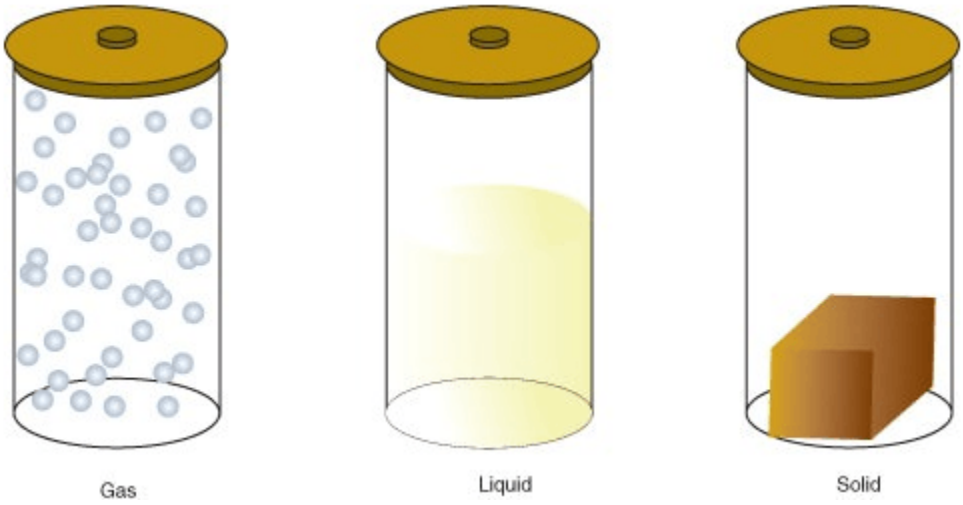


Figure 6.1.1: States of Matter. All three containers contain a substance with the same mass, but the substances are in different states. In the left-hand container, the substance is a gas, which has spread to fill its container. It takes both the shape and volume of the container. In the middle container, the substance is a liquid, which has spread to take the shape of its container but not the volume. In the right-hand container, the substance is a solid, which takes neither the shape nor the volume of its container.

In Figure 6.1.2, all three phases are shown at the submicroscopic level in animations. Notice how the movement and freedom of molecules steadily increases as attractive forces decrease from solid to liquid to gas phase.

Solid matter Liquid matter Gas

SOLID LIQUID GAS

Figure 6.1.2 *Animation of all three phases at the submicroscopic level.*

The change from solid to liquid usually does not significantly change the volume of a substance. However, the change from a liquid to a gas significantly increases the volume of a substance, by a factor of 1,000 or more. Figures 6.1.3 and 6.1.4 show the differences among solids, liquids, and gases at the molecular level, while Table 6.1.1 lists the different characteristics of these states.

Table 6.1.1 Characteristics of the Three States of Matter

Characteristic	Solid	Liquid	Gas
shape	definite	indefinite	indefinite
volume	definite	definite	indefinite
relative intermolecular interaction strength	strong	moderate	weak
relative particle positions	in contact and fixed in place	in contact but not fixed	not in contact, random positions

Example 6.1.1

What state or states of matter does each statement, describe?

a. This state has a definite volume.
b. This state has no definite shape.
c. This state allows the individual particles to move about while remaining in contact.

Solution

a. This statement describes either the liquid state or the solid state.
b. This statement describes either the liquid state or the gas state.
c. This statement describes the liquid state.

Exercise 6.1.1

What state or states of matter does each statement describe?

a. This state has individual particles in a fixed position with regard to each other.
b. This state has individual particles far apart from each other in space.
c. This state has indefinite shape.

Answer a available at the end of this section.

Phase Changes

A phase change is a physical process in which a substance goes from one phase to another. Usually the change occurs when adding or removing heat at a particular temperature, known as the melting point or the boiling point of the substance. The **melting point** is the temperature at which the substance goes from a solid to a liquid (or from a liquid to a solid). The **boiling point** is the temperature at which a substance goes from a liquid to a gas (or from a gas to a liquid). The nature of the phase change depends on the direction of the heat transfer. Heat going *into* a substance changes it from a solid to a liquid or a liquid to a gas. Removing heat *from* a substance changes a gas to a liquid or a liquid to a solid.

Two key points are worth emphasizing. First, at a substance's melting point or boiling point, two phases can exist simultaneously. Take water (H_2O) as an example. On the Celsius scale, H_2O has a melting point of 0°C and a boiling point of 100°C. At 0°C, both the solid and liquid phases of H_2O can coexist. However, if heat is added, some of the solid H_2O will melt and turn into liquid H_2O. If heat is removed, the opposite happens: some of the liquid H_2O turns into solid H_2O. A similar process can occur at 100°C: adding heat increases the amount of gaseous H_2O, while removing heat increases the amount of liquid H_2O (Figure 6.1.3).

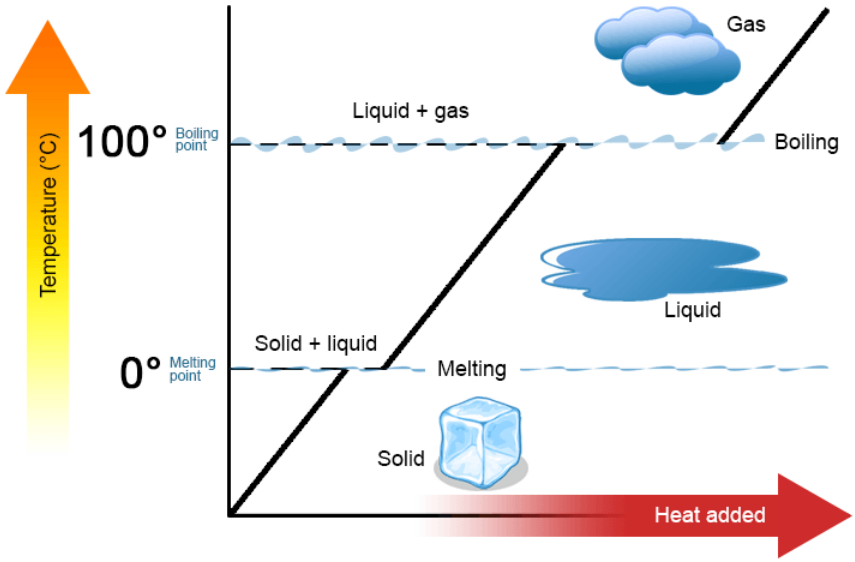


Figure 6.1.3: Heating curve for water. As heat is added to solid water, the temperature increases until it reaches 0 °C, *the melting point. At this point, the phase change, added heat goes into changing the state from a solid to liquid. Only when this phase change is complete, the temperature can increase. (CC BY 3.0 Unported; Community College Consortium for Bioscience Credentials).*

> Water is a good substance to use as an example because many people are already familiar with it. Other substances have melting points and boiling points as well.

Second, as shown in Figure 6.1.3, **the temperature of a substance does not change** as the substance goes **from one phase to another**. In other words, phase changes are isothermal (isothermal means "constant temperature"). Again, consider H_2O as an example. Solid water (ice) can exist at 0°C. If heat is added to ice at 0°C, some of the solid changes phase to make liquid, which is also at 0°C. Remember, the solid and liquid phases of H_2O can coexist at 0°C. Only after all of the solid has melted into liquid does the addition of heat change the temperature of the substance.

Summary of Phase Changes

All of the changes of state that occur between solid, liquid, and gas are summarized in the diagram in the figure below. **Freezing** is the opposite of melting, and both represent the equilibrium between the solid and liquid states. **Evaporation** occurs when a liquid turns to a gas. **Condensation** is the opposite of vaporization, and both represent the equilibrium between the liquid and gas states. **Deposition** is the opposite of sublimation, and both represent the equilibrium between the solid and gas states.

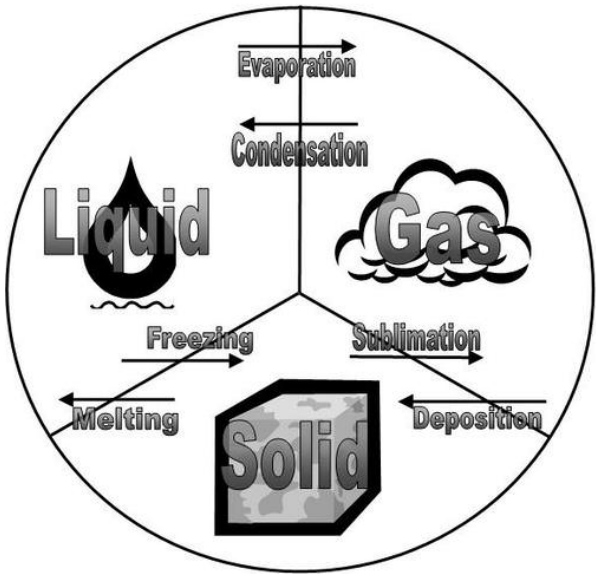


Figure 6.1.4: Solid, liquid, and gas states with the terms for each change of state that occurs between them.
Liquid evaporates into gas in freezes into a solid; gas condenses into a liquid depositions into a solid; solids melt into a liquid and sublimation into a gas

Summary

- Solids, liquids, and gases are different phases that have their own unique properties.
- A change of state (or phase chnage) can be brought about by putting heat into a system or removing it from the system.

Contributors and Attributions

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- Libretexts: The Basics of GOB (Ball et.al.)
- Marisa Alviar-Agnew (Sacramento City College)
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Answers

Exercise 6.1.1

solid
gas
liquid or gas

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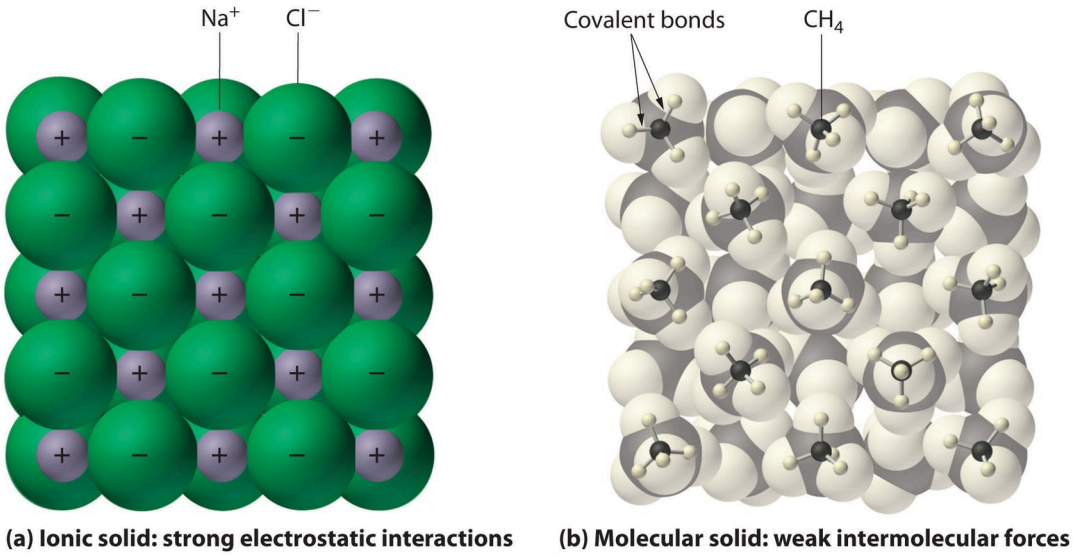
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6.2: Comparing Ionic and Molecular Substances

Learning Objectives

- Know the physical properties of ionic and molecular substances.

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



(a) The positively and negatively charged ions in an ionic solid such as sodium chloride (NaCl) are held together by strong electrostatic interactions. (b) In this representation of the packing of methane (CH4) molecules in solid methane, a prototypical molecular solid, the methane molecules are held together in the solid only by relatively weak intermolecular forces, even though the atoms within each methane molecule are held together by strong covalent bonds.

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** between molecules is far less than the energy required to break the ionic bonds in a crystalline ionic compound (Figure 6.2.1) . Ionic solids typically melt at high temperatures and boil at even higher temperatures. For example, sodium chloride melts at 801 °C and boils at 1413 °C. (As a comparison, the molecular compound water melts at 0 °C and boils at 100 °C.). The water solubility of molecular compounds is variable and depends primarily on the type of intermolecular forces involved.

Figure 6.2.1 Interactions in Ionic and Covalent Solids.

Since molecular compounds are composed of neutral molecules, their electrical conductivity is generally quite poor, whether in the solid or liquid state. In solid form, an ionic compound is not electrically conductive because its ions are unable to flow (“electricity” is the flow of charged particles). When molten, however, it can conduct electricity because its ions are able to move freely through the liquid (Figure 6.2.2; Video 6.2.1).

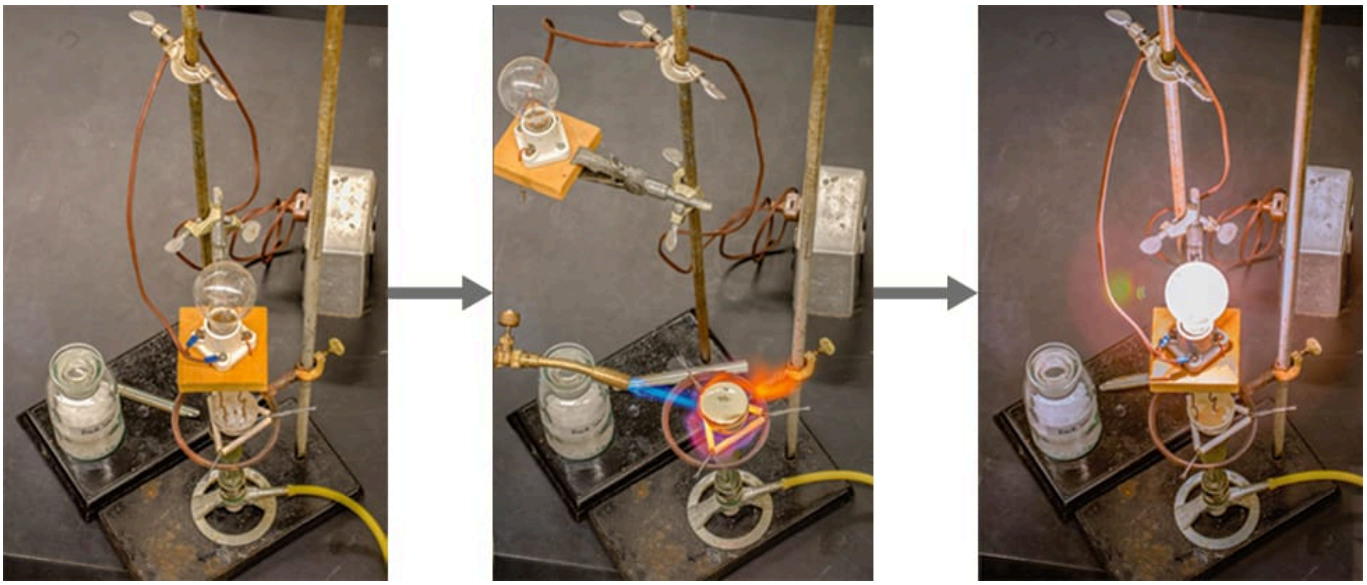


Figure 6.2.2 Sodium chloride melts at 801 °C and conducts electricity when molten. (credit: modification of work by Mark Blaser and Matt Evans)

This figure shows three photos connected by right-facing arrows. The first shows a light bulb as part of a complex lab equipment setup. The light bulb is not lit. The second photo shows a substances being heated or set on fire. The third shows the light bulb again which is lit.

Conductivity of Molten Salt

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 6.2.1 Watch this video to see a mixture of salts melt and conduct electricity.

The table below summarizes some of the differences between ionic and molecular compounds.

Table 6.2.1 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

Table 6.2.1 Comparison of Ionic and Molecular Compounds		
Electrical conductivity	Good when molten or in solution	Poor

One type of molecular compound behaves quite differently than that described so far. A covalent network solid is a compound in which all of the atoms are connected to one another by covalent bonds. Diamond is composed entirely of carbon atoms, each bonded to four other carbon atoms in a tetrahedral geometry. Melting a covalent network solid is not accomplished by overcoming the relatively weak intermolecular forces. Rather, all of the covalent bonds must be broken, a process that requires extremely high temperatures. Diamond, in fact, does not melt at all. Instead, it vaporizes to a gas at temperatures above $3500^{\circ}\mathrm{C}$.

Summary

- The physical properties of a material are affected by the intermolecular forces holding the molecules together.
- Ionic compounds usually form hard crystalline solids with high melting points. Covalent molecular compounds, in contrast, consist of discrete molecules held together by weak intermolecular forces and can be gases, liquids, or solids at room temperature and pressure.
- Ionic compounds in molten form or in solution can conduct electricity while molecular compounds do not..

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6.3: Forces between Molecules

Learning Objectives

- Describe the types of intermolecular forces possible between atoms or molecules in condensed phases (dispersion forces, dipole-dipole attractions, and hydrogen bonding)
- Identify the types of intermolecular forces experienced by specific molecules based on their structures

Under appropriate conditions, the attractions between all gas molecules will cause them to form liquids or solids. This is due to intermolecular forces, not *intra*molecular forces. *Intra*molecular forces are those *within* the molecule that keep the molecule together, for example, the bonds between the atoms. *Inter*molecular forces are the attractions *between* molecules, which determine many of the physical properties of a substance. Figure 6.3.1 illustrates these different molecular forces. The strengths of these attractive forces vary widely, though usually the IMFs between small molecules are weak compared to the intramolecular forces that bond atoms together within a molecule. For example, to overcome the IMFs in one mole of liquid HCl and convert it into gaseous HCl requires only about 17 kilojoules. However, to break the covalent bonds between the hydrogen and chlorine atoms in one mole of HCl requires about 25 times more energy—430 kilojoules.

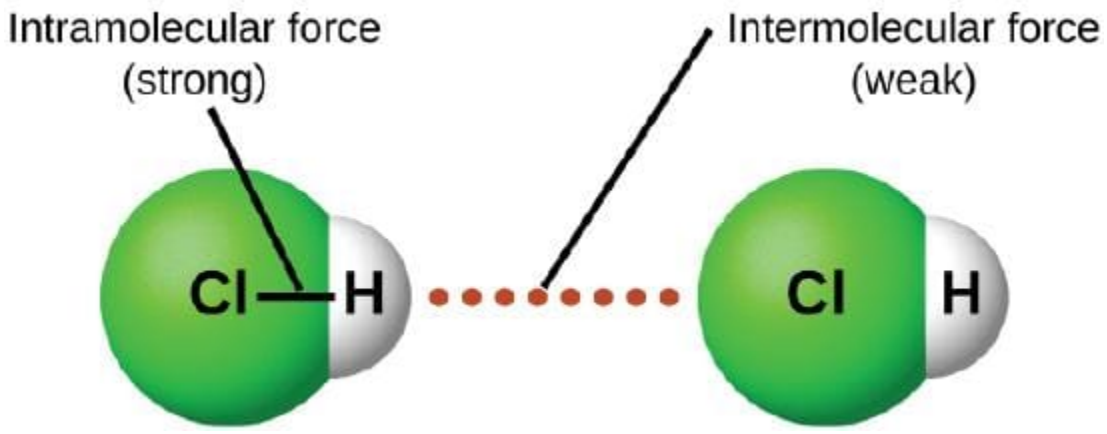


Figure 6.3.1 Intramolecular forces keep a molecule intact. Intermolecular forces hold multiple molecules together and determine many of a substance's properties.

An image is shown in which two molecules composed of a green sphere labeled "C l" connected on the right to a white sphere labeled "H" are near one another with a dotted line labeled "Intermolecular force (weak)" drawn between them. A line connects the two spheres in each molecule and the line is labeled "Intramolecular force (strong)."

Dipole–Dipole Forces

Dipole-dipole forces *are the attractive forces that occur between polar molecules* (see figure below). A molecule of hydrogen chloride has a partially positive hydrogen atom and a partially negative chlorine atom. A collection of many hydrogen chloride molecules will align themselves so that the oppositely charged regions of neighboring molecules are near each other.

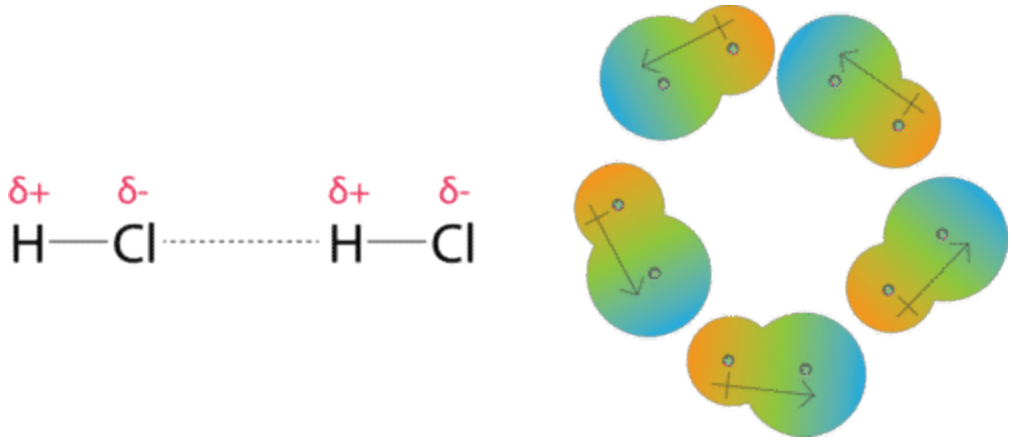


Figure 6.3.2 *Dipole-dipole forces result from the attraction between the positive end of one dipole and the negative end of a neighboring dipole. Dipole-dipole forces are similar to ionic bonds, but because they involve only partial charges, they are much weaker.*

Dipole-dipole forces in hydrogen chloride

The strength of the intermolecular interactions increases as the dipole moment of the molecules increases, as shown in Table 6.3.1.

Table 6.3.1: Relationships between the Dipole Moment and the Boiling Point for Organic Compounds of Similar Molar Mass

Compound	Molar Mass (g/mol)	Dipole Moment (D)	Boiling Point (K)
C_3H_6 (cyclopropane)	42	0	240
CH_3OCH_3 (dimethyl ether)	46	1.30	248
CH_3CN (acetonitrile)	41	3.9	355

The attractive energy between two ions is proportional to 1/r, whereas the attractive energy between two dipoles is proportional to 1/r6.

Example 6.3.1 Dipole-Dipole Forces and Their Effects

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

Solution

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

A common method for preparing oxygen is the decomposition

Exercise 6.3.1

Predict which will have the higher boiling point: ICl or $\mathrm{Br_2}$. Explain your reasoning.

Answer available at the end of this section.

Dispersion Forces

Dispersion forces are the weakest of all intermolecular forces. They are often called London forces after Fritz London (1900 -

1954), who first proposed their existence in 1930. **London dispersion forces** *are intermolecular forces that occur between all atoms and molecules due to the random motion of electrons.*

For example, the electron cloud of a helium atom contains two electrons, and, when averaged over time, these electrons will distribute themselves evenly around the nucleus. However, at any given moment, the electron distribution may be uneven, resulting in an *instantaneous dipole*. This weak and temporary dipole can subsequently influence neighboring helium atoms through electrostatic attraction and repulsion. The formation of an induced dipole is illustrated below.



Figure 6.3.3 *Random fluctuations in the electron density within the electron cloud of a helium atom results in a short-lived ("instantaneous") dipole. The attractive force between instantaneous dipoles and the resulting induced dipoles in neighboring molecules is called the London dispersion force.*

From left to right: instantaneous uneven distribution of electrons in helium atom; nonpolar helium atom; instantaneous dipole; induce dipole on neighboring helium atom press resulting in an attractive force

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 6.3.1.

Table 6.3.2: Melting and Boiling Points of the Halogens

Halogen	Molar Mass	Atomic Radius	Melting Point	Boiling Point
fluorine, F_2	38 g/mol	72 pm	53 K	85 K
chlorine, Cl_2	71 g/mol	99 pm	172 K	238 K
bromine, Br_2	160 g/mol	114 pm	266 K	332 K
iodine, I_2	254 g/mol	133 pm	387 K	457 K
astatine, At_2	420 g/mol	150 pm	575 K	610 K

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

For similar substances, London dispersion forces get stronger with increasing atomic or molecular size.

The strengths of London dispersion forces also depend significantly on molecular shape because shape determines how much of one molecule can interact with its neighboring molecules at any given time. For example, part (b) in Figure 6.3.4 shows 2,2-dimethylpropane (neopentane) and *n*-pentane, both of which have the empirical formula C_5H_{12}. Neopentane is almost spherical, with a small surface area for intermolecular interactions, whereas *n*-pentane has an extended conformation that enables it to come into close contact with other *n*-pentane molecules. As a result, the boiling point of neopentane (9.5°C) is more than 25°C lower than the boiling point of *n*-pentane (36.1°C).

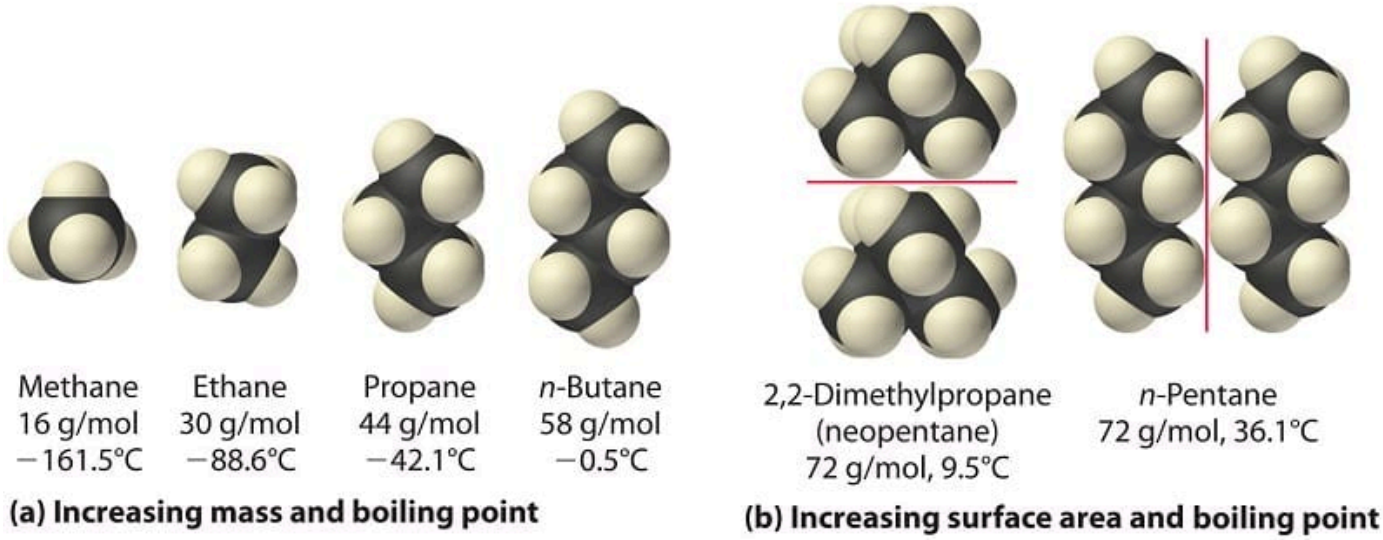


Figure 6.3.4 Mass and Surface Area Affect the Strength of London Dispersion Forces. (a) In this series of four simple alkanes, larger molecules have stronger London forces between them than smaller molecules and consequently higher boiling points. (b) Linear *n*-pentane molecules have a larger surface area and stronger intermolecular forces than spherical neopentane molecules. As a result, neopentane is a gas at room temperature, whereas *n*-pentane is a volatile liquid.

London dispersion forces

All molecules, whether polar or nonpolar, are attracted to one another by London dispersion forces in addition to any other attractive forces that may be present.

Example 6.3.2 London Forces and Their Effects

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.

Given: compounds

Asked for: order of increasing boiling points

Strategyy:

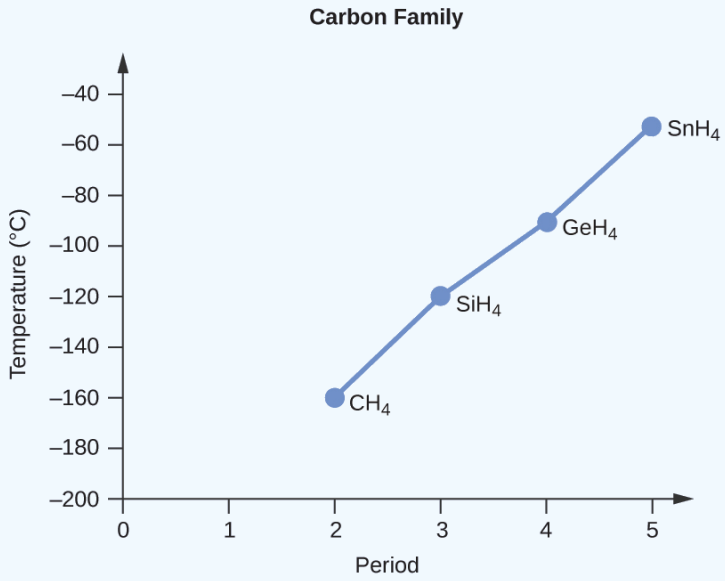
Determine the intermolecular forces in the compound. Also, compare the molar masses and surface area of compounds with similar types of intermolecular force. The substance with the weakest forces and the lowest molar masses and least surface area have the lowest boiling point.

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:



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

Exercise 6.3.2

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.

Hydrogen Bonds

The attractive force between water molecules is an unusually strong type of dipole-dipole interaction. Water contains hydrogen atoms that are bound to a highly electronegative oxygen atom, making for very polar bonds. The partially positive hydrogen atom of one molecule is then attracted to the oxygen atom of a nearby water molecule (see figure below).

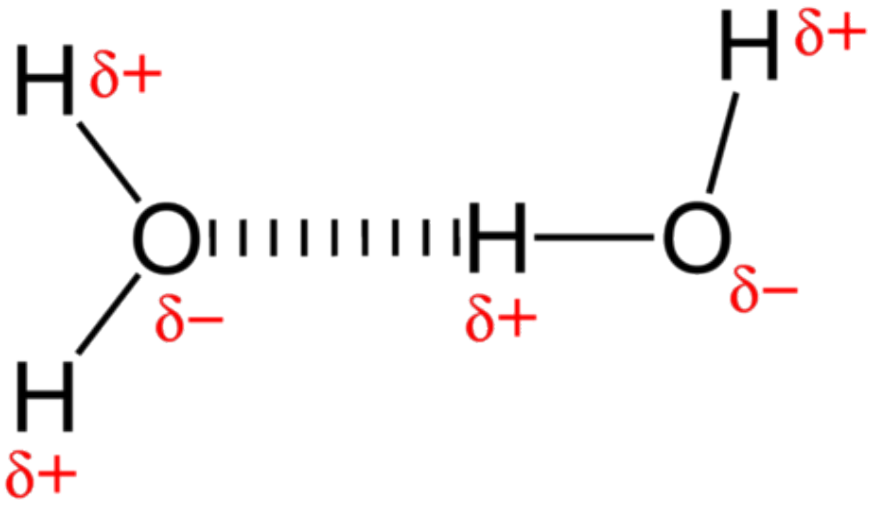


Figure 6.3.5 A hydrogen bond in water occurs between the hydrogen atom of one water molecule and the lone pair of electrons on the oxygen atom of a neighboring water molecule.

A **hydrogen bond** *is an intermolecular attractive force in which a hydrogen atom, that is covalently bonded to a small, highly electronegative atom, is attracted to a lone pair of electrons on an atom in a neighboring molecule*. Hydrogen bonds are very strong compared to other dipole-dipole interactions, but still much weaker than a covalent bond. A typical hydrogen bond is about 5% as strong as a covalent bond.

Hydrogen bonding occurs only in molecules where hydrogen is covalently bonded to one of three elements: fluorine, oxygen, or nitrogen. These three elements are so electronegative that they withdraw the majority of the electron density from the covalent bond with hydrogen, leaving the H atom very electron-deficient. Because the hydrogen atom does not have any electrons other than the ones in the covalent bond, its positively charged nucleus is almost completely exposed, allowing strong attractions to other nearby lone pairs of electrons.

The hydrogen bonding that occurs in water leads to some unusual, but very important properties. Most molecular compounds that have a mass similar to water are gases at room temperature. However, because of the strong hydrogen bonds, water molecules are able to stay condensed in the liquid state. The figure below shows how its bent shape and the presence of two hydrogen atoms per molecule allows each water molecule to hydrogen bond with several other molecules.

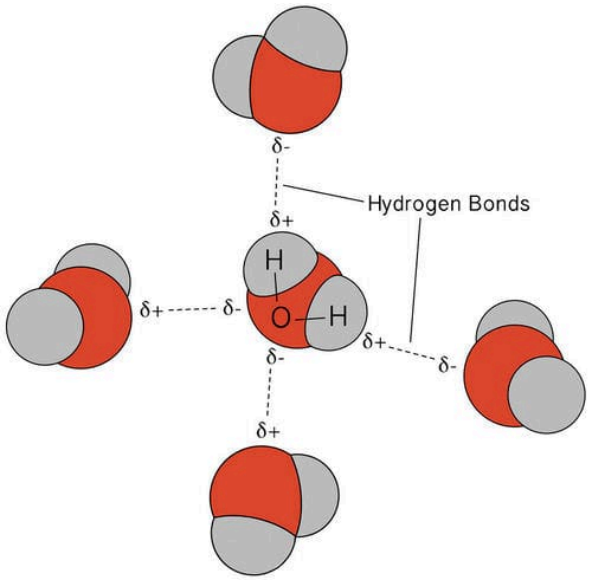


Figure 6.3.6Multiple hydrogen bonds occur simultaneously in water because of its bent shape and the presence of two hydrogen atoms per molecule.

In the liquid state, the hydrogen bonds of water can break and reform as the molecules flow from one place to another. When water is cooled, the molecules begin to slow down. Eventually, when water is frozen to ice, the hydrogen bonds become more rigid and form a well-defined network (Figure 6.3.7). The bent shape of the molecules leads to gaps in the hydrogen bonding network of ice. Ice has the very unusual property that its solid state is less dense than its liquid state. As a result, ice floats in liquid water. Virtually all other substances are denser in the solid state than in the liquid state. Hydrogen bonds also play a very important biological role in the physical structures of proteins and nucleic acids.

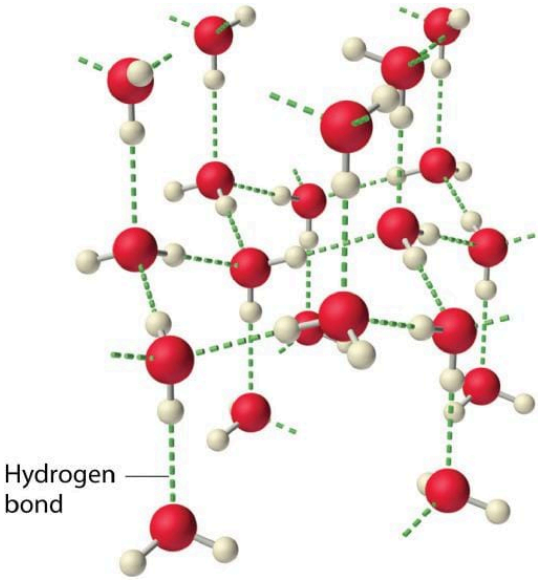


Figure 6.3.7 The Hydrogen-Bonded Structure of Ice.

Hydrogen bond formation requires both a hydrogen bond donor and a hydrogen bond acceptor.

Because ice is less dense than liquid water, rivers, lakes, and oceans freeze from the top down. In fact, the ice forms a protective surface layer that insulates the rest of the water, allowing fish and other organisms to survive in the lower levels of a frozen lake or sea. If ice were denser than the liquid, the ice formed at the surface in cold weather would sink as fast as it formed. Bodies of water would freeze from the bottom up, which would be lethal for most aquatic creatures. The expansion of water when freezing also explains why automobile or boat engines must be protected by “antifreeze” and why unprotected pipes in houses break if they are allowed to freeze.

Strength of Intermolecular Forces

Molecules with hydrogen atoms bonded to electronegative atoms such as O, N, and F tend to exhibit unusually strong intermolecular interactions due to hydrogen bonds as illustrated for the covalent hydrides of elements of groups 14–17 in Figure 6.3.8. These result in much higher boiling points than are observed for substances in which dipole-dipole forces or London dispersion forces dominate. All the polar molecules (with predominantly dipole-dipole forces) in group 16 (H_2S to H_2Te) have lower boiling points than H_2O (with hydrogen bonds). Methane and its heavier congeners in group 14 form a series whose boiling points increase smoothly with increasing molar mass. This is the expected trend in nonpolar molecules, for which London dispersion forces are the exclusive intermolecular forces. In contrast, the hydrides of the lightest members of groups 15–17 have boiling points that are more than 100°C greater than predicted on the basis of their molar masses. The effect is most dramatic for water: if we extend the straight line connecting the points for H_2Te and H_2Se to the line for period 2, we obtain an estimated boiling point of –130°C for water! Imagine the implications for life on Earth if water boiled at –130°C rather than 100°C.

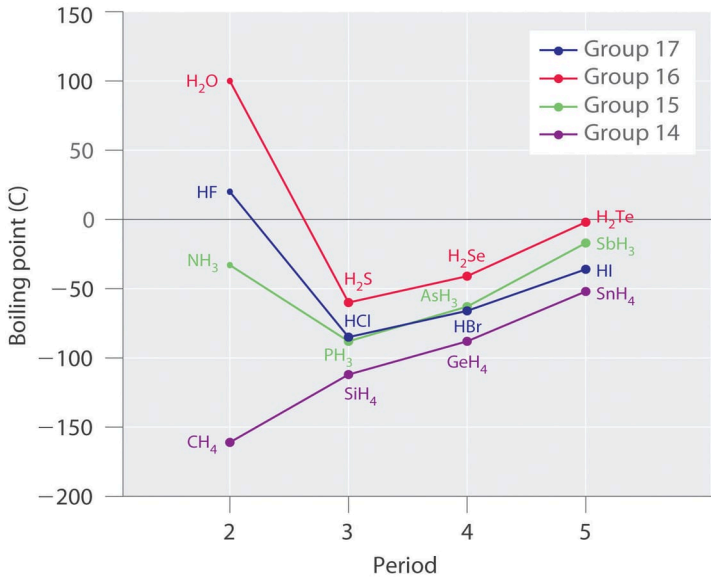


Figure 6.3.8 The Effects of Hydrogen Bonding on Boiling Points. These plots of the boiling points of the covalent hydrides of the elements of groups 14–17 show that the boiling points of the lightest members of each series for which hydrogen bonding is possible (HF, NH_3, and H_2O) are anomalously high for compounds with such low molecular masses.

Example 6.3.3

Considering CH_3OH, C_2H_6, Xe, and $(CH_3)_3N$, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Given: compounds

Asked for: formation of hydrogen bonds and structure

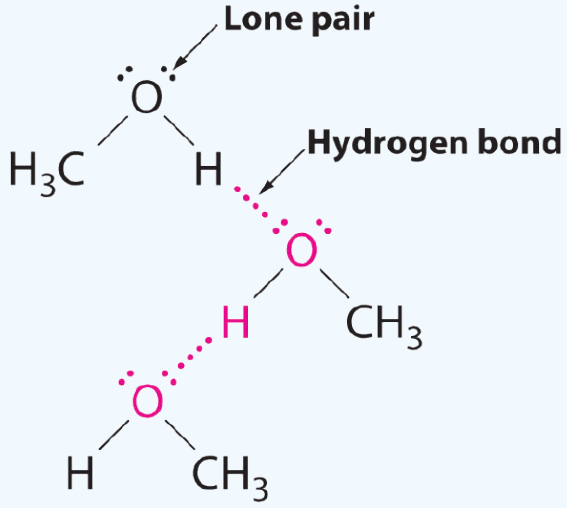
Strategy:

A. Identify the compounds with a hydrogen atom attached to O, N, or F. These are likely to be able to act as hydrogen bond donors.
B. Of the compounds that can act as hydrogen bond donors, identify those that also contain lone pairs of electrons, which allow them to be hydrogen bond acceptors. If a substance is both a hydrogen donor and a hydrogen bond acceptor, draw a structure showing the hydrogen bonding.

Solution:

A Of the species listed, xenon (Xe), ethane (C_2H_6), and trimethylamine [$(CH_3)_3N$] do not contain a hydrogen atom attached to O, N, or F; hence they cannot act as hydrogen bond donors.

B The one compound that can act as a hydrogen bond donor, methanol (CH_3OH), contains both a hydrogen atom attached to O (making it a hydrogen bond donor) and two lone pairs of electrons on O (making it a hydrogen bond acceptor); methanol can thus form hydrogen bonds by acting as either a hydrogen bond donor or a hydrogen bond acceptor. The hydrogen-bonded structure of methanol is as follows:



Hydrogen bonding in methanol

Exercise 6.3.3

Considering CH_3CO_2H, $(CH_3)_3N$, NH_3, and CH_3F, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Answer available at the end of this section.

Although hydrogen bonds are significantly weaker than covalent bonds, with typical dissociation energies of only 15–25 kJ/mol, they have a significant influence on the physical properties of a compound. Compounds such as HF can form only two hydrogen bonds at a time as can, on average, pure liquid NH_3. Consequently, even though their molecular masses are similar to that of water, their boiling points are significantly lower than the boiling point of water, which forms *four* hydrogen bonds at a time.

Example 6.3.4: Buckyballs

Arrange C_{60} (buckminsterfullerene, which has a cage structure), NaCl, He, Ar, and N_2O in order of increasing boiling points.

Given: compounds

Asked for: order of increasing boiling points

Strategy:

Identify the intermolecular forces in each compound and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution:

Electrostatic interactions are strongest for an ionic compound, so we expect NaCl to have the highest boiling point. To predict the relative boiling points of the other compounds, we must consider their polarity (for dipole–dipole interactions), their ability to form hydrogen bonds, and their molar mass (for London dispersion forces). Helium is nonpolar and by far the lightest, so it should have the lowest boiling point. Argon and N_2O have very similar molar masses (40 and 44 g/mol, respectively), but N_2O is polar while Ar is not. Consequently, N_2O should have a higher boiling point. A C_{60} molecule is nonpolar, but its molar mass is 720 g/mol, much greater than that of Ar or N_2O. Because the boiling points of nonpolar substances increase rapidly with molecular mass, C_{60} should boil at a higher temperature than the other nonionic substances. The predicted order is thus as follows, with actual boiling points in parentheses:

He (−269°C) < Ar (−185.7°C) < N_2O (−88.5°C) < C_{60} (>280°C) < NaCl (1465°C).

Exercise 6.3.4

Arrange 2,4-dimethylheptane, Ne, CS_2, Cl_2, and KBr in order of decreasing boiling points.

Answer available at the end of this section.

Example 6.3.5:

Identify the most significant intermolecular force in each substance.

a. C_3H_8
b. CH_3OH
c. H_2S

Solution

a. Although C–H bonds are polar, they are only minimally polar. The most significant intermolecular force for this substance would be dispersion forces.

b. This molecule has an H atom bonded to an O atom, so it will experience hydrogen bonding.

c. Although this molecule does not experience hydrogen bonding, the Lewis electron dot diagram and VSEPR indicate that it is bent, so it has a permanent dipole. The most significant force in this substance is dipole-dipole interaction.

Exercise 6.3.5

Identify the most significant intermolecular force in each substance.

a. HF
b. HCl

Answer a available at the end of this section.

Summary

- Molecules in liquids are held to other molecules by intermolecular interactions, which are weaker than the intramolecular interactions that hold the atoms together within molecules and polyatomic ions.
- **Dipole–dipole interactions** arise from the electrostatic interactions of the positive and negative ends of molecules with permanent dipole moments.
- **London dispersion forces** are due to the formation of **instantaneous dipole moments** in polar and nonpolar molecules as a result of short-lived fluctuations of electron charge distribution, which in turn cause the temporary formation of an **induced dipole** in adjacent molecules.
- **Hydrogen bonds** are especially strong dipole–dipole interactions between molecules that have hydrogen bonded to a highly electronegative atom, such as O, N, or F. The resulting partially positively charged H atom on one molecule (the *hydrogen bond donor*) can interact strongly with a lone pair of electrons of a partially negatively charged O, N, or F atom on adjacent molecules (the *hydrogen bond acceptor*).

Contributors and Attributions

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Answers

Exercise 6.3.1

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

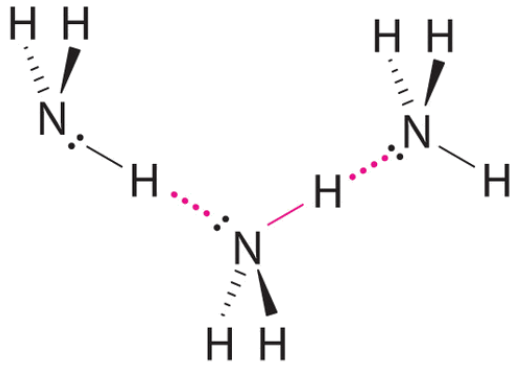
Exercise 6.3.2

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

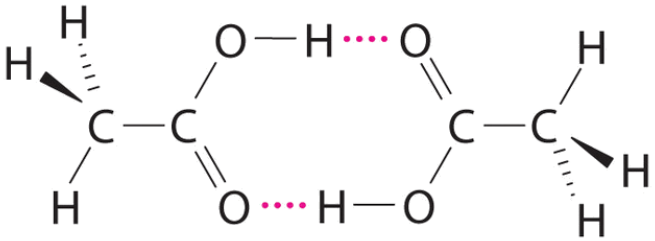
$$C_2H_6 < C_3H_8 < C_4H_{10}.$$

Exercise 6.3.3

CH_3CO_2H and NH_3;



Hydrogen bonding in ammonia



Hydrogen bonding in acetic acid

Exercise 6.3.4

KBr (1435°C) > 2,4-dimethylheptane (132.9°C) > CS_2 (46.6°C) > Cl_2 (–34.6°C) > Ne (–246°C)

Exercise 6.3.5

hydrogen bonding

dipole-dipole interactions

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6.4: Forces in Solutions

Learning Objectives

- Learn some terminology involving solutions.
- Explain the significance of the statement "like dissolves like".
- Explain why certain substances dissolve in other substances.

A **solution** is another name for a homogeneous mixture. A **mixture** as a material composed of two or more substances. In a solution, the combination is so intimate that the



Figure 6.4.1 Making a saline water solution by dissolving table salt (NaCl) in water. The salt is the solute and the water the solvent. (CC-BY-SA 3.0; Chris 73).

different substances cannot be differentiated by sight, even with a microscope. Compare, for example, a mixture of salt and pepper and another mixture consisting of salt and water. In the first mixture, we can readily see individual grains of salt and the flecks of pepper. A mixture of salt and pepper is not a solution. However, in the second mixture, no matter how carefully we look, we cannot see two different substances. Salt dissolved in water is a solution.

The major component of a solution, called the **solvent**, is typically the same phase as the solution itself. Each minor component of a solution (and there may be more than one) is called the **solute**. In most of the solutions we will describe in this textbook, there will be no ambiguity about whether a component is the solvent or the solute.) For example, in a solution of salt in water, the solute is salt, and solvent is water Figure 6.4.1.

Solutions come in all phases, and the solvent and the solute do not have to be in the same phase to form a solution (such as salt and water). For example, air is a gaseous solution of about 80% nitrogen and about 20% oxygen, with some other gases present in much smaller amounts. An alloy is a solid solution consisting of a metal (like iron) with some other metals or nonmetals dissolved in it. Steel, an alloy of iron and carbon and small amounts of other metals, is an example of a solid solution. Table 6.4.1 lists some common types of solutions, with examples of each.

Table 6.4.1 Types of Solutions

Solvent Phase	Solute Phase	Example
gas	gas	air
liquid	gas	carbonated beverages

Solvent Phase	Solute Phase	Example
liquid	liquid	ethanol (C_2H_5OH) in H_2O (alcoholic beverages)
liquid	solid	salt water
solid	gas	H_2 gas absorbed by Pd metal
solid	liquid	Hg(ℓ) in dental fillings
solid	solid	steel alloys

Example 6.4.1: Sugar and Water

A solution is made by dissolving 1.00 g of sucrose ($C_{12}H_{22}O_{11}$) in 100.0 g of liquid water. Identify the solvent and solute in the resulting solution.

Solution

Either by mass or by moles, the obvious minor component is **sucrose**, so it is **the solute**. **Water**—the majority component—is **the solvent**. The fact that the resulting solution is the same phase as water also suggests that water is the solvent.

Exercise 6.4.1

A solution is made by dissolving 3.33 g of $HCl(g)$ in 40.0 g of liquid methyl alcohol (CH_3OH). Identify the solvent and solute in the resulting solution.

Answer available at the end of this section.

Like Dissolves Like

A simple way to predict which compounds will dissolve in other compounds is the phrase "like dissolves like". What this means is that polar compounds dissolve polar compounds, nonpolar compounds dissolve nonpolar compounds, but polar and nonpolar do not dissolve in each other.

Even some nonpolar substances dissolve in water but only to a limited degree. Have you ever wondered why fish are able to breathe? Oxygen gas, an nonpolar molecules, does dissolve in water and it is this oxygen that the fish take in through their gills. Or, one more example of a nonpolar compound that dissolves in water is the reason we can enjoy carbonated sodas. Pepsi-cola and all the other sodas have carbon dioxide gas, CO_2, a nonpolar compound, dissolved in a sugar-water solution. In this case, to keep as much gas in solution as possible, the sodas are kept under pressure.

This general trend of "like dissolves like" is summarized in the following table:

Table 6.4.2 Summary of Solubilities

Solute	Solvent	Is Solution Formed?
Polar Covalent	Polar	yes
Non-polar Covalent	Non-polar	yes
Polar Covalent	Non-polar	no
Non-polar Covalent	Polar	no
Ionic	Polar	yes
Ionic	Non-polar	no

Note that every time charged particles (ionic compounds or polar substances) are mixed, a solution is formed. When particles

with no charges (nonpolar compounds) are mixed, they will form a solution. However, if substances with charges are mixed with other substances without charges a solution does not form.

> When an ionic compound is considered "insoluble", it doesn't necessarily mean the compound is completely untouched by water. All ionic compounds dissolve to some extent. An insoluble compound just doesn't dissolve in any noticeable or appreciable amount.

What is it that makes a solute soluble in some solvents but not others?

The answer is intermolecular interactions. The intermolecular interactions include London dispersion forces, dipole-dipole interactions, and hydrogen bonding (as described in



Figure 6.4.1 Making a saline water solution by dissolving table salt (NaCl) in water. The salt is the solute and the water the solvent. (CC-BY-SA 3.0; Chris 73).

the previous section). From experimental studies, it has been determined that if molecules of a solute experience the same intermolecular forces that the solvent does, the solute will likely dissolve in that solvent. So, NaCl—a very polar substance because it is composed of ions—dissolves in water, which is very polar, but not in oil, which is generally nonpolar. Nonpolar wax dissolves in nonpolar hexane, but not in polar water. *Liquids that dissolve in one another in all proportions are said to be* **miscible**. *Liquids that do not dissolve in one another are called* **immiscible**.

Figure 6.4.2 Water (clear liquid) and oil (yellow) do not form liquid solutions. (CC BY-SA 1.0 Generic; Victor Blacus)

Example 6.4.2: Polar and Nonpolar Solvents

Would I_2 be more soluble in CCl_4 or H_2O? Explain your answer.

Solution

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

Exercise 6.4.2

Would C_3H_7OH be more soluble in CCl_4 or H_2O? Explain your answer.

Answer available at the end of this section.

Example 6.4.3

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

a. methanol (CH_3OH)
b. sodium sulfate (Na_2SO_4)
c. octane (C_8H_{18})

Solution

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

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

Exercise 6.4.3

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

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

Answer available at the end of this section.

The Dissolving Process

Water typically dissolves most ionic compounds and polar molecules. Nonpolar molecules, such as those found in grease or oil, do not dissolve in water. We will first examine the process that occurs when an ionic compound, such as table salt (sodium chloride), dissolves in water.

Water molecules move about continuously due to their kinetic energy. When a crystal of sodium chloride is placed into water, the water's molecules collide with the crystal lattice. Recall that the crystal lattice is composed of alternating positive and negative ions. Water is attracted to the sodium chloride crystal because water is polar; it has both a positive and a negative end. The positively charged sodium ions in the crystal attract the oxygen end of the water molecules because they are partially negative. The negatively charged chloride ions in the crystal attract the hydrogen end of the water molecules because they are partially positive. The action of the polar water molecules takes the crystal lattice apart (see figure below).

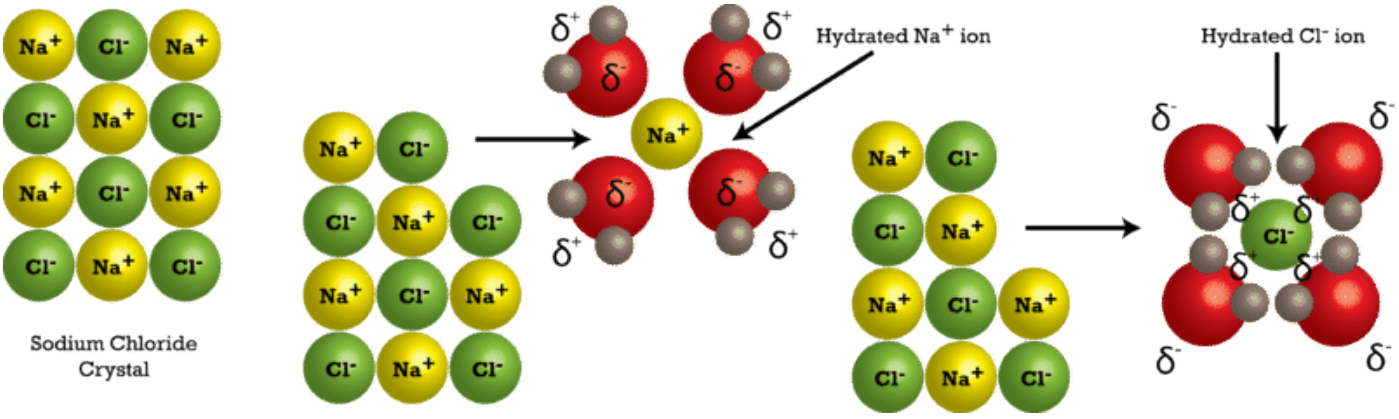


Figure 6.4.3: *The process of an ionic sodium chloride crystal being dissolved and hydrated by water.*

After coming apart from the crystal, *the individual ions are then surrounded by solvent particles in a process called* **solvation**. Note in the figure above that the individual $\mathrm{Na^+}$ ions are surrounded by water molecules with the oxygen atom oriented near the positive ion. Likewise, the chloride ions are surrounded by water molecules with the opposite orientation. Thus, numerous **ion-dipole** interactions are formed. **Hydration** *is the process of solute particles being surrounded by water molecules arranged in a specific manner*. Hydration helps to stabilize aqueous solutions by preventing the positive and negative ions from coming back together and forming a precipitate.

Table sugar is made of the molecular compound sucrose $(\mathrm{C_{12}H_{22}O_{11}})$. Solid sugar consists of individual sugar molecules held together by intermolecular attractive forces. When water dissolves sugar, it separates the individual sugar molecules by disrupting the attractive forces, but it *does not break the covalent bonds* between the carbon, hydrogen, and oxygen atoms. Dissolved sugar molecules are also hydrated. The hydration shell around a molecule of sucrose is arranged so that its partially negative oxygen atoms are near the partially positive hydrogen atoms in the solvent, and vice versa.

Summary

- Solutions are composed of a solvent (major component) and a solute (minor component).
- “Like dissolves like” is a useful rule for deciding if a solute will be soluble in a solvent.
- Liquids that dissolve in one another in all proportions are said to be **miscible**.
- Liquids that do not dissolve in one another are called **immiscible**.
- **Ion-dipole** interactions are formed when ionic compounds dissolve in water.

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Answers

Exercise 6.4.1

solute: HCl(g); solvent: $\mathrm{CH_3OH}$

Exercise 6.4.2

$\mathrm{H_2O}$ because both experience hydrogen bonding

Exercise 6.4.3

octane ($\mathrm{C_8H_{18}}$) will dissolve. It is also non-polar.

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6.5: Gases- 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**. It 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 6.5.1 shows a representation of how we mentally picture the gas phase.

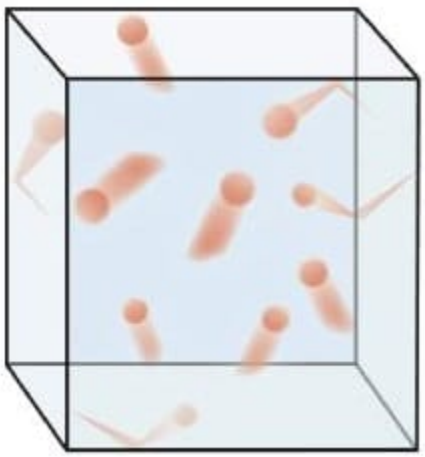


Figure 6.5.1 The kinetic -molecular theory of gases. The kinetic theory of gases describes this state of matter as composed of tiny particles in constant motion with a lot of distance between the particles.

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 so well that 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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6.6: The Simple Gas Laws

Learning Objectives

- Learn what is meant by the term *gas laws*.
- Know the different units of pressure.
- Learn and apply Boyle's law.
- Learn and apply Charles's law.
- Learn and apply Gay-Lussac's law.

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. 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.

Pressure Units

A barometer measures gas pressure by the height of the column of mercury. One unit of gas pressure is the millimeter of mercury (mm Hg). An equivalent unit to the mm Hg is called the torr, in honor of the inventor of the barometer, Evangelista Torricelli. The **pascal** (Pa) is the standard unit of pressure. A pascal is a very small amount of pressure, so the most useful unit for everyday gas pressures is the kilopascal (kPa). A kilopascal is equal to 1000 pascals. Another commonly used unit of pressure is the **atmosphere** (atm). Standard atmospheric pressure is called $1\ \text{atm}$ of pressure and is equal to $760\ \text{mm Hg}$ and $101.3\ \text{kPa}$. Atmospheric pressure is also often stated as pounds per square inch (psi). The atmospheric pressure at sea level is $14.7\ \text{psi}$.

$$1\ \text{atm} = 760\ \text{mm Hg} = 760\ \text{torr} = 101.3\ \text{kPa} = 14.7\ \text{psi}$$

Boyle's Law: Pressure and Volume

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 for a given amount of gas at a constant temperature:

$$P \times V = \text{ constant at constant n and T}$$

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

$$P_1V_1 = \text{constant} = P_2V_2$$

where the properties are assumed to be multiplied together. Leaving out the middle part, we have simply

$$P_1V_1 = P_2V_2 \text{ at constant n and T}$$

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 ia called **Boyle's law**, after the English scientist Robert Boyle, who first announced it in 1662. Figure $6.6.1$ shows two representations of how Boyle's law works.

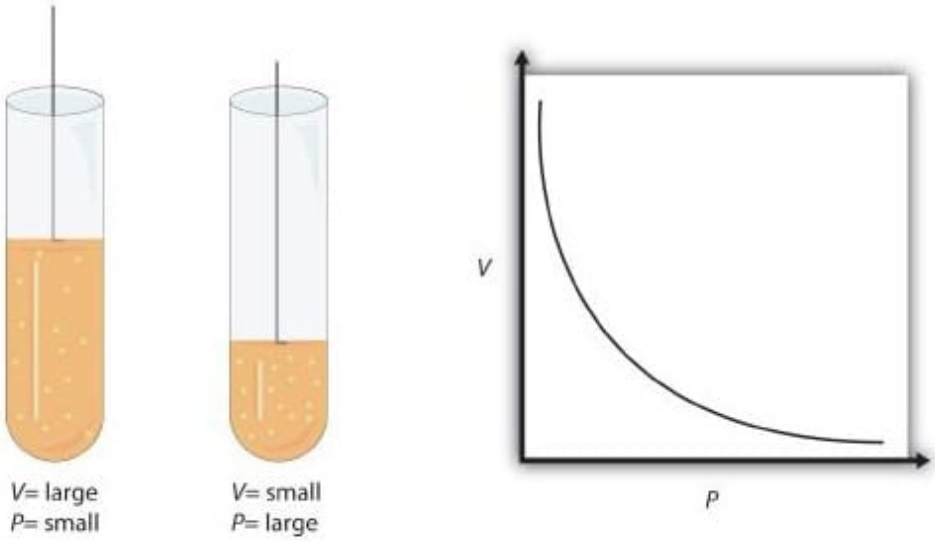


Figure 6.6.1 Boyle's Law. A piston having a certain pressure and volume (left piston) will have half the volume when its pressure is twice as much (right piston). One can also plot P versus V for a given amount of gas at a certain temperature; such a plot will look like the graph on the right.

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 6.6.1

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

Example 6.6.1: Steps for Problem Solving volume and pressure changes.

Steps for Problem Solving	**Example 6.6.1**
Identify the "given"information and what the problem is asking you to "find."	Given: P_1 = 2.44 atm and V_1 = 4.01 L P_2 = 1.93 atm Find: V_2 = ? L
List other known quantities.	none

Steps for Problem Solving	Example 6.6.1
Plan the problem.	First, rearrange the equation algebraically to solve for V_2. $$V_2 = \frac{P_1 \times V_1}{P_2}$$
Cancel units and calculate.	Now substitute the known quantities into the equation and solve. $$V_2 = \frac{2.44 \ \cancel{\text{atm}} \times 4.01 \text{ L}}{1.93 \ \cancel{\text{atm}}} = 5.07 \text{ L}$$
Think about your result.	We know that pressure and volume are inversely related; as one decreases, the other increases. Pressure is d 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 th sense based on Boyle's law.

Exercise 6.6.1

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 6.6.2:

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

Example 6.6.2:Steps for Problem Solving volume and pressure changes

Steps for Problem Solving	Example 6.6.2
Identify the "given"information and what the problem is asking you to "find."	Given: P_1 = 722 torr and V_1 = 88.8 mL V_2 = 0.633 L Find: P_2 = ? torr
List other known quantities.	1 L = 1000 mL to have the same units for volume.

Steps for Problem Solving	Example 6.6.2
Plan the problem.	1. Perform the conversion of the second volume unit from L to mL. 2. Rearrange the equation algebraically to solve for P_2. $$P_2 = \frac{P_1 \times V_1}{V_2}$$
Cancel units and calculate.	1. $$0.663 \cancel{L} \times \frac{1000\,ml}{1\,\cancel{L}} = 663\,ml$$ 2. Substitute the known quantities into the equation and solve. $$P_2 = \frac{722\text{ torr} \times 88.8\,\cancel{\text{mL}}}{663\,\cancel{\text{mL}}} = 96.7\text{ torr}$$
Think about your result.	When the volume increased, the pressure decreased, which is as expected for Boyle's law.

Exercise 6.6.2

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.

Charles's Law: Temperature and Volume

French physicist Jacques Charles (1746 - 1823) studied the effect of temperature on the volume of a gas at constant pressure. **Charles's Law** states that the volume of a given mass of gas varies directly with the absolute temperature of the gas when pressure is kept constant. The absolute temperature is temperature measured with the Kelvin scale. The Kelvin scale must be used because zero on the Kelvin scale corresponds to a complete stoppage of molecular motion.

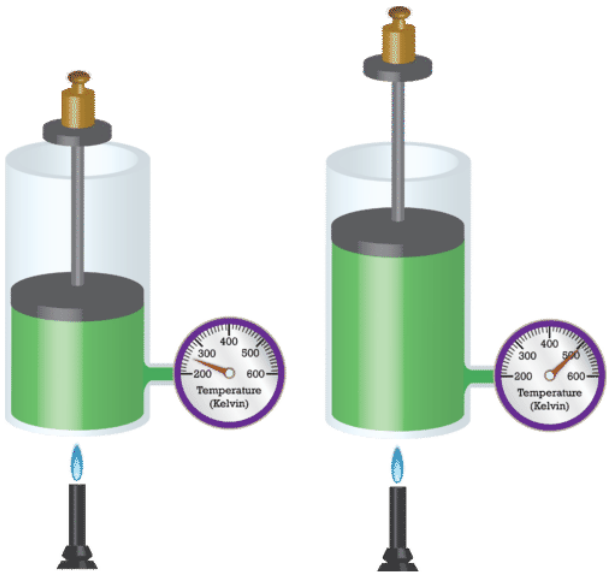


Figure 6.6.2 As a container of confined gas is heated, its molecules increase in kinetic energy and push the movable piston outward, resulting in an increase in volume.

Mathematically, the direct relationship of Charles's Law can be represented by the following equation:

$$\frac{V}{T} = k$$

As with Boyle's Law, k is constant only for a given gas sample. The table below shows temperature and volume data for a set amount of gas at a constant pressure. The third column is the constant for this particular data set and is always equal to the volume divided by the Kelvin temperature.

Table 6.6.1 Temperature-Volume Data

Temperature (K)	**Volume** (mL)	$\frac{V}{T} = k\ \left(\frac{\mathrm{mL}}{\mathrm{K}}\right)$
50	20	0.40
100	40	0.40
150	60	0.40
200	80	0.40
300	120	0.40
500	200	0.40
1000	400	0.40

When this data is graphed, the result is a straight line, indicative of a direct relationship, shown in the figure below.

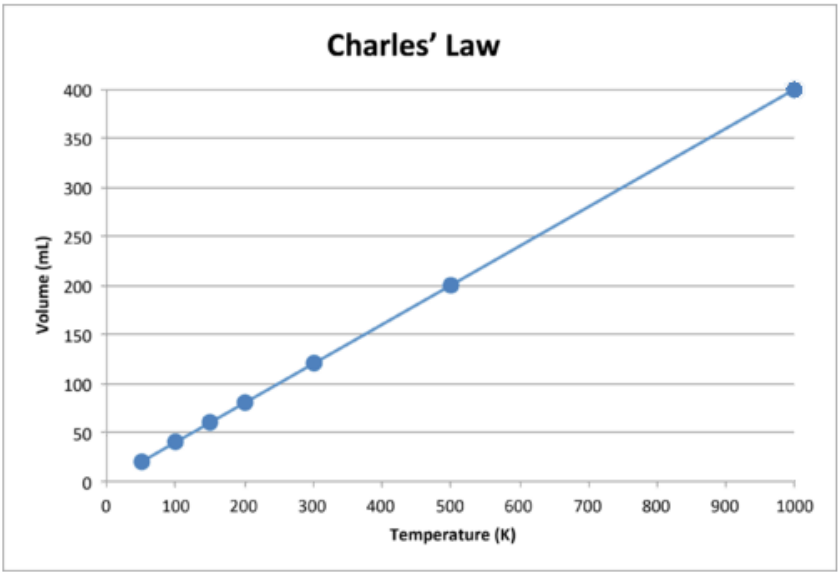


Figure 6.6.3 graph plots how the volume of a gas increases as the Kelvin temperature increases. The increase is linear.

Notice that the line goes exactly toward the origin, meaning that as the absolute temperature of the gas approaches zero, its volume approaches zero. However, when a gas is brought to extremely cold temperatures, its molecules would eventually condense into the liquid state before reaching absolute zero. The temperature at which this change into the liquid state occurs varies for different gases.

Charles's Law can also be used to compare changing conditions for a gas. Now we use V_1 and T_1 to stand for the initial volume and temperature of a gas, while V_2 and T_2 stand for the final volume and temperature. The mathematical relationship of Charles's Law becomes:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

This equation can be used to calculate any one of the four quantities if the other three are known. The direct relationship will only hold if the temperatures are expressed in Kelvin. Temperatures in Celsius will not work. Recall the relationship that $\mathrm{K} = {}^{\circ}\mathrm{C} + 273$.

Example 6.6.3:

A balloon is filled to a volume of $2.20\ \mathrm{L}$ at a temperature of $22^{\circ}\mathrm{C}$. The balloon is then heated to a temperature of $71^{\circ}\mathrm{C}$. Find the new volume of the balloon.

Solution

Steps for Problem Solving	**Example** 6.6.3
Identify the "given"information and what the problem is asking you to "find."	Given: $V_1 = 2.20\ \mathrm{L}$ and $T_1 = 22^{\circ}\mathrm{C} = 295\ \mathrm{K}$ $T_2 = 71^{\circ}\mathrm{C} = 344\ \mathrm{K}$ Find: $V2$ = ? L

Steps for Problem Solving	Example 6.6.3
List other known quantities.	The temperatures have first been converted to Kelvin.
Plan the problem.	First, rearrange the equation algebraically to solve for V_2. $$V_2 = \frac{V_1 \times T_2}{T_1}$$
Cancel units and calculate.	Now substitute the known quantities into the equation and solve. $$V_2 = \frac{2.20\ \text{L} \times 344\ \cancel{\text{K}}}{295\ \cancel{\text{K}}} = 2.57\ \text{L}$$
Think about your result.	The volume increases as the temperature increases. The result has three significant figures.

Exercise 6.6.3

If $V1$ = 3.77 L and $T1$ = 255 K, what is $V2$ if $T2$ = 123 K?

Answer available at the end of this section.

Example 6.6.4:

A sample of a gas has an initial volume of 34.8 L and an initial temperature of −67°C. What must be the temperature of the gas for its volume to be 25.0 L?

Solution

Example 6.6.4: Steps for Problem Solving Volume and Tempature Changes

Steps for Problem Solving	Example 6.6.4
Identify the "given"information and what the problem is asking you to "find."	Given: Given:$T1$ = -27°C and $V1$ = 34.8 L $V2$ = 25.0 L Find: $T2$ = ? K
List other known quantities.	K = -27°C + 273

Steps for Problem Solving	Example 6.6.4
Plan the problem.	1. Convert the initial temperature to Kelvin 2. Rearrange the equation algebraically to solve for T_2. $$T_2 = \frac{V_2 \times T_1}{V_1}$$
Cancel units and calculate.	1. −67°C + 273 = 206 K 2. Substitute the known quantities into the equation and solve. $$T_2 = \frac{25.0 \cancel{L} \times 206 \text{ K}}{34.8 \cancel{L}} = 148 \text{ K}$$
Think about your result.	This is also equal to −125°C. As temperature decreases, volume decreases, which it does in this example.

Exercise 6.6.4

If $V1$ = 623 mL, $T1$ = 255°C, and $V2$ = 277 mL, what is $T2$?

Answer available at the end of this section.

Gay-Lussac's Law: Temperature and Pressure

When the temperature of a sample of gas in a rigid container is increased, the pressure of the gas increases as well. The increase in kinetic energy results in the molecules of gas striking the walls of the container with more force, resulting in a greater pressure. The French chemist Joseph Gay-Lussac (1778 - 1850) discovered the relationship between the pressure of a gas and its absolute temperature. **Gay-Lussac's Law** states that the pressure of a given mass of gas varies directly with the absolute temperature of the gas, when the volume is kept constant. Gay-Lussac's Law is very similar to Charles's Law, with the only difference being the type of container. Whereas the container in a Charles's Law experiment is flexible, it is rigid in a Gay-Lussac's Law experiment.



Figure 6.6.4 Joseph Gay-Lussac.

The mathematical expressions for Gay-Lussac's Law are likewise similar to those of Charles's Law:

$$\frac{P}{T} \text{ and } \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

A graph of pressure vs. temperature also illustrates a direct relationship. As a gas is cooled at constant volume its pressure continually decreases until the gas condenses to a liquid.

Example 6.6.5

The gas in an aerosol can is under a pressure of $3.00\ \text{atm}$ at a temperature of 25°C. It is dangerous to dispose of an aerosol can by incineration. What would the pressure in the aerosol can be at a temperature of 845°C?

Solution

Example 6.6.5: Steps for Problem Solving Volume and Tempature Changes

Steps for Problem Solving	Example 6.6.5
Identify the "given"information and what the problem is asking you to "find."	Given: $P_1 = 3.00\ \text{atm}$ $T_1 = 25^\circ\text{C} = 298\ \text{K}$ $T_2 = 845^\circ\text{C} = 1118\ \text{K}$ Find: $P_2 = ?\ \text{atm}$
List other known quantities	The temperatures have first been converted to Kelvin.
Plan the problem	First, rearrange the equation algebraically to solve for P_2. $P_2 = \frac{P_1 \times T_2}{T_1}$
Calculate	Now substitute the known quantities into the equation and solve. $P_2 = \frac{3.00\ \text{atm} \times 1118\ \cancel{\text{K}}}{298\ \cancel{\text{K}}} = 11.3\ \text{atm}$
Think about your result.	The pressure increases dramatically due to large increase in temperature.

Molar Volume

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 compare more directly the properties of gases that differ from each other.

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:

$$(1\,atm)V = (1\,mol)(0.08205\frac{L.atm}{mol.K})(273\,K)$$

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 (Fig. 6.6.1 Molar Volume). 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 not 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.

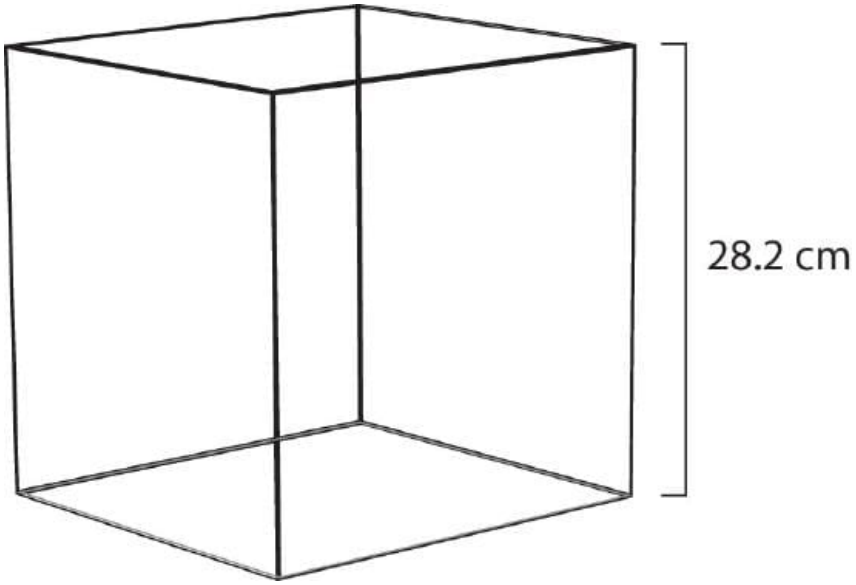


Figure 6.6.5 Molar volume. A mole of gas at STP occupies 22.4 L, the volume of a cube that is 28.2 cm on a side.

Example 6.6.6:

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 6.6.5

What volume does 4.87 mol of Kr have at STP?

Figure 6.6.5 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.

109 L

Note

Chemistry Is Everywhere: Breathing

Breathing (more properly called *respiration*) is the process by which we draw air into our lungs so that our bodies can take up oxygen from the air. Let us apply the gas laws to breathing.

Start by considering pressure. We draw air into our lungs because the diaphragm, a muscle underneath the lungs, moves down to reduce pressure in the lungs, causing external air to rush in to fill the lower-pressure volume. We expel air by the diaphragm pushing against the lungs, increasing pressure inside the lungs and forcing the high-pressure air out. What are the pressure changes involved? A quarter of an atmosphere? A tenth of an atmosphere? Actually, under normal conditions, it's only 1 or 2 torr of pressure difference that makes us breathe in and out.

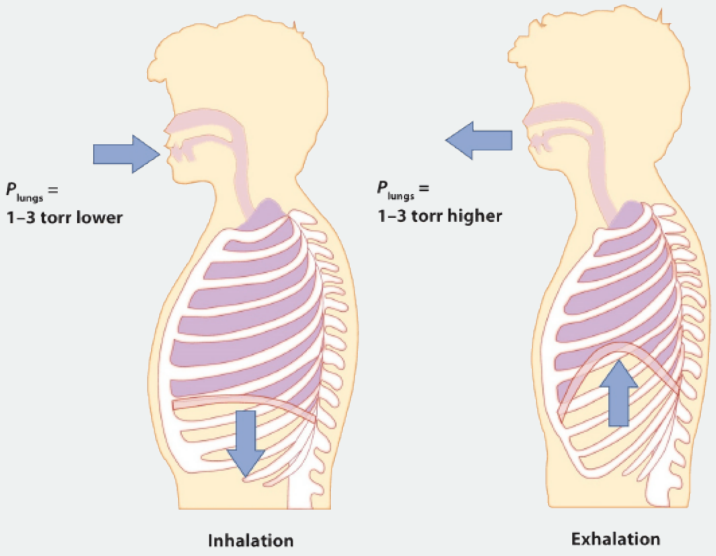


Fig. 6.6.2 Breathing Mechanics. Breathing involves pressure differences between the inside of the lungs and the air outside. The pressure differences are only a few torr.

A normal breath is about 0.50 L. If room temperature is about 22°C, then the air has a temperature of about 295 K. With normal pressure being 1.0 atm, how many moles of air do we take in for every breath? The ideal gas law gives us an answer:

$$(1.0\,atm)(0.50\,L) = n(0.08205\frac{L.atm}{mol.K})(295\,K)$$

Solving for the number of moles, we get

n = 0.021 mol air

This ends up being about 0.6 g of air per breath—not much but enough to keep us alive.

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.
- Charles's law relates a gas's volume and temperature at constant pressure and amount.
- Gay-Lussac's Law states that the pressure of a given mass of gas varies directly with the absolute temperature of the gas, when the volume is kept constant.
- In gas laws, temperatures must always be expressed in Kelvins.

Contributors and Attributions

-
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- Henry Agnew (UC Davis)

Answers

Exercise 6.6.1
124 mL

Exercise 6.6.2
119 mL

Exercise 6.6.3
1.82 L

Exercise 6.6.4
235 K, or −38°

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6.7: The Ideal Gas Law

Learning Objectives

- Learn and apply the ideal gas law.
- Learn and apply the combined gas law.

There are a number of chemical reactions that require ammonia. In order to carry out the reaction efficiently, we need to know how much ammonia we have for stoichiometric purposes. Using gas laws, we can determine the number of moles present in the tank if we know the volume, temperature, and pressure of the system.

Ideal Gas Law

As with the other gas laws, we can also say that $\frac{(P \times V)}{(T \times n)}$ is equal to a constant. The constant can be evaluated provided that the gas being described is considered to be ideal.

The **ideal gas law** is a single equation which relates the pressure, volume, temperature, and number of moles of an ideal gas. If we substitute in the variable R for the constant, the equation becomes:

$$\frac{P \times V}{T \times n} = R$$

The ideal gas law is conveniently rearranged to look this way, with the multiplication signs omitted:

$$PV = nRT$$

The variable R in the equation is called the **ideal gas constant**.

Evaluating the Ideal Gas Constant

The value of R, the ideal gas constant, depends on the units chosen for pressure, temperature, and volume in the ideal gas equation. It is necessary to use Kelvin for the temperature and it is conventional to use the SI unit of liters for the volume. However, pressure is commonly measured in one of three units: kPa, atm, or $\mathrm{mm\ Hg}$. Therefore, R can have three different values.

We will demonstrate how R is calculated when the pressure is measured in kPa. The volume of $1.00\ \mathrm{mol}$ of any gas at STP (Standard temperature, 273.15 K and pressure, 1 atm)is measured to be $22.414\ \mathrm{L}$. We can substitute $101.325\ \mathrm{kPa}$ for pressure, $22.414\ \mathrm{L}$ for volume, and $273.15\ \mathrm{K}$ for temperature into the ideal gas equation and solve for R.

$$\begin{aligned} R &= \frac{PV}{nT} \\ &= \frac{101.325\ \mathrm{kPa} \times 22.414\ \mathrm{L}}{1.000\ \mathrm{mol} \times 273.15\ \mathrm{K}} \\ &= 8.314\ \mathrm{kPa \cdot L/K \cdot mol} \end{aligned}$$

This is the value of R that is to be used in the ideal gas equation when the pressure is given in kPa. The table below shows a summary of this and the other possible values of R. It is important to choose the correct value of R to use for a given problem.

Table 6.7.1 *Values of the Ideal Gas Constant*

Unit of P	Unit of V	Unit of n	Unit of T	Value and Unit of R
kPa	L	mol	K	$8.314\ \mathrm{J/K \cdot mol}$
atm	L	mol	K	$0.08206\ \mathrm{L \cdot atm/K \cdot mol}$

Unit of P	Unit of V	Unit of n	Unit of T	Value and Unit of R
mm Hg	L	mol	K	$62.36\ \text{L} \cdot \text{mm Hg}/\text{K} \cdot \text{mol}$

Notice that the unit for R when the pressure is in kPa has been changed to $\text{J}/\text{K} \cdot \text{mol}$. A kilopascal multiplied by a liter is equal to the SI unit for energy, a joule (J).

Example 6.7.1 Oxygen Gas

What volume is occupied by $3.76\ \text{g}$ of oxygen gas at a pressure of $88.4\ \text{kPa}$ and a temperature of 19°C? Assume the oxygen is ideal.

Solution

Example 6.7.1 *Steps for Problem Solving volume of oxygen gas*

Steps for Problem Solving	Example 6.7.1
Identify the "given"information and what the problem is asking you to "find."	Given: • $P = 88.4\ \text{kPa}$ • $T = 19^\circ\text{C} = 292\ \text{K}$ Mass $\text{O}_2 = 3.76\ \text{g}$ Find: *V* = ? L
List other known quantities	$\text{O}_2 = 32.00\ \text{g/mol}$ $R = 8.314\ \text{J}/\text{K} \cdot \text{mol}$
Plan the problem	1. First, determine the number of moles of O_2 from the given mass and the molar mass. 2. Then, rearrange the equation algebraically to solve for V $$V = \frac{nRT}{P}$$
Calculate	1. $$3.76\ \cancel{\text{g}} \times \frac{1\ \text{mol O}_2}{32.00\ \cancel{\text{g}}\ \text{O}_2} = 0.1175\ \text{mol O}_2$$ 2. Now substitute the known quantities into the equation and solve. $$V = \frac{nRT}{P} = \frac{0.1175\ \cancel{\text{mol}} \times 8.314\ \cancel{\text{J/K}} \cdot \cancel{\text{mol}} \times 292\ \cancel{\text{K}}}{88.4\ \cancel{\text{kPa}}} = 3.23\ \text{L O}_2$$
Think about your result.	The number of moles of oxygen is far less than one mole, so the volume should be fairly small compared to r $(22.4\ \text{L/mol})$ since the pressure and temperature are reasonably close to standard. The result has three signi because of the values for T and P. Since a joule $(\text{J}) = \text{kPa} \cdot \text{L}$, the units cancel out correctly, leaving a volume

Example 6.7.2: Argon Gas

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

Example 6.7.2: Steps for Problem Solving volume of argon gas

Steps for Problem Solving	Example 6.7.2
Identify the "given"information and what the problem is asking you to "find."	Given: n = 4.22 mol P = 1.21 atm T = 34°C Find: *V* = ? L
List other known quantities	none
Plan the problem	1. The first step is to convert temperature to kelvin. 2. Then, rearrange the equation algebraically to solve for V $$V = \frac{nRT}{P}$$
Calculate	1. 34 + 273 = 307 K 2. Now substitute the known quantities into the equation and solve. \[\begin{align*} V=\frac{(4.22\, \cancel{mol})(0.08205\frac{L.\cancel{atm}}{\cancel{mol.K}})(307\, \ca cancel{atm}} \[4pt] &= 87.9 \,L \end{align*} \nonumber \]
Think about your result.	The number of moles of Ar is large so the expected volume should also be large.

Exercise 6.7.1

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

3.94 L

Exercise 6.7.2

For a 0.00554 mol sample of H_2, *P* = 23.44 torr and *T* = 557 K. What is its volume?

Answer

8.21 L

One thing we notice about all the gas laws is that, collectively, 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 Kelvin.

Example 6.7.3:

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

Example 6.7.3: Steps for Problem Solving pressure of gas

Steps for Problem Solving	**Example 6.7.3**
Identify the "given"information and what the problem is asking you to "find."	Given: V_1 = 8.33 L, P_1 = 1.82 atm, and T_1 = 286 K V2 = 5.72 L and T_2 = 355 K Find: P_2 = ? atm
List other known quantities	none
Plan the problem	First, rearrange the equation algebraically to solve for V_2. $$P_2 = \frac{P_1V_1T_2}{T_1V_2}$$
Calculate	Now substitute the known quantities into the equation and solve. $$P_2 = \frac{(1.82\,atm)(8.33\,\cancel{L})(355\,\cancel{K})}{(286\,\cancel{K})(5.72\,\cancel{L})} = 3.22atm$$
Think about your result.	Ultimately, the pressure increased, which would have been difficult to predict because two properties of the changing.

Exercise 6.7.3

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.

As with other gas laws, if you need to determine the value of a variable in the denominator of the combined gas law, you can either cross-multiply all the terms or just take the reciprocal of the combined gas law. Remember, the variable you are solving for must be in the numerator and all by itself on one side of the equation.

Summary

- The ideal gas constant is calculated to be $8.314\ \mathrm{J/K \cdot mol}$ when the pressure is in kPa.
- The ideal gas law is a single equation which relates the pressure, volume, temperature, and number of moles of an ideal gas.
- The combined gas law relates pressure, volume, and temperature of a gas.

Contributors and Attributions

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Answers

Exercise 6.7.3

105 mL

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7: ACIDS AND BASES

7.1: Acids and Bases - Experimental Definitions

7.2: Acids and Bases

7.3: Acidic and Basic Anhydrides

7.4: Strong and Weak Acids and Bases

7.5: Neutralization

7.6: The pH Scale

7.7: Buffers and Conjugate Acid-Base Pairs

7.8: Acids and Bases in Industry and in Daily Life

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7.1: Acids and Bases - Experimental Definitions

Learning Objectives

- Examine properties of acids and bases.

Many people enjoy drinking coffee. A cup first thing in the morning helps start the day. But keeping the coffee maker clean can be a problem. Lime deposits build up after a while and slow down the brewing process. The best cure for this is to put vinegar (dilute acetic acid) in the pot and run it through the brewing cycle. The vinegar dissolves the deposits and cleans the maker, which will speed up the brewing process back to its original rate. Just be sure to run water through the brewing process after the vinegar, or you will get some really horrible coffee.

Perhaps you have eaten too much pizza and felt very uncomfortable hours later. This feeling is due to excess stomach acid being produced. The discomfort can be dealt with by taking an antacid. The base in the antacid will react with the HCl in the stomach and neutralize it, taking care of that unpleasant feeling. Figure $7.1.1$ provides some examples of acids and bases.



Figure $7.1.1$ Some examples of common household acids and bases.

Acids

Acids are very common in some of the foods that we eat. Citrus fruits such as oranges and lemons contain citric acid and ascorbic acid, which is better known as vitamin C. Carbonated sodas contain phosphoric acid. Vinegar contains acetic acid. Your own stomach utilizes hydrochloric acid to digest food. Acids are a distinct class of compounds because of the properties of their aqueous solutions as outlined below:

1. Aqueous solutions of acids are electrolytes, meaning that they conduct electrical current. Some acids are strong electrolytes because they ionize completely in water, yielding a great many ions. Other acids are weak electrolytes that exist primarily in a non-ionized form when dissolved in water.
2. Acids have a sour taste. Lemons, vinegar, and sour candies all contain acids.
3. Acids change the color of certain acid-base indicators. Two common indicators are litmus and phenolphthalein. Blue litmus turns red in the presence of an acid, while phenolphthalein turns colorless.
4. Acids react with active metals to yield hydrogen gas. Recall that an activity series is a list of metals in descending order of reactivity. Metals that are above hydrogen in the activity series will replace the hydrogen from an acid in a single-replacement reaction, as shown below:

$$\mathrm{Zn}\,(s) + \mathrm{H_2SO_4}\,(aq) \rightarrow \mathrm{ZnSO_4}\,(aq) + \mathrm{H_2}\,(g) \tag{7.1.1}$$

5. Acids react with bases to produce a salt compound and water. When equal moles of an acid and a base are combined, the acid is neutralized by the base. The products of this reaction are an ionic compound, which is labeled as a salt, and water.

Common examples: Lemons, oranges, vinegar, urine, sulfuric acid, hydrochloric acid

Bases

Bases have properties that mostly contrast with those of acids.

1. Aqueous solutions of bases are also electrolytes. Bases can be either strong or weak, just as acids can.
2. Bases often have a bitter taste and are found in foods less frequently than acids. Many bases, like soaps, are slippery to the touch.
3. Bases also change the color of indicators. Litmus turns blue in the presence of a base while phenolphthalein turns pink.
4. Bases do not react with metals in the way that acids do.
5. Bases react with acids to produce a salt and water.

Common Examples: Soap, toothpaste, bleach, cleaning agents, limewater, ammonia water, sodium hydroxide.



Figure 7.1.2 Phenolphthalein indicator in presence of base.

Warning

Tasting chemicals and touching them are NOT good lab practices and should be avoided - in other words, don't do this at home.

Summary

- A brief summary of properties of acids and bases are given.
- Properties of acids and bases mostly contrast each other.

Contributors and Attributions

-
- Peggy Lawson (Oxbow Prairie Heights School). Funded by Saskatchewan Educational Technology Consortium.
- Wikipedia
- Marisa Alviar-Agnew (Sacramento City College)
- Henry Agnew (UC Davis)

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7.2: Acids and Bases

Learning Objectives

- Identify an Arrhenius acid and an Arrhenius base.
- Identify a Brønsted-Lowry acid and a Brønsted-Lowry base.
- Write chemical reactions between an Arrhenius acid and an Arrhenius base and between Brønsted-Lowry acid and a Brønsted-Lowry base.

There are three major classifications of substances known as acids or bases. The Arrhenius definition states that an acid produces H^+ in solution and a base produces OH^-. This theory was developed by Svante Arrhenius in 1883. Later, two more sophisticated and general theories were proposed. These are the Brønsted-Lowry and the Lewis definitions of acids and bases. The Lewis theory is discussed elsewhere.

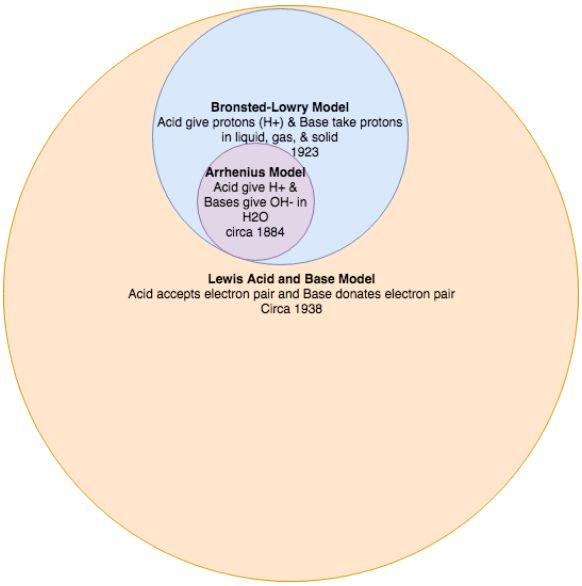


Figure 7.2.1 Acid base reaction theories as superset and subset models.

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** $\mathrm{H^+}$ **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.

$$\mathrm{HCl\,(aq)\ \rightarrow H^+\,(aq) + Cl^-\,(aq)}$$

In this reaction, hydrochloric acid (HCl) dissociates completely into hydrogen (H^+) and chlorine (Cl^-) ions when dissolved in water, thereby releasing H^+ ions into solution. Formation of the hydronium ion equation:

$$\mathrm{HCl\,(aq) + H_2O\,(l)\ \rightarrow H_3O^+\,(aq) + Cl^-\,(aq)}$$

An **Arrhenius base** is a compound that **increases the concentration of** $\mathrm{OH^-}$ **ions** that are present when added to water. The dissociation is represented by the following equation:

$$\mathrm{NaOH}\ \ (\mathrm{aq})\ \rightarrow \mathrm{Na}^{+}\ \ (\mathrm{aq}) + \mathrm{OH}^{-}\ \ (\mathrm{aq})$$

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. Also, the Arrhenius definition of acid and base is 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 (PD)**, while **a Brønsted-Lowry base** is a **proton acceptor (PA)**.

> 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:

$$\mathrm{NH_3\,(aq) + H_2O\ (\ell) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)} \tag{7.2.1}$$

What has happened in this reaction is that the original water molecule has donated a hydrogen ion to the original ammonia molecule, which in turn has accepted the hydrogen ion. We can illustrate this as follows (Figure 7.2.2):

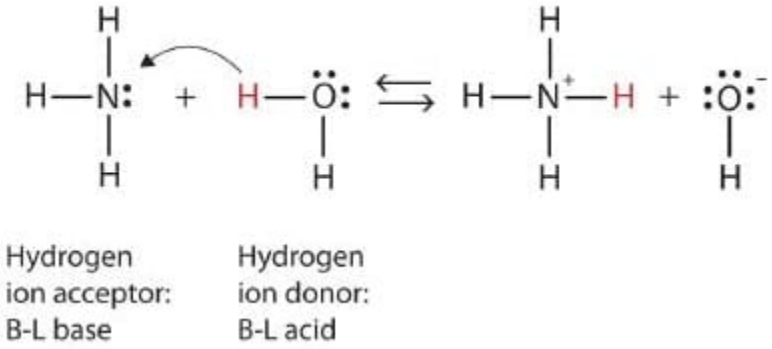


Figure 7.2.2 reaction of ammonia and water.

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.

The Hydronium Ion

A proton in aqueous solution may be surrounded by more than one water molecule, leading to formulas like $H_5O_2^+$ or $H_9O_4^+$ rather than H_3O^+. It is simpler, however, to use H_3O^+ to represent the hydronium ion.

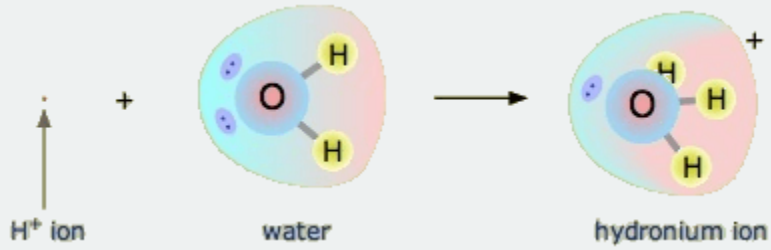


Figure 7.2.3 reaction of hydrogen and water to form hydronium. (CC BY-NC 3.0)

With this in mind, how do we define HCl as an acid in the Brønsted-Lowry sense? Consider what happens when HCl is dissolved in H_2O:

$$HCl(g) + H_2O\ (\ell)\ \rightarrow H_3O^+(aq) + Cl^-(aq) \tag{7.2.2}$$

We can depict this process using Lewis electron dot diagrams (Figure 7.2.4):

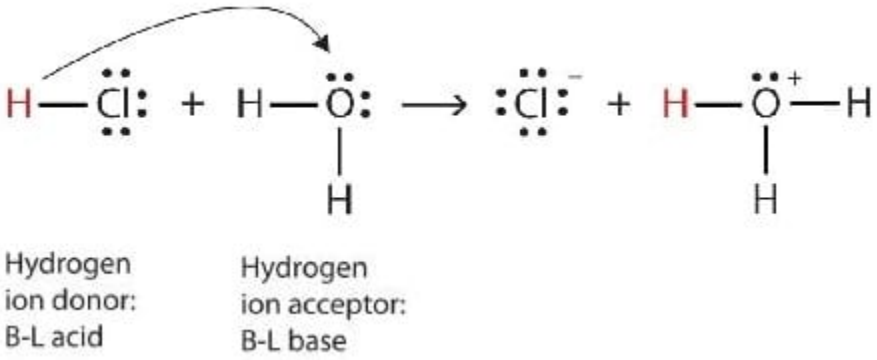


Figure 7.2.4 Lewis electron dot diagram of HCl dissolved in H_2O

Now we see that a hydrogen ion is transferred from the HCl molecule to the H_2O molecule to make chloride ions and hydronium ions. As the hydrogen ion donor, HCl acts as a Brønsted-Lowry acid; as a hydrogen ion acceptor, H_2O is a Brønsted-Lowry base. So HCl is an acid not just in the Arrhenius sense but also in the Brønsted-Lowry sense. Moreover, by the Brønsted-Lowry definitions, H_2O is a base in the formation of aqueous HCl. So the Brønsted-Lowry definitions of an acid and a base classify the dissolving of HCl in water as a reaction between an acid and a base—although the Arrhenius definition would not have labeled H_2O a base in this circumstance.

A summary of the acid-base definitions based on the Arrhenius and Bronstes-Lowry theories is given in Table 7.2.1.

Table 7.2.1 Acid-Base Definitions

Type	Acid	Base
Arrhenius	H^+ ions in solution	OH^- ions in solution
Brønsted-Lowry	H^+ donor	H^+ 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 7.2.1

Aniline ($C_6H_5NH_2$) is slightly soluble in water. It has a nitrogen atom that can accept a hydrogen ion from a water molecule just like the nitrogen atom in ammonia does. Write the chemical equation for this reaction and identify the Brønsted-Lowry acid and base.

Solution

$C_6H_5NH_2$ and H_2O are the reactants. When $C_6H_5NH_2$ accepts a proton from H_2O, it gains an extra H and a positive charge and leaves an OH^- ion behind. The reaction is as follows:

$$C_6H_5NH_2\,(aq) + H_2O(\ell) \rightleftharpoons C_6H_5NH_3{}^+\,(aq) + OH^-\,(aq)$$

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 7.2.1

Identify the Brønsted-Lowry acid and the Brønsted-Lowry base in this chemical equation.

$$H_2PO_4{}^- + H_2O \rightleftharpoons HPO_4{}^{2-} + H_3O^+$$

Answer available at the end of this section.

Exercise 7.2.2

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.

Summary

- An Arrhenius acid is a compound that increases the H^+ ion concentration and an Arrhenius base is a compound that increases the OH^- ion concentration in aqueous solution.
- A Brønsted-Lowry acid is a proton donor; a Brønsted-Lowry base is a proton 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.

Contributors and Attributions

- Libretext: The Basics of GOB Chemistry (Ball et al.)
- Marisa Alviar-Agnew (Sacramento City College)
- Libretext: Chemistry for Allied Health (Soult)

Answers

Exercise 7.2.1

Brønsted-Lowry acid: $H_2PO_4^-$; Brønsted-Lowry base: H2O

Exercise 7.2.2

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-}.**

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7.3: Acidic and Basic Anhydrides

Learning Objectives

- Identify acid anyhdrides and basic anhydrides.
- Know the reactions of acid and basic anhydrides with water.

Metal oxides are substances used in the manufacture of commonly used bases like calcium hydroxide (traditionally known as slaked lime), sodium hydroxide and potassium hydroxide. Acid anhydrides (non-metal oxides) are environmentally relevant. Sulfur and nitrogen oxides are considered air pollutants as they react with atmospheric water vapor to produce acid rain (Chapter 13).

Nonmetal Oxides: Acid Anhydrides

Acid anhydrides are compounds that turn into an acid when you add water. They are non-metal oxides. The oxides of period three elements demonstrate periodicity with respect to acidity. As you move across the period, the oxides become more acidic. Sodium and magnesium oxides are alkaline. Aluminium oxides are amphoteric (reacting both as a base or acid). Silicon, phosphorus, sulfur, and chlorine oxides are acidic. Some non-metal oxides, such as nitrous oxide (N_2O) and carbon monoxide (CO), do not display any acid/base characteristics. These are a little more complicated than basic anhydrides, so don't worry too much about them right now.

Several examples of reactions involving nonmetal oxides are as follows:

1. Carbon dioxide is the anhydride of carbonic acid:

$CO_2(g) + H_2O(l) \rightarrow H_2CO_3\,(aq)$

2. Sulfur dioxide reacts with water to form the weak acid, sulfurous acid:

$SO_2(g) + H_2O\,(l) \rightarrow H_2SO_3\,(aq)$

3. Sulfur trioxide forms the strong sulfuric acid with water (so, sulfur trioxide is the anhydride of sulfuric acid):

$SO_3(g) + H_2O(l) \rightarrow H_2SO_4\,(aq)$

This reaction is important in the manufacture of the acid.

Metal Oxides: Basic Anhydrides

Oxides of more electropositive elements like the alkali or alkaline earth metals tend to be basic. They are called *basic anhydrides*. Exposed to water, they may form bases (basic hydroxides). Sodium oxide is basic—when hydrated, it forms sodium hydroxide. Here's another example:

$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2\,(aq)$

If the metal is an alkali or alkaline earth, the reaction probably happens quickly and produces a lot of heat. If the metal is a transition metal, the reaction might not happen so easily or at all.

Summary

- Acid anhydrides are nonmetal oxides that react with water to form acids.
- Basic anhydrides are metal oxides that react with water to form bases.

Contributors and Attributions

- Wikipedia
- Marisa Alviar-Agnew (Sacramento City College)

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7.4: Strong and Weak Acids and Bases

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 HCl(aq). When HCl is dissolved in H_2O, it completely dissociates into H^+(aq) and Cl^-(aq) ions; all the HCl molecules become ions:

$$HCl \overset{100\%}{\rightarrow} H^+(aq) + Cl^-(aq)$$

Any acid that dissociates 100% into ions is called a **strong acid**. If it does not dissociate 100%, it is a **weak acid**. $HC_2H_3O_2$ is an example of a weak acid:

$$HC_2H_3O_2 \overset{\sim 5\%}{\longrightarrow} H^+(aq) + C_2H_3O_2^-(aq)$$

Because this reaction does not go 100% to completion, it is more appropriate to write it as **a reversible reaction**:

$$HC_2H_3O_2 \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$$

As it turns out, there are very few strong acids, which are given in Table 7.4.1. 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.

Table 7.4.1 Strong Acids and Bases

Acids	Bases
HCl	LiOH
HBr	NaOH
HI	KOH
HNO_3	RbOH
H_2SO_4	CsOH
$HClO_3$	$Mg(OH)_2$
$HClO_4$	$Ca(OH)_2$
	$Sr(OH)_2$
	$Ba(OH)_2$

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 7.4.1); 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 7.4.1: 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 7.4.1, it is a strong acid.
b. Because $Mg(OH)_2$ is listed in Table 7.4.1, 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 7.4.1

Identify each acid or base as strong or weak.

a. RbOH
b. $\mathrm{HNO_2}$

Answer a available at the end of this section.

Example 7.4.2: 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 7.4.1, this reaction proceeds 100% to products.

Exercise 7.4.2

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.

Summary

- Strong acids and bases are 100% ionized in aqueous solution.

- Weak acids and bases are less than 100% ionized in aqueous solution.

Contributors and Attributions

- Libretext: Beginning Chemistry (Ball et al.)
- Marisa Alviar-Agnew (Sacramento City College)
- Henry Agnew (UC Davis)

Answers

Exercise 7.4.1

strong base

weak acid

Exercise 7.4.2

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.

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7.5: Neutralization

Learning Objective

- Write acid-base neutralization reactions.

What happens when an acid such as HCl is mixed with a base such as NaOH:

$$\mathrm{HCl\,(aq) + NaOH\,(aq) \longrightarrow NaCl\,(aq) + H_2O\,(l)}$$

When an acid and a base are combined, water and a salt are the products. Double displacement reactions of this type are called **neutralization reactions**. We can write an expanded version of this equation, with aqueous substances written in their longer form:

$$\mathrm{H^+\,(aq) + Cl^-\,(aq) + Na^+\,(aq) + OH^-\,(aq) \longrightarrow Na^+\,(aq) + Cl^-\,(aq) + H_2O\,(l)}$$

Removing the spectator ions we get the net ionic equation:

$$\mathrm{H^+\,(aq) + OH^-\,(aq) \longrightarrow H_2O\,(l)}$$

When a strong acid and a strong base are combined in the proper amounts - when $\mathrm{[H^+]}$ equals $\mathrm{[OH^-]}$\) - a neutral solution results in which pH = 7. The acid and base have neutralized each other, and the acidic and basic properties are no longer present.

Salt solutions do not always have a pH of 7, however. Through a process known as **hydrolysis**, the ions produced when an acid and base combine may react with the water molecules to produce a solution that is slightly acidic or basic. We will not go into details here, but generally if a strong acid is mixed with a weak base there the resulting solution will be slightly acidic; if a strong base is mixed with a weak acid the solution will be slightly basic.

Neutralization

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 7.5.1 *Acid-base neutralization reaction.*

Example 7.5.1: propionic acid + calcium hydroxide

Calcium propionate is used to inhibit the growth of molds in foods, tobacco, and some medicines. Write a balanced chemical equation for the reaction of aqueous propionic acid ($CH_3CH_2CO_2H$) with aqueous calcium hydroxide [$Ca(OH)_2$].

Solution

Example 7.5.1: steps for problem solving the reaction of propionic acid + calcium hydroxide

Steps	Reaction
Write the unbalanced equation. This is a double displacement reaction, so the cations and anions swap to create the water and the salt.	$CH_3CH_2CO_2H(aq) + Ca(OH)_2(aq) \rightarrow (CH_3CH_2CO_2)_2Ca(aq) + H_2O(l)$
Balance the equation. Because there are two OH^- ions in the formula for $Ca(OH)_2$, we need two moles of propionic acid, $CH_3CH_2CO_2H$ to provide H^+ ions.	$\underline{2}CH_3CH_2CO_2H(aq) + Ca(OH)_2(aq) \rightarrow (CH_3CH_2CO_2)_2Ca(aq) + \underline{2}H_2O(l)$

Exercise 7.5.1

Write a balanced chemical equation for the reaction of solid barium hydroxide with dilute acetic acid.

Answer available at the end of this section.

Applications

In analytical laboratories, chemical methods are used for determining the amounts of acids or bases in foods and household and industrial chemicals.

In , chemical neutralization methods are often applied to reduce the damage that an effluent may cause upon release to the environment.

There are many uses of neutralization reactions that are acid-alkali reactions. A very common use is antacid tablets (section 7.8).

In chemical synthesis of nanomaterials, the heat of neutralization reaction can be used to facilitate the chemical reduction of metal precursors.

Also in the digestive tract, neutralization reactions are used when food is moved from the stomach to the intestines. In order for the nutrients to be absorbed through the intestinal wall, an alkaline environment is needed, so the pancreas produce an antacid bicarbonate to cause this transformation to occur.

Another common use, though perhaps not as widely known, is in fertilizers and control of soil pH. Slaked lime (calcium hydroxide) or limestone (calcium carbonate) may be worked into soil that is too acidic for plant growth. Fertilizers that improve plant growth are made by neutralizing sulfuric acid (H_2SO_4) or nitric acid (HNO_3) with ammonia gas (NH_3), making or . These are salts utilized in the fertilizer.

Industrially, a by-product of the burning of coal, gas, may combine with water vapor in the air to eventually produce sulfuric acid, which falls as acid rain. To prevent the sulfur dioxide from being released, a device known as a scrubber gleans the gas from smoke stacks. This device first blows calcium carbonate into the combustion chamber where it decomposes into calcium oxide (lime) and carbon dioxide. This lime then reacts with the sulfur dioxide produced forming calcium sulfite. A suspension of lime is then injected into the mixture to produce a slurry, which removes the and any remaining unreacted sulfur dioxide.

Fluffy Cakes

Q: How do acid-base reactions make cake fluffy?



Figure 7.5.1 Cake with buttercream frosting. Image use with permission (Public domain; Scheinwerfermann)..png

A: Usually cakes include an acidic ingredient (this varies) and sodium bicarbonate, a base. When they react, the proton from the acid is transferred to the bicarbonate, making the weak acid carbonic acid. Carbonic acid is the product of an acid anhydride reaction between carbon dioxide and water. This reaction can be reversed, or carbonic acid can decompose into water and carbon dioxide. Especially at the high temperatures inside a baking cake, this decomposition will happen, and produce carbon dioxide gas. The pressure of the hot gas will form bubbles inside the cake, making it fluffy.

Summary

- Acids and bases combine and produce salt and water.

Contributors and Attributions

- Peggy Lawson (Oxbow Prairie Heights School). Funded by Saskatchewan Educational Technology Consortium.
- Marisa Alviar-Agnew (Sacramento City College)
- Henry Agnew (UC Davis)
- Wikipedia

Answers

Exercise 7.5.1

$$\mathrm{Ba(OH)_2\,(s) + 2\,CH_3CO_2H\ (aq) \longrightarrow Ba(CH_3CO_2)_2\,(aq) + 2\,H_2O\,(l)}$$

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7.6: The pH Scale

Learning Objectives

- Define pH.
- Determine the pH of acidic and basic solutions.
- Determine the hydrogen (hydronium) ion concentration from pH and vice versa.

Molar concentration values of hydrogen $[H^+]$ can be markedly different from one aqueous solution to another. So chemists defined a new scale that succinctly indicates the concentrations of either of these two ions. This is known as the pH scale. The range of values from 0 to 14 that describes the acidity or basicity of a solution. You can use pH to make a quick determination whether a given aqueous solution is acidic, basic, or neutral.

pH is a *logarithmic* scale. A solution that has a pH of 1.0 has 10 times the $[H^+]$ as a solution with a pH of 2.0, which in turn has 10 times the $[H^+]$ as a solution with a pH of 3.0 and so forth.

Warning: The pH scale has no limits

pH is usually (but not always) between 0 and 14. Knowing the dependence of pH on $[H+]$, we can summarize as follows:

- If pH < 7, then the solution is acidic.
- If pH = 7, then the solution is neutral.
- If pH > 7, then the solution is basic.

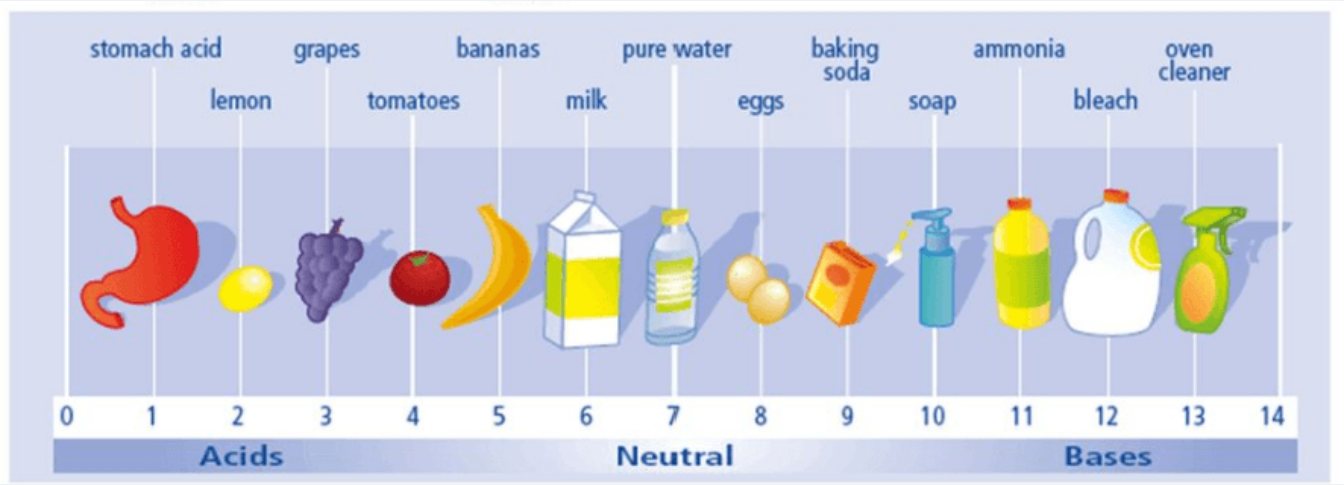


Figure 7.6.1 The pH scale.

Figure 7.6.2 illustrates the relationship between pH and the hydrogen ion concentration, 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** $[H^+]$, which will give a positive value for pH.

The general formula for determining $[H^+]$ from pH is as follows:

$$[H^+] = 10^{-pH}$$

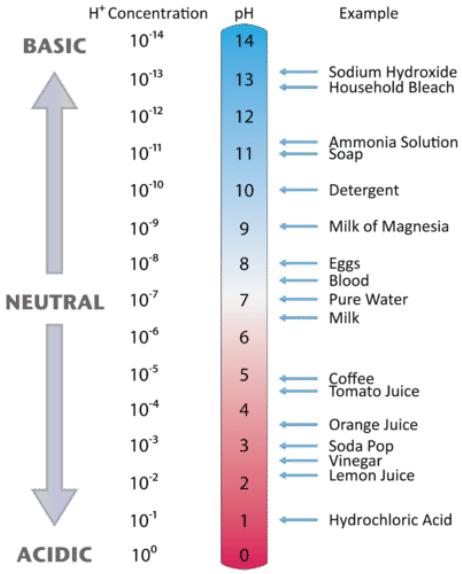


Figure 7.6.2 The pH values for several common materials with corresponding hydrogen ion concentration, [H+] .

Example 7.6.1

Label each solution as acidic, basic, or neutral based only on the stated pH.

a. milk of magnesia, pH = 10.5
b. pure water, pH = 7
c. wine, pH = 3.0

Answer

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 7.6.1

Identify each substance as acidic, basic, or neutral based only on the stated pH.

a. human blood with pH = 7.4
b. household ammonia with pH = 11.0
c. cherries with pH = 3.6

Answer a 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.

Table 7.6.1: gives the typical pH values of some common substances. Note that several food items are on the list, and most of them are acidic.

*Table 7.6.1 Typical pH Values of Various Substances**

Substance	pH
stomach acid	1.7
lemon juice	2.2
vinegar	2.9
soda	3.0
wine	3.5
coffee, black	5.0
milk	6.9
pure water	7.0
blood	7.4
seawater	8.5
milk of magnesia	10.5
ammonia solution	12.5
1.0 M NaOH	14.0
***Actual values may vary depending on conditions**	

Example 7.6.2:

What is the $[H^+]$ for an aqueous solution whose pH is 6?

Solution

The pH value of 6 denotes that the exponent of 10 is -6. Therefore the answer is

$$[H^+] = 1.0 \times 10^{-6} M$$

Exercise 7.6.2

What is the $[H^+]$ for an aqueous solution whose pH is 11?

Answer

$[H^+] = 1.0 \times 10^{-11}$ M

Example 7.6.3:

What is the pH of an aqueous solution whose hydrogen ion concentration is 1.0×10^{-7}M? Is the solution acidic, basic, or neutral.

Solution

The hydrogen ion concentration is 1.0 x 10^{-7}M. The exponent of 10 is -7, which denoted that pH= -(-7) = **7**. The solution is **neutral**.

Exercise 7.6.3

What is the pH of an aqueous solution whose hydrogen ion concentration is 1.0 x 10^{-3}M? Is the solution acidic, basic, or neutral.

Solution

The hydrogen ion concentration is 1.0 x 10^{-3}M. The exponent of 10 is -3, which denoted that pH= -(-3) = **3**. The solution is **acidic**.

Summary

To make pH even easier to work with, pH is defined as the ***negative*** **log of** $[H^+]$, which will give a positive value for pH.

pH is usually (but not always) between 0 and 14.

- If pH < 7, then the solution is acidic.
- If pH = 7, then the solution is neutral.
- If pH > 7, then the solution is basic.

Contributors and Attributions

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-
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Answers

Exercise 7.6.1
basic

Exercise 7.6.1
basic

Exercise 7.6.1
acidic

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7.7: Buffers and Conjugate Acid-Base Pairs

Learning Objectives

- Identify conjugate acid base pair.
- Define buffers and know the composition of different buffer systems.
- Describe how buffers work.

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, $\mathrm{OH^-}$, and the conjugate acid of ammonia, $\mathrm{NH_4^+}$:

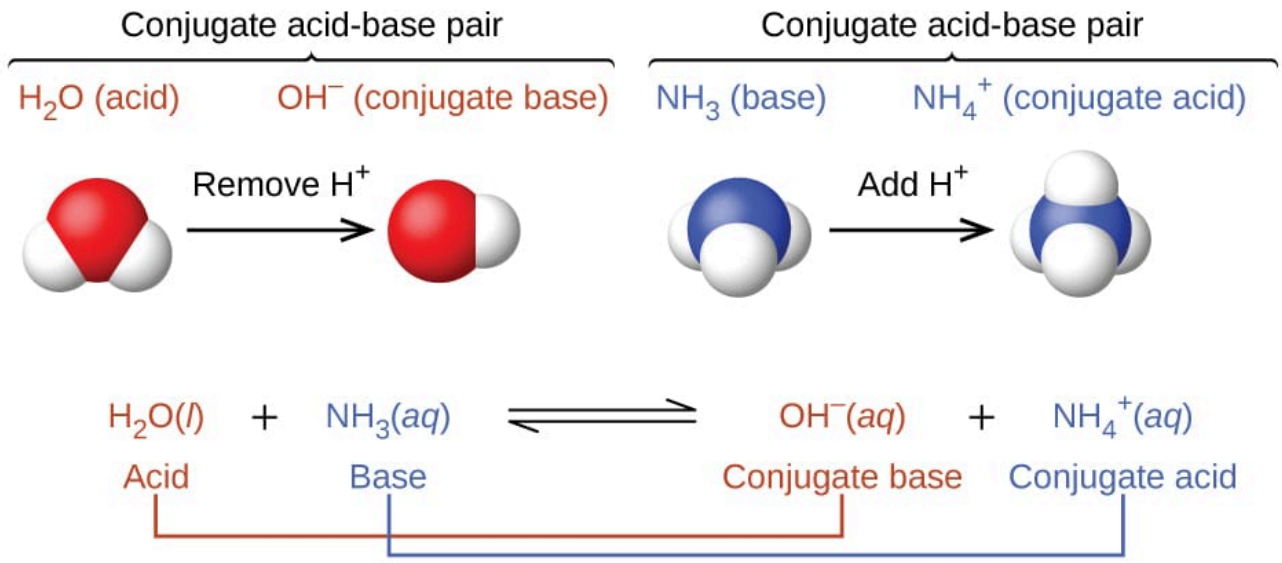
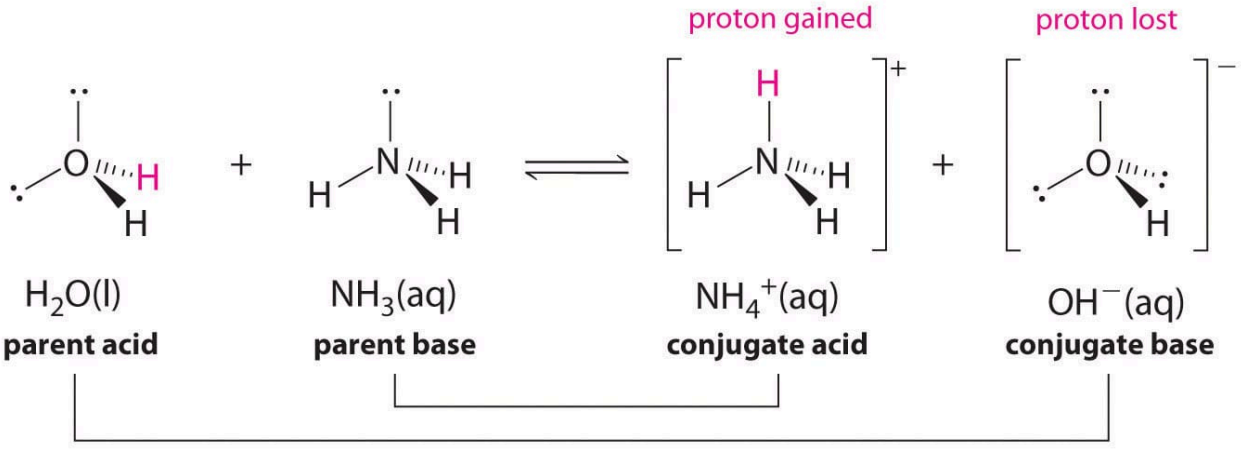


Figure 7.7.2.This figure has three parts in two rows. In the first row, two diagrams of acid-base pairs are shown. On the left, a space filling model of H subscript 2 O is shown with a red O atom at the center and two smaller white H atoms attached in a bent shape. Above this model is the label “H subscript 2 O (acid)” in purple. An arrow points right, which is labeled “Remove H superscript plus.” To the right is another space filling model with a single red O atom to which a single smaller white H atom is attached. The label in purple above this model reads, “O H superscript negative (conjugate base).” Above both of these red and white models is an upward pointing bracket that is labeled “Conjugate acid-base pair.” To the right is a space filling model with a central blue N atom to which three smaller white H atoms are attached in a triangular pyramid arrangement. A label in green above reads “N H subscript 3 (base).” An arrow labeled “Add H superscript plus” points right. To the right of the arrow is another space filling model with a blue central N atom and four smaller white H atoms in a tetrahedral arrangement. The green label above reads “N H subscript 3 superscript plus (conjugate acid).” Above both of these blue and white models is an upward pointing bracket that is labeled “Conjugate acid-base pair.” The second row of the figure shows the chemical reaction, H subscript 2 O (l) is shown in purple, and is labeled below in purple as “acid,” plus N H subscript 3 (a q) in green, labeled below in green as “base,” followed by a double sided arrow arrow and O H superscript negative (a q) in purple, labeled in purple as “conjugate base,” plus N H subscript 4 superscript plus (a q)” in green, which is labeled in green as “conjugate acid.” The acid on the left side of the equation is connected to the conjugate base on the right with a purple line. Similarly, the base on the left is connected to the conjugate acid on the right side.

In the 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^-.



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Figure 7.7.2. 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

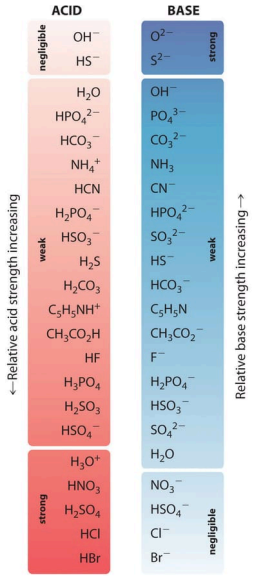


Figure 7.7.3 The Relative Strengths of Some Common Conjugate Acid–Base Pairs

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 7.7.1

Identify the conjugate acid-base pairs in this equilibrium.

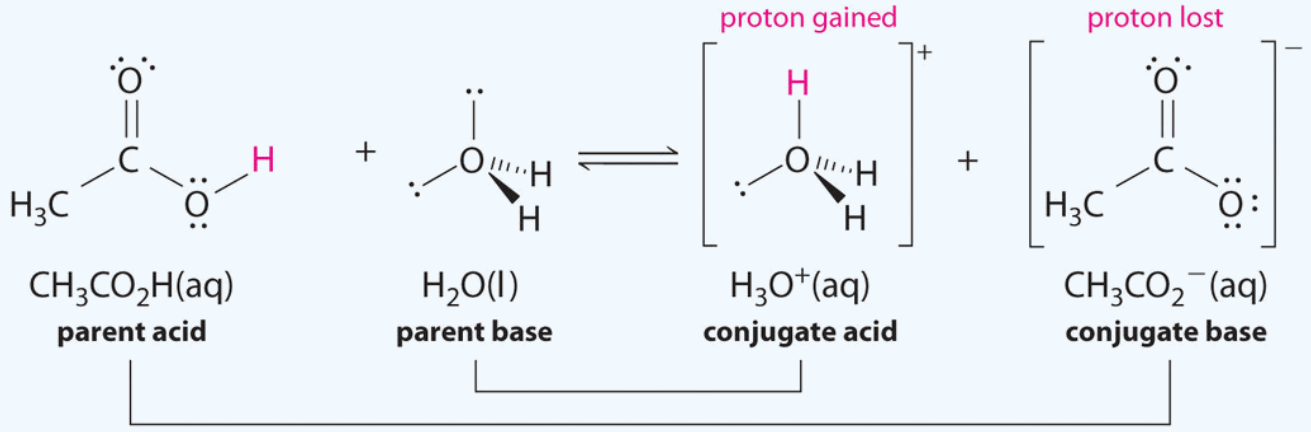
$$\mathrm{CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-}$$

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 7.7.1 the reaction of acetic acid with water

Example 7.7.2

Identify the conjugate acid-base pairs in this equilibrium.

$$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$$

Solution

One pair is H2O and OH^-, where H2O 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 (CH3)3N and $(CH_3)_3NH^+$, where $(CH_3)_3NH^+$ is the conjugate acid (it has an additional proton) and (CH3)3N is the conjugate base.

Exercise 7.7.1

Identify the conjugate acid-base pairs in this equilibrium.

$$NH_2^- + H_2O \rightleftharpoons NH_3 + OH^-$$

Answer: available at the end of this section.

Buffer Solutions

Weak acids are relatively common, even in the foods we eat. But we occasionally encounter a strong acid or base, such as stomach acid, which has a strongly acidic pH of 1.7. By definition, strong acids and bases can produce a relatively large amount of H^+ or OH^- ions and consequently have marked chemical activities. In addition, very small amounts of strong acids and bases can change the pH of a solution very quickly. If 1 mL of stomach acid [approximated as 0.1 M HCl(aq)] were added to the bloodstream and no correcting mechanism were present, the pH of the blood would decrease from about 7.4 to about 4.7—a pH that is not conducive to continued living. Fortunately, the body has a mechanism for minimizing such dramatic pH changes.

This mechanism involves a **buffer**, a solution that resists dramatic changes in pH. Buffers do so by being composed of certain pairs of solutes: either a weak acid plus a salt derived from that weak acid, or a weak base plus a salt of that weak base. For example, a buffer can be composed of dissolved HC2H3O2 (a weak acid) and NaC2H3O2 (the salt derived from that weak acid). Another example of a buffer is a solution containing NH3 (a weak base) and NH4Cl (a salt derived from that weak base).

Let us use an $HC_2H_3O_2/NaC_2H_3O_2$ buffer to demonstrate how buffers work. If a strong base—a source of $OH^-(aq)$ ions—is added to the buffer solution, those OH^- ions will react with the $HC_2H_3O_2$ in an acid-base reaction:

$$HC_2H_3O_2\,(aq) + OH^-\,(aq) \rightarrow H_2O(\ell) + C_2H_3O_2^-\,(aq) \tag{7.7.1}$$

Rather than changing the pH dramatically by making the solution basic, the added OH^- ions react to make H_2O, so the pH does not change much.

If a strong acid—a source of H^+ ions—is added to the buffer solution, the H^+ ions will react with the anion from the salt. Because $HC_2H_3O_2$ is a weak acid, it is not ionized much. This means that if lots of H^+ ions and $C_2H_3O_2^-$ ions are present in the same solution, they will come together to make $HC_2H_3O_2$:

$$H^+\,(aq) + C_2H_3O_2^-\,(aq) \rightarrow HC_2H_3O_2\,(aq) \tag{7.7.2}$$

Rather than changing the pH dramatically and making the solution acidic, the added H^+ ions react to make molecules of a weak acid. Figure 7.7.2 illustrates both actions of a buffer.

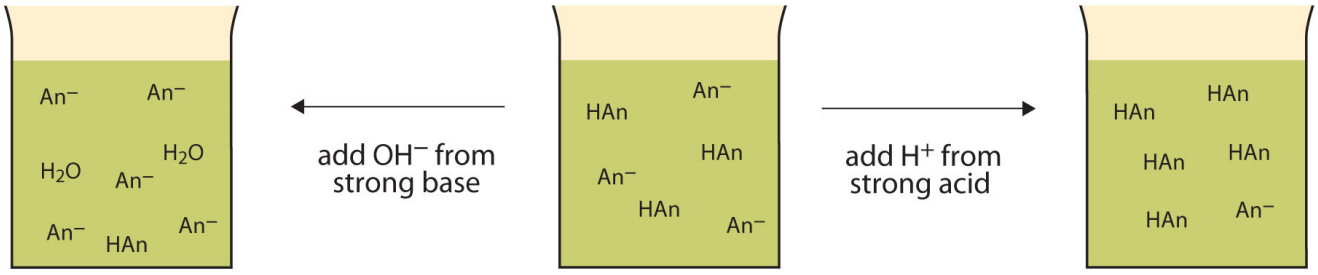


Figure 7.7.4 The actions of buffers. Buffers can react with both strong acids (top) and strong bases (side) to minimize large changes in pH.

Buffers made from weak bases and salts of weak bases act similarly. For example, in a buffer containing NH_3 and NH_4Cl, NH_3 molecules can react with any excess H^+ ions introduced by strong acids:

$$NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq)$$

while the $NH_4^+(aq)$ ion can react with any OH^- ions introduced by strong bases:

$$NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(aq) + H_2O(\ell)$$

Some common buffer systems are listed in the table below.

Table 7.7.1 Some Common Buffers

Table 7.7.1 Some Common Buffers		
Buffer System	**Buffer Components**	**pH of buffer (equal molarities of both components)**
Acetic acid/acetate ion	CH_3COOH/CH_3COO^-	4.74
Carbonic acid/hydrogen carbonate ion	H_2CO_3/HCO_3^-	6.38
Dihydrogen phosphate ion/hydrogen phosphate ion	$H_2PO_4^-/HPO_4^{2-}$	7.21
Ammonia/ammonium ion	NH_3/NH_4^+	9.25

Buffers work well only for limited amounts of added strong acid or base. Once either solute is completely reacted, the solution is no longer a buffer, and rapid changes in pH may occur. We say that a buffer has a certain **capacity**. Buffers that have more solute dissolved in them to start with have larger capacities, as might be expected.

Human blood has a buffering system to minimize extreme changes in pH. One buffer in blood is based on the presence of HCO_3^- and H_2CO_3 [the second compound is another way to write $CO_2(aq)$]. With this buffer present, even if some stomach acid were to find its way directly into the bloodstream, the change in the pH of blood would be minimal. Inside many of the body's cells, there is a buffering system based on phosphate ions.

Example 7.7.3:

Which combinations of compounds can make a buffer solution?

1. $HCHO_2$ and $NaCHO_2$
2. HCl and NaCl
3. CH_3NH_2 and CH_3NH_3Cl
4. NH_3 and NaOH

Solution

1. $HCHO_2$ is formic acid, a weak acid, while $NaCHO_2$ is the salt made from the anion of the weak acid (the formate ion [CHO_2^-]). The combination of these two solutes would make a buffer solution.
2. HCl is a strong acid, not a weak acid, so the combination of these two solutes would not make a buffer solution.
3. CH_3NH_2 is methylamine, which is like NH_3 with one of its H atoms substituted with a CH_3 group. Because it is not listed in Table 7.7.1, we can assume that it is a weak base. The compound CH_3NH_3Cl is a salt made from that weak base, so the combination of these two solutes would make a buffer solution.
4. NH_3 is a weak base, but NaOH is a strong base. The combination of these two solutes would not make a buffer solution.

Exercise 7.7.2

Which combinations of compounds can make a buffer solution?

1. $NaHCO_3$ and NaCl
2. H_3PO_4 and NaH_2PO_4
3. NH_3 and $(NH_4)_3PO_4$
4. NaOH and NaCl

Answer a 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.

Food and Drink Application: the Acid that Eases Pain

Although medicines are not exactly "food and drink," we do ingest them, so let's take a look at an acid that is probably the most common medicine: acetylsalicylic acid, also known as aspirin. Aspirin is well known as a pain reliever and antipyretic (fever reducer).

The structure of aspirin is shown in the accompanying figure. The acid part is circled; it is the H atom in that part that can be donated as aspirin acts as a Brønsted-Lowry acid. Because it is not given in Table 7.7.1, acetylsalicylic acid is a weak acid. However, it is still an acid, and given that some people consume relatively large amounts of aspirin daily, its acidic nature can cause problems in the stomach lining, despite the stomach's defenses against its own stomach acid.

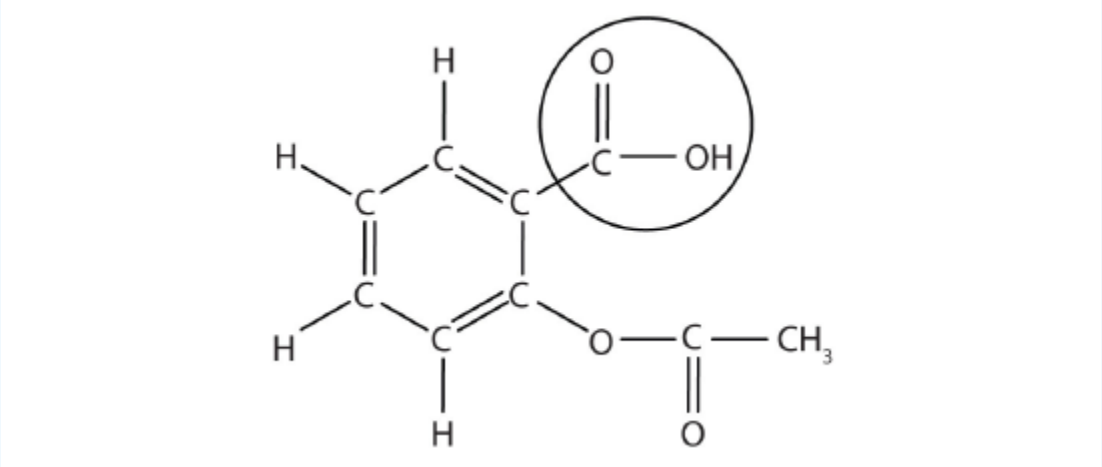


Figure 7.7.5: The Molecular Structure of Aspirin. The circled atoms are the acid part of the molecule.

Because the acid properties of aspirin may be problematic, many aspirin brands offer a "buffered aspirin" form of the medicine. In these cases, the aspirin also contains a buffering agent—usually MgO—that regulates the acidity of the aspirin to minimize its acidic side effects.

As useful and common as aspirin is, it was formally marketed as a drug starting in 1899. The US Food and Drug Administration (FDA), the governmental agency charged with overseeing and approving drugs in the United States, wasn't formed until 1906. Some have argued that if the FDA had been formed before aspirin was introduced, aspirin may never have gotten approval due to its potential for side effects—gastrointestinal bleeding, ringing in the ears, Reye's syndrome (a liver problem), and some allergic reactions. However, recently aspirin has been touted for its effects in lessening heart attacks and strokes, so it is likely that aspirin will remain on the market.

Summary

- A buffer is a solution that resists sudden changes in pH.
- Reactions showing how buffers regulate pH are described.

Contributors and Attributions

-
- TextMap: Beginning Chemistry (Ball et al.)
- Marisa Alviar-Agnew (Sacramento City College)

Answers

Exercise 7.7.1

H_2O (acid) and OH^- (base); NH_2^- (base) and NH_3 (acid)

Exercise 7.7.2

Yes.

Exercise 7.7.2

No. Need a weak acid or base and a salt of its conjugate base or acid.

Exercise 7.7.2

Yes.

Exercise 7.7.2

No. Need a weak base or acid.

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7.8: Acids and Bases in Industry and in Daily Life

Learning Objective

- Know the many uses of common acids and bases.

Antacids: A Basic Remedy

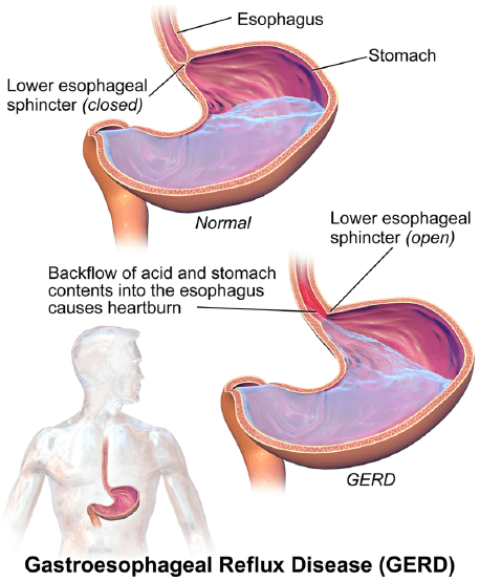


Figure 7.8.1. Antacids are available over the counter and are taken by mouth to quickly relieve occasional heartburn, the major symptom of gastroesophageal reflux disease and also indigestion. Treatment with antacids alone is symptomatic and only justified for minor symptoms.

Antacids contain alkaline ions that chemically neutralize stomach gastric acid, reducing damage and relieving pain. For example, Tums is a very commonly used antacid that can be bought over the counter. Other antacids, such as Alka Seltzer, work in similar ways. Below, show the mechanism and products for reaction in which calcium carbonate (the active ingredient in Tums) neutralizes HCl in a simple proton transfer reaction.

$$CaCO_3\,(s) + HCl\,(aq) \rightarrow H_2CO_3\,(aq) + CaCl_2\,(aq)$$

Following this acid-base reaction, carbonic acid quickly degrades into CO_2 and H_2O.

$$H_2CO_3\,(aq) \rightarrow CO_2(g) + H_2O(l)$$

Figure 7.8.1 *A comparison of a healthy condition to GERD. I*

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Under the generic name algeldrate, aluminium hydroxide is used as an antacid. Aluminium hydroxide is preferred over other alternatives such as sodium bicarbonate because $Al(OH)_3$, being insoluble, does not increase the pH of stomach above 7 and hence, does not trigger secretion of excess stomach acid. Brand names include Alu-Cap, Aludrox, Gaviscon, and Pepsamar. In 2016 Gaviscon was one of the biggest selling branded over-the-counter medications sold in Great Britain, with sales of £62 million. It reacts with excess acid in the stomach, reducing the acidity of the stomach content, which may relieve the symptoms of ulcers, heartburn or dyspepsia. Such products can cause constipation, because the aluminum ions inhibit the contractions of smooth muscle cells in the gastrointestinal tract, slowing peristalsis and lengthening the time needed for stool to pass through the colon. Some such products are formulated to minimize such effects through the inclusion of equal concentrations of magnesium hydroxide or magnesium carbonate, which have counterbalancing laxative effects.

Antacids are distinct from acid-reducing drugs like H_2-receptor antagonists or proton pump inhibitors and they do not kill the bacteria *Helicobacter pylori*, which causes most ulcers. Ranitidine (Zantac), famotidine (Pepcid AC), and cimetidine (Tagamet) are in a class of medications called H_2 blockers. It decreases the amount of acid made in the stomach and are used to treat ulcers; gastroesophageal reflux disease (GERD), a condition in which backward flow of acid from the stomach causes heartburn and injury of the food pipe (esophagus); and conditions where the stomach produces too much acid, such as Zollinger-Ellison syndrome. These over-the-counter medications are used to prevent and treat symptoms of heartburn associated with acid indigestion and sour stomach. Omeprazole (Prilosec) also works by decreasing the amount of acid made in the stomach and is in a class of medications called proton-pump inhibitors.

Acids and Bases in Industry and at Home

Common Acids

It should not be hard for you to name several common acids, but you might find that listing bases is just a little more difficult. Here's a partial list of some common acids, along with some chemical formulas:

Table 7.8.1 *Common Acids and Their Uses*

Chemist Name	Common Name	Uses
hydrochloric acid, HCl	muriatic acid (used in pools) and stomach acid	Used in cleaning (refining) metals, in maintenance of swimming pools, and for household cleaning.
sulfuric acid, H_2SO_4		Used in car batteries, and in the manufacture of fertilizers.
nitric acid, HNO_3		Used in the manufacture of fertilizers, explosives and in extraction of gold.
acetic acid, $HC_2H_3O_2$	vinegar	Main ingredient in vinegar.
carbonic acid, H_2CO_3	responsible for the "fiz" in carbonated drinks	As an ingredient in carbonated drinks.

Chemist Name	Common Name	Uses
citric acid, $C_6H_8O_7$		Used in food and dietary supplements. Also added as an acidulant in creams, gels, liquids, and lotions.
acetylsalicylic acid, $C_6H_4(OCOCH_3)CO_2H$	aspirin	The active ingredient in aspirin.

Hydrochloric Acid

Hydrochloric acid is a corrosive, strong mineral acid with many industrial uses. One of the most important applications of hydrochloric acid is in the pickling of steel, to remove rust or iron oxide scale from iron or steel before subsequent processing. Another major use of hydrochloric acid is in the production of organic compounds, such as vinyl chloride and dichloroethane for PVC. Other organic compounds produced with hydrochloric acid include bisphenol A for polycarbonate, activated carbon, and ascorbic acid, as well as numerous pharmaceutical products. Other inorganic compounds produced with hydrochloric acid include road application salt calcium chloride, nickel(II) chloride for electroplating, and zinc chloride for the galvanizing industry and battery production.

Sulfuric Acid

Sulfuric acid is a very important commodity chemical, and indeed, a nation's sulfuric acid production is a good indicator of its industrial strength. World production in the year 2004 was about 180 million tonnes, with the following geographic distribution: Asia 35%, North America (including Mexico) 24%, Africa 11%, Western Europe 10%, Eastern Europe and Russia 10%, Australia and Oceania 7%, South America 7%. Most of this amount (≈60%) is consumed for fertilizers, particularly superphosphates, ammonium phosphate and ammonium sulfates. About 20% is used in chemical industry for production of detergents, synthetic resins, dyestuffs, pharmaceuticals, petroleum catalysts, insecticides and antifreeze, as well as in various processes such as oil well acidicizing, aluminium reduction, paper sizing, water treatment. About 6% of uses are related to pigments and include paints, enamels, printing inks, coated fabrics and paper, and the rest is dispersed into a multitude of applications such as production of explosives, cellophane, acetate and viscose textiles, lubricants, non-ferrous metals, and batteries.



Figure 7.8.2: Drops of concentrated sulfuric acid rapidly decompose a piece of cotton towel by dehydration. (CC BY-SA 3.0; Toxic Walker).

Because the hydration of sulfuric acid is thermodynamically favorable (and is highly exothermic) and the affinity of it for water is sufficiently strong, sulfuric acid is an excellent dehydrating agent. Concentrated sulfuric acid has a very powerful dehydrating property, removing water (H_2O) from other compounds including sugar and other carbohydrates and producing carbon, heat, steam. Sulfuric acid behaves as a typical acid in its reaction with most metals by generating hydrogen gas (Equation ???).

Nitric Acid

Nitric acid (HNO_3) is a highly corrosive mineral acid and is also commonly used as a strong oxidizing agent. Nitric acid is normally considered to be a strong acid at ambient temperatures. The main industrial use of nitric acid is for the production of fertilizers. Nitric acid is neutralized with ammonia to give ammonium nitrate. This application consumes 75–80% of the 26 million tonnes produced annually (1987). The other main applications are for the production of explosives, nylon precursors, and specialty organic compounds.



Figure 7.8.3: Second degree burn caused by nitric acid. (CC BY-SA 3.0; Alcamán).

Table 7.8.2 Common Bases and Its Uses

Some Common Bases	Uses
sodium hydroxide, NaOH (lye or caustic soda)	Used in the manufacture of soaps and detergents and as the main ingredient in oven and drain cleaners.
potassium hydroxide, KOH (lye or caustic potash)	Used in the production of liquid soaps and soft soaps. Used in alkaline batteries.
magnesium hydroxide, $Mg(OH)_2$ (milk of magnesia)	Used as an ingredient in laxatives, antacids, and deodorants. Also used in the neutralization of acidic wastewater.
calcium hydroxide, $Ca(OH)_2$ (slaked lime)	Used in the manufacture of cement and lime water. Also, added to neutralize acidic soil.
aluminum hydroxide	Used in water purification and as an ingredient in antacids.
ammonia, NH_3	Used as a building block for the synthesis of many pharmaceutical products and in many commercial cleaning products. Used in the manufacture of fertilizers.

Sodium Hydroxide

Sodium hydroxide, also known as lye and caustic soda, is an inorganic compound with formula NaOH.

It is a popular strong base used in industry. Around 56% of sodium hydroxide produced is used by industry, 25% of which is used in the paper industry. Sodium hydroxide is also used in the manufacture of sodium salts and detergents, pH regulation, and organic synthesis. It is used in the Bayer process of aluminium production. In bulk, it is most often handled as an aqueous solution, since solutions are cheaper and easier to handle.

Sodium hydroxide is used in many scenarios where it is desirable to increase the alkalinity of a mixture, or to neutralize acids.



Figure 7.8.4 Sample of sodium hydroxide as pellets in a watchglass. (Public Domain; Walkerma).

Calcium Hydroxide

Calcium hydroxide (traditionally called slaked lime) is an inorganic compound with the chemical formula $\mathrm{Ca(OH)_2}$. It is a colorless crystal or white powder. It has many names including hydrated lime, caustic lime, builders' lime, slaked lime, cal, or pickling lime.

One significant application of calcium hydroxide is as a flocculant, in water and sewage treatment. It is also used in fresh water

treatment for raising the pH of the water so that pipes will not corrode where the base water is acidic, because it is self-regulating and does not raise the pH too much.

It is also used in the preparation of ammonia gas (NH_3), using the following reaction:

$$Ca(OH)_2 + 2NH_4Cl \rightarrow 2NH_3 + CaCl_2 + 2H_2O$$

Another large application is in the paper industry, where it is an intermediate in the reaction in the production of sodium hydroxide. Because of its low toxicity and the mildness of its basic properties, slaked lime is widely used in the food industry:

Ammonia

Ammonia is a compound of nitrogen and hydrogen with the formula $\mathrm{NH_3}$ and is a colorless gas with a characteristic pungent smell. It is the active product of “smelling salts,” and can quickly revive the faint of heart and light of head. Although common in nature and in wide use, ammonia is both caustic and hazardous in its concentrated form.

Globally, approximately 88% (as of 2014) of ammonia is used as fertilizers either as its salts, solutions or anhydrously. When applied to soil, it helps provide increased yields of crops such as maize and wheat. 30% of agricultural nitrogen applied in the US is in the form of anhydrous ammonia and worldwide 110 million tonnes are applied each year. Ammonia is also a building block for the synthesis of many pharmaceutical products and is used in many commercial cleaning products.

Summary

Common acids and bases have many and various uses in industry and in daily life.

Contributors and Attributions

-
- Peggy Lawson (Oxbow Prairie Heights School). Funded by Saskatchewan Educational Technology Consortium.
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8: OXIDATION AND REDUCTION

8.1: Oxidation and Reduction - Four Views
8.2: Oxidizing and Reducing Agents
8.3: Electrochemistry- Cells and Batteries
8.4: Corrosion and Explosion
8.5: Oxygen - An Abundant and Essential Oxidizing Agent
8.6: Some Common Reducing Agents
8.7: Oxidation, Reduction, and Living Things

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8.1: Oxidation and Reduction - Four Views

Learning Objectives

- Define *oxidation* and *reduction*.
- Assign oxidation numbers to atoms in simple compounds.
- Recognize a reaction as an oxidation-reduction reaction.

Oxygen is an element that has been known for centuries. In its pure elemental form, oxygen is highly reactive, and it readily makes compounds with most other elements. It is also the most abundant element by mass in the Earth's crust. The class of reactions called oxidation and reduction were originally defined with respect to the element oxygen.

Many elements simply combine with oxygen to form the oxide of that element. Heating magnesium in air allows it to combine with oxygen to form magnesium oxide.

$$2\mathrm{Mg}\,(s) + \mathrm{O_2}\,(g) \rightarrow 2\mathrm{MgO}\,(s)$$

Many compounds react with oxygen as well, often in very exothermic processes that are generally referred to as combustion reactions. For example, when methane burns, carbon dioxide and water are produced.

$$\mathrm{CH_4}\,(g) + 2\mathrm{O_2}\,(g) \rightarrow \mathrm{CO_2}\,(g) + 2\mathrm{H_2O}\,(g)$$

Carbon dioxide is an oxide of carbon, while water is an oxide of hydrogen. Early scientists viewed oxidation as a process in which a substance was reacted with oxygen to produce one or more oxides. In the previous examples, magnesium and methane are being oxidized.

The definitions of oxidation and reduction were eventually broadened to include similar types of reactions that do not necessarily involve oxygen. Oxygen is more electronegative than any element except for fluorine. Therefore, when oxygen is bonded to any element other than fluorine, electrons from the other atom are shifted away from that atom and toward the oxygen atom. An **oxidation-reduction reaction** (sometimes abbreviated as a **redox reaction**) *is a reaction that involves the full or partial transfer of electrons from one reactant to another*. **Oxidation** *involves a full or partial loss of electrons,* while **reduction** *involves a full or partial gain of electrons*.

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 **oxidation number** is a positive or negative number that is assigned to an atom to indicate its degree of oxidation or reduction. In oxidation-reduction processes, the driving force for chemical change is in the exchange of electrons between chemical species. A series of rules have been developed to help us.

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.
   Examples: $\mathrm{H_2}$, $\mathrm{Br_2}$, Na, Be, K, $\mathrm{O_2}$, $\mathrm{P_4}$, all have oxidation number of 0.
2. Atoms in monatomic (i.e., one-atom) ions are assigned an oxidation number equal to their charge.
   Example: In MgCl2, magnesium has an oxidation number of +2, while each chlorine atom has an oxidation number of –1

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].
   Example: 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.
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).
   Example: 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.

Note

Oxidation numbers are usually written with the sign first, then the magnitude, to differentiate them from charges.

Example 8.1.1

Assign oxidation numbers to the atoms in each substance.

1. Cl_2
2. GeO_2
3. $CaCl_2$

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. The Ca^{2+} ion has an oxidation number of +2 by rule 2. Also according to rule 2, each chlorine atom is assigned an oxidation number of –1.

Exercise 8.1.1: Phosphoric Acid

Assign oxidation numbers to the atoms in H_3PO_4.

Answer available at the end of this section.

Oxidation and Reduction Reactions

The processes of oxidation and reduction are commonly viewed in terms of the gain or loss of electrons or the increase or decrease in oxidation numbers. However, many reactions in organic chemistry that involve the gain or loss of oxygen or hydrogen are also considered as redox reactions.

The table below summarizes the processes of oxidation and reduction.

Table 8.1.1 The Processes of Oxidation and Reduction.

Oxidation	Reduction
Complete loss of electrons (ionic reaction)	Complete gain of electrons (ionic reaction)

Oxidation	Reduction
Increase in oxidation number	Decrease in oxidation number
Gain of oxygen	Loss of oxygen
Loss of hydrogen in a molecular compound	Gain of hydrogen in a molecular compound

1. Oxidation is complete loss of electrons. Reduction is complete gain of electrons

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.

Electrons that are lost are written as products; electrons that are gained are written as reactants. For example, the reaction below represents when acid is added to zinc metal.

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

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.

Note: "LEO says GER"

LEO stands for Losing Electrons is Oxidation, while GER stands for Gaining Electrons is Reduction.



Figure 8.1.1

> *This guy knows his redox reactions.*

2. Oxidation is an increase in oxidation number. Reduction is a decrease in oxidation number.

Consider the reaction below between elemental iron and copper sulfate:

$$\mathrm{Fe + CuSO_4 \rightarrow FeSO_4 + Cu}$$

In the course of the reaction, the oxidation number of Fe increases from zero to $+2$. The oxidation number of copper decreases from $+2$ to 0. This result is in accordance with the activity series. Iron is above copper in the series, so will be more likely to form $\mathrm{Fe^{2+}}$ while converting the $\mathrm{Cu^{2+}}$ to metallic copper $(\mathrm{Cu^0})$.

3. Oxidation is gain of oxygen. Reduction is loss of oxygen.

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 ($CH3CHO$) molecule takes on an oxygen atom to become acetic acid ($\mathrm{CH_3COOH}$).

$$\mathrm{2\,CH_3CHO + O_2 \longrightarrow 2\,CH_3COOH}$$

Thus, acetaldehyde is being oxidized.

4. Oxidation is loss of hydrogen in a molecular compound. Reduction is gain of hydrogen in a molecular compound.

Oxidation and reduction can be defined in terms of the gain or loss of hydrogen atoms. If a molecule adds hydrogen atoms, it is being reduced. If a molecule loses hydrogen atoms, the molecule is being oxidized. For example, in the conversion of acetaldehyde into ethanol CH_3CHO, hydrogen atoms are added to acetaldehyde, so the acetaldehyde is being reduced:

$$\mathrm{CH_3CHO + H_2 \longrightarrow CH_3CH_2OH}$$

Example 8.1.2

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 8.1.2

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. $CH_2{=}CH_2 \rightarrow CH_3CH_3$

Answers

a. oxidation

b. reduction
c. reduction

Example 8.1.3:

Identify what is being oxidized and reduced in this redox reaction.

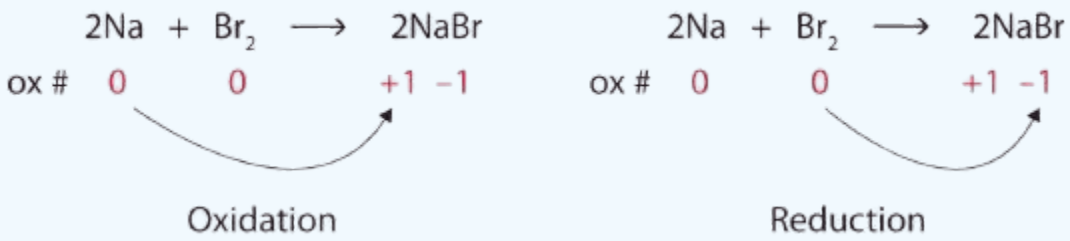
$$2\,\mathrm{Na} + \mathrm{Br_2} \longrightarrow 2\,\mathrm{NaBr}$$

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:



Example 8.1.3

$$2\,\mathrm{Na} + \mathrm{Br_2} \longrightarrow 2\,\mathrm{NaBr}$$

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 8.1.3

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.

Example 8.1.4: Gain or Loss of Electrons

For each half reaction, identify if there was a loss or gain of electrons.

a. $2N^{3-} \rightarrow N_2$
b. $Cr^{6+} \rightarrow Cr^{3+}$

Solutions

a. When we compare the overall charges on each side of the equation, we find a charge of 2(-3)=-6 on the left but a charge of 0 on the right. This equation is not properly balanced. To balance it, six electrons must be added on the right side as follows:

\[\ce{2N^{3-} → N2 + 6e^{-}}\nonumber \]

So there was a *loss of six electrons*. Now the equation is balanced, not only in terms of elements but also in terms of charge.

b. When we compare the overall charges on each side of the equation, we find a charge of +6 on the left and a charge of +3 on the right. This equation is not properly balanced. To end up with an oxidation number of +3 on the right side 3 electrons must be added on the left side as follows:

\[\ce{Cr^{6+} + 3e^{-} → Cr^{3+}\nonumber \]

So there was a *gain of three electrons*. Now the equation is balanced in terms of charge.

Exercise 8.1.4 Gain or Loss of Electrons

For each half reaction, identify if there was a loss or gain of electrons.

a. $O_2 \rightarrow 2O^{2-}$
b. $Cu^{+} \rightarrow Cu^{2+}$

Answers

a. gain of four electrons

b. loss of one electron

Example 8.1.5: 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.

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:

$$\mathrm{Ag^+ + e^- \longrightarrow Ag}$$

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

$$\mathrm{Al \longrightarrow Al^{3+} + 3\,e^-}$$

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

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

Example 8.1.5 Silver reduction reaction

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

Exercise 8.1.5

Write and balance the redox reaction that has calcium ions and potassium metal as reactants and calcium metal and potassium ions as products.

Summary

- Rules for determining oxidation numbers are listed.
- Examples of oxidation number determinations are provided.
- Chemical reactions in which electrons are transferred are called oxidation-reduction, or redox, reactions.
- Oxidation is defined in terms of the loss of electrons, gain of oxygen, loss of hydrogen, or an increase in oxidation number.
- Reduction is defined in terms of gain of electrons, loss of oxygen, gain of hydrogen, or a decrease in oxidation number.
- Oxidation and reduction always occur together, even though they can be written as separate chemical equations.

Contributors and Attributions

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Answers

Exercise 8.1.1: Phosphoric Acid

H: +1; O: −2; P: +5

Exercise 8.1.3

C is being oxidized from 0 to +4; O is being reduced from 0 to −2.

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8.2: Oxidizing and Reducing Agents

Learning Objective

- Identify oxidizing and reducing agents.

Life on planet Earth is a complicated and well-organized set of processes. Animals are designed to breathe oxygen and plants are designed to produce oxygen. Photosynthesis is the means by which we get the oxygen we need for life. Light striking a plant pigment known as chlorophyll initiates a complex series of reactions, many of which involve redox processes complete with movement of electrons. In this series of reactions, water is converted to oxygen gas, and we have something to sustain our lives.

The reaction below is a redox reaction that produces zinc sulfide:

$$\mathrm{Zn} + \mathrm{S} \rightarrow \mathrm{ZnS}$$

The half-reactions can be written:

$$\text{Oxidation: } \mathrm{Zn} \rightarrow \blacksquare + 2\mathrm{e}^-$$
$$\text{Reduction: } \mathrm{S} + 2\mathrm{e}^- \rightarrow \blacksquare$$

In the reaction above, zinc is being oxidized by losing electrons. However, there must be another substance present that gains those electrons and in this case that is the sulfur. In other words, the sulfur is causing the zinc to be oxidized. Sulfur is called the oxidizing agent. The zinc causes the sulfur to gain electrons and become reduced and so the zinc is called the reducing agent. The **oxidizing agent** is a substance that causes oxidation by accepting electrons; therefore, its oxidation state decreases. The **reducing agent** is a substance that causes reduction by losing electrons; therefore its oxidation state increases. The simplest way to think of this is that the oxidizing agent is the substance that is reduced, while the reducing agent is the substance that is oxidized as shown in Figure 8.2.1 and summarized in Table 8.2.1.

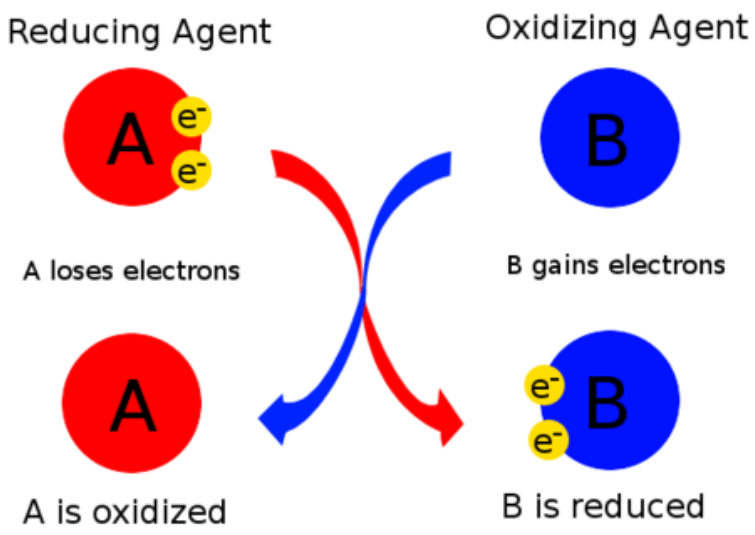


Figure 8.2.1 A reducing agent is oxidized and an oxidizing agent is reduced.

Note

Both the oxidizing and reducing agents are the *reactants* and therefore appear on the *left*-hand side of an equation.

Table 8.2.1: A Comparison of Oxidizing and Reducing Agents.

	Oxidizing Agents	Reducing Agents
Oxidation State	Decreases	Increases
# of Electrons	Gained	Lost
Substance is...	Reduced	Oxidized

The examples below show how to analyze a redox reaction and identify oxidizing and reducing agents.

Example 8.2.1 Half-equations

When chlorine gas is bubbled into a solution of sodium bromide, a reaction occurs which produces aqueous sodium chloride and bromine. Determine what is being oxidized and what is being reduced. Identify the oxidizing and reducing agents.

$$\mathrm{Cl_2}\,(g) + 2\mathrm{NaBr}\,(aq) \rightarrow 2\mathrm{NaCl}\,(aq) + \mathrm{Br_2}\,(l)$$

Solution:

Step 1: Plan the problem.

Break the reaction down into a net ionic equation and then into half-reactions. The substance that loses electrons is being oxidized and is the reducing agent. The substance that gains electrons is being reduced and is the oxidizing agent.

Step 2: Solve.

$$\mathrm{Cl_2}\,(g) + \cancel{2\mathrm{Na^+}\,(aq)} + 2\mathrm{Br^-}\,(aq) \rightarrow \cancel{2\mathrm{Na^+}\,(aq)} + 2\mathrm{Cl^-}\,(aq) + \mathrm{Br_2}\,(l)$$

$$\mathrm{Cl_2}\,(g) + 2\mathrm{Br^-}\,(aq) \rightarrow 2\mathrm{Cl^-}\,(aq) + \mathrm{Br_2}\,(l) \quad \text{(net ionic equation)}$$

$$\text{Reduction: } \mathrm{Cl_2}\,(g) + 2\mathrm{e^-} \rightarrow 2\mathrm{Cl^-}\,(aq)$$
$$\text{Oxidation: } 2\mathrm{Br^-}\,(aq) \rightarrow \mathrm{Br_2}\,(l) + 2\mathrm{e^-}$$

The $\mathrm{Cl_2}$ is being reduced and is the oxidizing agent. The $\mathrm{Br^-}$ is being oxidized and is the reducing agent.

Exercise 8.2.1 : Half-equations

Write the following reaction in the form of half-equations. Identify each half-equation as an oxidation or a reduction. Also identify the oxidizing agent and the reducing agent in the overall reaction

$$\mathrm{Zn} + 2\,\mathrm{Fe^{3+}} \longrightarrow \mathrm{Zn^{2+}} + 2\,\mathrm{Fe^{2+}}$$

Answer

The half-equations are

$\mathrm{Zn} \longrightarrow \mathrm{Zn^{2+}} + 2\,\mathrm{e^-}$ oxidation—loss of electrons

$2\,\mathrm{e^-} + 2\,\mathrm{Fe^{3+}} \longrightarrow 2\,\mathrm{Fe^{2+}}$ reduction—gain of electrons

Zinc has been oxidized, the oxidizing *agent* must have been the other reactant, namely, iron(III).

Iron(III) ion has been reduced, the zinc must be the reducing agent.

Example 8.2.2: Identify reducing and oxidizing agents

Identify the reducing and oxidizing agents in the balanced redox reaction:

$$Cl_2(aq) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$$

Oxidation half reaction

$$2Br^-(aq) \rightarrow Br_2(aq)$$

Oxidation States: -1 to 0

Reduction Half Reaction

$$Cl_2(aq) \rightarrow 2Cl^-(aq)$$

Oxidation States: 0 to -1

Overview

- Br^- *loses* an electron; it is *oxidized* from Br^- to Br_2; thus, Br^- is the *reducing agent*.
- Cl_2 *gains* one electron; it is *reduced* from Cl_2 to 2 Cl^-; thus, Cl_2 is the *oxidizing agent*.

Exercise 8.2.2: Identify reducing and oxidizing agents

Identify the oxidizing agent and the reducing agent in the following redox reaction:

$$MnO_4^- + SO_3^{2-} \rightarrow Mn^{2+} + SO_4^{2-}$$

Solution

S is the reducing agent and Mn is the oxidizing agent.

Summary

- An oxidizing agent is a substance that causes oxidation by accepting electrons; therefore, it gets reduced.
- A reducing agent is a substance that causes reduction by losing electrons; therefore it gets oxidized.
- Examples of how to identify oxidizing and reducing agents are shown.

Contributors and Attributions

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8.3: Electrochemistry- Cells and Batteries

Learning Objectives

- Define electrochemistry.
- Describe the basic components of electrochemical cells.
- List some of the characteristics, applications and limitations of cells and batteries.
- Know the difference between galvanic and electrolytic cells.
- Define electrolysis and list several of its applications.

Metal exposed to the outside elements will usually corrode if not protected. The corrosion process is a series of redox reactions involving the metal of the sculpture. In some situations, the metals are deliberately left unprotected so that the surface will undergo changes that may enhance the esthetic value of the work.

Electrochemical Reactions

Chemical reactions either absorb or release energy, which can be in the form of electricity. **Electrochemistry** is a branch of chemistry that deals with the interconversion of chemical energy and electrical energy. Electrochemistry has many common applications in everyday life. All sorts of batteries, from those used to power a flashlight to a calculator to an automobile, rely on chemical reactions to generate electricity. Electricity is used to plate objects with decorative metals like gold or chromium. Electrochemistry is important in the transmission of nerve impulses in biological systems. Redox chemistry, the transfer of electrons, is behind all electrochemical processes.

An **electrochemical cell** is any device that converts chemical energy into electrical energy or electrical energy into chemical energy. There are three components that make up an electrochemical reaction. There must be a solution where redox reactions can occur. These reactions generally take place in water to facilitate electron and ion movement. A conductor must exist for electrons to be transferred. This conductor is usually some kind of wire so that electrons can move from one site to another. Ions also must be able to move through some form of salt bridge that facilitates ion migration.

Luigi Galvani

Luigi Galvani (1737 - 1798) was an Italian physician and scientist who did research on nerve conduction in animals. His accidental observation of the twitching of frog legs when they were in contact with an iron scalpel while the legs hung on copper hooks led to studies on electrical conductivity in muscles and nerves. He believed that animal tissues contained an "animal electricity" similar to the natural electricity that caused lightning to form.



Figure 8.3.1: Alessandro Giuseppe Antonio Anastasio Volta (Public Domain; via Wikipedia)

Alessandro Volta developed the first "voltaic cell" in 1800. This battery consisted of alternating disks of zinc and silver with pieces of cardboard soaked in brine separating the disks. Since there were no voltmeters at the time (and no idea that the electric current was due to electron flow), Volta had to rely on another measure of battery strength: the amount of shock produced (it's never a good idea to test things on yourself). He found that the intensity of the shock increased with the number of metal plates in the system. Devices with twenty plates produced a shock that was quite painful. It's a good thing we have voltmeters today to measure electric current instead of the "stick your finger on this and tell me what you feel" method.

Galvanic (Voltaic) Cells

Galvanic cells, also known as voltaic cells, are electrochemical cells in which spontaneous oxidation-reduction reactions produce electrical energy. In writing the equations, it is often convenient to separate the oxidation-reduction reactions into half-reactions to facilitate balancing the overall equation and to emphasize the actual chemical transformations.

Consider what happens when a clean piece of copper metal is placed in a solution of silver nitrate (Figure 8.3.1). As soon as the copper metal is added, silver metal begins to form and copper ions pass into the solution. The blue color of the solution on the far right indicates the presence of copper ions. The reaction may be split into its two half-reactions. Half-reactions separate the oxidation from the reduction, so each can be considered individually.

$$\begin{aligned}
&\text{oxidation: } \mathrm{Cu}(s) \longrightarrow \mathrm{Cu}^{2+}(aq) + 2\,\mathrm{e}^- \\
&\text{reduction: } 2 \times (\mathrm{Ag}^+(aq) + \mathrm{e}^- \longrightarrow \mathrm{Ag}(s)) \qquad \text{or} \qquad 2\,\mathrm{Ag}^+(aq) + 2\,\mathrm{e}^- \longrightarrow 2\,\mathrm{Ag}(s) \\
&\text{overall: } 2\,\mathrm{Ag}^+(aq) + \mathrm{Cu}(s) \longrightarrow 2\,\mathrm{Ag}(s) + \mathrm{Cu}^{2+}(aq)
\end{aligned}$$

The equation for the reduction half-reaction had to be doubled so the number electrons “gained” in the reduction half-reaction equaled the number of electrons “lost” in the oxidation half-reaction.

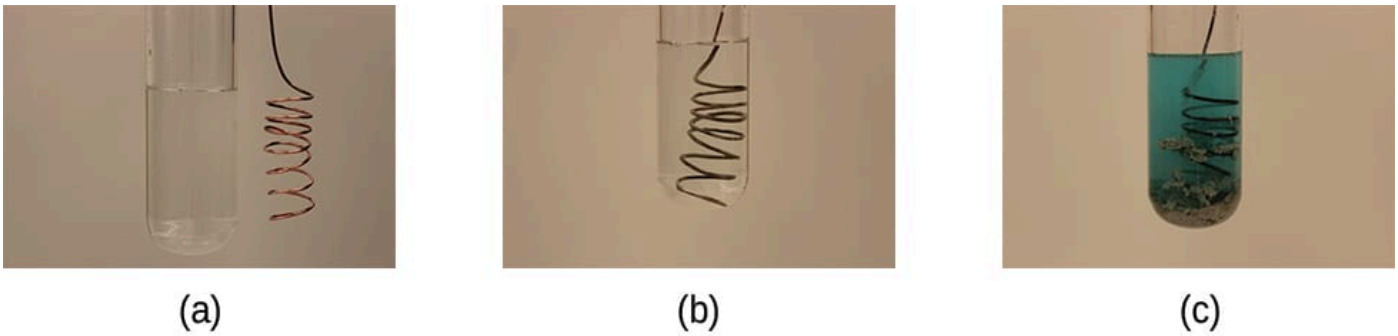


Figure 8.3.1 When a clean piece of copper metal is placed into a clear solution of silver nitrate (a), an oxidation-reduction reaction occurs that results in the exchange of Cu2+ for Ag+ ions in solution. As the reaction proceeds (b), the solution turns blue (c) because of the copper ions present, and silver metal is deposited on the copper strip as the silver ions are removed from solution. (CC BY 4.0; modification of work by Mark Ott via OpenStax)

Galvanic or voltaic cells involve spontaneous electrochemical reactions in which the half-reactions are separated (Figure 8.3.2) so that current can flow through an external wire. The beaker on the left side of the figure is called a half-cell, and contains a 1 *M* solution of copper(II) nitrate [$Cu(NO_3)_2$] with a piece of copper metal partially submerged in the solution. The copper metal is an electrode. The copper is undergoing oxidation; therefore, the copper electrode is the **anode**. The anode is connected to a voltmeter with a wire and the other terminal of the voltmeter is connected to a silver electrode by a wire. The silver is undergoing reduction; therefore, the silver electrode is the **cathode**. The half-cell on the right side of the figure consists of the silver electrode in a 1 *M* solution of silver nitrate ($AgNO_3$). At this point, no current flows—that is, no significant movement of electrons through the wire occurs because the circuit is open. The circuit is closed using a salt bridge, which transmits the current with moving ions.

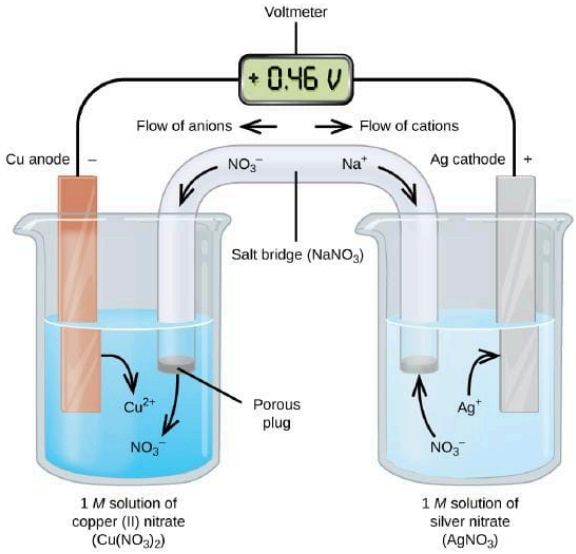


Figure 8.3.2 A standard Cu-Ag galvanic cell.

The salt bridge consists of a concentrated, nonreactive, electrolyte solution such as the sodium nitrate ($NaNO_3$) solution used in this example. As electrons flow from left to right through the electrode and wire, nitrate ions (anions) pass through the porous plug on the left into the copper(II) nitrate solution. This keeps the beaker on the left electrically neutral by neutralizing the charge on the copper(II) ions that are produced in the solution as the copper metal is oxidized. At the same time, the nitrate ions are moving to the left, sodium ions (cations) move to the right, through the porous plug, and into the silver nitrate solution on the right. These added cations “replace” the silver ions that are removed from the solution as they were reduced to silver metal, keeping the beaker on the right electrically neutral.

When the electrochemical cell is constructed in this fashion, a positive cell potential (0.46 V) indicates a spontaneous reaction *and* that the electrons are flowing from the left to the right.

Key Features of a Standard Galvanic Cell (as shown in Figure 8.3.2

- Electrons flow from the anode to the cathode: left to right in the standard galvanic cell.
- The electrode in the left half-cell is the anode because oxidation occurs here. The name refers to the flow of anions in the salt bridge toward it.
- The electrode in the right half-cell is the cathode because reduction occurs here. The name refers to the flow of cations in the salt bridge toward it.
- Oxidation occurs at the anode (the left half-cell in the figure).
- Reduction occurs at the cathode (the right half-cell in the figure).
- The salt bridge must be present to close (complete) the circuit and both an oxidation and reduction must occur for current to flow.

Example 8.3.1: Chromium-Copper Galvanic Cell

Consider a galvanic cell consisting of

$$2\,\mathrm{Cr}(s) + 3\,\mathrm{Cu}^{2+}(aq) \longrightarrow 2\,\mathrm{Cr}^{3+}(aq) + 3\,\mathrm{Cu}(s)$$

Write the oxidation and reduction half-reactions. Which reaction occurs at the anode? The cathode?

Solution

By inspection, Cr is oxidized when three electrons are lost to form Cr^{3+}, and Cu^{2+} is reduced as it gains two electrons to form Cu. Balancing the charge gives

$$\begin{aligned}&\text{oxidation: } 2\,\mathrm{Cr}(s) \longrightarrow 2\,\mathrm{Cr}^{3+}(aq) + 6\,\mathrm{e}^-\\&\text{reduction: } 3\,\mathrm{Cu}^{2+}(aq) + 6\,\mathrm{e}^- \longrightarrow 3\,\mathrm{Cu}(s)\\&\overline{\text{overall: } 2\,\mathrm{Cr}(s) + 3\,\mathrm{Cu}^{2+}(aq) \longrightarrow 2\,\mathrm{Cr}^{3+}(aq) + 3\,\mathrm{Cu}(s)}\end{aligned}$$

Cell notation uses the simplest form of each of the equations, and starts with the reaction at the anode. No concentrations were specified so:

$$\mathrm{Cr}(s)\,|\,\mathrm{Cr}^{3+}(aq)\,\|\,\mathrm{Cu}^{2+}(aq)\,|\,\mathrm{Cu}(s).$$

Oxidation occurs at the anode and reduction at the cathode.

Exercise 8.3.1 Copper-Zinc Galvanic Cell

Consider a galvanic cell consisting of

$$\mathrm{Zn}(s) + \mathrm{Cu}^{2+}(aq) \longrightarrow \mathrm{Zn}^{2+}(aq) + \mathrm{Cu}(s)$$

Write the oxidation and reduction half-reactions. Which reaction occurs at the anode? The cathode?

Answer available at the end of this section.

Batteries

A battery is an electrochemical cell or series of cells that produces an electric current. In principle, any galvanic cell could be used as a battery. An ideal battery would never run down, produce an unchanging voltage, and be capable of withstanding environmental extremes of heat and humidity. Real batteries strike a balance between ideal characteristics and practical limitations. For example, the mass of a car battery is about 18 kg or about 1% of the mass of an average car or light-duty truck. This type of battery would supply nearly unlimited energy if used in a smartphone, but would be rejected for this application because of its mass. Thus, no single battery is “best” and batteries are selected for a particular application, keeping things like

the mass of the battery, its cost, reliability, and current capacity in mind. There are two basic types of batteries: primary and secondary. A few batteries of each type are described next.

Visit this site to learn more about batteries.

Dry Cells (Primary Batteries)

Primary batteries are single-use batteries because they cannot be recharged. A common primary battery is the **dry cell** (Figure 8.3.1). The dry cell is a zinc-carbon battery. The zinc can serves as both a container and the negative electrode. The positive electrode is a rod made of carbon that is surrounded by a paste of manganese(IV) oxide, zinc chloride, ammonium chloride, carbon powder, and a small amount of water. The reaction at the anode can be represented as the ordinary oxidation of zinc:

$$\mathrm{Zn}(s) \longrightarrow \mathrm{Zn}^{2+}(aq) + 2\,\mathrm{e}^-$$

[Original Image Removed]

Figure 8.3.3 A diagram of a cross section of a dry cell battery is shown. The overall shape of the cell is cylindrical. The lateral surface c cylinder, indicated as a thin red line, is labeled “zinc can (electrode).” Just beneath this is a slightly thicker dark grey surface that cove lateral surface, top, and bottom of the battery, which is labeled “Porous separator.” Inside is a purple region with many evenly spaced darker purple dots, labeled “Paste of M n O subscript 2, N H subscript 4 C l, Z n C l subscript 2, water (cathode).” A dark grey rod, lab “Carbon rod (electrode),” extends from the top of the battery, leaving a gap of less than one-fifth the height of the battery below the rod bottom of the cylinder. A thin grey line segment at the very bottom of the cylinder is labeled “Metal bottom cover (negative).” The very the cylinder has a thin grey surface that curves upward at the center over the top of the carbon electrode at the center of the cylinder. upper surface is labeled “Metal top cover (positive).” A thin dark grey line just below this surface is labeled “Insulator.” Below this, abo purple region, and outside of the carbon electrode at the center is an orange region that is labeled “Seal.”

The reaction at the cathode is more complicated, in part because more than one reaction occurs. The series of reactions that occurs at the cathode is approximately

$$2\,\mathrm{MnO_2}(s) + 2\,\mathrm{NH_4Cl}(aq) + 2\,\mathrm{e}^- \longrightarrow \mathrm{Mn_2O_3}(s) + 2\,\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) + 2\,\mathrm{Cl}^-$$

The overall reaction for the zinc–carbon battery can be represented as

$$2\,\mathrm{MnO_2}(s) + 2\,\mathrm{NH_4Cl}(aq) + \mathrm{Zn}(s) \longrightarrow \mathrm{Zn}^{2+}(aq) + \mathrm{Mn_2O_3}(s) + 2\,\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) + 2\,\mathrm{Cl}^-$$

with an overall cell potential which is initially about 1.5 V, but decreases as the battery is used. It is important to remember that the voltage delivered by a battery is the same regardless of the size of a battery. For this reason, D, C, A, AA, and AAA batteries all have the same voltage rating. However, larger batteries can deliver more moles of electrons.

Take Note

The dry cell is not very efficient in producing electrical energy because only the relatively small fraction of the MnO_2 that is near the cathode is actually reduced and only a small fraction of the zinc cathode is actually consumed as the cell discharges. In addition, dry cells have a limited shelf life because the Zn anode reacts spontaneously with NH_4Cl in the electrolyte, causing the case to corrode and allowing the contents to leak out (Figure 8.3.2).



Figure 8.3.2 A dry cell with a leak. Source: Photo courtesy of Mitchclanky2008, http://www.flickr.com/photos/25597837@N05/2422765479/.

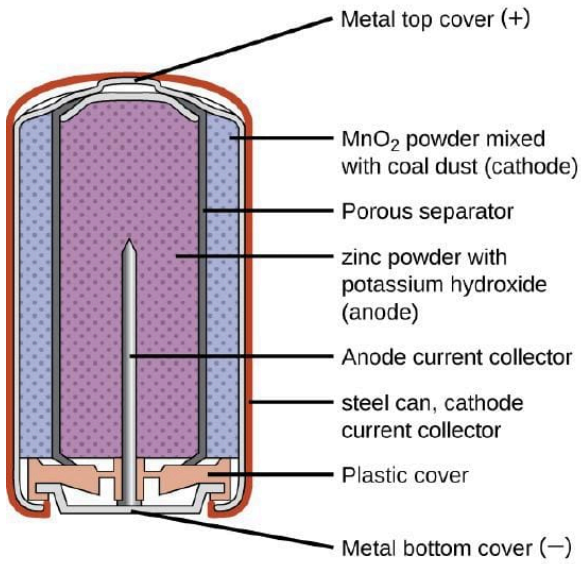


Figure 8.3.4 A cross section of an alkaline battery.

Alkaline batteries (Figure 8.3.4) were developed in the 1950s partly to address some of the performance issues with zinc–carbon dry cells. They are manufactured to be exact replacements for zinc-carbon dry cells. As their name suggests, these types of batteries use alkaline electrolytes, often potassium hydroxide.

An alkaline battery can deliver about three to five times the energy of a zinc-carbon dry cell of similar size. Alkaline batteries are prone to leaking potassium hydroxide, so these should also be removed from devices for long-term storage. While some alkaline batteries are rechargeable, most are not.

Warning

Attempts to recharge an alkaline battery that is not rechargeable often leads to rupture of the battery and leakage of the potassium hydroxide electrolyte.

Lead Storage Batteries (Secondary Batteries)

The lead acid battery (Figure 8.3.5) is the type of secondary battery used in your automobile. Secondary batteries are rechargeable. The lead acid battery is inexpensive and capable of producing the high current required by automobile starter motors. The reactions for a lead acid battery are

$$\begin{aligned}&\text{anode: } \mathrm{Pb}(s) + \mathrm{HSO_4}^-(aq) \longrightarrow \mathrm{PbSO_4}(s) + \mathrm{H}^+(aq) + 2\,\mathrm{e}^-\\ &\underline{\text{cathode: } \mathrm{PbO_2}(s) + \mathrm{HSO_4}^-(aq) + 3\,\mathrm{H}^+(aq) + 2\,\mathrm{e}^- \longrightarrow \mathrm{PbSO_4}(s) + 2\,\mathrm{H_2O}(l)}\\ &\text{overall: } \mathrm{Pb}(s) + \mathrm{PbO_2}(s) + 2\,\mathrm{H_2SO_4}(aq) \longrightarrow 2\,\mathrm{PbSO_4}(s) + 2\,\mathrm{H_2O}(l)\end{aligned}$$

Each cell produces 2 V, so six cells are connected in series to produce a 12-V car battery. Lead acid batteries are heavy and contain a caustic liquid electrolyte, but are often still the battery of choice because of their high current density. The lead acid battery in your automobile consists of six cells connected in series to give 12 V. Their low cost and high current output makes these excellent candidates for providing power for automobile starter motors.

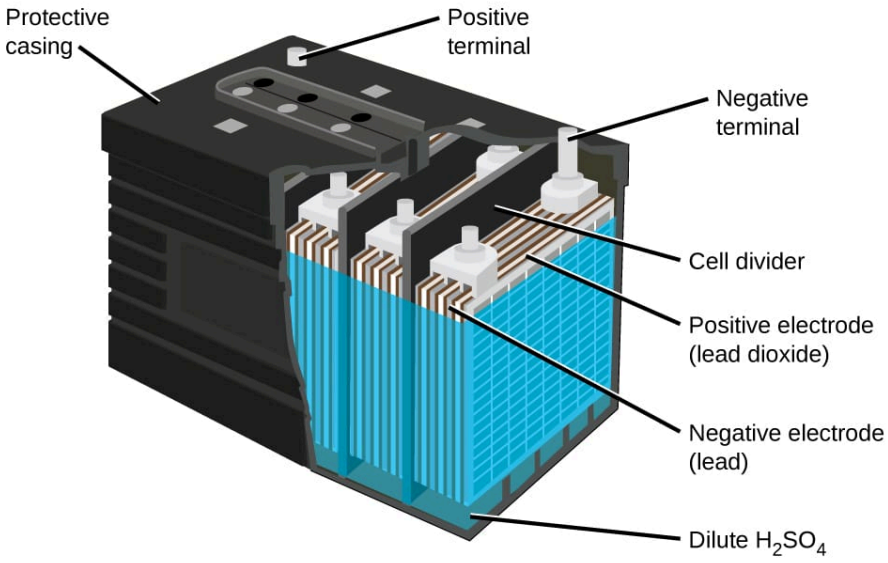


Figure 8.3.5 A lead (acid) storage battery.

As mentioned earlier, unlike a dry cell, the lead storage battery is rechargeable. Note that the forward redox reaction generates solid lead (II) sulfate which slowly builds up on the plates. Additionally, the concentration of sulfuric acid decreases. When the car is running normally, its generator **recharges** the battery by forcing the above reactions to run in the opposite, or non spontaneous direction.

$$2\mathrm{PbSO_4}\,(s) + 2\mathrm{H_2O}\,(l) \rightarrow \mathrm{Pb}\,(s) + \mathrm{PbO_2}\,(s) + 4\mathrm{H}^+\,(aq) + 2{\mathrm{SO_4}}^{2-}\,(aq)$$

This reaction regenerates the lead, lead (IV) oxide, and sulfuric acid needed for the battery to function properly. Theoretically, a lead storage battery should last forever. In practice, the recharging is not 100% efficient because some of the lead (II) sulfate falls from the electrodes and collects on the bottom of the cells.

Warning

Lead storage batteries contain a significant amount of lead so they must always be disposed of properly.

Other Batteries

The **nickel–cadmium**, or NiCad, battery (Figure 8.3.6) is used in small electrical appliances and devices like drills,

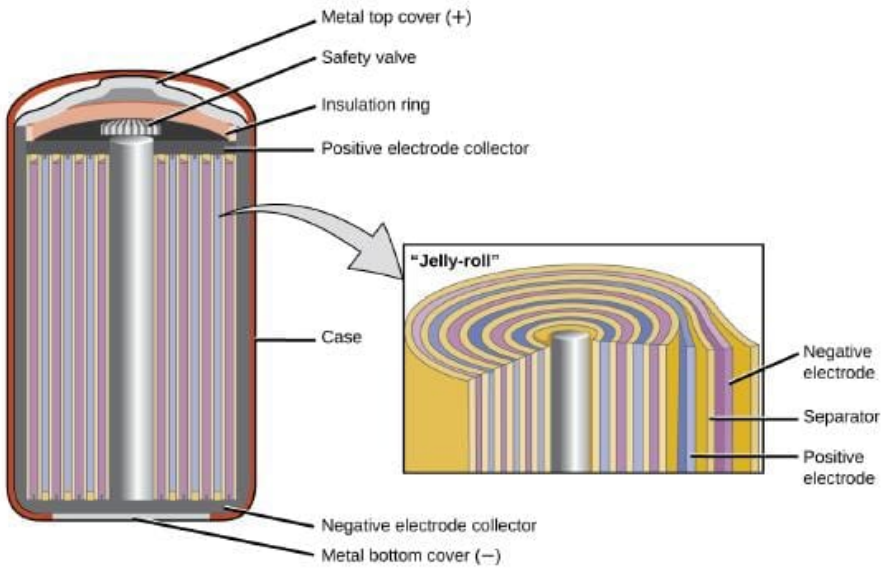


Figure 8.3.6 NiCd battery with “jelly-roll” design.

portable vacuum cleaners, and AM/FM digital tuners. It consists of a nickel-plated cathode, cadmium-plated anode, and a potassium hydroxide electrode. The positive and negative plates, which are prevented from shorting by the separator, are rolled together and put into the case. This is a “jelly-roll” design and allows the NiCd cell to deliver much more current than a similar-sized alkaline battery.

The voltage is about 1.2 V to 1.25 V as the battery discharges. When properly treated, a NiCd battery can be recharged about 1000 times.

Warning

Cadmium is a toxic heavy metal so NiCd batteries should never be opened or put into the regular trash.

Lithium ion batteries are among the most popular rechargeable batteries and are used in many portable electronic devices. The battery voltage is about 3.7 V. Lithium batteries are popular because they can provide a large amount current, are lighter than comparable batteries of other types, produce a nearly constant voltage as they discharge, and only slowly lose their charge when stored. Specialized **lithium-iodide (polymer) batteries** find application in many long-life, critical devices, such as pacemakers and other implantable electronic medical devices. These devices are designed to last 15 or more years.

Disposable primary lithium batteries must be distinguished from secondary lithium-ion or a lithium-polymer. The term "lithium battery" refers to a family of different lithium-metal chemistries, comprising many types of cathodes and electrolytes but all with metallic lithium as the anode. Lithium batteries are widely used in portable consumer electronic devices, and in electric vehicles ranging from full sized vehicles to radio controlled toys.

A **watch battery, coin** or **button cell** (Figure 8.3.7) is a small single cell battery shaped as a squat cylinder typically 5 to 25 mm

(0.197 to 0.984 in) in diameter and 1 to 6 mm (0.039 to 0.236 in) high — like a button on a garment, hence the name. A metal can forms the bottom body and positive terminal of the cell. An insulated top cap is the negative terminal. Button cells are single cells, usually disposable primary cells. Common anode materials are zinc or lithium. Common cathode materials are manganese dioxide, silver oxide, carbon monofluoride, cupric oxide or oxygen from the air. Mercuric oxide button cells were formerly common, but are no longer available due to the toxicity and environmental effects of mercury.

Warning

Button cells are very dangerous for small children. Button cells that are swallowed can cause severe internal burns and significant injury or death.

Fuel Cells

A fuel cell is a device that converts chemical energy into electrical energy. Fuel cells are similar to

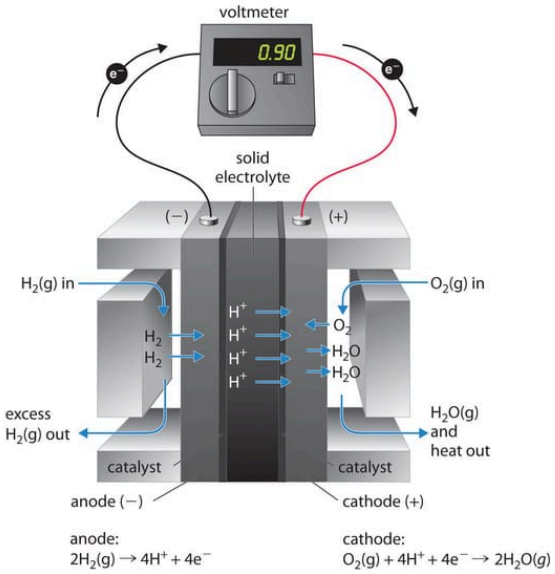


Figure 8.3.8 A hydrogen fuel cell.

batteries but require a continuous source of fuel, often hydrogen. They will continue to produce electricity as long as fuel is available. Hydrogen fuel cells have been used to supply power for satellites, space capsules, automobiles, boats, and submarines (Figure 8.3.8).

The voltage is about 0.9 V. The efficiency of fuel cells is typically about 40% to 60%, which is higher than the typical internal combustion engine (25% to 35%) and, in the case of the hydrogen fuel cell, produces only water as exhaust. Although fuel cells are an essentially pollution-free means of obtaining electrical energy, their expense and technological complexity have thus far limited their applications.

Electrolysis

In this chapter, we have described various galvanic cells in which a spontaneous chemical reaction is used to generate electrical energy. In an electrolytic cell, however, the opposite process, called electrolysis, occurs: an external voltage is applied to drive a nonspontaneous reaction. Electrolysis has many commercial and industrial applications. Electrometallurgy is the process of reduction of metals from metallic compounds to obtain the pure form of metal using electrolysis. Aluminium, lithium, sodium, potassium, magnesium, calcium, and in some cases copper, are produced in this way. Chlorine and sodium hydroxide are the major products of the electrolysis of brine, a water/sodium chloride mixture. Water electrolysis is used to generate oxygen for spacecraft and nuclear submarines.

Electrolysis is also used in the cleaning and preservation of old artifacts. Because the process separates the non-metallic particles from the metallic ones, it is very useful for cleaning a wide variety of metallic objects, from old coins to even larger objects including rusted cast iron cylinder blocks and heads when rebuilding automobile engines. Rust removal from small iron or steel objects by electrolysis can be done in a home workshop using simple materials such as a plastic bucket, tap water, lengths of rebar, washing soda, baling wire, and a battery charger.

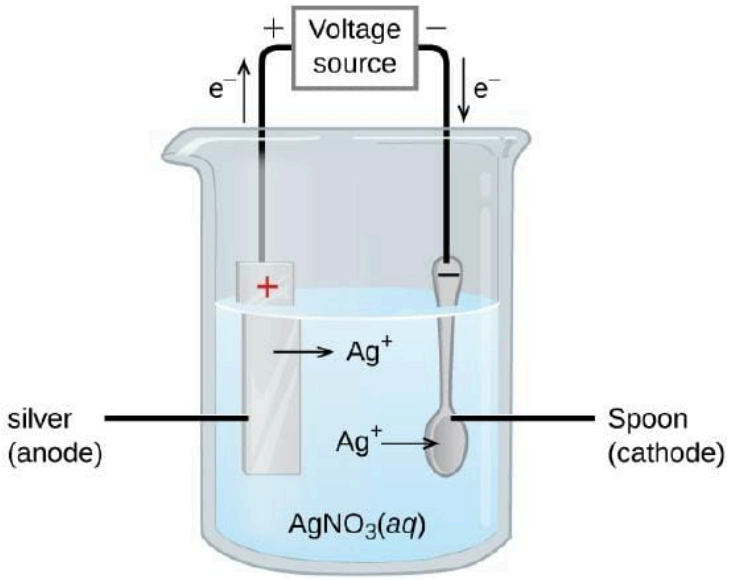


Figure 8.3.9: Silver plating of a spoon.

An important use for electrolytic cells is in **electroplating**. Electroplating results in a thin coating of one metal on top of a conducting surface. Reasons for electroplating include making the object more corrosion resistant, strengthening the surface, producing a more attractive finish, or for purifying metal. The metals commonly used in electroplating include cadmium, chromium, copper, gold, nickel, silver, and tin. Common consumer products include silver-plated or gold-plated tableware, chrome-plated automobile parts, and jewelry. We can get an idea of how this works by investigating how silver-plated tableware is produced (Figure 8.3.9).

Summary

- Electrochemistry is a branch of chemistry that deals with the interconversion of chemical energy and electrical energy.
- Batteries are galvanic cells, or a series of cells, that produce an electric current.
- There are two basic types of batteries: primary and secondary.
- Primary batteries are “single use” and cannot be recharged. Dry cells and (most) alkaline batteries are examples of primary batteries.
- The second type is rechargeable and is called a secondary battery. Examples of secondary batteries include nickel-cadmium (NiCd), lead acid, and lithium ion batteries.
- Fuel cells are similar to batteries in that they generate an electrical current, but require continuous addition of fuel and oxidizer. The hydrogen fuel cell uses hydrogen and oxygen from the air to produce water, and is generally more efficient than internal combustion engines.
- Electrolysis occurs when an external voltage is applied to drive a nonspontaneous reaction.

Contributors and Attributions

-

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- TextMap: Chemistry-The Central Science (Brown et al.)

- Marisa Alviar-Agnew (Sacramento City College)

- Wikipedia

Answers

Exercise 8.3.1 **Copper-Zinc Galvanic Cell**

From the information given in the problem:

anode (oxidation): $\mathrm{Zn}(s) \longrightarrow \mathrm{Zn}^{2+}(aq) + 2\,\mathrm{e}^-$

cathode (reduction): $\mathrm{Cu}^{2+}(aq) + 2\,\mathrm{e}^- \longrightarrow \mathrm{Cu}(s)$

overall: $\mathrm{Zn}(s) + \mathrm{Cu}^{2+}(aq) \longrightarrow \mathrm{Zn}^{2+}(aq) + \mathrm{Cu}(s)$

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8.4: Corrosion and Explosion

Learning Objectives

- Understand the process of corrosion.
- Understand the process of explosion.

Corrosion is a galvanic process by which metals deteriorate through oxidation—usually but not always to their oxides. For example, when exposed to air, iron rusts, silver tarnishes, and copper and brass acquire a bluish-green surface called a patina. Of the various metals subject to corrosion, iron is by far the most important commercially. An estimated $100 billion per year is spent in the United States alone to replace iron-containing objects destroyed by corrosion.

Explosions can occur in nature due to a large influx of energy. Most natural explosions arise from volcanic processes of various sorts. Chemical explosions, usually involve a rapid and violent oxidation reaction that produces large amounts of hot gas. Gunpowder was the first explosive to be discovered and put to use. Other notable early developments in chemical explosive technology were Frederick Augustus Abel's development of nitrocellulose in 1865 and Alfred Nobel's invention of dynamite in 1866. Chemical explosions (both intentional and accidental) are often initiated by an electric spark or flame in the presence of oxygen. Accidental explosions may occur in fuel tanks, rocket engines, etc.

The Rusting of Iron

Perhaps the most familiar example of corrosion is the formation of rust on iron. Iron will rust when it is exposed to oxygen and water. The main steps in the rusting of iron appear to involve the following. Once exposed to the atmosphere, iron rapidly oxidizes.

$$\mathrm{Fe\,(s)} \longrightarrow \mathrm{Fe^{2+}\,(aq)} + 2\,\mathrm{e^-} \qquad \text{(cathode)}$$

The electrons reduce oxygen in the air in acidic solutions.

$$\mathrm{O_2\,(g)} + 4\,\mathrm{H^+\,(aq)} + 4\,\mathrm{e^-} \longrightarrow 2\,\mathrm{H_2O\,(l)} \qquad \text{(anode)}$$

$$2\,\mathrm{Fe\,(s)} + \mathrm{O_2\,(g)} + 4\,\mathrm{H^+\,(aq)} \longrightarrow 2\,\mathrm{Fe^{2+}\,(aq)} + 2\,\mathrm{H_2O\,(l)} \qquad \text{(over all)}$$

What we call rust is hydrated iron(III) oxide, which forms when iron(II) ions react further with oxygen.

$$4\,\mathrm{Fe^{2+}\,(aq)} + \mathrm{O_2\,(g)} + (4+2\,\mathrm{x})\mathrm{H_2O\,(l)} \longrightarrow 2\,\mathrm{Fe_2O_3}\ \cdot x\,\mathrm{H_2O\,(s)} + 8\,\mathrm{H^+\,(aq)}$$

The number of water molecules is variable, so it is represented by *x*. Unlike the patina on copper, the formation of rust does not create a protective layer and so corrosion of the iron continues as the rust flakes off and exposes fresh iron to the atmosphere.

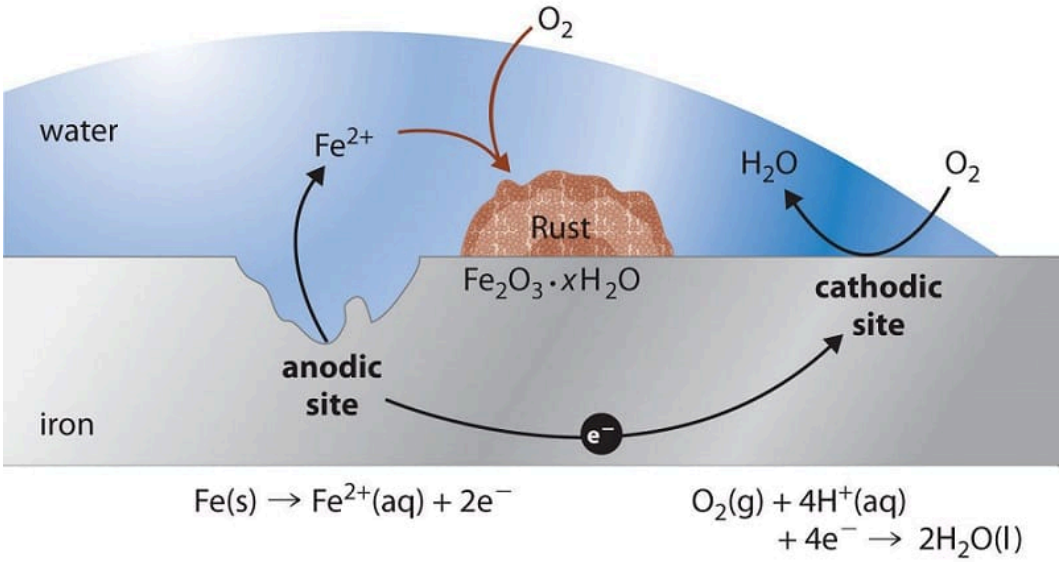


Figure 8.4.1 Rust, the Result of Corrosion of Metallic Iron. Iron is oxidized to Fe2+(aq) at an anodic site on the surface of the iron, which is often an impurity or a lattice defect. Oxygen is reduced to water at a different site on the surface of the iron, which acts as the cathode. Electrons are transferred from the anode to the cathode through the electrically conductive metal.

One way to keep iron from corroding is to keep it painted. Other strategies include alloying the iron with other metals. For example, stainless steel is mostly iron with a bit of chromium. Zinc-plated or galvanized iron uses a different strategy. Zinc is more easily oxidized than iron because zinc has a lower reduction potential. Since zinc has a lower reduction potential, it is a more active metal. Thus, even if the zinc coating is scratched, the zinc will still oxidize before the iron. This suggests that this approach should work with other active metals.

Changing Colors

The Statue of Liberty is a landmark every American recognizes. The Statue of Liberty is easily identified by its height, stance, and unique blue-green color. When this statue was first delivered from France, its appearance was not green. It was brown, the color of its copper "skin." So how did the Statue of Liberty change colors? The change in appearance was a direct result of corrosion. The copper that is the primary component of the statue slowly underwent oxidation from the air. The oxidation-reduction reactions of copper metal in the environment occur in several steps. Copper metal is oxidized to copper(I) oxide ($\mathrm{Cu_2O}$), which is red, and then to copper(II) oxide, which is black.

$$2\,\mathrm{Cu\,(s)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)} \rightarrow \underset{\text{red}}{\mathrm{Cu_2O\,(s)}}$$

$$\mathrm{Cu_2O\,(s)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)} \rightarrow \underset{\text{black}}{2\,\mathrm{CuO\,(s)}}$$

Coal, which was often high in sulfur, was burned extensively in the early part of the last century. As a result, sulfur trioxide, carbon dioxide, and water all reacted with the CuO.

$$2\,\mathrm{CuO\,(s)} + \mathrm{CO_2\,(g)} + \mathrm{H_2O\,(l)} \rightarrow \underset{\text{green}}{\mathrm{Cu_2CO_3(OH)_2\,(s)}}$$

$$3\,\mathrm{CuO\,(s)} + 2\,\mathrm{CO_2\,(g)} + \mathrm{H_2O\,(l)} \rightarrow \underset{\text{blue}}{\mathrm{Cu_2(CO_3)_2(OH)_2\,(s)}}$$

$$4\,\mathrm{CuO\,(s)} + \mathrm{SO_3\,(g)} + 3\,\mathrm{H_2O\,(l)} \rightarrow \underset{\text{green}}{\mathrm{Cu_4SO_4(OH)_6\,(s)}}$$

These three compounds are responsible for the characteristic blue-green patina seen today. Fortunately, formation of the patina created a protective layer on the surface, preventing further corrosion of the copper skin. The formation of the protective layer is a form of passivation, which is discussed elsewhere.



Figure 8.4.2: (a) The Statue of Liberty is covered with a copper skin, and was originally brown, as shown in this painting. (b) Exposure to the elements has resulted in the formation of the blue-green patina seen today.

Silver Tarnishes

Even though coinage metals are known to be resistant to oxygen in air, silver will tarnish due to $\mathrm{H_2S\,(g)}$

$$\mathrm{2\,Ag\,(s) + H_2S\,(g) \longrightarrow Ag_2S\,(s) + H_2\,(g)}$$

Explosive Reactions

TNT is one of the most commonly used explosives for military, industrial, and mining applications. TNT has been used in conjunction with hydraulic fracturing, a process used to recover oil and gas from shale formations. The technique involves displacing and detonating nitroglycerin in hydraulically induced fractures followed by wellbore shots using pelletized TNT.

TNT is valued partly because of its insensitivity to shock and friction, with reduced risk of accidental detonation compared to more sensitive explosives such as nitroglycerin. TNT melts at 80 °C (176 °F), far below the temperature at which it will spontaneously detonate, allowing it to be poured or safely combined with other explosives. TNT neither absorbs nor dissolves in water, which allows it to be used effectively in wet environments. To detonate, TNT must be triggered by a pressure wave from a starter explosive, called an explosive booster.

Although blocks of TNT are available in various sizes (e.g. 250 g, 500 g, 1,000 g), it is more commonly encountered in synergistic explosive blends comprising a variable percentage of TNT plus other ingredients

Upon detonation, TNT decomposes as follows:

$$\mathrm{2\,C_7H_5N_3O_6 \longrightarrow 3\,N_2 + 5\,H_2O + 7\,CO + 7\,C}$$

$$\mathrm{2\,C_7H_5N_3O_6 \longrightarrow 3\,N_2 + 5\,H_2 + 12\,CO + 2\,C}$$

The reaction is exothermic but has a high activation energy in the gas phase (~62 kcal/mol). The condensed phases (solid or liquid) show markedly lower activation energies of roughly 35 kcal/mol due to unique bimolecular decomposition routes at elevated densities. Because of the production of carbon, TNT explosions have a sooty appearance. Because TNT has an excess of carbon, explosive mixtures with oxygen-rich compounds can yield more energy per kilogram than TNT alone. During the 20th century, amatol, a mixture of TNT with ammonium nitrate was a widely used military explosive.

TNT can be detonated with a high velocity initiator or by efficient concussion. For many years, TNT used to be the reference point for the Figure of Insensitivity. TNT had a rating of exactly 100 on the "F of I" scale. The reference has since been changed to a more sensitive explosive called RDX, which has an F of I rating of 80.

ANFO (or AN/FO, for ammonium nitrate/fuel oil) is a widely used bulk industrial explosive. Its name is commonly pronounced as "an-fo". It consists of 94% porous prilled ammonium nitrate ($\mathrm{NH_4NO_3}$) (AN), which acts as the oxidizing agent and absorbent for the fuel, and 6% number 2 fuel oil (FO). The fuel component of ANFO is typically diesel, but kerosene, coal dust, racing fuel, or even molasses have been used instead. Finely powdered aluminium in the mixture will sensitise it to detonate more readily.

The chemistry of ANFO detonation is the reaction of ammonium nitrate with a long-chain alkane ($\mathrm{C_nH_{2n+2}}$) to form nitrogen, carbon dioxide, and water.

$$\mathrm{NH_4NO_3 + C_nH_{2n+2} \longrightarrow \mathit{x}\,N_2 + \mathit{y}\,H_2O + \mathit{z}\,CO_2}$$

In an ideal stoichiometrically balanced reaction, ANFO is composed of about 94.3% AN and 5.7% FO by \(\ce{weight. In practice, a slight excess of fuel oil is added, as underdosing results in reduced performance while overdosing merely results in more post-blast fumes. When detonation conditions are optimal, the aforementioned gases are the only products. In practical use, such conditions are impossible to attain, and blasts produce moderate amounts of toxic gases such as carbon monoxide and nitrogen oxides (NOx).

$$\mathrm{NH_4NO_3 + C_nH_{2n+2} \longrightarrow \mathit{v}\,CO + \mathit{w}\,NOx + \mathit{y}\,H_2O + \mathit{z}\,CO_2}$$

ANFO has found wide use in coal mining, quarrying, metal mining, and civil construction in applications where its low cost and ease of use may outweigh the benefits of other explosives, such as water resistance, oxygen balance, higher detonation velocity, or performance in small-diameter columns. ANFO is also widely used in avalanche hazard mitigation.

Summary

- Corrosion and explosion are two major redox processes.
- Examples of corrosion (metal deterioration) and explosion (using TNT and ANFO) are given.

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- Marisa Alviar-Agnew (Sacramento City College)

- TextMap: Chemistry-A Central Science (Brown et al.)
- Wikipedia

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8.5: Oxygen - An Abundant and Essential Oxidizing Agent

Learning Objectives

- Know the occurrence and properties of oxygen.
- Know reactions involving oxygen as an oxidizing agent.

Elemental oxygen is a strong oxidizing agent. It reacts with most other elements and many compounds. Oxygen was isolated by Michael Sendivogius before 1604, but it is commonly believed that the element was discovered independently by Carl Wilhelm Scheele, in Uppsala, in 1773 or earlier, and Joseph Priestley in Wiltshire, in 1774. The name oxygen was coined in 1777 by Antoine Lavoisier, who first recognized oxygen as a chemical element and correctly characterized the role it plays in combustion.

Oxygen: Occurrence and Properties

By mass, oxygen is the third-most abundant element in the universe, after hydrogen and helium. Oxygen is the most abundant element on the earth's crust. About 50% of the mass of the earth's crust consists of oxygen (combined with other elements, principally silicon). Oxygen occurs as O_2 molecules and, to a limited extent, as O_3 (ozone) molecules in air. It forms about 20% of the mass of the air. About 89% of water by mass consists of combined oxygen. In combination with carbon, hydrogen, and nitrogen, oxygen is a large part of plants and animals.

Oxygen is a colorless, odorless, and tasteless gas at ordinary temperatures. It is slightly denser than air. Although it is only slightly soluble in water (49 mL of gas dissolves in 1 L at STP), oxygen's solubility is very important to aquatic life.

Oxygen is essential in combustion processes such as the burning of fuels. All combustion reactions are also examples of redox reactions. A combustion reaction occurs when a substance reacts with oxygen to create heat. One example is the combustion of octane, the principle component of gasoline:

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

Combustion reactions are a major source of energy for modern industry. Plants and animals use the oxygen from the air in respiration. The administration of oxygen-enriched air is an important medical practice when a patient is receiving an inadequate supply of oxygen because of shock, pneumonia, or some other illness.

The chemical industry employs oxygen for oxidizing many substances. A significant amount of oxygen produced commercially is important in the removal of carbon from iron during steel production. Large quantities of pure oxygen are also necessary in metal fabrication and in the cutting and welding of metals with oxyhydrogen and oxyacetylene torches. Liquid oxygen is important to the space industry. It is an oxidizing agent in rocket engines. It is also the source of gaseous oxygen for life support in space.

As we know, oxygen is very important to life. The energy required for the maintenance of normal body functions in human beings and in other organisms comes from the slow oxidation of chemical compounds. Oxygen is the final oxidizing agent in these reactions. In humans, oxygen passes from the lungs into the blood, where it combines with hemoglobin, producing oxyhemoglobin. In this form, blood transports the oxygen to tissues, where it is transferred to the tissues. The ultimate products are carbon dioxide and water. The blood carries the carbon dioxide through the veins to the lungs, where the blood releases the carbon dioxide and collects another supply of oxygen. Digestion and assimilation of food regenerate the materials consumed by oxidation in the body; the energy liberated is the same as if the food burned outside the body.

Oxygen: Reactions with Other Elements

Oxygen reacts directly at room temperature or at elevated temperatures with all other elements except the noble gases, the halogens, and few second- and third-row transition metals of low reactivity (those with higher reduction potentials than copper). Rust is an example of the reaction of oxygen with iron. The more active metals form peroxides or superoxides. Less active metals and the nonmetals give oxides. Two examples of these reactions are:

$$2\,\mathrm{Mg\,(s)} + \mathrm{O_2\,(g)} \longrightarrow 2\,\mathrm{MgO\,(s)}$$

$$\mathrm{P_4(s)}^{+}\ 5\,\mathrm{O_2\,(g)} \longrightarrow \mathrm{P_4O_{10}\,(s)}$$

The oxides of halogens, at least one of the noble gases, and metals with higher reduction potentials than copper do not form by the direct action of the elements with oxygen.

Oxygen: Reaction with Compounds

Elemental oxygen also reacts with some compounds. If it is possible to oxidize any of the elements in a given compound, further oxidation by oxygen can occur. For example, hydrogen sulfide, H_2S, contains sulfur with an oxidation state of 2–. Because the sulfur does not exhibit its maximum oxidation state, we would expect H_2S to react with oxygen. It does, yielding water and sulfur dioxide. The reaction is:

$$2\,\mathrm{H_2S}(g)+3\,\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{H_2O}(l)+2\,\mathrm{SO_2}(g)$$

It is also possible to oxidize oxides such as CO and P_4O_6 that contain an element with a lower oxidation state. The ease with which elemental oxygen picks up electrons is mirrored by the difficulty of removing electrons from oxygen in most oxides. Of the elements, only the very reactive fluorine can oxidize oxides to form oxygen gas.

Most nonmetals react with oxygen to form nonmetal oxides. Depending on the available oxidation states for the element, a variety of oxides might form. Fluorine will combine with oxygen to form fluorides such as OF_2, where the oxygen has a 2+-oxidation state.

Sulfur Oxygen Compounds

The two common oxides of sulfur are sulfur dioxide, SO_2, and sulfur trioxide, SO_3. The odor of burning sulfur comes from sulfur dioxide. Sulfur dioxide, occurs in volcanic gases Figure 8.5.1 and in the atmosphere near industrial plants that burn fuel containing sulfur compounds.



Figure 8.5.1: Mount Mayon volcano (Philippines) erupting in the early morning of January 23, 2018. (CC BY-SA 4.0; Ezra Acayan via Wikipedia)

Ozone: Another Form of Oxygen

When dry oxygen is passed between two electrically charged plates, ozone (O_3, illustrated in Figure 8.5.2), an allotrope of oxygen possessing a distinctive odor, forms. The formation of ozone from oxygen is an endothermic reaction, in which the energy comes from an electrical discharge, heat, or ultraviolet light:

$$3\,O_2(g) \xrightarrow{\text{electric discharge}} 2\,O_3(g)$$

The sharp odor associated with sparking electrical equipment is due, in part, to ozone.

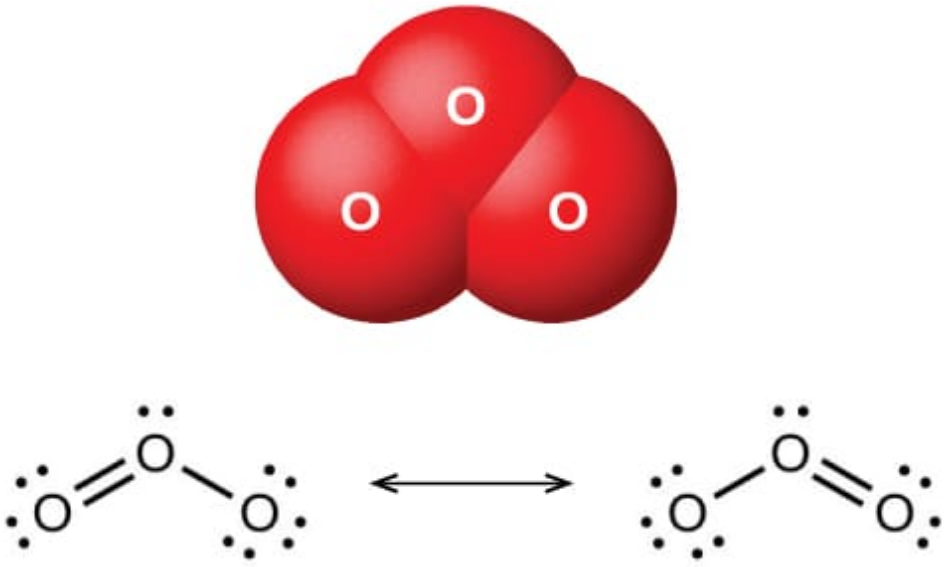


Figure 8.5.2 The image shows the bent ozone (O3) molecule and the resonance structures necessary to describe its bonding.

Ozone forms naturally in the upper atmosphere by the action of ultraviolet light from the sun on the oxygen there. Most atmospheric ozone occurs in the stratosphere, a layer of the atmosphere extending from about 10 to 50 kilometers above the earth's surface. This ozone acts as a barrier to harmful ultraviolet light from the sun by absorbing it via a chemical decomposition reaction:

$$O_3(g) \xrightarrow{\text{ultraviolet light}} O(g) + O_2(g)$$

The reactive oxygen atoms recombine with molecular oxygen to complete the ozone cycle. The presence of stratospheric ozone decreases the frequency of skin cancer and other damaging effects of ultraviolet radiation. It has been clearly demonstrated that chlorofluorocarbons, CFCs (known commercially as Freons), which were present as aerosol propellants in spray cans and as refrigerants, caused depletion of ozone in the stratosphere. This occurred because ultraviolet light also causes CFCs to decompose, producing atomic chlorine. The chlorine atoms react with ozone molecules, resulting in a net removal of O_3 molecules from stratosphere. This process is explored in detail in our coverage of chemical kinetics. There is a worldwide effort to reduce the amount of CFCs used commercially, and the ozone hole is already beginning to decrease in size as atmospheric concentrations of atomic chlorine decrease. While ozone in the stratosphere helps protect us, ozone in the troposphere is a problem. This ozone is a toxic component of photochemical smog.

The uses of ozone depend on its reactivity with other substances. It can be used as a bleaching agent for oils, waxes, fabrics, and starch: It oxidizes the colored compounds in these substances to colorless compounds. It is an alternative to chlorine as a disinfectant for water.

Low level ozone (or tropospheric ozone) is an atmospheric pollutant.[42] It is not emitted directly by car engines or by industrial operations, but formed by the reaction of sunlight on air containing hydrocarbons and nitrogen oxides that react to form ozone directly at the source of the pollution or many kilometers down wind.

Ozone reacts directly with some hydrocarbons such as aldehydes and thus begins their removal from the air, but the products are themselves key components of smog.

Ozone can be used to remove iron and manganese from water, forming a precipitate which can be filtered:

$$2Fe^{2+} + O_3 + 5H_2O \rightarrow 2Fe(OH)_3(s) + O_2 + 4H^+$$

$$2Mn^{2+} + 2O_3 + 4H_2O \rightarrow 2MnO(OH)_2(s) + 2O_2 + 4H^+$$

Ozone will also oxidize dissolved hydrogen sulfide in water to sulfurous acid:

$$3O_3 + H_2S \rightarrow H_2SO_3 + 3O_2$$

These three reactions are central in the use of ozone based well water treatment.

Ozone will also detoxify cyanides by converting them to cyanates.

$$CN^- + O_3 \rightarrow CNO^- + O_2$$

Ozone will also completely decompose urea:

$$(NH_2)_2CO + O_3 \rightarrow N_2 + CO_2 + 2H_2O$$

Other Common Oxidizing Agents

Chlorine is usually used (in the form of hypochlorous acid) to kill bacteria and other microbes in drinking water supplies and public swimming pools. In most private swimming pools, chlorine itself is not used, but rather sodium hypochlorite, formed from chlorine and sodium hydroxide, or solid tablets of chlorinated isocyanurates. The drawback of using chlorine in swimming pools is that the chlorine reacts with the proteins in human hair and skin. The distinctive 'chlorine aroma' associated with swimming pools is not the result of chlorine itself, but of chloramine, a chemical compound produced by the reaction of free dissolved chlorine with amines in organic substances. As a disinfectant in water, chlorine is more than three times as effective against Escherichia coli as bromine, and more than six times as effective as iodine. Increasingly, chloramine itself is being directly added to drinking water for purposes of disinfection, a process known as chloramination.

It is often impractical to store and use poisonous chlorine gas for water treatment, so alternative methods of adding chlorine are used. These include hypochlorite solutions, which gradually release chlorine into the water, and compounds like sodium dichloro-s-triazinetrione (dihydrate or anhydrous), sometimes referred to as "dichlor", and trichloro-s-triazinetrione, sometimes referred to as "trichlor". These compounds are stable while solid and may be used in powdered, granular, or tablet form. When added in small amounts to pool water or industrial water systems, the chlorine atoms hydrolyze from the rest of the molecule forming hypochlorous acid (HOCl), which acts as a general biocide, killing germs, micro-organisms, algae, and so on.

Breathalizers

The breathalyzer is a redox reaction. When the potassium dichromate reacts with ethanol it loses an oxygen atom (gets reduced), going from the orange dichromate to the green chromium sulfate. At the same time dichromate is being reduced, ethanol gains an oxygen atom (gets oxidized), forming acetic acid. The sulfuric acid helps to remove the ethanol from the exhaled air into the test solution and also provides the necessary acidic conditions.

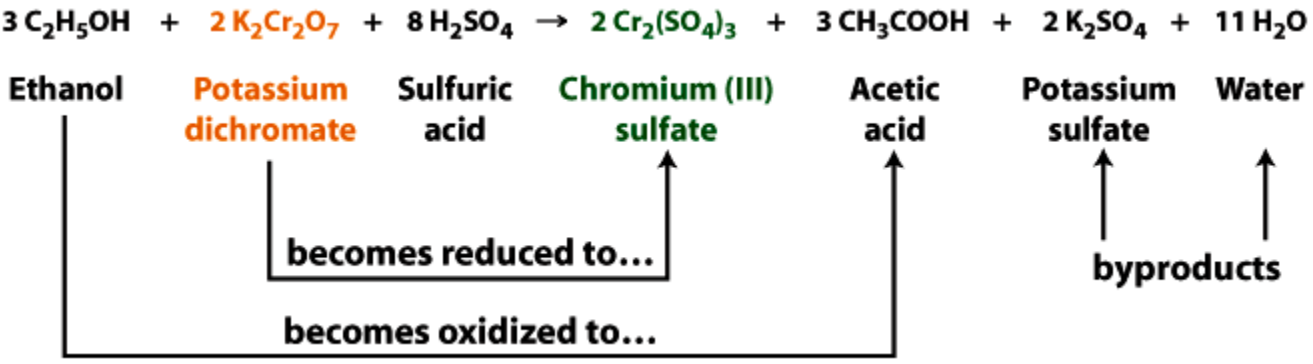


Figure 8.5.3 In this reaction, the chromium atom is reduced from Cr^{6+} to Cr^{3+}, and the ethanol is oxidized to acetic acid.

In this reaction, the chromium atom is reduced from Cr^{6+} to Cr^{3+}, and the ethanol is oxidized to acetic acid.

Hydrogen peroxide can be used for the sterilization of various surfaces, including surgical tools and may be deployed as a vapor (VHP) for room sterilization. H_2O_2 demonstrates broad-spectrum efficacy against viruses, bacteria, yeasts, and bacterial spores. In general, greater activity is seen against Gram-positive than Gram-negative bacteria; however, the presence of catalase or other

peroxidases in these organisms can increase tolerance in the presence of lower concentrations. Higher concentrations of H_2O_2 (10 to 30%) and longer contact times are required for sporicidal activity.

Hydrogen peroxide is seen as an environmentally safe alternative to chlorine-based bleaches, as it degrades to form oxygen and water and it is generally recognized as safe as an antimicrobial agent by the U.S. Food and Drug Administration (FDA).

Historically hydrogen peroxide was used for disinfecting wounds, partly because of its low cost and prompt availability compared to other antiseptics. It is now thought to inhibit healing and to induce scarring because it destroys newly formed skin cells. Only a very low concentration of

H_2O_2 can induce healing, and only if not repeatedly applied. Surgical use can lead to gas embolism formation. Despite this, it is still used for wound treatment in many countries but is also prevalent as a major first aid antiseptic in the United States

Diluted H_2O_2 (between 1.9% and 12%) mixed with aqueous ammonia is used to bleach human hair. The chemical's bleaching property lends its name to the phrase "peroxide blonde". Hydrogen peroxide is also used for tooth whitening. It can be found in most whitening toothpastes.



Figure 8.5.3: Skin shortly after exposure to 35% H_2O_2. (Public Domain; Olli Niemitalo via Wikipedia)

Almost all applications of potassium permanganate ($KMnO_4$) exploit its oxidizing properties. As a strong oxidant that does not generate toxic byproducts, $KMnO_4$ has many niche uses. Potassium permanganate is used for a number of skin conditions. This includes fungal infections of the foot, impetigo, pemphigus, superficial wounds, dermatitis, and tropical ulcers. It is on the WHO Model List of Essential Medicines, the most important medications needed in a basic health system. Potassium permanganate is used extensively in the water treatment industry.

Benzoyl peroxide (BPO) is a medication and industrial chemical. As a medication, it is used to treat mild to moderate acne. For more severe cases, it may be used with other treatments. Some versions are sold mixed with antibiotics such as clindamycin. Other uses include bleaching flour, hair bleaching, teeth whitening, and textile bleaching.[5] It is also used in the plastic industry

Sodium hypochlorite is most often encountered as a pale greenish-yellow dilute solution commonly known as liquid bleach or simply bleach, a household chemical widely used (since the 18th century) as a disinfectant or a bleaching agent. The compound in solution is unstable and easily decomposes, liberating chlorine, which is the active principle of such products. Indeed, sodium hypochlorite is the oldest and still most important chlorine-based bleach.

Warning

While sodium hypochlorite is non-toxic, its corrosive properties, common availability, and reaction products make it a significant safety risk. In particular, mixing liquid bleach with other cleaning products, such as acids or ammonia, may produce toxic fumes.

Summary

- Oxygen is one of the most reactive elements. This reactivity, coupled with its abundance, makes the chemistry of oxygen very rich and well understood.
- Many compounds of the representative metals and non metals react with oxygen to form oxides.
- Other than oxygen, ozone, chlorine, potassium dichromate, hydrogen peroxide, potassium peroxide, benzoyl peroxide, sodium hypochlorite are common oxidizing agents mentioned in this section, that have many beneficial uses.

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8.6: Some Common Reducing Agents

Learning Objectives

- Know the occurrence and properties of hydrogen.
- Know reactions involving common reducing agents such as carbon, hydrogen, and antioxidants.

Metal Extraction

Smelting is a process of applying heat to ore in order to extract a base metal. It uses heat and a chemical reducing agent to decompose the ore, leaving the metal base behind. It is used to extract many metals from their ores, including silver, iron, copper, and other base metals. The reducing agent is commonly a source of carbon, such as coke—or, in earlier times, charcoal. **Coke** is a grey, hard, and porous fuel with a high carbon content and few impurities, made by heating coal or oil in the absence of air.

Coke is used in smelting iron ore for example in a blast furnace. The reaction can be represented as follows:

$$2Fe_2O_3 + 3C \rightarrow 4Fe + 3CO_2$$

Antioxidants

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

$$\mathrm{C_6H_8O_6 + 2\,H^+ + 2\,NO_2}^- \rightarrow \mathrm{C_6H_6O_6 + 2\,H_2O + 2\,NO} \tag{8.6.1}$$

> If reaction in Equation 8.6.1 did not occur, nitrite ions from foods would oxidize the iron in hemoglobin, destroying its ability to carry oxygen.

Tocopherol (vitamin E) is also an antioxidant. In the body, vitamin E is thought to act by scavenging harmful by-products of metabolism, such as the highly reactive molecular fragments called free radicals. In foods, vitamin E acts to prevent fats from being oxidized and thus becoming rancid. Vitamin C is also a good antioxidant (Figure 8.6.2).



Figure 8.6.2: Citrus Fruits. Citrus fruits, such as oranges, lemons, and limes, are good sources of vitamin C, which is an antioxidant. Wedges of pink grapefruit, lime, and lemon, and a half orange (clockwise from top). from Wikipedia.

Hydrogen as a Reducing Agent

Large quantities of H_2 are needed in the petroleum and chemical industries. The largest application of H_2 is for the processing ("upgrading") of fossil fuels, and in the production of ammonia. Mass production of Ammonia mostly uses the Haber–Bosch process, reacting hydrogen (H_2) and nitrogen (N_2) at a moderately-elevated temperature (450 °C) and high pressure (100 standard atmospheres (10,000 kPa)):

$$3H_2(g) + N_2(g) \rightarrow 2NH_3(g)$$

H_2 has several other important uses. H_2 is used as a hydrogenating agent (Chapter 17), particularly in increasing the level of saturation of unsaturated fats and oils (found in items such as margarine), and in the production of methanol. It is similarly the source of hydrogen in the manufacture of hydrochloric acid. H_2 is also used as a reducing agent of metallic ores.

Hydrogen gas is highly flammable producing a large amount of heat when it reacts with oxygen gas as shown below.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) + 572kJ$$

Hydrogen gas forms explosive mixtures with air in concentrations from 4–74% and with chlorine at 5–95%. The explosive reactions may be triggered by spark, heat, or sunlight.

A Closer Look at Hydrogen

Hydrogen is among the ten most abundant elements on the planet, but very little is found in elemental form due to its low density and reactivity. Much of the terrestrial hydrogen is locked up in water molecules and organic compounds like hydrocarbons.

Hydrogen is the fuel for reactions of the Sun and other stars (fusion reactions). Hydrogen is the lightest and most abundant element in the universe. About 70%- 75% of the universe is composed of hydrogen by mass. All stars are essentially large masses of hydrogen gas that produce enormous amounts of energy through the fusion of hydrogen atoms at their dense cores. In smaller stars, hydrogen atoms collided and fused to form helium and other light elements like nitrogen and carbon(essential for life). In the larger stars, fusion produces the lighter and heavier elements like calcium, oxygen, and silicon.

YouTube Video

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

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On Earth, hydrogen is mostly found in association with oxygen; its most abundant form being water (H_2O). Hydrogen is only .9% by mass and 15% by volume abundant on the earth, despite water covering about 70% of the planet. Because hydrogen is so light, there is only 0.5 ppm (parts per million) in the atmosphere, which is a good thing considering it is EXTREMELY flammable.

Hydrogen gas can be prepared by reacting a dilute strong acid like hydrochloric acids with an active metal. The metal becomes oxides, while the H^+ (from the acid) is reduced to hydrogen gas. This method is only practical for producing small amounts of hydrogen in the lab, but is much too costly for industrial production:

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

The purest form of H_2(g) can come from electrolysis of H_2O(l), the most common hydrogen compound on this plant. This method is also not commercially viable because it requires a significant amount of energy ($\Delta H = 572 \ \ kJ$):

$$2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)}$$

\(H_2O\) is the most abundant form of hydrogen on the planet, so it seems logical to try to extract hydrogen from water without electrolysis of water. To do so, we must reduce the hydrogen with +1 oxidation state to hydrogen with 0 oxidation state (in hydrogen gas).

Three commonly used reducing agents are carbon (in coke or coal), carbon monoxide, and methane. These react with water vapor form H_2(g):

$$C_{(s)} + 2H_2O_{(g)} \rightarrow CO(g) + H_{2(g)}$$

$$CO_{(g)} + 2H_2O_{(g)} \rightarrow CO2 + H_{2(g)}$$

Reforming of Methane:

$$CH_{4(g)} + H_2O_{(g)} \rightarrow CO(g) + 3H_{2(g)}$$

These three methods are most industrially feasible (cost effective) methods of producing H_2(g).

Summary

- Common reducing agents include carbon (in the form of coke or coal), hydrogen gas, as well as those substances referred to in the food chemistry as antioxidants (e.g. ascorbic acid and vitamin E).
- Various reactions involving reducing agents were given.

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8.7: Oxidation, Reduction, and Living Things

Learning Objective

- Know the overall reactions involved in respiration and photosynthesis.

Oxidation and reduction reactions are especially crucial in biological processes such as cellular respiration and photosynthesis.

Cellular respiration is a set of metabolic reactions and processes that take place in the cells of organisms to convert biochemical energy from nutrients into adenosine triphosphate (ATP), and then release waste products. Cellular respiration is considered an exothermic redox reaction which releases heat. The overall reaction occurs in a series of biochemical steps, most of which are redox reactions themselves. Although cellular respiration is technically a combustion reaction, it clearly does not resemble one when it occurs in a living cell because of the slow release of energy from the series of reactions.

Nutrients that are commonly used by animal and plant cells in respiration include sugar, amino acids and fatty acids, and the most common oxidizing agent (electron acceptor) is molecular oxygen (O_2).

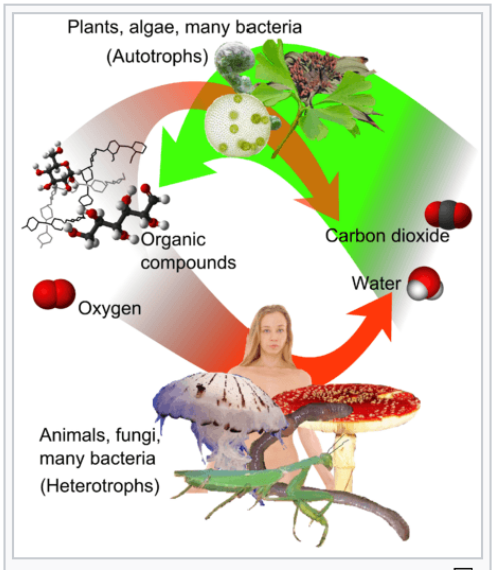


Figure 8.7.1 Aerobic respiration (red arrows) is the main means by which both fungi and animals utilize chemical energy in the form of organic compounds that were previously created through photosynthesis (green arrow). (CC-BY-SA 2.0, Mikael Häggström, Wikimedia)

The reaction for aerobic respiration is essentially the reverse of photosynthesis and is simplified as:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + 2880kJ/mol$$

Green plants carry out the redox reaction that makes possible almost all life on Earth. They do this through a process called **photosynthesis**, in which carbon dioxide and water are converted to glucose ($C_6H_{12}O_6$). The synthesis of glucose requires a variety of proteins called enzymes and a green pigment called chlorophyll that converts sunlight into chemical energy

A simplified overall formula for photosynthesis is:

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

or simply

carbon dioxide + water + sunlight → glucose + oxygen gas

In this reaction, carbon dioxide is reduced to glucose, and water is oxidized to oxygen gas. Other reactions convert the glucose

to more complex carbohydrates, plant proteins, and oils.

Summary

- Redox reactions are common in organic and biological chemistry, including aerobic respiration, and photosynthesis.

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9: ORGANIC CHEMISTRY

Scientists of the 18th and early 19th centuries studied compounds obtained from plants and animals and labeled them *organic* because they were isolated from "organized" (living) systems. Compounds isolated from nonliving systems, such as rocks and ores, the atmosphere, and the oceans, were labeled *inorganic*. For many years, scientists thought organic compounds could be made by only living organisms because they possessed a vital force found only in living systems. The vital force theory began to decline in 1828, when the German chemist Friedrich Wöhler synthesized urea from inorganic starting materials. He reacted silver cyanate (AgOCN) and ammonium chloride (NH_4Cl), expecting to get ammonium cyanate (NH_4OCN). What he expected is described by the following equation.

$$AgOCN + NH_4Cl \rightarrow AgCl + NH_4OCN \tag{9.1}$$

Instead, he found the product to be urea (NH_2CONH_2), a well-known organic material readily isolated from urine. This result led to a series of experiments in which a wide variety of organic compounds were made from inorganic starting materials. The vital force theory gradually went away as chemists learned that they could make many organic compounds in the laboratory.

Today **organic chemistry** is the study of the chemistry of the carbon compounds, and inorganic chemistry is the study of the chemistry of all other elements. It may seem strange that we divide chemistry into two branches—one that considers compounds of only one element and one that covers the 100-plus remaining elements. However, this division seems more reasonable when we consider that of tens of millions of compounds that have been characterized, the overwhelming majority are carbon compounds.

> The word *organic* has different meanings. Organic fertilizer, such as cow manure, is organic in the original sense; it is derived from living organisms. Organic foods generally are foods grown without synthetic pesticides or fertilizers. Organic chemistry is the chemistry of compounds of carbon.

Carbon is unique among the other elements in that its atoms can form stable covalent bonds with each other and with atoms of other elements in a multitude of variations. The resulting molecules can contain from one to millions of carbon atoms. We previously surveyed organic chemistry by dividing its compounds into families based on functional groups. We begin with the simplest members of a family and then move on to molecules that are organic in the original sense—that is, they are made by and found in living organisms. These complex molecules (all containing carbon) determine the forms and functions of living systems and are the subject of biochemistry.



Figure 9.1 All organic compounds contain carbon and most are formed by living things, although they are also formed by geological and artificial processes. (credit left: modification of work by Jon Sullivan; credit left middle: modification of work by Deb Tremper; credit right middle: modification of work by "annszyp"/Wikimedia Commons; credit right: modification of work by George Shuklin)

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 9.1.

Table 9.1: General Contrasting Properties and Examples of Organic and Inorganic Compounds

Organic	Hexane	Inorganic	NaCl
low melting points	−95°C	high melting points	801°C
low boiling points	69°C	high boiling points	1,413°C
low solubility in water; high solubility in nonpolar solvents	insoluble in water; soluble in gasoline	greater solubility in water; low solubility in nonpolar solvents	soluble in water; insoluble in gasoline
flammable	highly flammable	nonflammable	nonflammable
aqueous solutions do not conduct electricity	nonconductive	aqueous solutions conduct electricity	conductive in aqueous solution
exhibit covalent bonding	covalent bonds	exhibit ionic bonding	ionic bonds

Keep in mind, however, that there are exceptions to every category in this table. To further illustrate typical differences among organic and inorganic compounds, Table 9.1 also lists properties of the inorganic compound sodium chloride (common table salt, NaCl) and the organic compound hexane (C_6H_{14}), a solvent that is used to extract soybean oil from soybeans (among other uses). Many compounds can be classified as organic or inorganic by the presence or absence of certain typical properties, as illustrated in Table 9.1.

Today, organic compounds are key components of plastics, soaps, perfumes, sweeteners, fabrics, pharmaceuticals, and many other substances that we use every day. The value to us of organic compounds ensures that organic chemistry is an important discipline within the general field of chemistry. In this chapter, we discuss why the element carbon gives rise to a vast number and variety of compounds, how those compounds are classified, and the role of organic compounds in representative biological and industrial settings.

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- 9.1: Prelude to Organic Chemistry
  9.2: Aliphatic Hydrocarbons
  9.3: Aromatic Compounds- Benzene and Its Relatives
  9.4: Halogenated Hydrocarbons- Many Uses, Some Hazards
  9.5: The Functional Group
  9.6: Alcohols, Phenols, and Ethers
  9.7: Aldehydes and Ketones
  9.8: Carboxylic Acids and Esters
  9.9: Nitrogen-Containing Compounds- Amines and Amides

- TextMap: The Basics of GOB Chemistry (Ball et al.)

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9.1: Prelude to Organic Chemistry

Scientists of the 18th and early 19th centuries studied compounds obtained from plants and animals and labeled them *organic* because they were isolated from "organized" (living) systems. Compounds isolated from nonliving systems, such as rocks and ores, the atmosphere, and the oceans, were labeled *inorganic*. For many years, scientists thought organic compounds could be made by only living organisms because they possessed a vital force found only in living systems. The vital force theory began to decline in 1828, when the German chemist Friedrich Wöhler synthesized urea from inorganic starting materials. He reacted silver cyanate (AgOCN) and ammonium chloride (NH_4Cl), expecting to get ammonium cyanate (NH_4OCN). What he expected is described by the following equation.

$$AgOCN + NH_4Cl \rightarrow AgCl + NH_4OCN \tag{9.1.1}$$

Instead, he found the product to be urea (NH_2CONH_2), a well-known organic material readily isolated from urine. This result led to a series of experiments in which a wide variety of organic compounds were made from inorganic starting materials. The vital force theory gradually went away as chemists learned that they could make many organic compounds in the laboratory.

Today **organic chemistry** is the study of the chemistry of the carbon compounds, and inorganic chemistry is the study of the chemistry of all other elements. It may seem strange that we divide chemistry into two branches—one that considers compounds of only one element and one that covers the 100-plus remaining elements. However, this division seems more reasonable when we consider that of tens of millions of compounds that have been characterized, the overwhelming majority are carbon compounds.

> The word *organic* has different meanings. Organic fertilizer, such as cow manure, is organic in the original sense; it is derived from living organisms. Organic foods generally are foods grown without synthetic pesticides or fertilizers. Organic chemistry is the chemistry of compounds of carbon.

Carbon is unique among the other elements in that its atoms can form stable covalent bonds with each other and with atoms of other elements in a multitude of variations. The resulting molecules can contain from one to millions of carbon atoms. We previously surveyed organic chemistry by dividing its compounds into families based on functional groups. We begin with the simplest members of a family and then move on to molecules that are organic in the original sense—that is, they are made by and found in living organisms. These complex molecules (all containing carbon) determine the forms and functions of living systems and are the subject of biochemistry.



Figure 9.1.1 All organic compounds contain carbon and most are formed by living things, although they are also formed by geological and artificial processes. (credit left: modification of work by Jon Sullivan; credit left middle: modification of work by Deb Tremper; credit right middle: modification of work by "annszyp"/Wikimedia Commons; credit right: modification of work by George Shuklin)

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 9.1.1.

Table 9.1.1: General Contrasting Properties and Examples of Organic and Inorganic Compounds

Organic	Hexane	Inorganic	NaCl
low melting points	−95°C	high melting points	801°C
low boiling points	69°C	high boiling points	1,413°C
low solubility in water; high solubility in nonpolar solvents	insoluble in water; soluble in gasoline	greater solubility in water; low solubility in nonpolar solvents	soluble in water; insoluble in gasoline
flammable	highly flammable	nonflammable	nonflammable
aqueous solutions do not conduct electricity	nonconductive	aqueous solutions conduct electricity	conductive in aqueous solution
exhibit covalent bonding	covalent bonds	exhibit ionic bonding	ionic bonds

Keep in mind, however, that there are exceptions to every category in this table. To further illustrate typical differences among organic and inorganic compounds, Table 9.1.1 also lists properties of the inorganic compound sodium chloride (common table salt, NaCl) and the organic compound hexane (C_6H_{14}), a solvent that is used to extract soybean oil from soybeans (among other uses). Many compounds can be classified as organic or inorganic by the presence or absence of certain typical properties, as illustrated in Table 9.1.1.

Today, organic compounds are key components of plastics, soaps, perfumes, sweeteners, fabrics, pharmaceuticals, and many other substances that we use every day. The value to us of organic compounds ensures that organic chemistry is an important discipline within the general field of chemistry. In this chapter, we discuss why the element carbon gives rise to a vast number and variety of compounds, how those compounds are classified, and the role of organic compounds in representative biological and industrial settings.

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9.2: Aliphatic Hydrocarbons

Learning Objectives

- Define and identify alkanes, alkenes, alkynes, and cyclic hydrocarbons.
- List some properties of hydrocarbons.
- Identify and name simple (straight-chain) alkanes given formulas and write formulas for straight-chain alkanes given their names.
- Define structural and geometric isomers.
- Write condensed structural formulas and draw line-angle formulas given complete structural formulas for alkanes,alkenes, alkynes, and cyclic hydrocarbons.

The simplest organic compounds are those composed of only two elements: carbon and hydrogen. These compounds are called **hydrocarbons**. Hydrocarbons themselves are separated into two types: aliphatic hydrocarbons and aromatic hydrocarbons. **Aliphatic hydrocarbons** are hydrocarbons based on chains of C atoms. There are three types of aliphatic hydrocarbons. **Alkanes** are aliphatic hydrocarbons with only single covalent bonds. **Alkenes** are hydrocarbons that contain at least one C–C double bond, and a**lkynes** are hydrocarbons that contain a C–C triple bond. Occasionally, we find an aliphatic hydrocarbon with a ring of C atoms; these hydrocarbons are called ***cycloalkanes*** (or *cycloalkene*s or *cycloalkyne*s). Because alkanes have the maximum number of H atoms possible according to the rules of covalent bonds, alkanes are also referred to as **saturated hydrocarbons**.

Note

The word *saturated* has the same meaning for hydrocarbons as it does for the dietary fats and oils: the molecule has no carbon-to-carbon double bonds (C=C).

Alkanes

The simplest alkanes have their C atoms bonded in a straight chain; these are called *normal* alkanes. They are named according to the number of C atoms in the chain. The smallest alkane is methane:

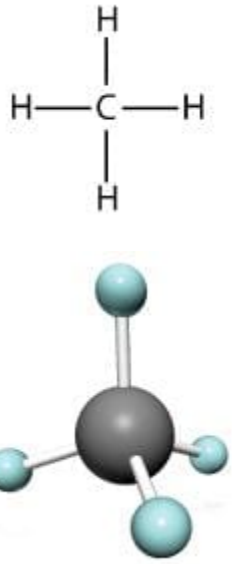
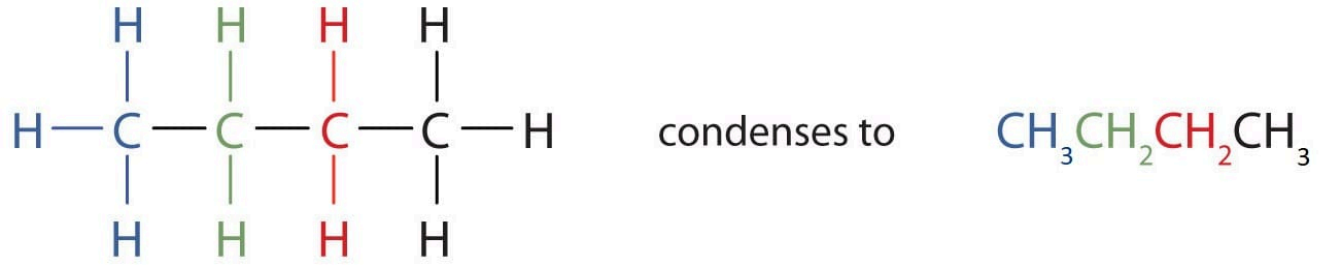


Figure 9.2.1. Two dimensional model of methane (top); *Three-dimensional representation of methane © Thinkstock. The methane molecule is three dimensional, with the H atoms in the positions of the four corners of a tetrahedron. (bottom)*

The diagrams representing alkanes are called **structural formulas** because they show the structure of the molecule. As molecules get larger, structural formulas become more and more complex. One way around this is to use a **condensed structural formula**, which lists the formula of each C atom in the backbone of the molecule.

condensed structural formula

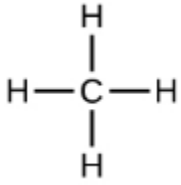
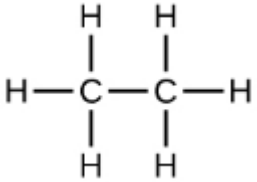
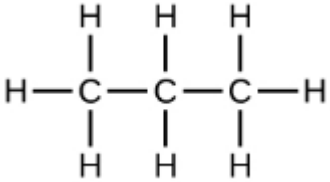
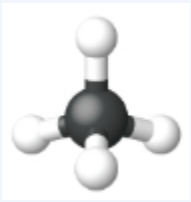
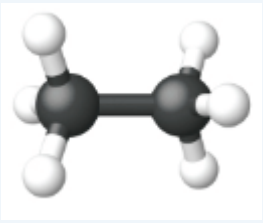
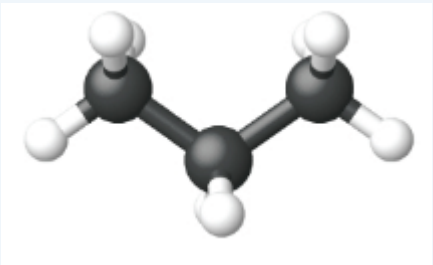
The condensed formulas show hydrogen atoms right next to the carbon atoms to which they are attached, as illustrated for butane:

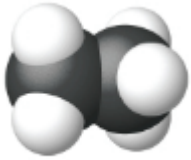
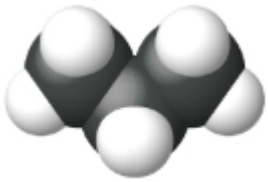


The ultimate condensed formula is a **line-angle formula (or line drawing)** , in which carbon atoms are implied at the corners and ends of lines, and each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds. For example, we can represent pentane ($CH_3CH_2CH_2CH_2CH_3$) and isopentane [$(CH_3)_2CHCH_2CH_3$] as follows:



Table 9.2.1 *Structural formulas for methane, ethane , and propane*

Structural Formula			
Ball and Stick Model			

Space Filling model			
Name	Methane	Ethane	Propane
Condensed Structural Formula	CH_4	CH_3CH_3	$CH_3CH_2CH_3$
Molecular Formula	CH_4	C_2H_6	C_3H_8
Line angle drawing			

Example 9.2.1

Provide the molecular formula, the complete structural formula, the condensed structural formula and the line angle formula for a straight chain alkane with 8 carbon atoms.

Solutions

Example 9.2.2 writing formulas for a straight chain alkane with eight carbon atoms.

structural formula	Explanation	Answer
Molecular Formula	The general formula for an alkane is C_nH_{2n+2} For an alkane with 8 carbon atoms, $C_8H_{(2\times 8)+2} = C_8H_{18}$.	C_8H_{18}.
Complete Structural Formula	Eight carbons first linked together and all remaining bonds to hydrogen to fulfill the octet rule.	C_1-C_2-C_3-C_4-C_5-C_6-C_7-C_8
Condensed Structural Formula	The terminal carbon atoms (C_1 and C_8) are bonded to three hydrogen atoms each and the six middle carbon atoms are bonded to two hydrogen atoms each. The six middle carbon atoms are all bonded to two hydrogen atoms so the structural formula can be simplified further.	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ $CH_3(CH_2)_6CH_3$
Line Angle Drawing	Eight carbon atoms are implied at the corners and ends of lines, and each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds.	

Exercise 9.2.1

Provide the molecular formula, the complete structural formula, the condensed structural formula, and the line angle formula for a straight chain alkane with 7 carbon atoms.

Answer available at the end of this section.

Homologous Series

Methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) are the beginning of a series of compounds in which any two members in a sequence differ by one carbon atom and two hydrogen atoms—namely, a CH_2 unit. The first 10 members of this series are given in Table 9.2.1.

Table 9.2.1 The First 10 Straight-Chain Alkanes

Molecular Formula	Condensed Structural Formula	Name
CH4	CH4	methane
C2H6	CH3CH3	ethane
C3H8	CH3CH2CH3	propane
C4H10	CH3CH2CH2CH3	butane
C5H12	CH3CH2CH2CH2CH3	pentane
C6H14	CH3(CH2)4CH3	hexane
C7H16	CH3(CH2)5CH3	heptane
C8H18	CH3(CH2)6CH3	octane
C9H20	CH3(CH2)7CH3	nonane
C10H22	CH3(CH2)8CH3	decane

Note

Parentheses in condensed structural formulas indicate that the enclosed grouping of atoms is attached to the adjacent carbon atom.

Consider the series in Figure 9.2.2. The sequence starts with C_3H_8, and a CH_2 unit is added in each step moving up the series. Any family of compounds in which adjacent members differ from each other by a definite factor (here a CH_2 group) is called a homologous series. The members of such a series, called *homologs*, have properties that vary in a regular and predictable manner. The principle of *homology* gives organization to organic chemistry in much the same way that the periodic table gives organization to inorganic chemistry. Instead of a bewildering array of individual carbon compounds, we can study a few members of a homologous series and from them deduce some of the properties of other compounds in the series.

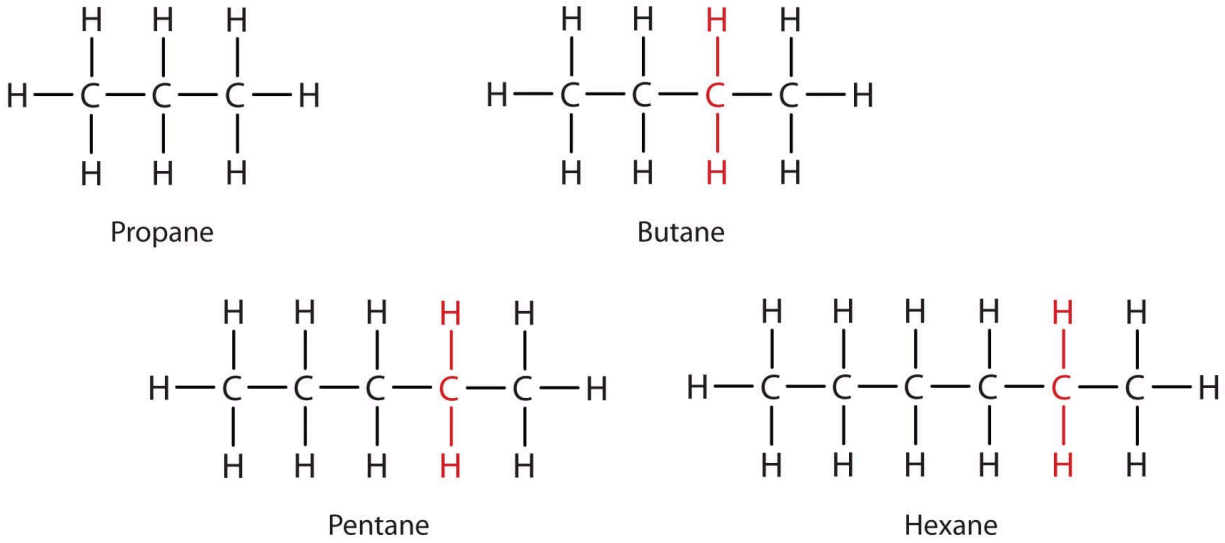


Figure 9.2.2 Members of a homologous series.

The principle of homology allows us to write a general formula for alkanes: $C_nH_{2n + 2}$. Using this formula, we can write a molecular formula for any alkane with a given number of carbon atoms. For example, an alkane with eight carbon atoms has the molecular formula $C_8H_{(2 \times 8) + 2} = C_8H_{18}$.

Naming (IUPAC Nomenclature)

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. A stem name in Table 9.2.1 indicates the number of carbon atoms in the longest continuous chain (LCC). Atoms or groups attached to this carbon chain, called *substituents*, are then named, with their positions indicated by numbers.

Table 9.2.2 Stems That Indicate the Number of Carbon Atoms in Organic Molecules

Stem	Number of C Atoms
meth-	1
eth-	2
prop-	3
but-	4
pent-	5
hex-	6
hept-	7
oct-	8
non-	9
dec-	10

Note

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.

Example 9.2.2

What is the name of an eight carbon alkane?

Solution

The stem that refers to eight carbon atoms is **oct** plus the suffix **-ane** for an alkane, so the answer is **Octane**.

Exercise 9.2.2

Provide the name for the following compounds:

a. seven carbon alkane

b. six carbon alkane

Answer available at the end of this section.

Isomerism-Branched Chain Alkanes

One of the interesting aspects of organic chemistry is that it is three-dimensional. A molecule can have a shape in space that may contribute to its properties. Molecules can differ in the way the atoms are arranged - the same combination of atoms can be assembled in more than one way. These compounds are known as **isomers**. Isomers are molecules with the same molecular formulas, but different arrangements of atoms. We will look at some isomer possibilities for alkanes and alkenes.

We can write the structure of butane (C_4H_{10}) by stringing four carbon atoms in a row,

–C–C–C–C–

and then adding enough hydrogen atoms to give each carbon atom four bonds:

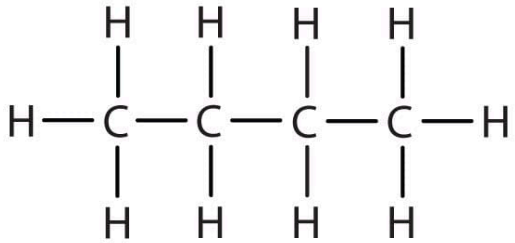


Figure 9.2.2 Complete structural formula of butane

The compound butane has this structure, but there is another way to put 4 carbon atoms and 10 hydrogen atoms together. Place 3 of the carbon atoms in a row and then branch the fourth one off the middle carbon atom:

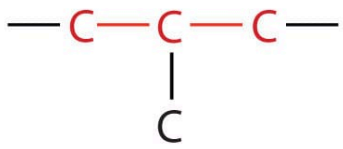
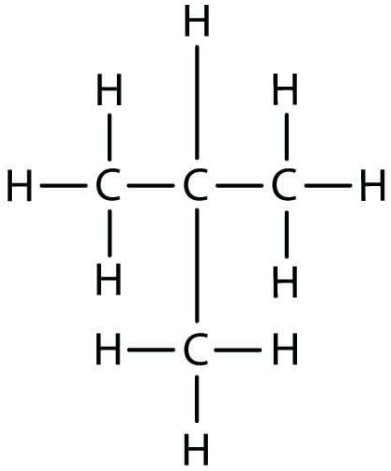


Figure 9.2.3 Incomplete structural formula

Now we add enough hydrogen atoms to give each carbon four bonds.



There is a hydrocarbon that corresponds to this structure, which means that two different compounds have the same molecular formula: C_4H_{10}. The two compounds have different properties—for example, one boils at –0.5°C; the other at –11.7°C. Different compounds having the same molecular formula are called isomers.

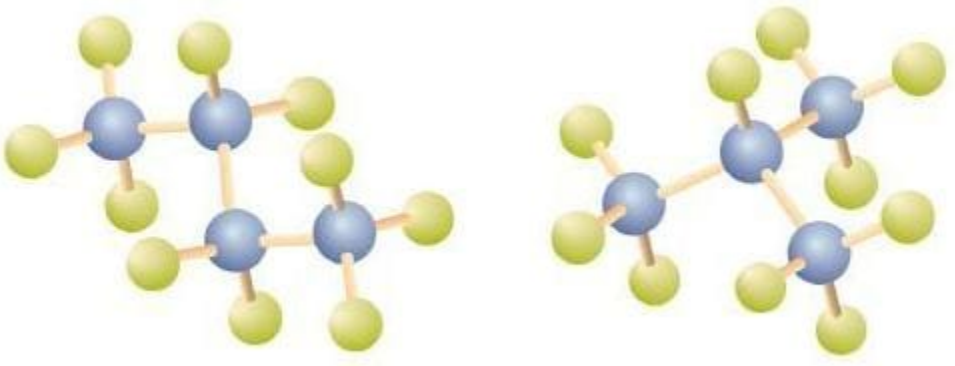
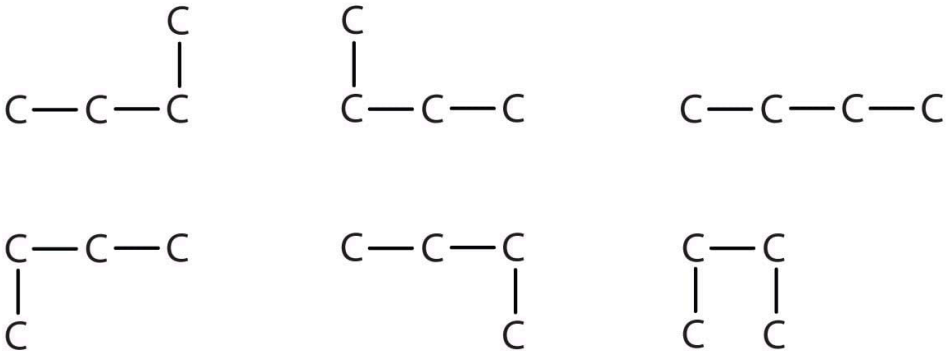


Figure 9.2.4 Butane and isobutane. The ball-and-stick models of these two compounds show them to be isomers; both have the molecular formula C4H10.

Notice that C_4H_{10} is depicted with a bent chain in Figure 9.2.4. The four-carbon chain may be bent in various ways because the groups can rotate freely about the C–C bonds. However, this rotation does not change the identity of the compound. It is important to realize that bending a chain does *not* change the identity of the compound; all of the following represent the same compound, butane:



The structure of isobutane shows a continuous chain of three carbon atoms only, with the fourth attached as a branch off the middle carbon atom of the continuous chain, which is different from the structures of butane (compare the two structures in Figure 9.2.4.

Unlike C_4H_{10}, the compounds methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) do not exist in isomeric forms because there is only one way to arrange the atoms in each formula so that each carbon atom has four bonds.

Next beyond C_4H_{10} in the homologous series is pentane. Each compound has the same molecular formula: C_5H_{12}. 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.

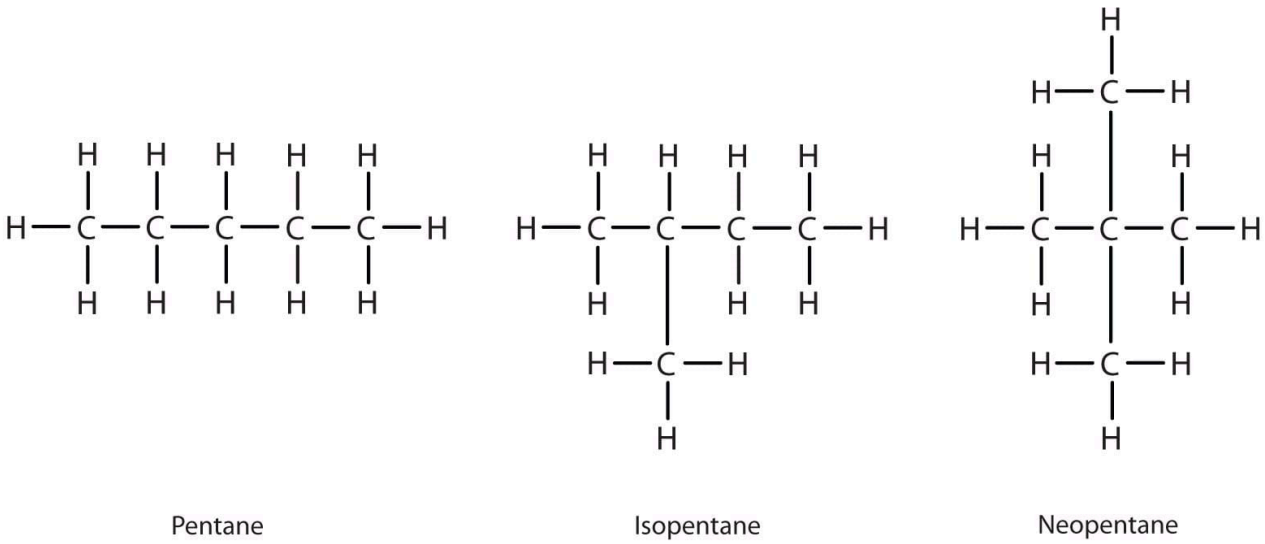


Figure 9.2.5 complete structural formulas for pentane isopentane and neopentane

Naming Branched Alkanes

You have already learned the basics of nomenclature-the names of the first 10 normal hydrocarbons. Here, we will add some steps to the procedure so you can name branched hydrocarbons.

First, given the structure of an alkane, identify the longest continuous chain of C atoms. Note that the longest chain may not be drawn in a straight line. The longest chain determines the parent name of the hydrocarbon. For example, in the molecule

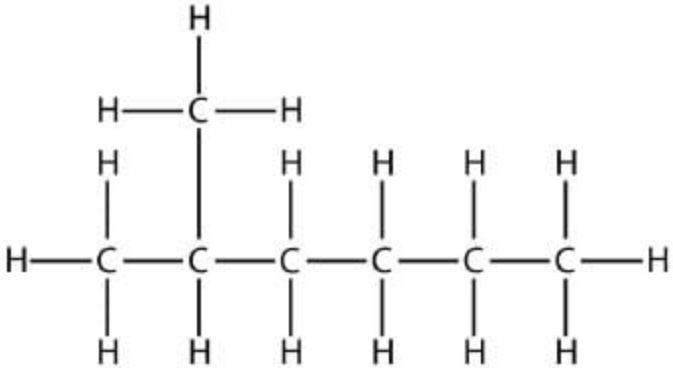


Figure 9.2.6 structural formula for hexane

the longest chain of carbons has six C atoms. Therefore, it will be named as a hexane. However, in the molecule

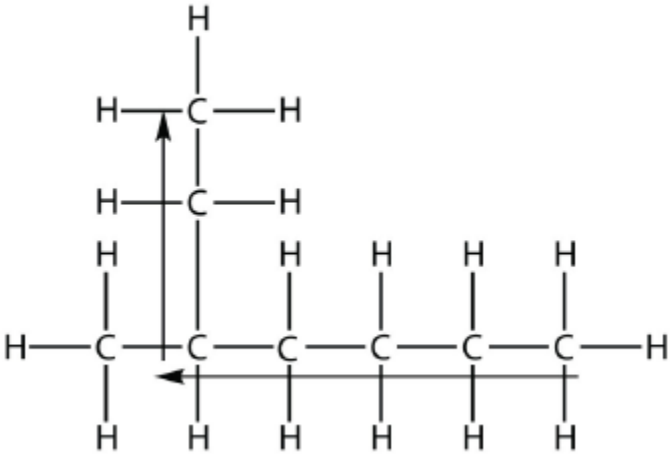


Figure 9.2.7 structural formula for heptane

the longest chain of C atoms is not six, but seven, as shown. So this molecule will be named as a heptane.

The next step is to identify the branches, or **substituents,** on the main chain. The names of the substituents, or *alkyl groups*, are derived from the names of the parent hydrocarbons; however, rather than having the ending *-ane*, the substituent name has the ending *-yl*. Table 9.2.3, lists the substituent names for the five smallest substituents.

Table 9.2.3 *Substituent Names.*

Substituent Formula	Number of C Atoms	Name of Substituent
CH_3	1	*methyl-*
CH_3CH_2	2	*ethyl-*
$CH_3CH_2CH_2$	3	*propyl-*
$CH_3CH_2CH_2CH_2$	4	*butyl-*
$CH_3CH_2CH_2CH_2CH_2$	5	*pentyl-*
and so forth	and so forth	and so forth

In naming the branched hydrocarbon, the name of the substituent is combined with the parent name of the hydrocarbon without spaces. However, there is likely one more step. The longest chain of the hydrocarbon must be numbered, and the numerical position of the substituent must be included to account for possible isomers. As with double and triple bonds, the main chain is numbered to give the substituent the lowest possible number. For example, in this alkane

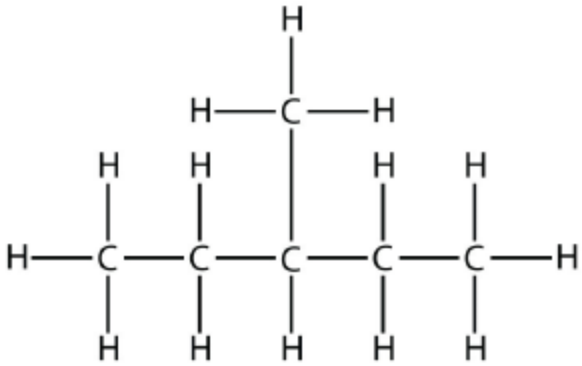


Figure 9.2.7 Structural formula for 3-methylpentane

the longest chain is five C atoms long, so it is a pentane. There is a one-carbon substituent on the third C atom, so there is a methyl group at position 3. We indicate the position using the number, which is followed by a hyphen, the substituent name, and the parent hydrocarbon name-in this case, **3-methylpentane**. That name is specific to that particular hydrocarbon and no other molecule. Organic chemistry nomenclature is very specific!

It is common to write the structural formula of a hydrocarbon without the H atoms, for clarity. So we can also represent 3-methylpentane as

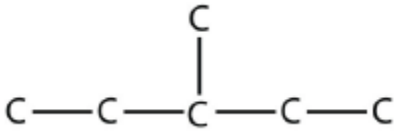
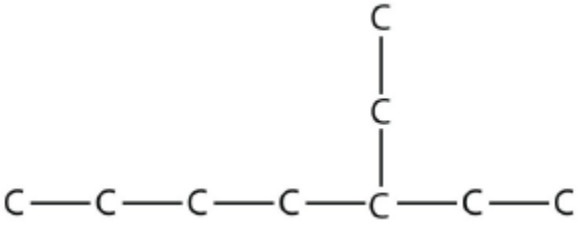


Figure 9.2.8 Structural formula for 3-methylpentane without the hydrogen atoms

where it is understood that any unwritten covalent bonds are bonds with H atoms. With this understanding, we recognize that the structural formula for 3-methylpentane refers to a molecule with the formula of C_6H_{14}.

Example 9.2.3:

Name this molecule.

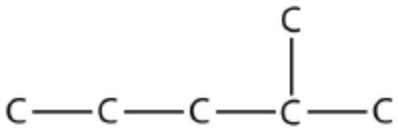


Solution

The longest continuous carbon chain has **seven** C atoms, so this molecule will be named as a **heptane**. There is a **two-carbon substituent** on the main chain, which is an **ethyl group**. To give the substituent the lowest numbering, we number the chain from the *right* side and see that **the substituent is on the third C atom**. So this hydrocarbon is **3-ethylheptane**.

Exercise 9.2.3

Name this molecule.



Answer

2-methylpentane

Branched hydrocarbons may have more than one substituent. If the substituents are different, then give each substituent a number (using the smallest possible numbers) and list the substituents in alphabetical order, with the numbers separated by hyphens and with no spaces in the name. So the molecule

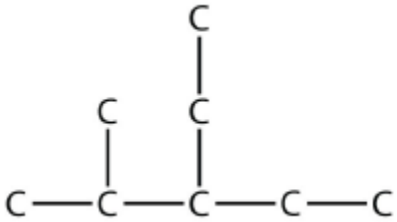


Figure 9.2.8 3-ethyl-2-methylpentane

is 3-ethyl-2-methylpentane.

If the substituents are the same, then use the name of the substituent only once, but use more than one number, separated by a comma. Also, put a numerical prefix before the substituent name that indicates the number of substituents of that type. The numerical prefixes are listed in Table 9.2.4. The number of the position values must agree with the numerical prefix before the substituent.

Table 9.2.4 Numerical Prefixes to Use for Multiple Substituents

Number of Same Substituent	Numerical Prefix
2	*di-*
3	*tri-*
4	*tetra-*
5	*penta-*
and so forth	and so forth

Consider this molecule:

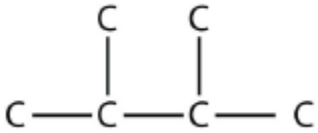
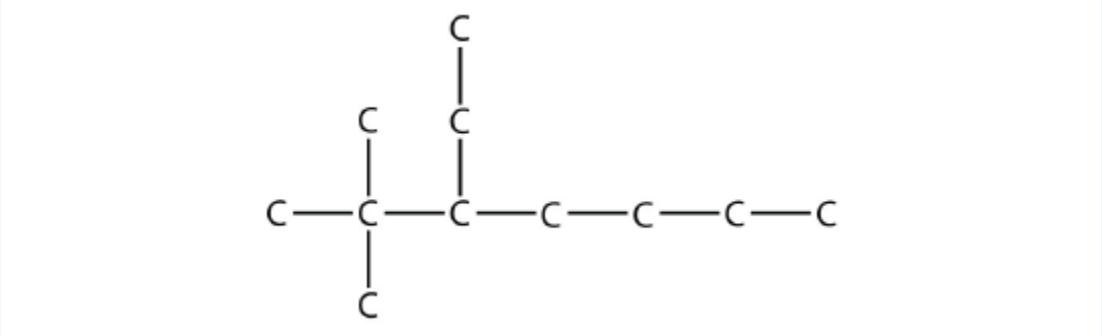


Figure 9.2.9 2,3-dimethylbutane

The longest chain has four C atoms, so it is a butane. There are two substituents, each of which consists of a single C atom; they are methyl groups. The methyl groups are on the second and third C atoms in the chain (no matter which end the numbering starts from), so we would name this molecule 2,3-dimethylbutane. Note the comma between the numbers, the hyphen between the numbers and the substituent name, and the presence of the prefix *di-* before the *methyl*. Other molecules-even with larger numbers of substituents-can be named similarly.

Example 9.2.4:

Name this molecule.

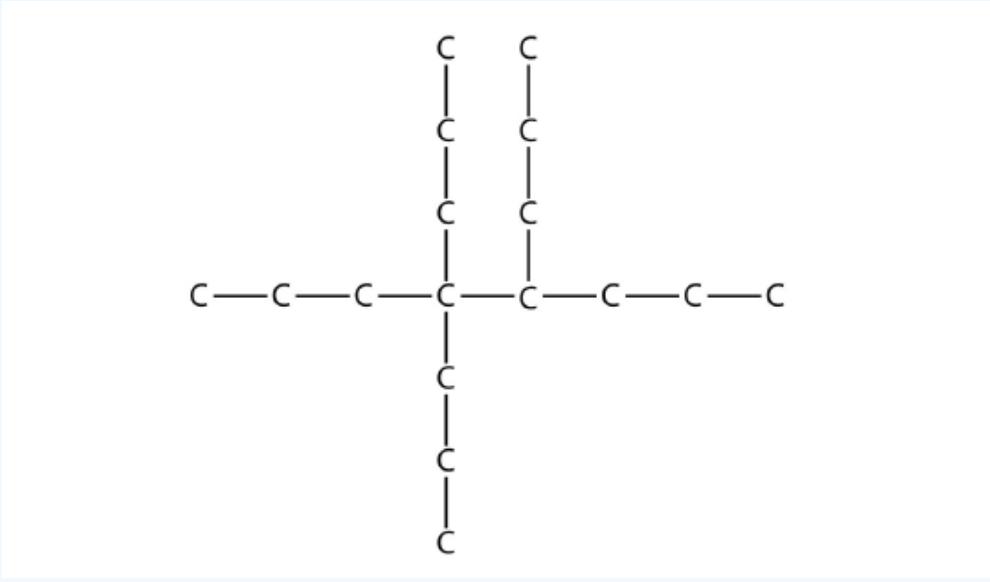


Solution

The longest chain has **seven** C atoms, so we name this molecule as a **heptane**. We find two one-carbon substituents on the second C atom and a **two-carbon substituent** on the third C atom. So this molecule is named **3-ethyl-2,2-dimethylheptane**.

Exercise 9.2.4

Name this molecule.



Answer

4,4,5-tripropyloctane

Properties of Alkanes

All alkanes are composed of carbon and hydrogen atoms, and have similar bonds, structures, and formulas; noncyclic alkanes all have a formula of C_nH_{2n+2}. The number of carbon atoms present in an alkane has no limit. Greater numbers of atoms in the molecules will lead to stronger intermolecular attractions (dispersion forces) and correspondingly different physical properties of

the molecules. Properties such as melting point and boiling point (Table 9.2.5) usually change smoothly and predictably as the number of carbon and hydrogen atoms in the molecules change.

Table 9.2.5 Properties of Some Alkanes

Alkane	Molecular Formula	Melting Point (°C)	Boiling Point (°C)	Phase at STP	Number of Structural Isomers
methane	CH_4	−182.5	−161.5	gas	1
ethane	C_2H_6	−183.3	−88.6	gas	1
propane	C_3H_8	−187.7	−42.1	gas	1
butane	C_4H_{10}	−138.3	−0.5	gas	2
pentane	C_5H_{12}	−129.7	36.1	liquid	3
hexane	C_6H_{14}	−95.3	68.7	liquid	5
heptane	C_7H_{16}	−90.6	98.4	liquid	9
octane	C_8H_{18}	−56.8	125.7	liquid	18
nonane	C_9H_{20}	−53.6	150.8	liquid	35
decane	$C_{10}H_{22}$	−29.7	174.0	liquid	75
tetradecane	$C_{14}H_{30}$	5.9	253.5	solid	1858
octadecane	$C_{18}H_{38}$	28.2	316.1	solid	60,523

Alkanes are relatively stable molecules, but heat or light will activate reactions that involve the breaking of C–H or C–C single bonds. Combustion is one such reaction:

$$\mathrm{CH_4}(g) + 2\,\mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(g)$$

Alkanes burn in the presence of oxygen, a highly exothermic oxidation-reduction reaction that produces carbon dioxide and water. 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 continuous- 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 9.2.10). You may recall that boiling point is a function of intermolecular interactions, which was discussed in the chapter on solutions and colloids.

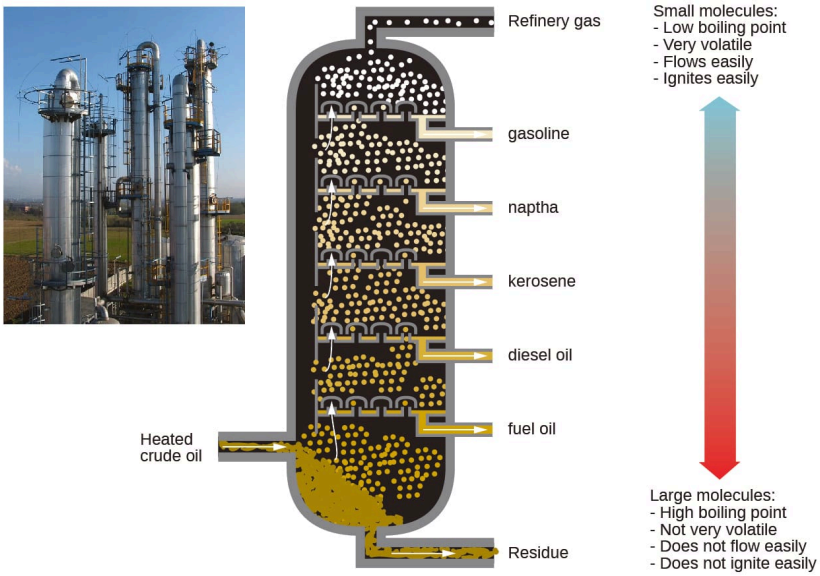


Figure 9.2.10 In a column for the fractional distillation of crude oil, oil heated to about 425 °C in the furnace vaporizes when it enters the base of the tower. The vapors rise through bubble caps in a series of trays in the tower. As the vapors gradually cool, fractions of higher, then of lower, boiling points condense to liquids and are drawn off. (credit left: modification of work by Luigi Chiesa)

In a substitution reaction, another typical reaction of alkanes, one or more of the alkane's hydrogen atoms is replaced with a different atom or group of atoms. No carbon-carbon bonds are broken in these reactions, and the hybridization of the carbon atoms does not change. For example, the reaction between ethane and molecular chlorine depicted here is a substitution reaction:

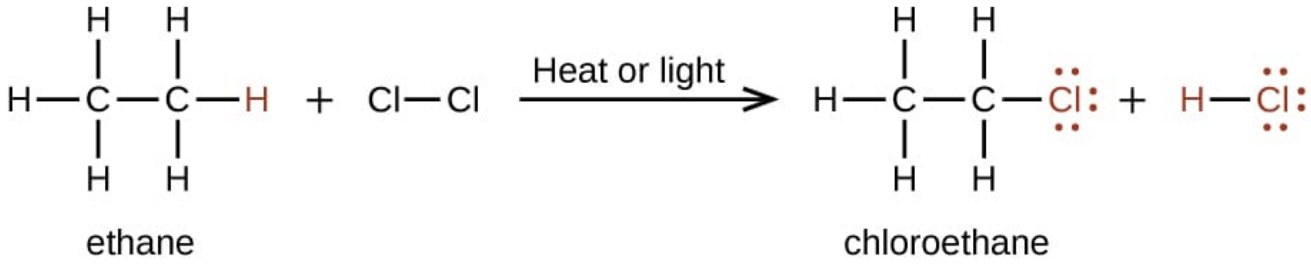


Figure 9.2.11 the reaction between ethane and molecular chlorine

The C–Cl portion of the chloroethane molecule is an example of a functional group, the part or moiety of a molecule that imparts a specific chemical reactivity. The types of functional groups present in an organic molecule are major determinants of its chemical properties and are used as a means of classifying organic compounds as detailed in the remaining sections of this chapter.

Cyclic Hydrocarbons

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. Like other alkanes, cycloalkanes are saturated compounds. Cycloalkanes have the general formula $\mathrm{C}_n\mathrm{H}_{2n}$. The simplest cycloalkane shown below is cyclopropane, a three-carbon ring.

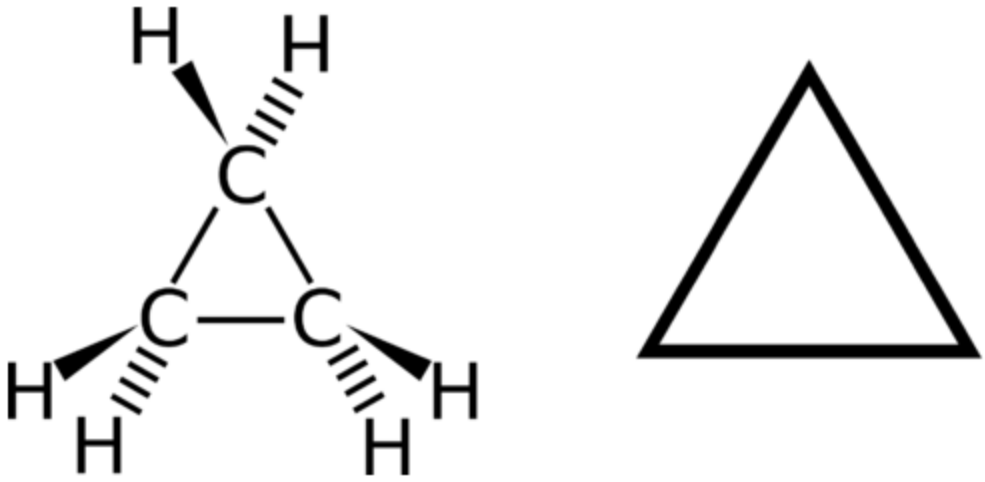


Figure 9.2.11 Cyclopropane the simplest cycloalkane.

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 are still sp^3 hybridized, with an ideal 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.

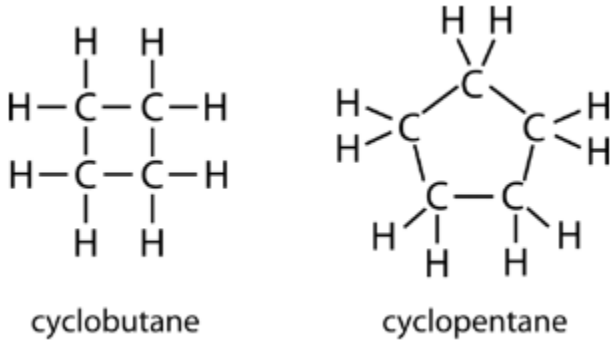


Figure 9.2.12 Cyclobutane and Cyclopentane

Cyclohexane is a six-carbon cycloalkane shown below

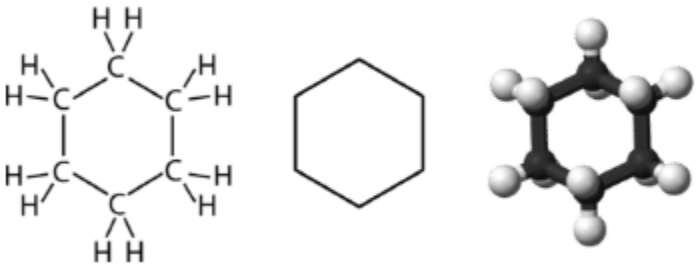


Figure 9.2.13 Cyclohexane

All three of the depictions of cyclohexane 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 puckered. The puckering of the ring means that every other carbon atom is above and below the plane. The figure below shows two possibilities for the puckered cyclohexane molecule. Each of the structures is called a conformation. The conformation on the right is called the boat conformation, while the one on

the left is called the chair conformation.



Figure 9.2.14 Chair (left) and boat (right) conformations for cyclohexane.

While both conformations reduce the ring strain compared to a planar molecule, the chair is preferred. This is because the chair conformation results in fewer repulsive interactions between the hydrogen atoms. However, interconversion readily occurs between the two conformations.

Larger cycloalkanes also exist, but are less common. Cyclic hydrocarbons may also be unsaturated. A **cycloalkene** is a cyclic hydrocarbon with at least one carbon-carbon double bond. A **cycloalkyne** is a cyclic hydrocarbon with at least one carbon-carbon triple bond. Shown below are the simplified structural formulas for cyclohexene and cyclooctyne.

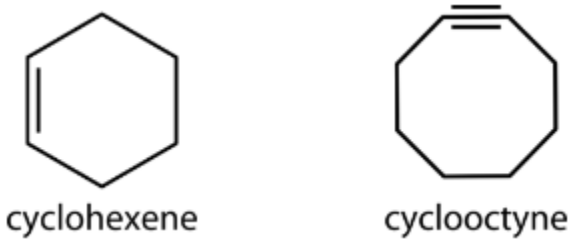


Figure 9.2.15 Cyclohexene(left) and cyclooctyne(right)

Unsaturated Hydrocarbons: Alkenes and Alkynes

Alkenes

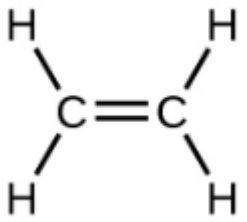
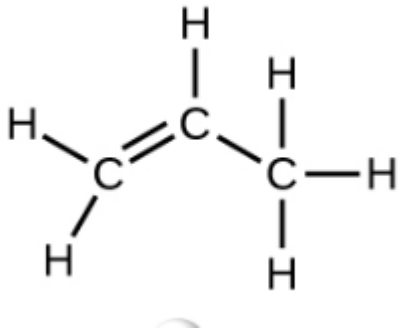
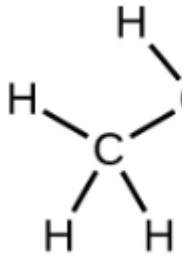
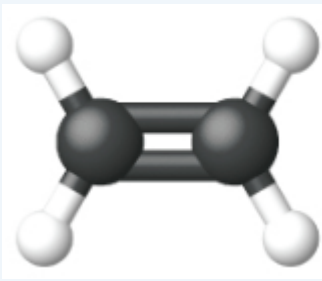
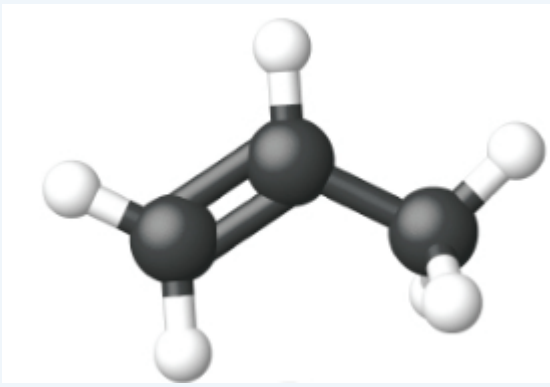
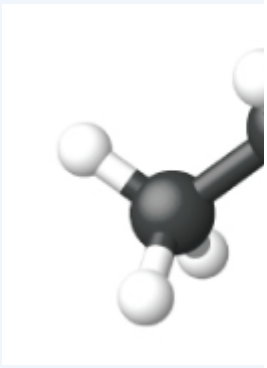
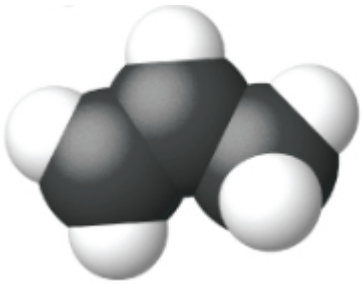
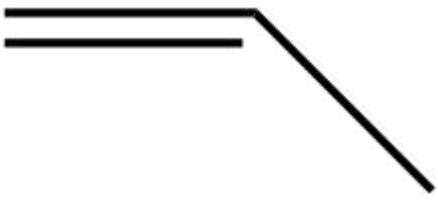
Organic compounds that contain one or more double or triple bonds between carbon atoms are described as unsaturated. Unsaturated hydrocarbons have less than the maximum number of H atoms possible. Unsaturated hydrocarbon molecules that contain one or more double bonds are called alkenes. Carbon atoms linked by a double bond are bound together by two bonds, one σ bond and one π bond. 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.

Note

The word un*saturated* has the same meaning for hydrocarbons as it does for the dietary fats and oils: the molecule has at least one carbon-to-carbon double (C=C) or triple bond (C≡C).

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 9.2.16); 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.

Structural formulas of Alkenes

Structural Formula			
Ball and Stick Model			
Space Filling model			
Name	ethene	propene	
Condensed Structural Formula	CH_2CH_2	CH_2CHCH_3	C
Molecular Formula	C_2H_2	C_3H_6	
Line angle drawing			

The name of an alkene is derived from the name of the alkane with the same number of carbon atoms. The presence of the double bond is signified by replacing the suffix *-ane* with the suffix *-ene*. The location of the double bond is identified by naming the smaller of the numbers of the carbon atoms participating in the double bond:

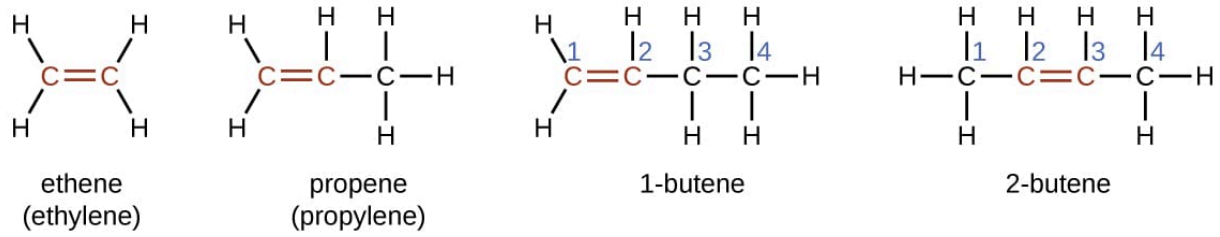


Figure 9.2.16 Four structural formulas and names are shown. The first shows two red C atoms connected by a red double bond illustrated with two parallel line segments. H atoms are bonded above and below to the left of the left-most C atom. Two more H atoms are similarly bonded to the right of the C atom on the right. Beneath this structure the name ethene and alternate name ethylene are shown. The second shows three C atoms bonded together with a red double bond between the red first and second C atoms moving left to right across the three-carbon chain. H atoms are bonded above and below to the left of the C atom to the left. A single H is bonded above the middle C atom. Three more H atoms are bonded above, below, and to the right of the third C atom. Beneath this structure the name propene and alternate name propylene is shown. The third shows four C atoms bonded together, numbered one through four moving left to right with a red double bond between the red first and second carbon in the chain. H atoms are bonded above and below to the left of the C atom to the left. A single H is bonded above the second C atom. H atoms are bonded above and below the third C atom. Three more H atoms are bonded above, below, and to the right of the fourth C atom. Beneath this structure the name 1 dash butene is shown. The fourth shows four C atoms bonded together, numbered one through four moving left to right with a red double bond between the red second and third C atoms in the chain. H atoms are bonded above, below, and to the left of the left-most C atom. A single H atom is bonded above the second C atom. A single H atom is bonded above the third C atom. Three more H atoms are bonded above, below, and to the right of the fourth C atom. Beneath this structure the name 2 dash butene is shown.

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 are bound together by one σ bond and two π bonds. The *sp*-hybridized carbons involved in the triple bond have bond angles of 180°, giving these types of bonds a linear, rod-like 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:



Figure 9.2.17 The structural formula and name for ethyne, also known as acetylene, are shown. In red, two C atoms are shown with a triple bond illustrated by three horizontal line segments between them. Shown in black at each end of the structure, a single H atom is bonded.

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.

Naming Alkenes and Alkynes

Alkenes and alkynes are named in a similar fashion. The biggest difference is that when identifying the longest carbon chain, it *must* contain the C–C double or triple bond. Furthermore, when numbering the main chain, the double or triple bond gets the lowest possible number. This means that there may be longer or higher-numbered substituents than may be allowed if the molecule were an alkane. For example, this molecule

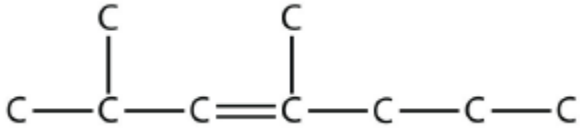
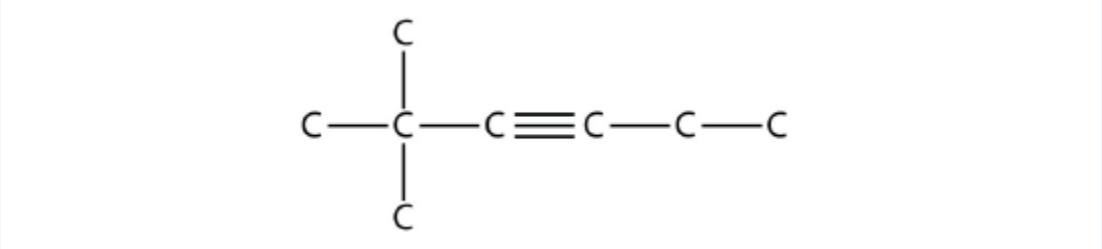


Figure 9.2.18 2,4-dimethyl-3-heptene

is 2,4-dimethyl-3-heptene (note the number and the hyphens that indicate the position of the double bond).

Example 9.2.5

Name this molecule.

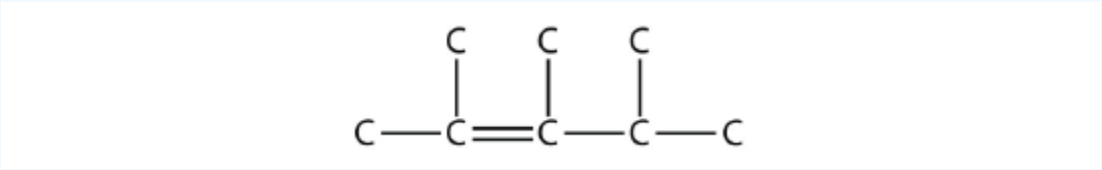


Solution

The longest chain that contains the C–C triple bond has six C atoms, so this is a hexyne molecule. The triple bond starts at the third C atom, so this is a 3-hexyne. Finally, there are two methyl groups on the chain; to give them the lowest possible number, we number the chain from the left side, giving the methyl groups the second position. So the name of this molecule is 2,2-dimethyl-3-hexyne.

Exercise 9.2.5

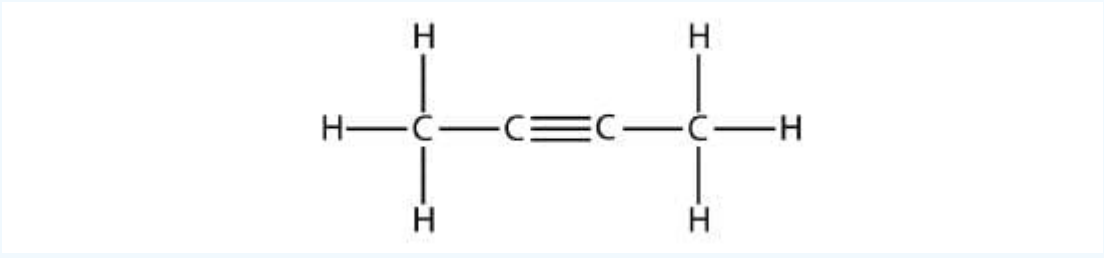
Name this molecule.



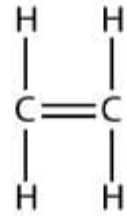
Answer available at the end of this section.

Example 9.2.6

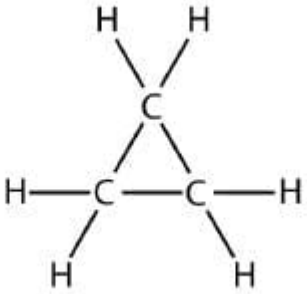
Identify the molecule as an alkane, an alkene, or an alkyne.

1. 

2.



3.



Solution

1. The molecule has at least one carbon-to-carbon triple bond (C≡C) so it is an **alkyne**.

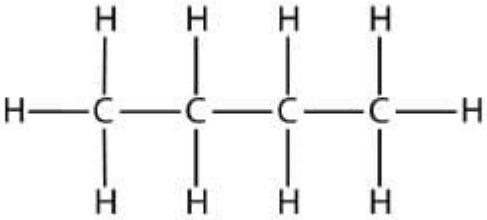
2. The molecule has a one carbon-to-carbon double bond (C=C) so it is an **alkene**.

3. The molecule only has carbon-to-carbon single bonds so it is an **alkane**.

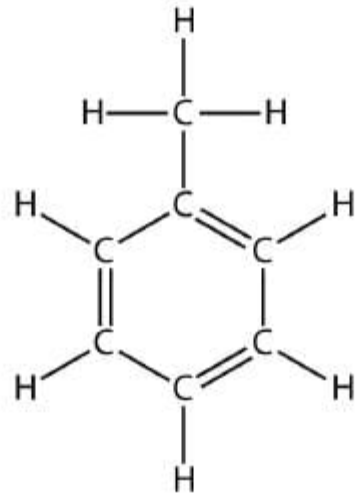
Exercise 9.2.6

Identify the molecule as an alkane, an alkene, or an alkyne.

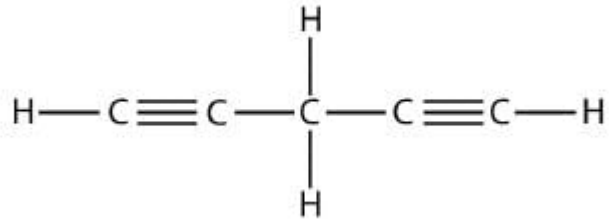
1.



2.



3.



Answer available at the end of this section.

Properties of Alkenes and Alkynes

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.

Halogens can also react with alkenes and alkynes, but the reaction is different. In these cases, the halogen reacts with the C–C double or triple bond and inserts itself onto each C atom involved in the multiple bonds. This reaction is called an **addition reaction**. One example is

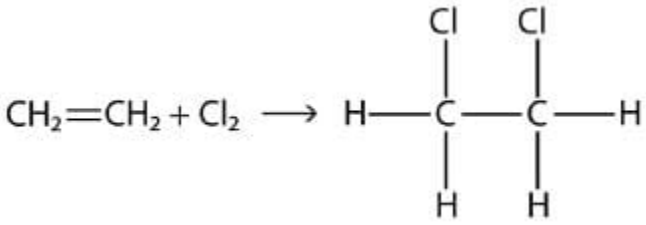


Figure 9.2.19

$$CH_2 = CH_2 + H_2 \overset{metal\ catalyst}{\rightarrow} CH_3CH_3$$

The reaction conditions are usually mild; in many cases, the halogen reacts spontaneously with an alkene or an alkyne.

Hydrogen can also be added across a multiple bond; this reaction is called a **hydrogenation reaction**. In this case, however, the reaction conditions may not be mild; high pressures of H_2 gas may be necessary. A platinum or palladium catalyst is usually

employed to get the reaction to proceed at a reasonable pace:

$$CH_2 = CH_2 + H_2 \overset{metal\ catalyst}{\rightarrow} CH_3CH_3$$

Geometric Isomers (Cis-Trans) Isomers

With a molecule such as 2-butene, a different type of isomerism called geometric isomerism can be observed. **Geometric isomers** are isomers in which the order of atom bonding is the same but the arrangement of atoms in space is different. The double bond in an alkene is not free to rotate because of the nature of the pi bond. Therefore, there are two different ways to construct the 2-butene molecule. The image below shows the two geometric isomers, called *cis*-2-butene and *trans*-2-butene.

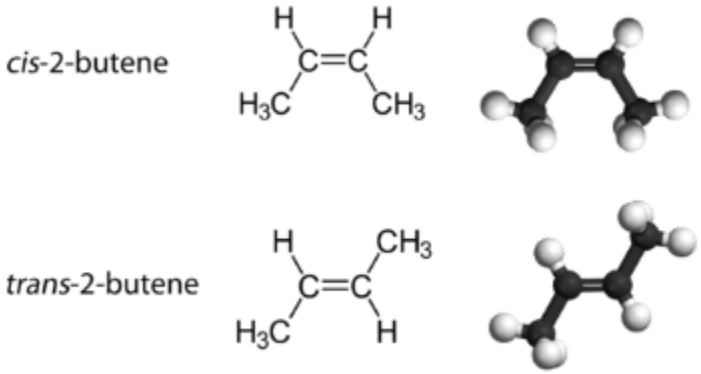


Figure 9.2.20\ *cis*-2-butene and *trans*-2-butene.

The ***cis* isomer** has the two single hydrogen atoms on the same side of the molecule, while the ***trans* isomer** has them on opposite sides of the molecule. In both molecules, the bonding order of the atoms is the same. In order for geometric isomers to exist, there must be a rigid structure in the molecule to prevent free rotation around a bond. If the double bond in an alkene was capable of rotating, the two geometric isomers above would not exist. In addition, the two carbon atoms must each have two different groups attached in order for there to be geometric isomers. Propene has no geometric isomers because one of the carbon atoms has two single hydrogens bonded to it.

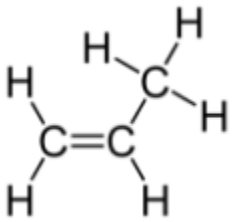


Figure 9.2.21\ Propene

Physical and chemical properties of geometric isomers are generally different. While *cis*-2-butene is a polar molecule, *trans*-2-butene is nonpolar. Heat or irradiation with light can be used to bring about the conversion of one geometric isomer to another. The input of energy must be large enough to break the pi bond between the two carbon atoms, which is weaker than the sigma bond. At that point,the now single bond is free to rotate and the isomers can interconvert.

As with alkenes, alkynes display structural isomerism beginning with 1-butyne and 2-butyne. However, there are no geometric isomers with alkynes because there is only one other group bonded to the carbon atoms that are involved in the triple bond.

Summary

- Simple alkanes exist as a homologous series, in which adjacent members differ by a CH_2 unit.
- Condensed chemical formulas show the hydrogen atoms (or other atoms or groups) right next to the carbon atoms to which they are attached.
- Line-angle formulas imply a carbon atom at the corners and ends of lines. Each carbon atom is understood to be attached to enough hydrogen atoms to give each carbon atom four bonds.

- Alkanes have both common names and systematic names, specified by IUPAC.
- Names and structures of typical cyclic hydrocarbons are given.
- Structural and geometric isomers are defined.
- Examples of alkane and alkene isomers are given.

Contributors and Attributions

- OpenSTAX
- TextMap: Beginning Chemistry (Ball et al.)
-

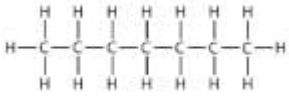
- Marisa Alviar-Agnew (Sacramento City College)

- Henry Agnew (UC Davis)

Answers

Exercise 9.2.1

molecular formula: C_7H_{16}

complete structural formula: 

condensed structural formula: $CH_3(CH_2)_5CH_3$

line angle drawing: 

Exercise 9.2.2

a. heptane

b. hexane

Exercise 9.2.5

2,3,4-trimethyl-2-pentene

Exercise 9.2.6

1. alkane, 2. alkene, 3. alkyne

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9.3: Aromatic Compounds- Benzene and Its Relatives

Learning Objective

- Name and identify aromatic compounds.

Benzene is the parent compound of the large family of organic compounds known as aromatic compounds. Unlike cyclohexane, benzene only contains six hydrogen atoms, giving the impression that the ring is unsaturated and each carbon atom participates in one double bond. Two different structures with alternating single and double bonds around the ring can be written for benzene.

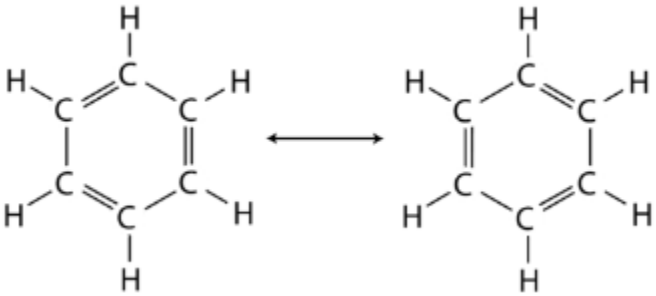


Figure 9.3.1 benzene

In benzene, the true bonding between carbon atoms is neither a single nor a double bond. Rather, all of the bonds are a hybrid of a single and double bond. In benzene, the pi bonding electrons are free to move completely around the ring. **Delocalized electrons** are electrons that are not confined to the bond between two atoms, but are instead allowed to move between three or more. The delocalization of the electrons in benzene can best be shown by showing benzene with a ring inside the hexagon, with the hydrogen atoms understood.

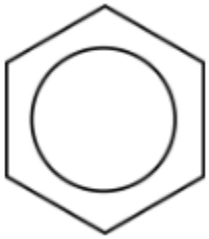


Figure 9.3.2 Delocalized electrons

Delocalization of the electrons makes for a more stable molecule than a similar molecule that does not have delocalized electrons. Benzene is a more stable and less reactive compound than straight-chain hexenes. The sp^2 hybridization of the carbon atoms results in a planar molecule as opposed to the puckered structure of cyclohexane.

There are many derivatives of benzene. The hydrogen atoms can be replaced by many different substituents. Aromatic compounds more readily undergo substitution reactions than addition reactions; replacement of one of the hydrogen atoms with another substituent will leave the delocalized double bonds intact. The following are typical examples of substituted benzene derivatives:

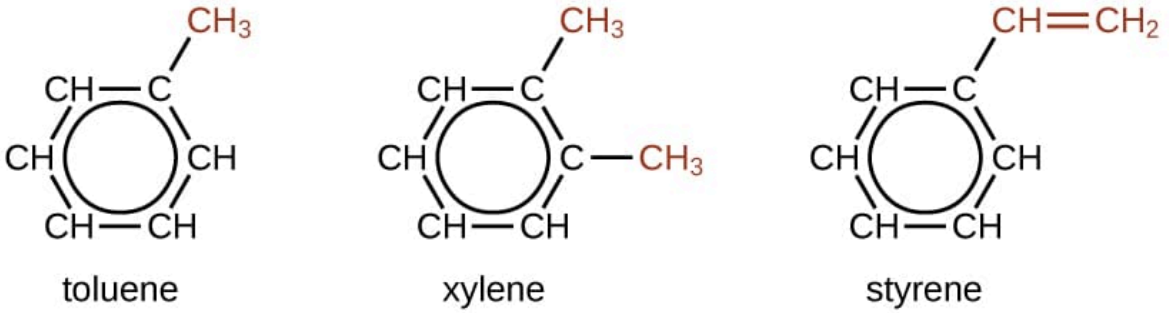


Figure 9.3.3 Three structural formulas are shown. The first is labeled toluene. This molecule has a six carbon hydrocarbon ring in which five of the C atoms are each bonded to only one H atom. At the upper right of the ring, the C atom that does not have a bonded H atom has a red C H subscript 3 group attached. A circle is at the center of the ring. The second is labeled xylene. This molecule has a six carbon hydrocarbon ring in which four of the C atoms are each bonded to only one H atom. At the upper right and right of the ring, the two C atoms that do not have bonded H atoms have C H subscript 3 groups attached. These C H subscript 3 groups appear in red. A circle is at the center of the ring. The third is labeled styrene. This molecule has a six carbon hydrocarbon ring in which five of the carbon atoms are each bonded to only one H atom. At the upper right of the ring, the carbon that does not have a bonded H atom has a red C H double bond C H subscript 2 group attached. A circle is at the center of the ring.

Toluene and xylene are important solvents and raw materials in the chemical industry. Styrene is used to produce the polymer polystyrene. The figure below shows the structural formulas for vanilla and naphthalene. Naphthalene is a chemical which is commonly used in mothballs. The vanilla molecule is extracted from vanilla beans.

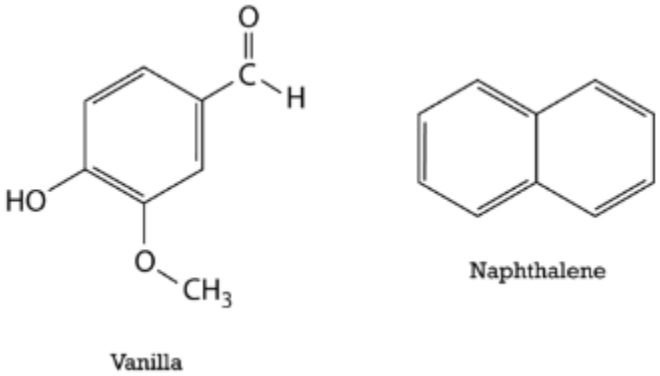


Figure 9.3.4 (left) vanilla molecule ; (right) naphthalene

Nomenclature of Aromatic Compounds

The simplest aromatic compounds are benzene rings with one substituent replacing one of the hydrogen atoms. If this substituent is an alkyl group, it is named first, followed in one word with "benzene". The molecule shown below is therefore called ethylbenzene.

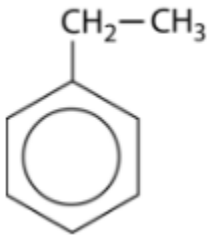


Figure 9.3.5 ethylbenzene

Substituents can be groups other than alkyl groups. If a chlorine atom were substituted for a hydrogen, the name becomes chlorobenzene. An $-NH_2$ group is called an amino group, so the corresponding molecule is called aminobenzene, often referred to as an aniline. An $-NO_2$ group is called a nitro group and so the third example below is nitrobenzene.

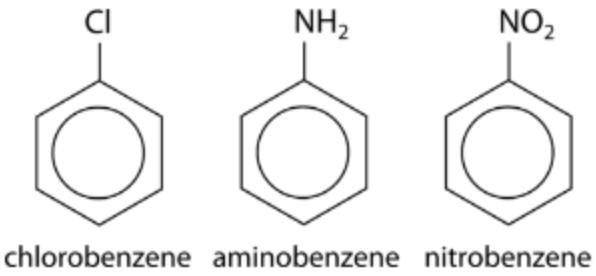


Figure 9.3.6 from left to right: chlorobenzene; aminobenzene; nitrobenzene

If more than one substituent is present, their location relative to each other can be indicated by numbering the positions on the benzene ring.

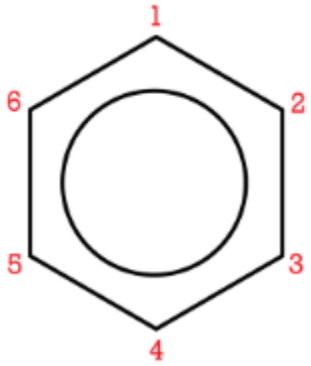


Figure 9.3.7 substituent locations relative to each other can be indicated by numbering the positions on the benzene ring

The number of the carbon location then precedes the name of the substituent in the overall name, with the numbers separated by a comma. As with branched alkanes, the system requires that the numbers be the lowest possible and that prefixes be used for more than one of the same substituent. If there are different substituents, the first in alphabetical order is given the lower number and listed first. The structures below are called 1,2-dimethylbenzene and 1-ethyl-4-methylbenzene.

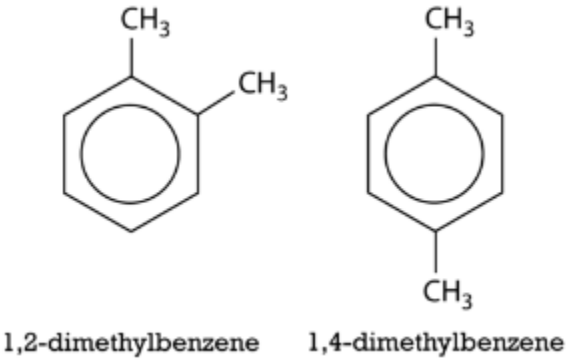


Figure 9.3.8 1,2-dimethylbenzene (left); 1-ethyl-4-methylbenzene (right)

An alternate system for naming di-substituted benzene rings uses three different prefixes: *ortho*, *meta*, and *para*. If two groups are in the **ortho** position, they are on adjacent carbon atoms. The **meta** positioning refers to being in a 1,3 arrangement. The **para** positioning refers to being in a 1,4 arrangement. Shown below are the three possibilities for dimethylbenzene, also called xylene.

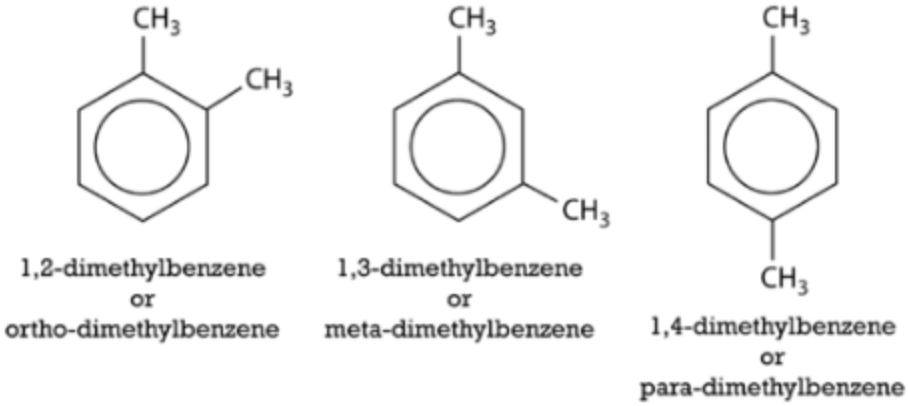


Figure 9.3.9 from left to right: ortho-dimethylbenzene; meta-dimethylbenzene ; para-dimethylbenzene

Lastly, a benzene ring missing one hydrogen atom $(-C_6H_5)$ can itself be considered the substituent on a longer chain of carbon atoms. That group is called a *phenyl* group and so the molecule below is called 2-phenylbutane.

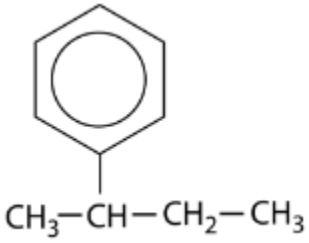


Figure 9.3.10 2-phenylbutane

Summary

- Aromatic hydrocarbons contain ring structures with delocalized π electron systems.
- Benzene is the parent compound of the large family of organic compounds known as aromatic compounds.
- Naming of aromatic compound i.e. benzene rings with different substituents is described.

Contributors and Attributions

-

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9.4: Halogenated Hydrocarbons- Many Uses, Some Hazards

Learning Objectives

- Identify haloalkanes (alkyl halides) and know their occurrence, uses, and properties.
- Learn how to name simple haloalkanes.

Haloalkanes also known as alkyl halides or halogenoalkanes, are a group of organic compounds in which one or more halogen atoms are substituted for one or more hydrogen atoms in a hydrocarbon. Haloalkanes are widely used commercially and, consequently, are known under many chemical and commercial names. Although these compounds were once widely used as dry cleaning solvents, coolants in refrigerators and air conditioners, and propellants in hairsprays and deodorants, increasing awareness of their toxicity and impact on the environment has led to a widespread decrease in applications for these materials.

The general formulas for organic molecules with functional groups use the letter R to stand for the rest of the molecule outside of the functional group. Because there are four possible halogen atoms (fluorine, chlorine, bromine, or iodine) that can act as the functional group, we use the general formula $\mathrm{R{-}X}$ to represent an alkyl halide.

Haloalkanes have higher boiling points than alkanes containing the same number of carbons. They are at best only slightly soluble in water but tend to dissolve in organic solvents.

Chloromethane (or methylchloride, CH_3Cl) was a widely used refrigerant, but its use has been discontinued due to its toxicity and flammability. Methyl chloride was also once used for producing lead-based gasoline additives (tetramethyllead).

The most important use of chloromethane today is as a chemical intermediate in the production of silicone polymers. Smaller quantities are used as a solvent in the manufacture of butyl rubber and in petroleum refining.

Large amounts of methyl chloride are produced naturally in the oceans by the action of sunlight on biomass and chlorine in sea foam. However, all methyl chloride that is used in industry is produced synthetically. Most methyl chloride is prepared by reacting methanol with hydrogen chloride, according to the chemical equation

$$CH_3OH + HCl \rightarrow CH_3Cl + H_2O$$

This can be carried out either by bubbling hydrogen chloride gas through boiling methanol with or without a zinc chloride catalyst, or by passing combined methanol and hydrogen chloride vapors over an alumina catalyst at 350 °C (662 °F).

A smaller amount of chloromethane is produced by heating a mixture of methane and chlorine to over 400 °C (752 °F). However, this method also results in more highly chlorinated compounds such as dichloromethane, chloroform, and carbon tetrachloride and is usually only used when these other products are also desired.

Short chain haloalkanes such as dichloromethane (CH_2Cl_2), trichloromethane (chloroform, $CHCl_3$) and tetrachloromethane (carbon tetrachloride, CCl4) are commonly used as hydrophobic solvents in chemistry. They were formerly very common in industry; however, their use has been greatly curtailed due to their toxicity and harmful environmental effects.

Some specific compounds are still used. Halothane (2-bromo-2-chloro-1,1,1-trifluoroethane) is still used in some situations as an inhalation anesthetic. The compound DDT is a very effective pesticide, but is only used when nothing else works because of its harmful effects on the environment.

Naming Alkyl Halides

IUPAC System: The rules for naming simple alkyl halides are listed below.

1. Name the parent compound by finding the longest continuous carbon atom chain that also contains the halogen. Add a prefix for the particular halogen atom. The prefixes for each of the four halogens are *fluoro-*, *chloro-*, *bromo-*, and *iodo-*. If more than one kind of halogen atom is present, put them in alphabetical order. If there is more than one of the same halogen on a given carbon atom, use the prefixes *di-*, *tri-*, or *tetra-* before the prefix for the halogen.
2. As with hydrocarbons, number the carbon chain in a way that makes the sum of halogen numbers as low as possible. If different halogens are in equivalent positions, give the lower number to the one that comes first in alphabetical order.
3. Add the numerical prefix into the name before the halogen prefix.
4. Separate numbers with commas and separate numbers from names or prefixes with a hyphen. There are no spaces in the name.

Listed below are some examples of names and structural formulas of a few alkyl halides.

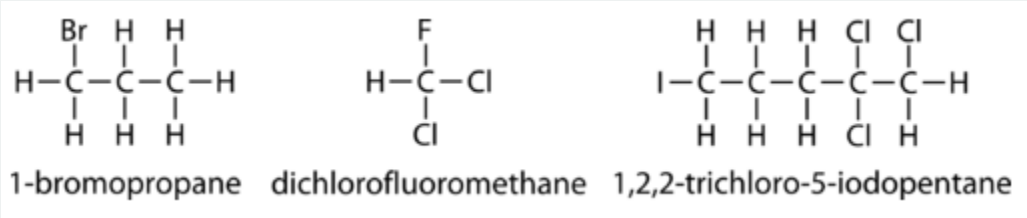


Figure 9.4.1 from left to right: 1-bromopropane; dichlorofluoromethane; 1,2,2-trichloro-5-iodpentane

Note that for the structure based on methane, no number needs to be used since there is only one carbon atom. In the third example, the *chloro-* is listed first alphabetically and the chain is numbered so that the sum of the numbers is as low as possible.

Common Names: The *common names* of alkyl halides consist of two parts: the name of the alkyl group plus the stem of the name of the halogen, with the ending *-ide*.

Alkyl halides with simple alkyl groups (one to four carbon atoms) are often called by common names. Those with a larger number of carbon atoms are usually given IUPAC names.

Example 9.4.1

Give the common and IUPAC names for each compound.

a. $CH_3CH_2CH_2Br$
b. $(CH_3)_2CHCl$

Solution

a. The alkyl group ($CH_3CH_2CH_2–$) is a propyl group, and the halogen is bromine (Br). The common name is therefore propyl bromide. For the IUPAC name, the prefix for bromine (bromo) is combined with the name for a three-carbon chain (propane), preceded by a number identifying the carbon atom to which the Br atom is attached, so the IUPAC name is 1-bromopropane.
b. The alkyl group [$(CH_3)_2CH–$] has three carbon atoms, with a chlorine (Cl) atom attached to the middle carbon atom. The alkyl group is therefore isopropyl, and the common name of the compound is isopropyl chloride. For the IUPAC name, the Cl atom (prefix *chloro-*) attached to the middle (second) carbon atom of a propane chain results in 2-chloropropane.

Exercise 9.4.1

Give common and IUPAC names for each compound.

a. CH_3CH_2I

b. $CH_3CH_2CH_2CH_2F$

Answers

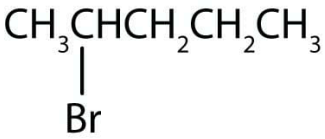
a. 1-iodoethane, ethyl iodide

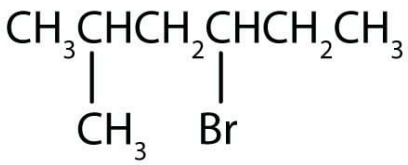
b. 1-fluorobutane, butyl fluoride

Example 9.4.2

Give the IUPAC name for each compound.

1.





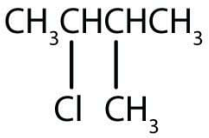
Solution

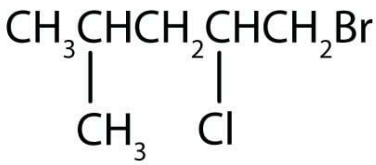
1. The parent alkane has five carbon atoms in the longest continuous chain; it is pentane. A bromo (Br) group is attached to the second carbon atom of the chain. The IUPAC name is 2-bromopentane.
2. The parent alkane is hexane. Methyl (CH_3) and bromo (Br) groups are attached to the second and fourth carbon atoms, respectively. Listing the substituents in alphabetical order gives the name 4-bromo-2-methylhexane.

Exercise 9.4.2

Give the IUPAC name for each compound.

a.





Answers

a. 2-chloro-3-methylbutane

b. 1-bromo-2-chloro-4-methylpentane

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 9.4.1, along with some of their uses.

Table 9.4.1: 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

Chlorofluorocarbons and Fluorocarbons

Chlorofluorocarbons (**CFCs**) and **hydrochlorofluorocarbons** (**HCFCs**) are fully or partly halogenated paraffin hydrocarbons that contain only carbon (C), hydrogen (H), chlorine (Cl), and fluorine (F), produced as volatile derivative of methane, ethane, and propane. They are also commonly known by the DuPont brand name **Freon**. The most common representative is dichlorodifluoromethane (R-12 or Freon-12). Many CFCs have been widely used as refrigerants, propellants (in aerosol applications), and solvents. Because CFCs contribute to ozone depletion in the upper atmosphere, the manufacture of such compounds has been phased out under the Montreal Protocol, and they are being replaced with other products such as **hydrofluorocarbons** (HFCs)

Chlorinated or fluorinated alkenes undergo polymerization. Important halogenated polymers include polyvinyl chloride (PVC), and polytetrafluoroethene (PTFE, or Teflon). Billions of kilograms of chlorodifluoromethane are produced annually as precursor to tetrafluoroethylene, the monomer that is converted into Teflon. The production of these materials releases substantial amounts of wastes. PVC and PTFE will be discussed in more detail in Chapter 10.

Summary

- **Haloalkanes** also known as alkyl halides or halogenoalkanes, are a group of organic compounds in which one or more halogen atoms are substituted for one or more hydrogen atoms in a hydrocarbon.
- These compounds are used as dry cleaning, industrial, and laboratory solvents, coolants in refrigerators and air conditioners, and propellants in hairsprays and deodorants
- The use of haloalkanes has been greatly curtailed due to their toxicity and harmful environmental effects.
- Naming of simple haloalkanes is described.

Contributors and Attributions

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9.5: The Functional Group

Learning Objectives

- Define *functional group*.
- Identify the functional group(s) present in organic compounds.

With over twenty million known organic compounds in existence, it would be very challenging to memorize chemical reactions for each one. Fortunately, molecules with similar functional groups tend to undergo similar reactions. A **functional group** is defined as an atom or group of atoms within a molecule that has similar chemical properties whenever it appears in various compounds. Even if other parts of the molecule are quite different, certain functional groups tend to react in certain ways.

We've already looked at alkanes, but they are generally unreactive. We primarily use alkanes as a source of energy when they are combusted. While the majority of functional groups involve atoms other than carbon and hydrogen, we will also look at some that include only carbon and hydrogen. Some of the most common functional groups are presented in the following sections.

Organic molecules vary greatly in size and when focusing on functional groups, we want to direct our attention to the atoms involved in the functional group. As a result, the abbreviation **R** is used in some examples. The letter **R** is used in molecular structures to represent the "**R**est of the molecule". It consists of a group of carbon and hydrogen atoms of any size. It is used as an abbreviation since a group of carbon and hydrogen atoms does not affect the functionality of the compound. In some molecules, you will see **R, R', or R''** which indicates that the R groups in the molecule can be different from one another. For example, R might be $-CH_2CH_3$ while R' is $-CH_2CH_2CH_2CH_3$.

The structure of capsaicin, the compound responsible for the heat in peppers, incorporates several functional groups, labeled in the figure below and explained throughout this section.

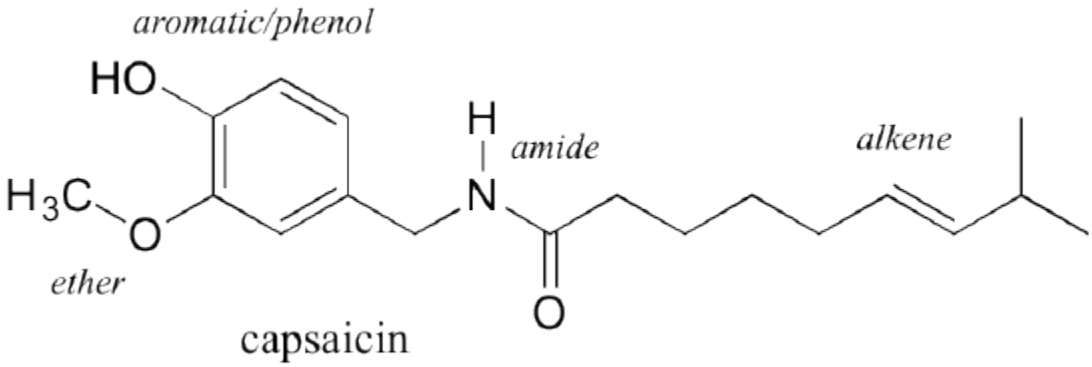


Figure 9.5.1 The structure of capsaicin

The table below summarizes the structures that will be discussed in this chapter:

Table 9.5.1 Selected Organic Functional Groups

Compound Name	Structure of Compound and Functional Group (red)	Example	
		Formula	Name
alkene	C═C	C_2H_4 	ethene
alkyne	C≡C	C_2H_2 	ethyne
alcohol	R—Ö—H	CH_3CH_2OH 	ethanol
ether	R—Ö—R′	$(C_2H_5)_2O$ 	diethyl ether
aldehyde	R—C(=O)—H	CH_3CHO 	ethanal
ketone	R—C(=O)—R′	$CH_3COCH_2CH_3$ 	methyl ethyl ketone
carboxylic acid	R—C(=O)—Ö—H	CH_3COOH 	acetic acid
ester	R—C(=O)—Ö—R′	$CH_3CO_2CH_2CH_3$ 	ethyl acetate
amine	R—N̈(H)—H R—N̈(R′)—H R—N̈(R′)—R″	$C_2H_5NH_2$ 	ethylamine
amine	R—N̈(H)—H R—N̈(R′)—H R—N̈(R′)—R″	$C_2H_5NH_2$	ethylamine
amide	R—C(=O)—N̈(H)—R′	CH_3CONH_2 	acetamide

Figure 9.5.1

Example 9.5.1

Identify the common functional groups for ATP.

3-1qu.png

Example 9.5.1

Solution

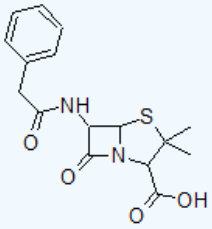
The common functional groups for ATP are **hydroxyl**, **ether** and **amine**. The other functional groups are covered in higher organic chemistry courses.

3.1.png

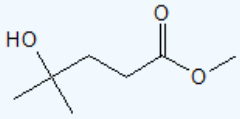
Example 9.5.1 ATP

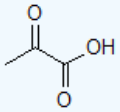
Exercise 9.5.1

Identify the functional groups (other than alkanes) in the following organic compounds. State whether alcohols and amines are primary, secondary, or tertiary.

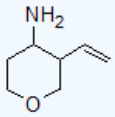


penicillin





pyruvic acid



Answer available at the end of this section.

Summary

- Functional groups consist of a single atom (such as Cl) or a group of atoms (such as CO_2H). It can determine the chemical reactivity of a molecule under a given set of conditions
- The major families of organic compounds are characterized by their functional groups.

Contributors and Attributions

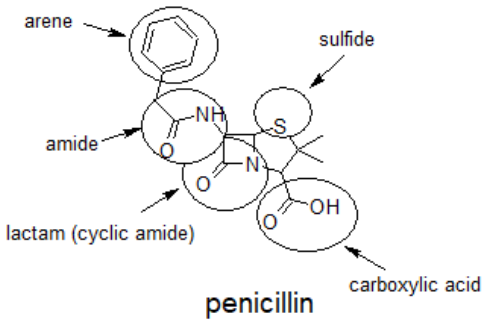
- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

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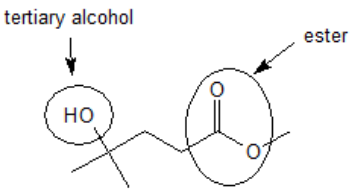
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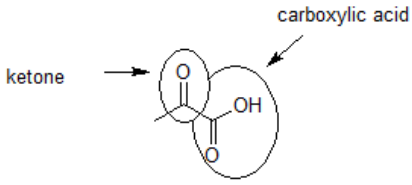
Answers

Exercise 9.5.1

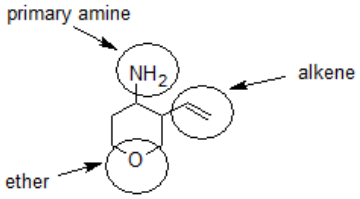


penicillin





pyruvic acid



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9.6: Alcohols, Phenols, and Ethers

Learning Objectives

- Describe the structure and properties of alcohols, ethers and phenols.
- Know the name and uses of simple alcohols, phenols and ethers.

An alcohol is an organic compound with a hydroxyl (OH) functional group on an aliphatic carbon atom. Because OH is the functional group of all alcohols, we often represent alcohols by the general formula ROH, where R is an alkyl group. Alcohols are common in nature. Most people are familiar with ethyl alcohol (ethanol), the active ingredient in alcoholic beverages, but this compound is only one of a family of organic compounds known as alcohols. The family also includes such familiar substances as cholesterol and the carbohydrates. Methanol (CH_3OH) and ethanol (CH_3CH_2OH) are the first two members of the homologous series of alcohols.

Nomenclature of Alcohols

Alcohols with one to four carbon atoms are frequently called by common names, in which the name of the alkyl group is followed by the word *alcohol*:

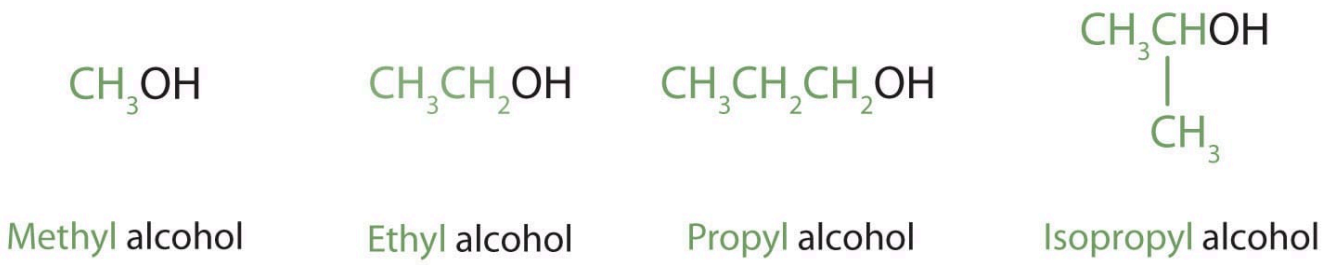
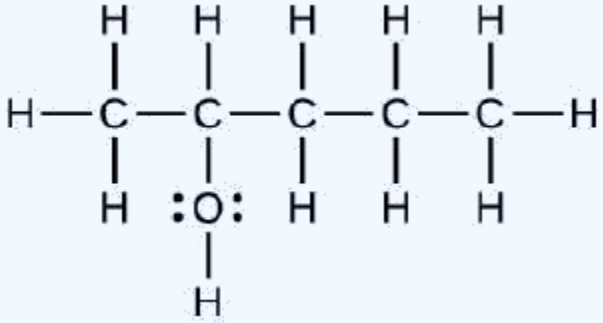


Figure 9.6.1:left to right: methyl alcohol; ethyl alcohol; propyl alcohol; isopropyl alcohol

According to the International Union of Pure and Applied Chemistry (IUPAC), the name of an alcohol comes from the hydrocarbon from which it was derived. The final *-e* in the name of the hydrocarbon is replaced by *-ol*, and the carbon atom to which the –OH group is bonded is indicated by a number placed before the name.

Example 9.6.1: Naming Alcohols

Consider the following example. How should it be named?

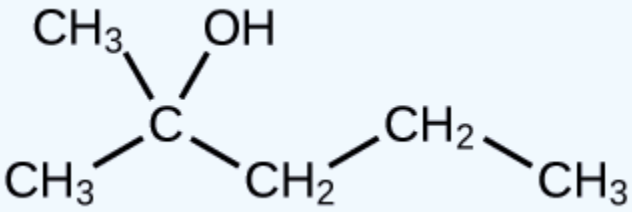


Solution

The carbon chain contains five carbon atoms. If the hydroxyl group was not present, we would have named this molecule pentane. To address the fact that the hydroxyl group is present, we change the ending of the name to *-ol*. In this case, since the –OH is attached to carbon 2 in the chain, we would name this molecule 2-pentanol.

Exercise 9.6.1

Name the following molecule:



Exercise 9.6.1: The structure shown has a C H subscript 3 group bonded up and to the right to a C atom. The C atom is bonded down and to the right to a C H subscript 2 group. The C H subscript 2 group is bonded up and to the right to a C H subscript 2 group. The C H subscript 2 group is bonded down and to the right to a C H subscript 3 group. The second C atom (from left to right) is bonded to a C H subscript 3 group and an O H group.

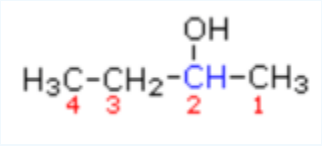
Answer available at the end of this section.

Note

The IUPAC adopted new nomenclature guidelines in 2013 that require this number to be placed as an “infix” rather than a prefix. For example, the new name for 2-propanol would be propan-2-ol. Widespread adoption of this new nomenclature will take some time, and students are encouraged to be familiar with both the old and new naming protocols.

Example 9.6.2: Naming Alcohols

Consider the following example. How should it be named according to the guidelines adopted in 2013?



Example 9.6.2:

Solution

The carbon chain contains four carbon atoms. If the hydroxyl group was not present, we would have named this molecule butane. To address the fact that the hydroxyl group is present, we change the ending of the name to *-ol*. In this case, since the –OH is attached to carbon 2 in the chain, we would name this molecule butan-2-ol.

Note

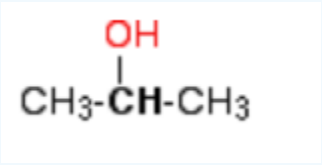
"Always place the OH on the lowest possible number for the chain."

In the previous example, if the carbon atoms were numbered from left to right then the OH would have been placed on the third carbon and the molecule would have been named butan-3-ol, but butan-2-ol is the more preferred name.

Exercise 9.6.2: Naming Alcohols

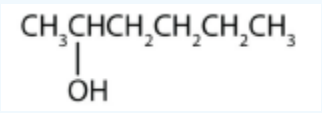
Name the following molecules according to the guidelines adopted in 2013?

a.



Exercise 9.6.2:

b.



Exercise 9.6.2:

Answer available at the end of this section.

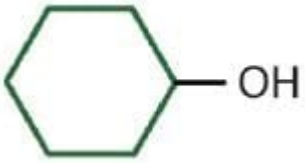
Table 9.6.1 names and classifies some of the simpler alcohols. Some of the common names reflect a compound's classification as secondary (*sec*-) or tertiary (*tert*-). These designations are not used in the IUPAC nomenclature system for alcohols. Note that there are four butyl alcohols in the table, corresponding to the four butyl groups: the butyl group ($CH_3CH_2CH_2CH_2$) discussed before, and three others:



Figure 9.6.2: from left to right: isobutyl alcohol press; sec-butyl alcohol;tert-butyl alcohol

Table 9.6.1: Classification and Nomenclature of Some Alcohols

Condensed Structural Formula	Common Name	IUPAC Name
CH_3OH	wood alcohol (methyl alcohol)	methanol
CH_3CH_2OH	grain alcohol (ethyl alcohol)	ethanol
$CH_3CH_2CH_2OH$	propyl alcohol	1-propanol
$(CH_3)_2CHOH$	rubbing alcohol (isopropyl alcohol)	2-propanol
$CH_3CH_2CH_2CH_2OH$	butyl alcohol	1-butanol
$CH_3CH_2CHOHCH_3$	*sec*-butyl alcohol	2-butanol
$(CH_3)_2CHCH_2OH$	isobutyl alcohol	2-methyl-1-propanol
$(CH_3)_3COH$	*tert*-butyl alcohol	2-methyl-2-propanol

Condensed Structural Formula	Common Name	IUPAC Name
	cyclohexyl alcohol	cyclohexanol

Methanol (Methyl Alcohol)

Methanol, also known as **methyl alcohol** among others, is a chemical with the formula CH_3OH (a methyl group linked to a hydroxyl group, often abbreviated MeOH). Methanol acquired the name **wood alcohol** because it was once produced chiefly by the destructive distillation of wood. Today, methanol is mainly produced industrially by hydrogenation of carbon monoxide.

$$CO(g) + 2H_2(g) \rightarrow CH_3OH(l)$$

Methanol is the simplest alcohol, consisting of a methyl group linked to a hydroxyl group. It is a light, volatile, colorless, flammable liquid with a distinctive odor similar to that of ethanol (drinking alcohol). At room temperature, it is a polar liquid. With more than 20 million tons produced annually, it is used as a fuel additive and as a precursor to other commodity chemicals, including formaldehyde, acetic acid, methyl tert-butyl ether, as well as a host of more specialized chemicals.

Ethanol (Ethyl Alcohol)

Ethanol (also called **ethyl alcohol**, **grain alcohol**, **drinking alcohol**, or simply **alcohol**) is a chemical compound, a simple alcohol with the chemical formula C_2H_6O. Its formula can be also written as $CH_3–CH_2–OH$ or C_2H_5OH (an ethyl group linked to a hydroxyl group), and is often abbreviated as **EtOH**. Ethanol is a volatile, flammable, colorless liquid with a slight characteristic odor. It is a psychoactive substance and is the principal type of alcohol found in alcoholic drinks.

Ethanol is naturally produced by the fermentation of sugars by yeasts or via petrochemical processes, and is most commonly consumed as a popular recreational drug. Ethanol is the alcohol produced by some species of yeast that is found in wine, beer, and distilled drinks. It has long been prepared by humans harnessing the metabolic efforts of yeasts in fermenting various sugars:

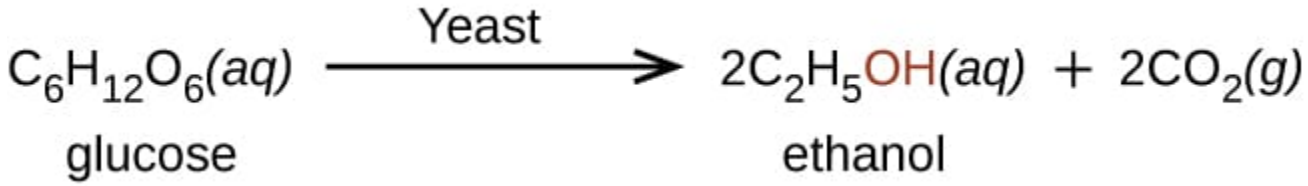


Figure 9.6.3: Fermentation of glucose to ethanol

Large quantities of ethanol (for industrial use) are synthesized from the addition reaction of water with ethylene using an acid as a catalyst:

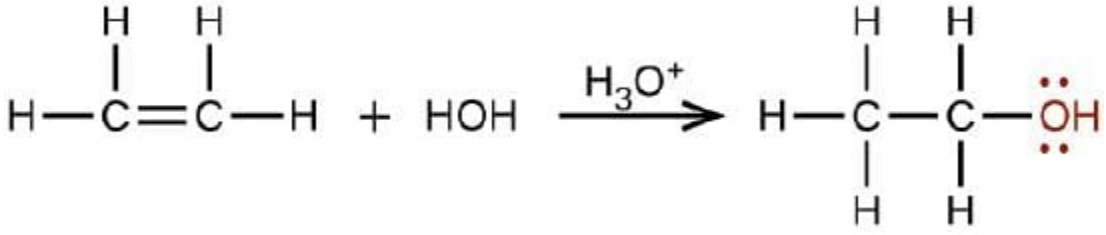


Figure 9.6.4 This reaction shows two carbons connected by a double bond, each with two bonded H atoms plus H O H arrow labeled “H subscript 3 O superscript plus” followed by two carbon atoms connected with a single bond with 5 bonded H atoms and an O H group shown in red at the right end of the molecule. The O of this group is shown with 2 pairs of electron dots.

Ethanol also has medical applications as an antiseptic and disinfectant. The compound is widely used as a chemical solvent, either for scientific chemical testing or in synthesis of other organic compounds, and is a vital substance used across many different kinds of manufacturing industries. Ethanol is also used as a clean-burning fuel source.

Toxicity of Alcohols

With respect to acute toxicity, simple alcohols have low acute toxicities. Doses of several milliliters are tolerated. For pentanols, hexanols, octanols and longer alcohols, LD50 (lethal dose, 50%) range from 2–5 g/kg (rats, oral). Methanol and ethanol are less acutely toxic. Methanol is however far more toxic than ethanol. All alcohols are mild skin irritants.

The metabolism of methanol (and ethylene glycol) is affected by the presence of ethanol, which has a higher affinity for liver alcohol dehydrogenase. In this way methanol will be excreted intact in urine.

The immediate effect of alcohol depends on the drinker's blood alcohol concentration (BAC). BAC can be different for each person depending on their age, sex, pre-existing health condition, even if they drink the same amount of alcohol.

Different BACs have different effects. Table 9.6.2 list the common effects of alcohol on the body depending on the BAC. However, tolerance varies considerably between individuals, as does individual response to a given dosage; the effects of alcohol differ widely between people. Hence in this context, BAC percentages are just estimates used for illustrative purposes.

Table 9.6.2 Blood Alcohol Levels and Effects Source: Wikipedia.

mg/dL	mM	Blood Alcohol Level % v/v	Effects
50	11	0.05%	Euphoria, talkativeness, relaxation
100	22	0.1%	Central nervous system depression, nausea, possible vomiting, impaired motor and sensory function, impaired cognition
>140	30	>0.14%	Decreased blood flow to brain
300	65	0.3%	Stupefaction, possible unconsciousness
400	87	0.4%	Possible death
500	109	>0.55%	Death

Rubbing alcohol refers to either isopropyl alcohol (propan-2-ol) or ethanol based liquids. Rubbing alcohol is undrinkable even if it is ethanol based, due to the bitterants added. Product labels for rubbing alcohol include a number of warnings about the chemical, including the flammability hazards and its intended use only as a topical antiseptic and not for internal wounds or consumption. It should be used in a well-ventilated area due to inhalation hazards. Poisoning can occur from ingestion, inhalation, absorption, or consumption of rubbing alcohol.

Multifunctional Alcohols

A **polyol** is an organic compound containing multiple hydroxyl groups. Examples of polyols discussed in this section include ethylene glycol, propylene glycol, and glycerol.

Alcohols containing two or more hydroxyl groups can be made. Examples include 1,2-ethanediol (ethylene glycol, used in antifreeze) and 1,2,3-propanetriol (glycerine, used as a solvent for cosmetics and medicines):

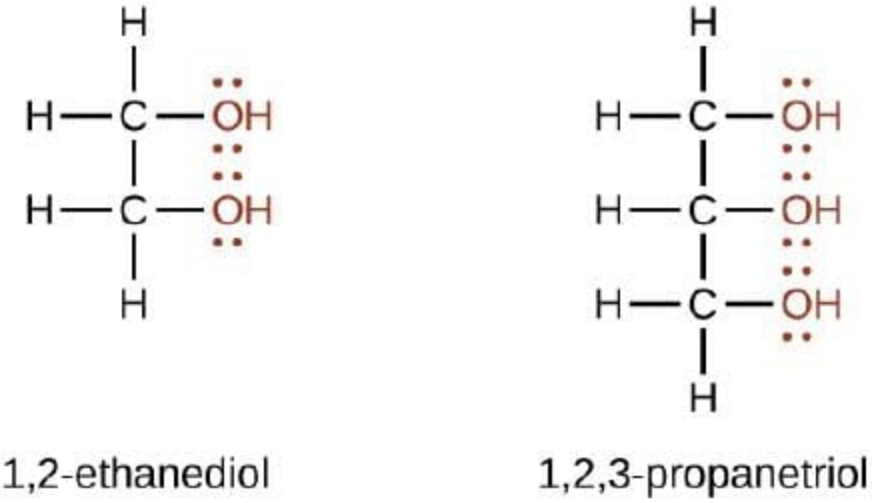


Figure 9.6.51,2-ethanediol; 1,2,3-propanetriol

Ethylene glycol (IUPAC name: ethane-1,2-diol) is an organic compound with the formula $(CH_2OH)_2$. It is mainly used for two purposes, as a raw material in the manufacture of polyester fibers and for antifreeze formulations. It is an odorless, colorless, sweet-tasting, viscous liquid. Ethylene glycol is toxic. Household pets are especially susceptible to ethylene glycol poisoning from vehicle antifreeze leaks.

undefinedundefined

Figure 9.6.6 from left to right:Ethylene glycol line model; Ethylene glycol ball and stick model*Fluorescent green-dyed antifreeze is visible in the radiator header tank when car radiator cap is removed.*

Propylene glycol (IUPAC name: **propane-1,2-diol**) is a organic compound with the chemical formula $CH_3CH(OH)CH_2OH$. It is a viscous, colorless liquid which is nearly odorless but possesses a faintly sweet taste. Containing two alcohol groups, it is classed as a diol. It is miscible with a broad range of solvents, including water, acetone, and chloroform. In general, glycols are non-irritating, have very low volatility and very low toxicity.

Figure 9.6.7 *A bottle of flavored "e-liquid" for "vaping" shows propylene glycol as the main ingredient. Source: Wikipedia*

undefined

Figure 9.6.8 **Propylene glycol**

Forty-five percent of propylene glycol produced is used as chemical feedstock for the production of unsaturated polyester resins. Propylene glycol is also used in various edible items such as coffee-based drinks, liquid sweeteners, ice cream, whipped dairy products and soda.Vaporizers used for delivery of pharmaceuticals or personal-care products often include propylene glycol among the ingredients. In alcohol-based hand sanitizers, it is used as a humectant to prevent the skin from drying. Propylene glycol is used as a solvent in many pharmaceuticals, including oral, injectable and topical formulations, such as for diazepam and lorazepam which are insoluble in water. Certain formulations of artificial tears, such as Systane, use proplyene glycol as an ingredient.Propylene glycol is frequently used as a substitute for ethylene glycol in low toxicity, environmentally friendly automotive antifreeze. It is also used to winterize the plumbing systems in vacant structures.

Glycerol (/ˈglɪsərɒl/; also called **glycerine** or **glycerin**; see spelling differences) is a simple polyol compound. It is a colorless, odorless, viscous liquid that is sweet-tasting and non-toxic. The glycerol backbone is found in many lipids which are known as glycerides. It is widely used in the food industry as a sweetener and humectant in pharmaceutical formulations. Glycerol has three hydroxyl groups that are responsible for its solubility in water and its hygroscopic nature.

Figure 9.6.9 Glycerol ball and stick model (top) line model (bottom)

In food and beverages, glycerol serves as a humectant, solvent, and sweetener, and may help preserve foods. It is also used as filler in commercially prepared low-fat foods (e.g., cookies), and as a thickening agent in liqueurs. Glycerol and water are used to preserve certain types of plant leaves. As a sugar substitute, it has approximately 27 kilocalories per teaspoon (sugar has 20) and is 60% as sweet as sucrose. It does not feed the bacteria that form plaques and cause dental cavities.[*citation needed*] As a food

additive, glycerol is labeled as E number E422. It is added to icing (frosting) to prevent it from setting too hard.

Glycerol is used in medical, pharmaceutical and personal care preparations, often as a means of improving smoothness, providing lubrication, and as a humectant. Ichthyosis and xerosis have been relieved by the topical use glycerin. It is found in allergen immunotherapies, cough syrups, elixirs and expectorants, toothpaste, mouthwashes, skin care products, shaving cream, hair care products, soaps, and water-based personal lubricants (Figure \(\PageIndex{10}\)). In solid dosage forms like tablets, glycerol is used as a tablet holding agent.

Table \({9{.}6{.}\eatSpaces{2} \endSpaces}\) Blood Alcohol Levels and Effects Source: Wikipedia.

Figure 9.6.10 *Personal lubricants commonly contain glycerol.*

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.

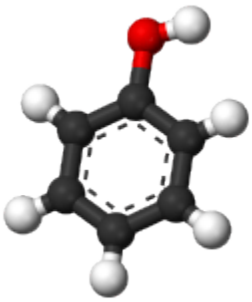


Figure 9.6.11 *Structure of phenol*



Figure 9.6.12
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.



Figure 9.6.13 *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.

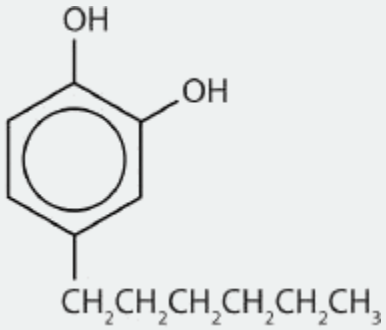


Figure 9.6.14 The compound 4-hexylresorcinol is mild enough to be used as the active ingredient in antiseptic preparations for use on the skin.

In addition to acting as an antiseptic, phenol is also a useful precursor in many chemical syntheses to produce pharmaceuticals, food preservatives, polymers, resins and adhesives. Phenolics are also present in a number of biological systems and natural products such as neurotransmitters, flavouring agents, and vitamins to name a few.

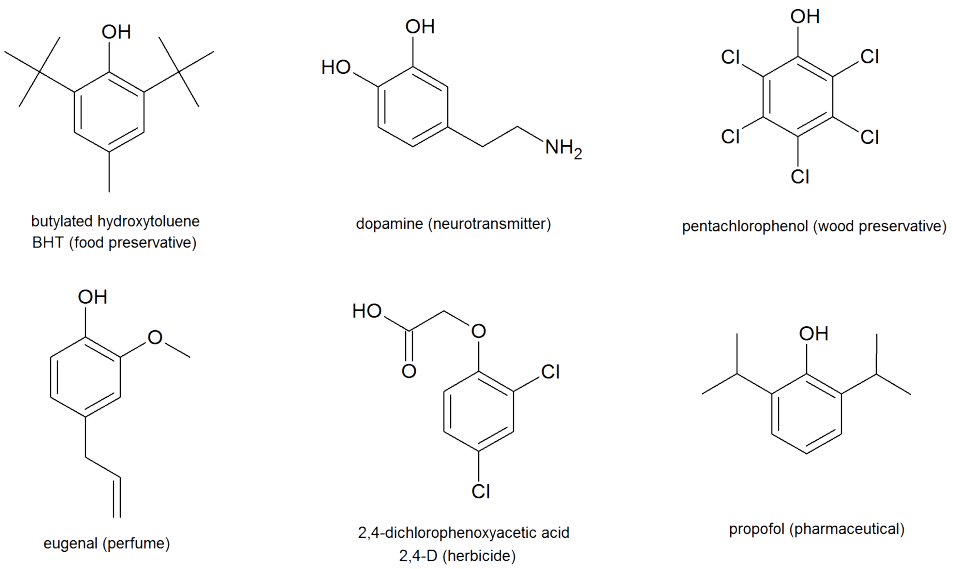


Figure 9.6.15 Top from left to right: line models of BHT; dopamine; pentachlorophenol; Bottom: eugenal; 2,4-dichlorophenoxyacetic acid; propofol

Ethers

Ethers are compounds that contain the functional group –O–. Ethers do not have a designated suffix like the other types of molecules we have named so far. In the IUPAC system, the oxygen atom and the smaller carbon branch are named as an alkoxy substituent and the remainder of the molecule as the base chain, as in alkanes. As shown in the following compound, the red symbols represent the smaller alkyl group and the oxygen atom, which would be named "methoxy." The larger carbon branch would be ethane, making the molecule methoxyethane. Many ethers as shown below, are referred to with common names instead of the IUPAC system names. For common names, the two branches connected to the oxygen atom are named separately and followed by "ether."

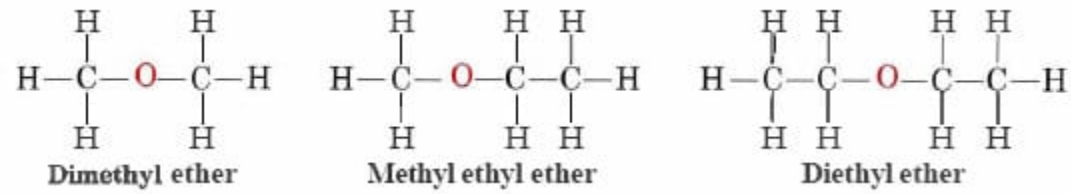


Figure 9.6.16 from left to right: Dimethyl ether; methyl ethyl ether; Diethyl ether

In the general formula for ethers, R—**O**—R, the hydrocarbon groups (R) may be the same or different.

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 9.6.3).

Table 9.6.3 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

Condensed Structural Formula	Name	Molar Mass	Boiling Point (°C)	Intermolecular Hydrogen Bonding in Pure Liquid?
$CH_3CH_2CH_2CH_2CH_3$	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).

Diethyl ether, the most widely used compound of this class, is a colorless, volatile liquid that is highly flammable. It was first used in 1846 as an anesthetic, but better anesthetics have now largely taken its place. Diethyl ether and other ethers are presently used primarily as solvents for gums, fats, waxes, and resins. *Tertiary*-butyl methyl ether, $C_4H_9OCH_3$ (abbreviated MTBE—italicized portions of names are not counted when ranking the groups alphabetically—so butyl comes before methyl in the common name), is used as an additive for gasoline. MTBE belongs to a group of chemicals known as oxygenates due to their capacity to increase the oxygen content of gasoline.

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.



Figure 9.6.17 *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.

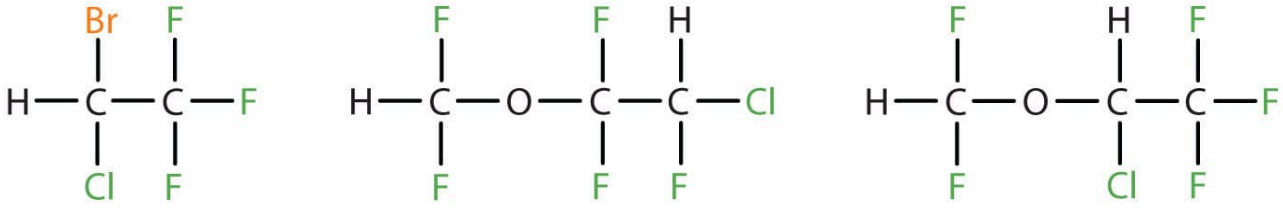


Figure 9.6.18 from left to right: halothane, enflurane, isoflurane. *These three modern, inhalant, halogen-containing, anesthetic compounds are less flammable than diethyl ether.*

A list of important ethers and their uses are given in Table 9.6.4

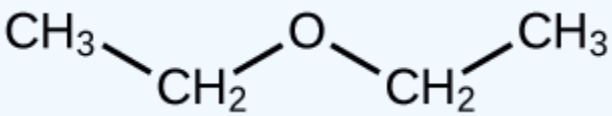
Table 9.6.4 Important Ethers and Their Uses

Ethylene oxide	**Ethylene oxide**	**Also the simplest epoxide. Most ethylene oxide is used for synthesis of ethylene glycols (antifreeze), including diethylene glycol and triethylene glycol, that accounts for up to 75% of global consumption.**
	Dimethyl ether	An aerosol spray propellant. A potential renewable alternative fuel for diesel engines with a cetane rating as high as 56–57.
	Diethyl ether	A common low boiling solvent (b.p. 34.6 °C) and an early anaesthetic. Used as starting fluid for diesel engines. Also used as a refrigerant and in the manufacture of smokeless gunpowder, along with use in perfumery.
	Dimethoxyethane(DME)	A water miscible solvent often found in lithium batteries (b.p. 85 °C):
	Dioxane	A cyclic ether and high-boiling solvent (b.p. 101.1 °C).

Example 9.6.2: classifying functional groups

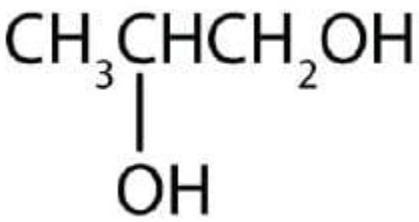
Identify the following compounds as alcohol, phenol or ether.

a.



Example 9.6.2:

b.



Example 9.6.2:

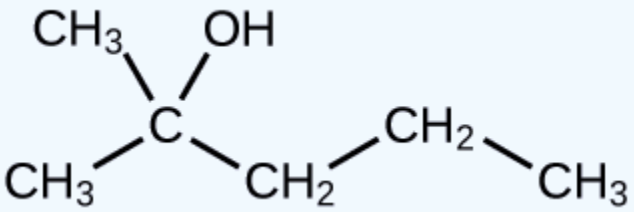
Solution

a. The compound has the general formula R—**O**—R, so it is an ether. b. The compound has two hydroxyl (–OH) groups, so it is an alcophol.

Exercise 9.6.2

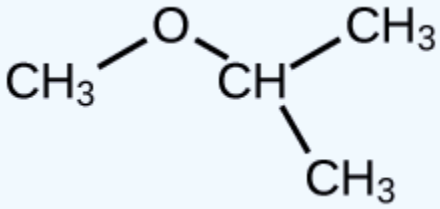
Identify the following compounds as alcohol, phenol or ether.

a.



Exercise 9.6.2: The structure shown has a C H subscript 3 group bonded up and to the right to a C atom. The C atom is bonded down and to the right to a C H subscript 2 group. The C H subscript 2 group is bonded up and to the right to a C H subscript 2 group. The C H subscript 2 group is bonded down and to the right to a C H subscript 3 group. The second C atom (from left to right) is bonded to a C H subscript 3 group and an O H group.

b.



Exercise 9.6.2: A molecular structure shows a C H subscript 3 group bonded up and to the right to an O atom. The O atom is bonded down and to the right to a C H group. The C H group is bonded up and to the right to a C H subscript 3 group. The C H group is also bonded down and to the right to another C H subscript 3 group.

Answer available at the end of this section.

Summary

- The –OH group is the functional group of an alcohol. Various alcohols have a wide range of applications in the medical field as well as in the transportation, food, cosmetic industries.
- The name of an alcohol comes from the hydrocarbon from which it was derived.
- The –R–O–R– group is the functional group of an ether. Diethyl ether and other ethers are presently used primarily as solvents for gums, fats, waxes, and resins. Ethylene oxide in particular is used in the manufacture of ethylene glycol (antifreeze).
- Phenols are compounds in which an OH group is attached directly to an aromatic ring. Many phenols are used as antiseptics.

Contributors and Attributions

- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

- TextMap: The Basics of GOB Chemistry (Ball et al.)

- Marisa Alviar-Agnew (Sacramento City College)

- Wikipedia

Answers

Exercise 9.6.1

2-methyl-2-pentanol

Exercise 9.6.2**: Naming Alcohols**

a. propan-2-ol

b. hexan-2-ol

Exercise 9.6.2

a. alcohol b. ether

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9.7: Aldehydes and Ketones

Learning Objectives

- Describe the structure and properties of aldehydes and ketones.
- Name common aldehydes and ketones.

Aldehydes and ketones are widespread in nature and are often combined with other functional groups. Examples of naturally occurring molecules which contain a aldehyde or ketone functional group are shown in the following two figures. The compounds in Figure $9.7.1$ are found chiefly in plants or microorganisms and those in Figure $9.7.2$ have animal origins. Aldehydes and ketones are known for their sweet and sometimes pungent odors. The odor from vanilla extract comes from the molecule vanillin. Likewise, benzaldehyde provides a strong scent of almonds and is this author's favorite chemical smell. Because of their pleasant fragrances aldehyde and ketone containing molecules are often found in perfumes. However, not all of the fragrances are pleasing. In particular, 2-Heptanone provides part of the sharp scent from blue cheese and (R)-Muscone is part of the musky smell from the Himalayan musk deer. Lastly, ketones show up in many important hormones such as progesterone (a female sex hormone) and testosterone (a male sex hormone). Notice how subtle differences in structure can cause drastic changes in biological activity. The ketone functionality also shows up in the anti-inflammatory steroid, Cortisone.

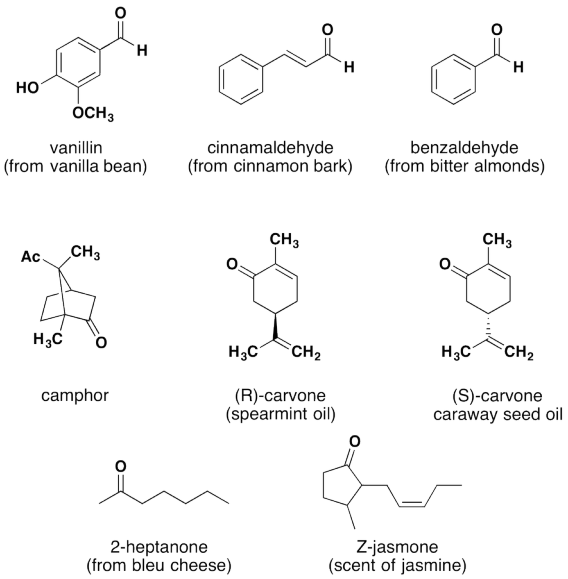


Figure $9.7.1$ Aldehyde and ketone containing molecules isolated from plant sources.

Figure $9.7.1$

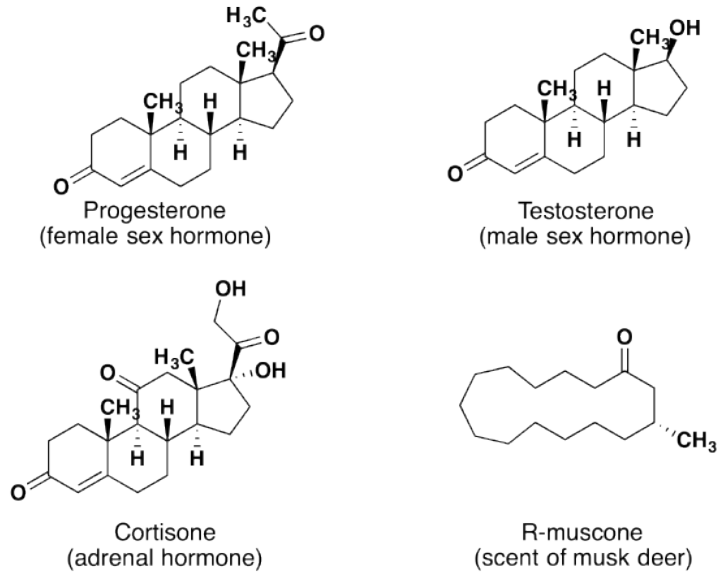


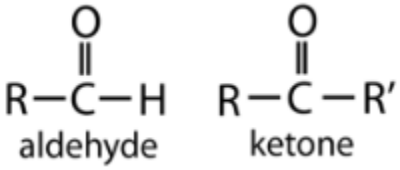
Figure 9.7.2 Aldehyde and ketone containing molecules isolated from animal sources.

Figure 9.7.1

Aldehydes and **ketones** are two related categories of organic compounds that both contain the **carbonyl group**, shown below



The difference between aldehydes and ketones is the placement of the carbonyl group within the molecule. An **aldehyde** is an organic compound in which the carbonyl group is attached to a carbon atom at the end of a carbon chain. A **ketone** is an organic compound in which the carbonyl group is attached to a carbon atom within the carbon chain. The general formulas for each are shown below.



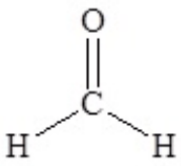
For aldehydes, the R group may be a hydrogen atom or any length carbon chain.

Naming Simple Aldehydes and Keones

Aldehydes are named by finding the longest continuous chain that contains the carbonyl group. Change the *-e* at the end of the name of the alkane to *-al*.

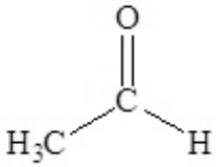
For the common name of aldehydes start with the common parent chain name and add the suffix ***-aldehyde***.

The IUPAC system names are given on top while the common name is given on the bottom in parentheses.



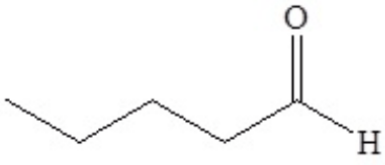
Methanal

(Formaldehyde)



Ethanal

(Acetaldehyde)



Pentanal

(Valeraldehyde)

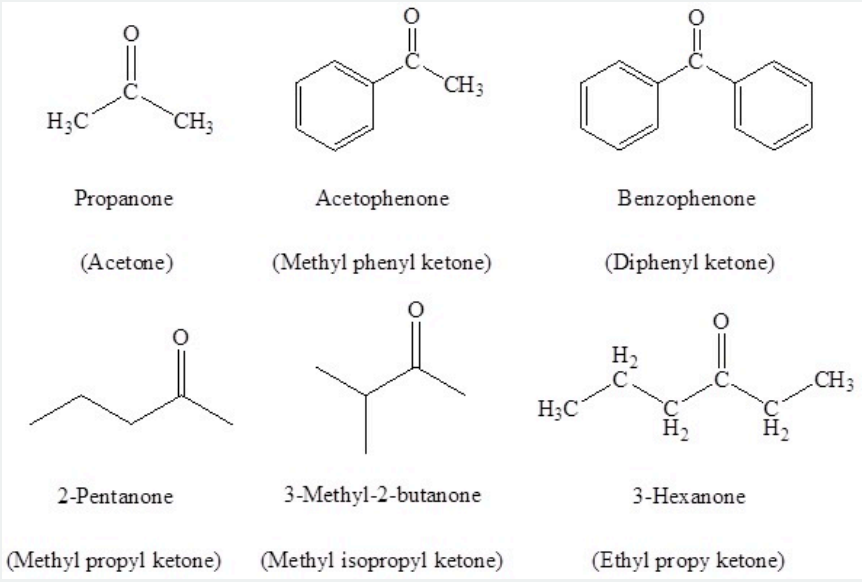
For ketones, R and R' must be carbon chains, of either the same or different lengths. The steps for naming ketones, followed by two examples, are shown below.

1. Name the parent compound by finding the longest continuous chain that contains the carbonyl group. Change the *-e* at the end of the name of the alkane to *-one*.
2. Number the carbon atoms in the chain in a way that the carbonyl group has the lowest possible number.
3. Add the numerical prefix into the name before the name of the ketone.
4. Use a hyphen between the number and the name of the ketone.

The common name for ketones are simply the **substituent groups listed alphabetically + *ketone*.**

Some common ketones are known by their generic names. Such as the fact that *propanone* is commonly referred to as *acetone*.

The IUPAC system names are given on top while the common name is given on the bottom in parentheses.



Top from left to right:propanone (acetone); acetophenone (methyl phenol ketone); benzophenone (diphenyl ketone; Bottom from left to right: 2 pentanone (methyl propyl ketone); 3 methyl 2 butanone (methyl isopropyl ketone); 3 hexanone (ethyl propyl ketone)

Properties of Aldehydes and Ketones

Aldehydes and ketones can work weak hydrogen bonds with water through the carbonyl oxygen atom. The lower members of both series (3 carbons or fewer) are soluble in water in all proportions. As the length of the carbon chain increases, water solubility decreases. Similar to ethers, neither aldehydes nor ketones can hydrogen bond with themselves. As a result, their boiling points are generally lower than those of alcohols. Unlike alkanes however, aldehydes and ketones are polar molecules due to the more electronegative oxygen atom. The dipole-dipole interactions are stronger than the dispersion forces present in alkanes. The

boiling points of aldehydes and ketones are intermediate between those of alkanes and alcohols. For example, the boiling point of ethane is $-89^{\circ}\mathrm{C}$, ethanal is $20^{\circ}\mathrm{C}$, and ethanol is $78^{\circ}\mathrm{C}$.

Methanal, commonly known as formaldehyde, was once commonly used as a biological preservative for dead animals. In recent years formaldehyde has been shown to be a carcinogen and so has been replaced for the purpose by safer alternatives. Aldehydes are currently used in the production of resins and plastics. The simplest ketone, propanone, is commonly called acetone. Acetone is a common organic solvent that was one used in most nail polish removers, but has largely been replaced by other solvents.

Some Common Aldehydes

Formaldehyde, an aldehyde with the formula HCHO, is a colorless gas with a pungent and irritating odor. It is sold in an aqueous solution called formalin, which contains about 37% formaldehyde by weight. Formaldehyde causes coagulation of proteins, so it kills bacteria (and any other living organism) and stops many of the biological processes that cause tissue to decay. Thus, formaldehyde is used for preserving tissue specimens and embalming bodies. It is also used to sterilize soil or other materials. Formaldehyde is used in the manufacture of Bakelite, a hard plastic having high chemical and electrical resistance.

Formaldehyde is produced industrially by the catalytic oxidation of methanol according to the chemical equation:

$$2\ CH_3OH + O_2 \rightarrow 2\ CH_2O + 2\ H_2O$$

Acetaldehyde (systematic name **ethanal**) is an organic chemical compound with the formula CH_3CHO, sometimes abbreviated by chemists as MeCHO (Me = methyl). It is one of the most important aldehydes, occurring widely in nature and being produced on a large scale in industry. Acetaldehyde occurs naturally in coffee, bread, and ripe fruit, and is produced by plants.

In 2003, global production was about 1 million tonnes. Before 1962, ethanol and acetylene were the major sources of acetaldehyde. Since then, ethylene is the dominant feedstock.

The main method of production is the oxidation of ethylene by the Wacker process, which involves oxidation of ethylene using a homogeneous palladium/copper system:

$$2\ CH_2{=}CH_2 + O_2 \rightarrow 2\ CH_3CHO$$

Propionaldehyde or **propanal** is the organic compound with the formula CH_3CH_2CHO. It is a saturated 3-carbon aldehyde and is a structural isomer of acetone. It is a colorless liquid with a slightly irritating, fruity odor. **Butyraldehyde**, also known as **butanal**, is an organic compound with the formula $CH_3(CH_2)_2CHO$. This compound is the aldehyde derivative of butane. It is a colourless flammable liquid with an unpleasant smell. It is miscible with most organic solvents. A major use of butyraldehyde is in the production of bis(2-ethylhexyl) phthalate, a major plasticizer. **Benzaldehyde** (C_6H_5CHO) is an organic compound consisting of a benzene ring with a formyl substituent. It is the simplest aromatic aldehyde and one of the most industrially useful.It is a colorless liquid with a characteristic almond-like odor. The primary component of bitter almond oil, benzaldehyde can be extracted from a number of other natural sources. Synthetic benzaldehyde is the flavoring agent in imitation almond extract, which is used to flavor cakes and other baked goods

Traces of many aldehydes are found in essential oils and often contribute to their favorable odors, e.g. cinnamaldehyde, cilantro, and vanillin.

Some Common Ketones

In terms of scale, the most important ketones are acetone, methylethyl ketone, and cyclohexanone. They are also common in biochemistry, but less so than in organic chemistry in general.

Dimethyl ketone, CH_3COCH_3, commonly called acetone, is the simplest ketone. **Acetone** is a colorless liquid. Among its many uses are as a solvent for lacquer (including fingernail polish), cellulose acetate, cellulose nitrate, acetylene, plastics, and varnishes; as a paint and varnish remover; and as a solvent in the manufacture of pharmaceuticals and chemicals.

Acetone is produced directly or indirectly from propylene. Approximately 83% of acetone is produced via the cumene process; as a result, acetone production is tied to phenol production. In the cumene process, benzene is alkylated with propylene to produce cumene, which is oxidized by air to produce phenol and acetone:

Overview of the cumene process

Other processes involve the direct oxidation of propylene (Wacker-Hoechst process), or the hydration of propylene to give 2-propanol, which is oxidized to acetone.

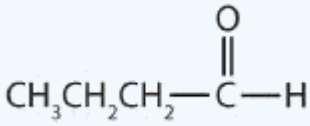
Butanone, also known as **methyl ethyl ketone** (**MEK**), is an organic compound with the formula $CH_3C(O)CH_2CH_3$. This colorless liquid ketone has a sharp, sweet odor reminiscent of butterscotch and acetone. It is produced industrially on a large scale, and also occurs in trace amounts in nature. It is soluble in water and is commonly used as an industrial solvent. Butanone is an effective and common solvent and is used in processes involving gums, resins, cellulose acetate and nitrocellulose coatings and in vinyl films. For this reason it finds use in the manufacture of plastics, textiles, in the production of paraffin wax, and in household products such as lacquer, varnishes, paint remover, a denaturing agent for denatured alcohol, glues, and as a cleaning agent. It has similar solvent properties to acetone but boils at a higher temperature and has a significantly slower evaporation rate.

Cyclohexanone is the organic compound with the formula $(CH_2)_5CO$. The molecule consists of six-carbon cyclic molecule with a ketonefunctional group. This colorless oil has an odor reminiscent of that of acetone. Over time, samples of cyclohexanone assume a yellow color. Cyclohexanone is slightly soluble in water and miscible with common organic solvents. Billions of kilograms are produced annually, mainly as a precursor to nylon.

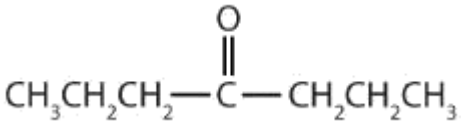
Example 9.7.1

Classify each compound as an aldehyde or a ketone.

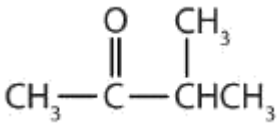
a.



b.



c.



Solution

a. This compound has the carbonyl group on an end carbon atom, so it is an aldehyde.

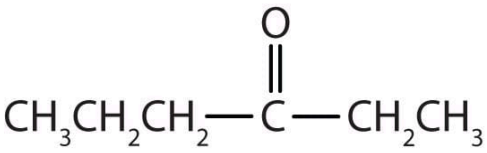
b. This compound has the carbonyl group on an interior carbon atom, so it is a ketone.

c. This compound has the carbonyl group between two alkyl groups, so it is a ketone.

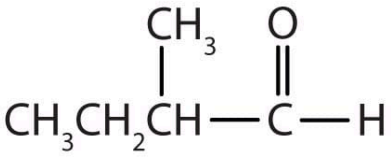
Exercise 9.7.1

Classify each compound as an aldehyde or a ketone.

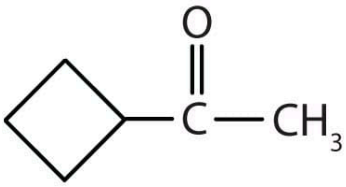
a.



b.



c.



Answer

a. ketone b. aldehyde c. ketone

Summary

- An aldehyde is an organic compound in which the carbonyl group is attached to a carbon atom at the end of a carbon chain.
- A ketone is an organic compound in which the carbonyl group is attached to a carbon atom within the carbon chain.The common names of aldehydes are taken from the names of the corresponding carboxylic acids: formaldehyde, acetaldehyde, and so on. The common names of ketones, like those of ethers, consist of the names of the groups attached to the carbonyl group, followed by the word *ketone*.
- Stem names of aldehydes and ketones are derived from those of the parent alkanes, using an *-al* ending for an aldehydes and an *-one* ending for a ketone.

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- Marisa Alviar-Agnew (Sacramento City College)

- Libretext: The Basics of GOB Chemistry (Ball et al.)
- Prof. Steven Farmer (Sonoma State University(opens in new window))

  William Reusch, Professor Emeritus (Michigan State U.(opens in new window)), Virtual Textbook of Organic Chemistry(opens in new window)

- Wikipedia

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9.8: Carboxylic Acids and Esters

Learning Objectives

- Describe the structure and properties of carboxylic acids and esters.
- Name common carboxylic acids and esters.

The odor of vinegar is caused by the presence of acetic acid, a carboxylic acid, in the vinegar. The odor of ripe bananas and many other fruits is due to the presence of esters, compounds that can be prepared by the reaction of a carboxylic acid with an alcohol. Because esters do not have hydrogen bonds between molecules, they have lower vapor pressures than the alcohols and carboxylic acids from which they are derived.

Both carboxylic acids and esters contain a carbonyl group with a second oxygen atom bonded to the carbon atom in the carbonyl group by a single bond. In a carboxylic acid, the second oxygen atom also bonds to a hydrogen atom. In an ester, the second oxygen atom bonds to another carbon atom. The names for carboxylic acids and esters include prefixes that denote the lengths of the carbon chains in the molecules and are derived following nomenclature rules similar to those for inorganic acids and salts (see these examples):

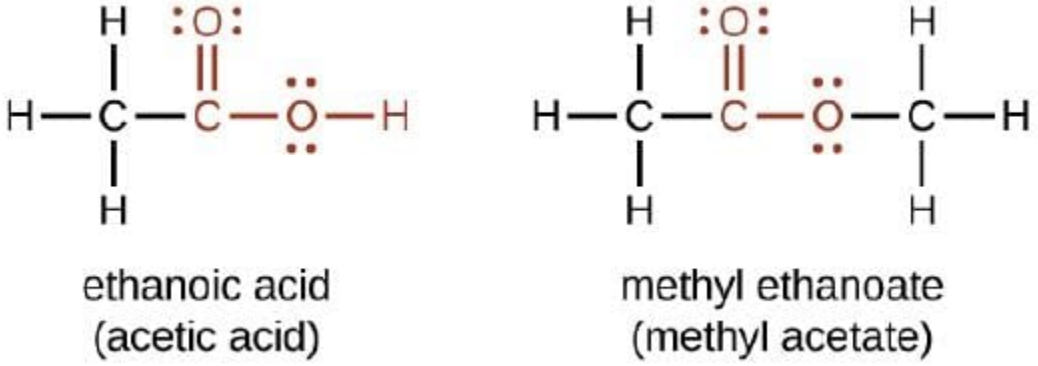


Figure 9.8.1 Two structures are shown. The first structure is labeled, “ethanoic acid,” and, “acetic acid.” This structure indicates a C atom to which H atoms are bonded above, below and to the left. To the right of this in red is a bonded group comprised of a C atom to which an O atom is double bonded above. To the right of the red C atom, an O atom is bonded which has an H atom bonded to its right. Both O atoms have two sets of electron dots. The second structure is labeled, “methyl ethanoate,” and, “methyl acetate.” This structure indicates a C atom to which H atoms are bonded above, below and to the left. In red, bonded to the right is a C atom with a double bonded O atom above and a single bonded O atom to the right. To the right of this last O atom in black is another C atom to which H atoms are bonded above, below and to the right. Both O atoms have two pairs of electron dots.

The functional groups for an acid and for an ester are shown in red in these formulas.

Carboxylic Acids

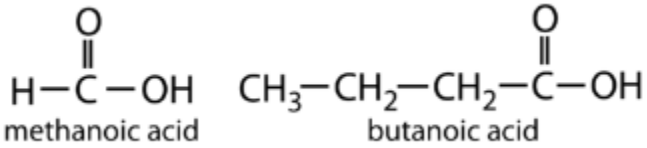
Carboxylic acids occur widely in nature, often combined with alcohols or other functional groups, as in fats, oils, and waxes. They are components of many foods, medicines, and household products (Figure 9.8.1). Not surprisingly, many of them are best known by common names based on Latin and Greek words that describe their source.



Figure 9.8.2 Carboxylic acids occur in many common household items. (a) Vinegar contains acetic acid, (b) aspirin is acetylsalicylic acid, (c) vitamin C is ascorbic acid, (d) lemons contain citric acid, and (e) spinach contains oxalic acid. © Thinkstock



The carboxyl group contains the $\mathrm{C{=}O}$ of the carbonyl group, with the carbon atom also being bonded to a hydroxyl $(\mathrm{-OH})$ group. A **carboxylic acid** is an organic compound that contains the carboxyl functional group. The general formula for a carboxylic acid can be abbreviated as $\mathrm{R{-}COOH}$. The carbon atom of the carboxyl group may be attached to a hydrogen atom or to a carbon chain. The naming of a carboxylic acid is as follows: Name the parent compound by finding the longest continuous chain that contains the carboxyl group. Change the *-e* at the end of the name of the alkane to *-oic acid*.



Carboxylic acids are weak acids, meaning they are not 100% ionized in water. Generally only about 1% of the molecules of a carboxylic acid dissolved in water are ionized at any given time. The remaining molecules are undissociated in solution.

We prepare carboxylic acids by the oxidation of aldehydes or alcohols whose –OH functional group is located on the carbon atom at the end of the chain of carbon atoms in the alcohol:

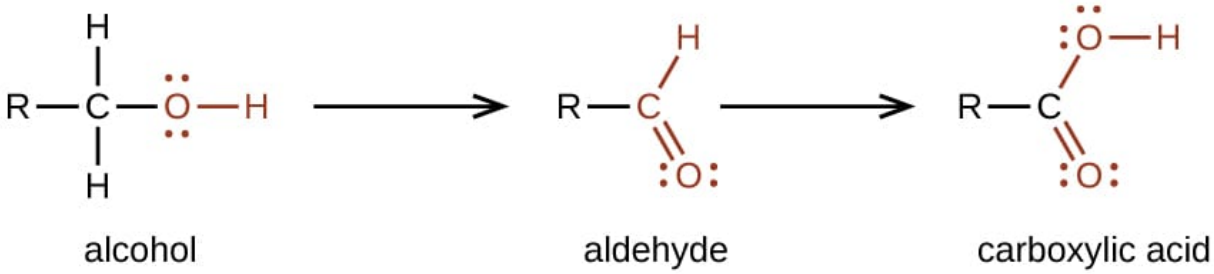
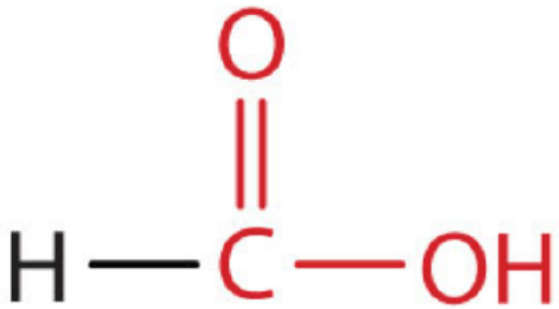


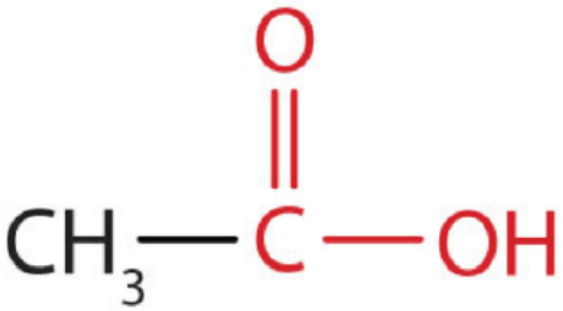
Figure 9.8.3 A chemical reaction with two arrows is shown. On the left, an alcohol, indicated with a C atom to which an R group is bonded to the left, H atoms are bonded above and below, and in red, a single bonded O atom with an H atom bonded to the right is shown. Following the first reaction arrow, an aldehyde is shown. This structure is represented with an R group bonded to a red C atom to which an H atom is bonded above and to the right, and an O atom is double bonded below and to the right. Appearing to the right of the second arrow, is a carboxylic acid comprised of an R group bonded to a C atom to which, in red, an O atom is single bonded with an H atom bonded to its right side. A red O is double bonded below and to the right. All O atoms have two pairs of electron dots.

The simplest carboxylic acid, formic acid (HCOOH, methanoic acid), was first obtained by the distillation of ants (Latin *formica*, meaning “ant”). The bites of some ants inject formic acid, and the stings of wasps and bees contain formic acid (as well as other poisonous materials).

The next higher homolog is acetic acid (CH_3COOH, ethanoic acid), which is made by fermenting cider and honey in the presence of oxygen. This fermentation produces vinegar, a solution containing 4%–10% acetic acid, plus a number of other compounds that add to its flavor. Acetic acid is probably the most familiar weak acid used in educational and industrial chemistry laboratories.



Formic acid



Acetic acid

> Pure acetic acid solidifies at 16.6°C, only slightly below normal room temperature. In the poorly heated laboratories of the late 19th and early 20th centuries in northern North America and Europe, acetic acid often "froze" on the storage shelf. For that reason, pure acetic acid (sometimes called concentrated acetic acid) came to be known as *glacial acetic acid*, a name that survives to this day.

The third homolog, propionic acid (CH_3CH_2COOH, propionic acid), is seldom encountered in everyday life. The fourth homolog, butyric acid ($CH_3CH_2CH_2COOH$), is one of the most foul-smelling substances imaginable. It is found in rancid butter and is one of the ingredients of body odor. By recognizing extremely small amounts of this and other chemicals, bloodhounds are able to track fugitives.

Many carboxylic acids occur naturally in plants and animals. Citrus fruits such as oranges and lemons contain citric acid (Figure 9.8.4). Ethanoic and citric acids are frequently added to foods to give them a tart flavor.

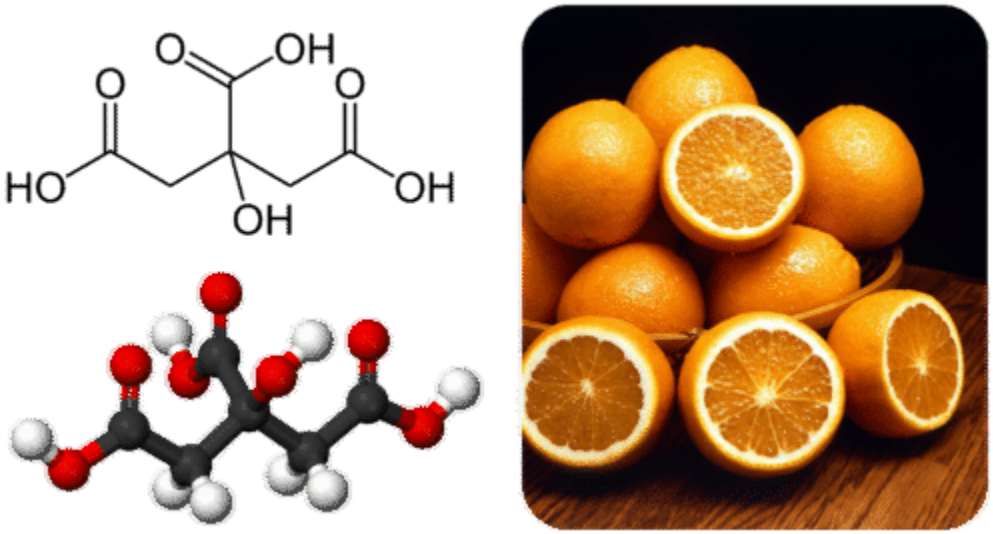
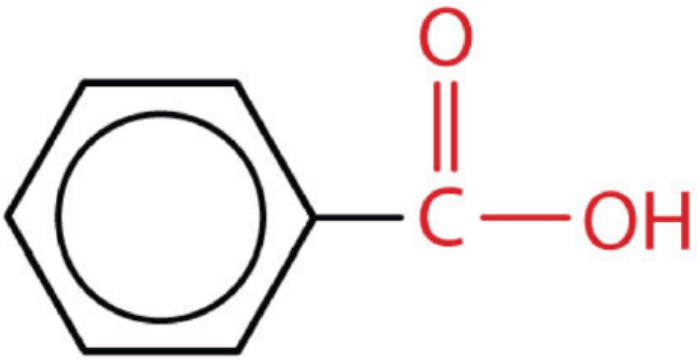


Figure 9.8.4: Citric acid is a large carboxylic acid with three ionizable hydrogen atoms. It is found in citrus fruits and gives them their sour or tart flavor.

Benzoic, propanoic, and sorbic acids are used as food preservatives because of their ability to kill microorganisms that can lead to spoilage. Methanoic and ethanoic acids are widely used in industry as starting points for the manufacture of paints, adhesives,

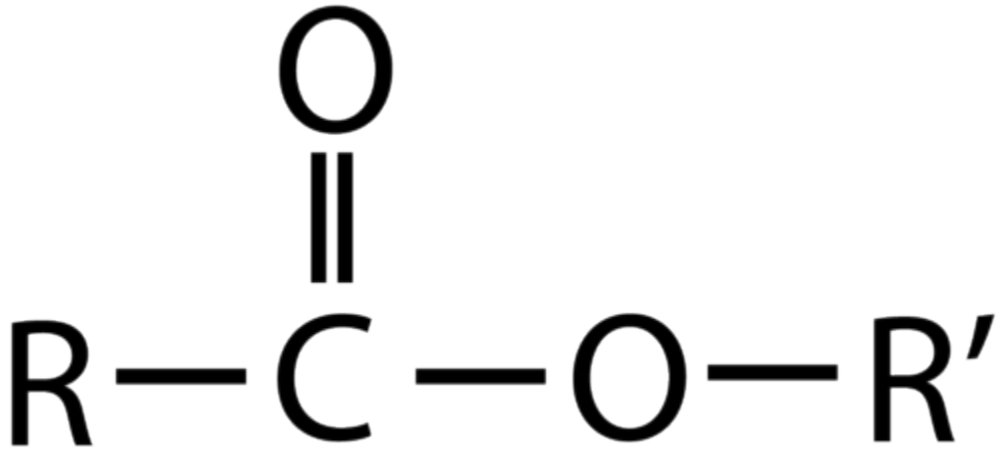
and coatings.



Benzoic acid

Esters: The Sweet Smell of RCOOR'

An **ester** is an organic compound that is a derivative of a carboxylic acid in which the hydrogen atom of the hydroxyl group has been replaced with an alkyl group. The structure is the product of a carboxylic acid (the R-portion) and an alcohol (the R'-portion). The general formula for an ester is shown below.



The R group can either be a hydrogen or a carbon chain. The R' group must be a carbon chain since a hydrogen atom would make the molecule a carboxylic acid.

Esters are produced by the reaction of acids with alcohols. For example, the ester ethyl acetate, $CH_3CO_2CH_2CH_3$, is formed when acetic acid reacts with ethanol:

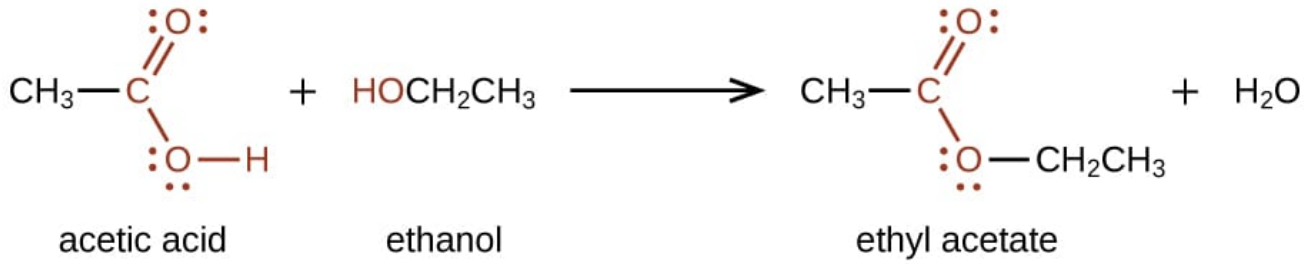


Figure 9.8.5). Once a flower or fruit has been chemically analyzed, flavor chemists can attempt to duplicate the natural odor or taste. Both natural and synthetic esters are used in perfumes and as flavoring agents.A chemical reaction is shown. On the left, a C H subscript 3 group bonded to a red C atom. The C atom forms a double bond with an O atom which is also in red. The C atom is also bonded to an O atom which is bonded to an H atom, also in red. A plus sign is shown, which is followed by H O C H subscript 2 C H subscript 3. The H O group is in red. Following a reaction arrow, a C H subscript 3 group is shown which is bonded to a red C atom with a double bonded O atom and a single bonded O. To the right of this single bonded O atom, a C H subscript 2 C H subscript 3 group is attached and shown in black. This structure is followed by a plus sign and H subscript 2 O. The O atoms in the first structure on the left and the structure following the reaction arrow have two pairs of electron dots.

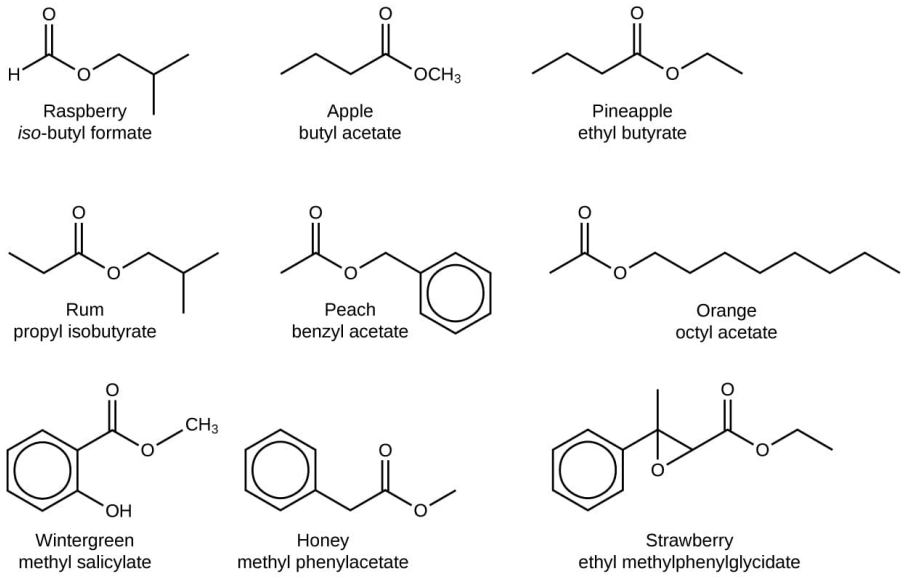


Figure 9.8.6 Esters are responsible for the odors associated with various plants and their fruits. There are nine structures represented in this figure. The first is labeled, “raspberry,” and, “iso-butyl formate.” It shows an H atom with a line going up and to the right which then goes down and to the right. It goes up and to the right again and down and to the right and up and to the right. At the first peak is a double bond to an O atom. At the first trough is an O atom. At the second trough, there is a line going straight down. The second is labeled, “apple,” and, “butyl acetate.” There is a line that goes up and to the right, down and to the right, up and to the right, and down and to the right. At the second peak is a double bond to an O atom. At the end, on the right is O C H subscript 3. The third is labeled, “pineapple,” and, “ethyl butyrate.” It is a line that goes up and to the right, down and to the right, up and to the right, down and to the right, up and to the right, and down and to the right. At the second peak is a double bond to an O atom and at the second trough is an O atom. The fourth is labeled, “rum,” and “propyl isobutyrate.” It shows a line that goes down and to the right, up and to the right, down and to the right, up and to the right, down and to the right and up and to the right. The first complete peak has a double bond to an O atom and the second trough has an O atom. The fifth is labeled, “peach,” and “benzyl acetate.” It shows a line that goes up and to the right, down and to the right, up and to the right and down and to the right. This line connects to a hexagon with a circle inside it. The first peak has a double bond to an O atom and the first trough has an O atom. The sixth is labeled, “orange,” and, “octyl acetate.” It shows a line that goes up and to the right and down and to the right and up and to the right and down and to the right and up and to the right and down and to the right and up and to the right and down and to the right and up and to the right and down and to the right. The first peak has a double bond to an O atom and the first complete trough has and an O atom. The seventh is labeled, “wintergreen,” and “methyl salicylate.” It shows a hexagon with a circle inside of it. On the right, is a bond down and to the right to an O H group. On the right is a bond to a line that goes up and to the right and down and two the right and up and to the right. At the first peak is a double bond to an O atom, the next trough shows and O atom and at the end of the line is a C H subscript 3 group. The eighth is labeled, “honey,” and “methyl phenylacetate.” It shows a hexagon with a circle inside of it. It shows it connecting to a line on the right that goes down and to the right then up and to the right and down and to the right and up and to the right. At the first peak that is not part of the hexagon is a double bond to an O atom. At the last trough is an O atom. The ninth is labeled, “strawberry,” and “ethyl methylphenylglycidate.” This shows a hexagon with a circle inside of it. On the right, it connects to a line that goes up and to the right and down and to the right and up and to the right and down and to the right and up and to the right and down and to the right. At the first peak is a line that extends above and below. Below, it connects to an O atom. At the next trough, the line extends down and to the left to the same O atom. At the next peak is a double bond to an O atom and at the next trough is an O atom.

Chemistry Is Everywhere: Esters, Fragrances, and Flavorings

Esters are very interesting compounds, in part because many have very pleasant odors and flavors. (Remember, never taste anything in the chemistry lab!) Many esters occur naturally and contribute to the odor of flowers and the taste of fruits. Other esters are synthesized industrially and are added to food products to improve their smell or taste; it is likely that if you eat a product whose ingredients include artificial flavorings, those flavorings are esters. Here are some esters and their uses, thanks to their odors, flavors, or both:

Table 9.8.1: Esters, Fragrances, and Flavorings

Ester	Tastes/Smells Like	Ester	Tastes/Smells Like
allyl hexanoate	pineapple	isobutyl formate	raspberry
benzyl acetate	pear	isobutyl acetate	pear
butyl butanoate	pineapple	methyl phenylacetate	honey
ethyl butanoate	banana	nonyl caprylate	orange
ethyl hexanoate	pineapple	pentyl acetate	apple
ethyl heptanoate	apricot	propyl ethanoate	pear
ethyl pentanoate	apple	propyl isobutyrate	rum

Among the most important of the natural esters are fats (such as lard, tallow, and butter) and oils (such as linseed, cottonseed, and olive oils), which are esters of the trihydroxyl alcohol glycerine, $C_3H_5(OH)_3$, with large carboxylic acids, such as palmitic acid, $CH_3(CH_2)_{14}CO_2H$, stearic acid, $CH_3(CH_2)_{16}CO_2H$, and oleic acid, $\mathrm{CH_3(CH_2)_7CH=CH(CH_2)_7CO_2H}$. Oleic acid is an unsaturated acid; it contains a $\mathrm{C=C}$ double bond. Palmitic and stearic acids are saturated acids that contain no double or triple bonds.

Note

Fats and vegetable oils are esters of long-chain fatty acids and glycerol. Esters of phosphoric acid are of the utmost importance to life.

Esters are common solvents. Ethyl acetate is used to extract organic solutes from aqueous solutions—for example, to remove caffeine from coffee. It also is used to remove nail polish and paint. Cellulose nitrate is dissolved in ethyl acetate and butyl acetate to form lacquers. The solvent evaporates as the lacquer “dries,” leaving a thin film on the surface. High boiling esters are used as softeners (plasticizers) for brittle plastics.

Summary

- A carboxylic acid is an organic compound that contains the carboxyl functional group.
- The general formula for a carboxylic acid can be abbreviated as $\mathrm{R-COOH}$.
- Many carboxylic acids are used in the food and beverage industry for flavoring and/or as preservatives.
- An ester has an OR group attached to the carbon atom of a carbonyl group.
- Fats and vegetable oils are esters of long-chain fatty acids and glycerol.
- Esters occur widely in nature and generally have pleasant odors and are often responsible for the characteristic fragrances of fruits and flowers.

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9.9: Nitrogen-Containing Compounds- Amines and Amides

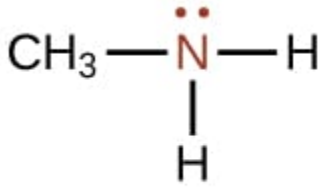
Learning Objectives

- Describe the structure and properties of amines and amides.
- Name simple amines and amides.

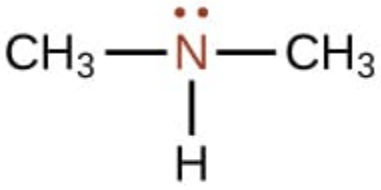
The addition of nitrogen into an organic framework leads to two families of molecules. Compounds containing a nitrogen atom bonded in a hydrocarbon framework are classified as amines. Compounds that have a nitrogen atom bonded to one side of a carbonyl group are classified as amides.

Amines

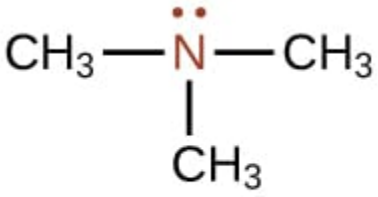
An **amine** is an organic compound that can be considered to be a derivative of ammonia (NH_3). Amines are molecules that contain carbon-nitrogen bonds. Amines are named by naming the alkyl groups attached to the nitrogen atom, followed by the suffix *-amine* as illustrated here for a few simple examples:



methyl amine



dimethyl amine



trimethyl amine

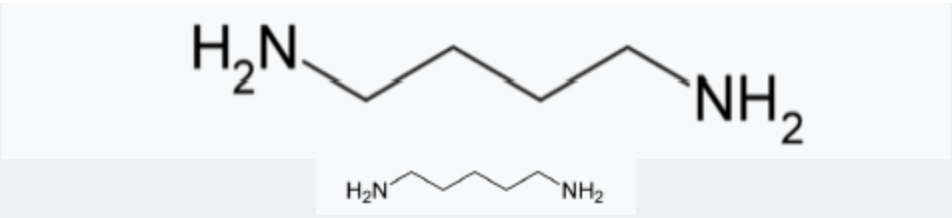
The name of larger molecules involve the class-identifying suffix *–ine* as you will see later in this section(e.g. caffeine and nicotine).

Methylamine and ethylamine are gases at room temperature, while larger amines are liquids. As with other organic compounds that form hydrogen bonds, water solubility is reflected in the length of the carbon chains. Smaller amines are soluble, while larger ones are less soluble.

Amines generally have rather pungent or noxious odors. Ammonia can be considered the simplest amine and has a very distinctive odor. Methylamine has an unpleasant odor associated with dead fish. Amines are often formed biologically during the breakdown of proteins in animal cells, and so many have the smell of death and decay. Putrescine and cadaverine are two such amines and are aptly named for their foul odors. The toxins which many animals use as a form of defense are frequently amines. Amines are used industrially as dyes and in many drugs.

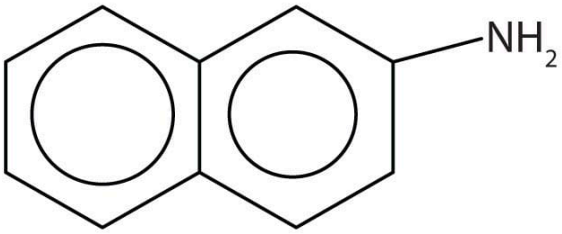
To Your Health: Amines in Death and Life

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.



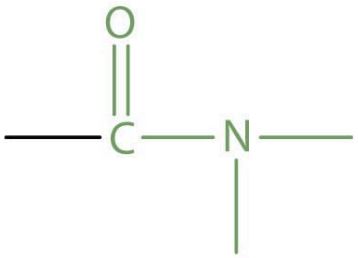
(Figure 9.9.1) Putrescine(left) Cadaverine (right)

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.

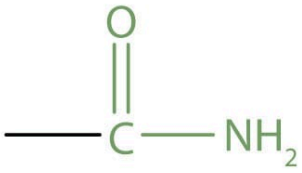


Amides

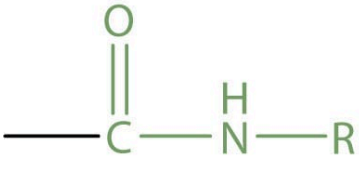
The amide functional group has an nitrogen atom attached to a carbonyl carbon atom. If the two remaining bonds on the nitrogen atom are attached to hydrogen atoms, the compound is a *simple amide*. If one or both of the two remaining bonds on the atom are attached to alkyl or aryl groups, the compound is a *substituted amide*.



The amide group

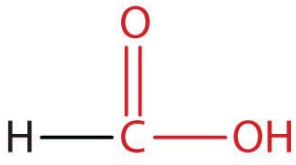


A simple amide

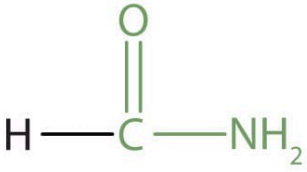


A substituted amide

Simple amides are named as derivatives of carboxylic acids. The *-ic* ending of the common name or the *-oic* ending of the International Union of Pure and Applied Chemistry (IUPAC) name of the carboxylic acid is replaced with the suffix *-amide*.



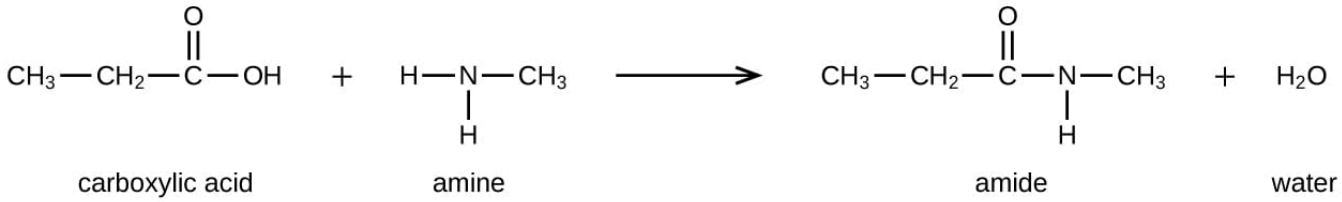
Formic acid
(methanoic acid)



Formamide
(methanamide)

Amides can be produced when carboxylic acids react with amines or ammonia in a process called amidation. A water molecule is eliminated from the reaction, and the amide is formed from the remaining pieces of the carboxylic acid and the amine (note the

similarity to formation of an ester from a carboxylic acid and an alcohol discussed in the previous section):



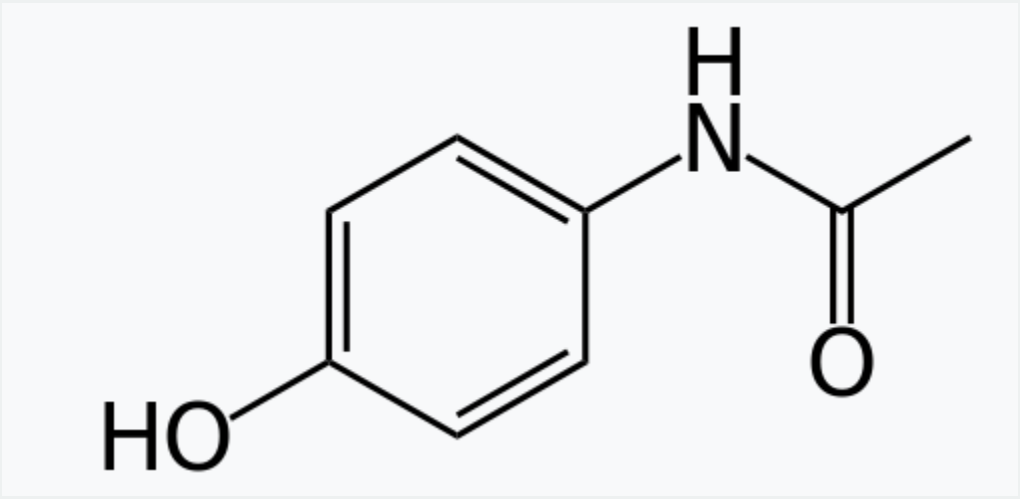
(Figure 9.9.2) reaction between carboxylic acid and amine to form amide and water

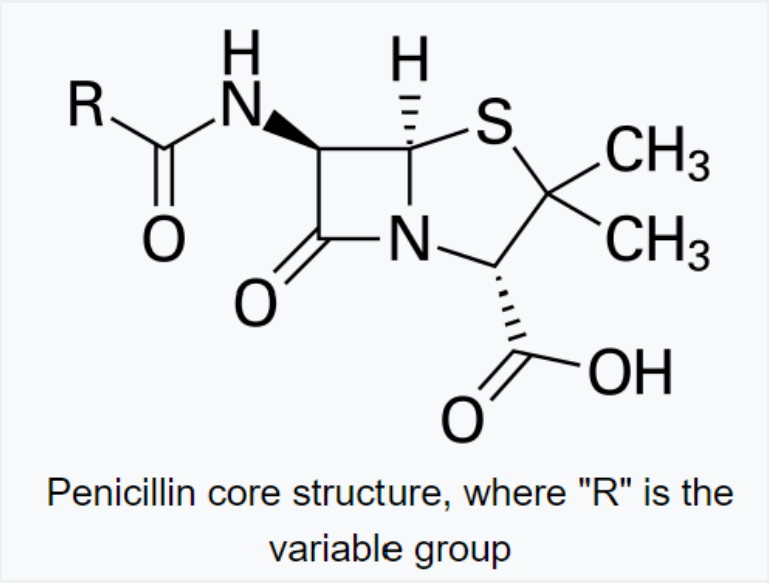
The reaction between amines and carboxylic acids to form amides is biologically important. It is through this reaction that amino acids (molecules containing both amine and carboxylic acid substituents) link together in a polymer to form proteins.

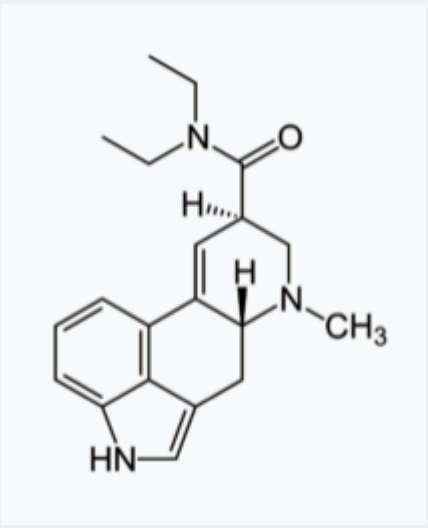
> The carbonyl carbon-to-nitrogen bond is called an *amide linkage*. This bond is quite stable and is found in the repeating units of protein molecules, where it is called a *peptide linkage*.

Amides are pervasive in nature and technology as structural materials. The amide linkage is easily formed, confers structural rigidity, and resists hydrolysis. Nylons are polyamides, as are the very resilient materials Aramid, Twaron, and Kevlar. Amide linkages constitute a defining molecular feature of proteins, the secondary structure of which is due in part to the hydrogen bonding abilities of amides. Amide linkages in a biochemicalcontext are called peptide bonds when they occur in the main chain of a protein and isopeptide bonds when they occur to a side-chain of the protein. Proteins can have structural roles, such as in hair or spider silk, but also nearly all enzymes are proteins. Low molecular weight amides, such as dimethylformamide ($HC(O)N(CH_3)_2$), are common solvents. Many drugs are amides, including paracetamol, penicillin and LSD. Moreover, plant *N*-alkylamides have a wide range of biological functionalities.

Drugs with the Amide Group







(Figure 9.9.3) Paracetamol (acetaminophen) LSD (Lysergic diethylamide)

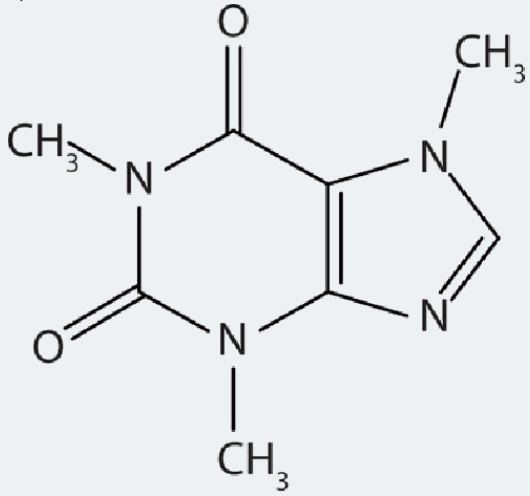
Heterocyclic Compounds: Alkaloids and Others

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.

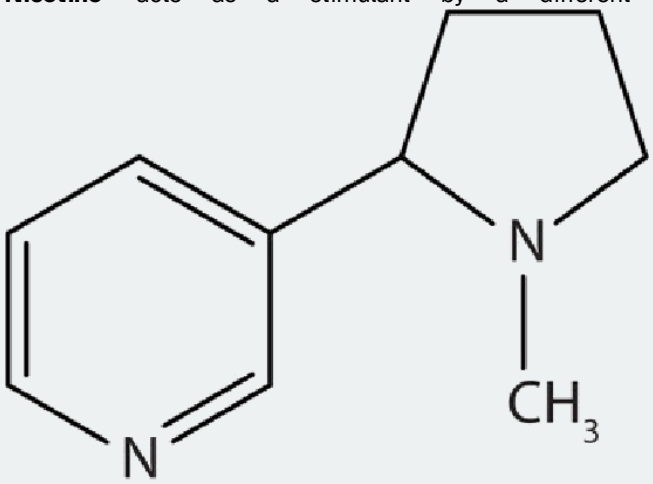
To Your Health: Three Well-Known Alkaloids

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.



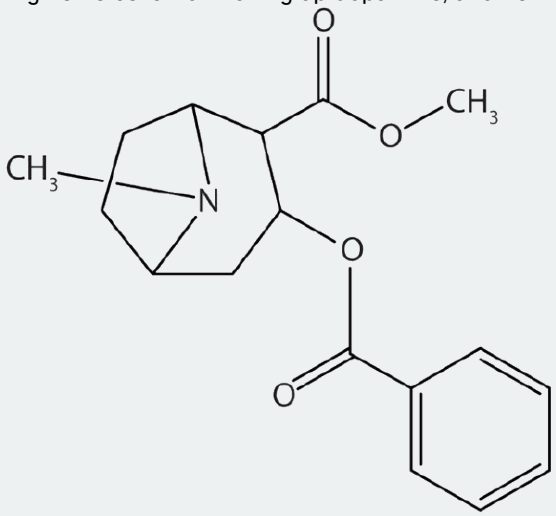
Caffeine

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.



Cocaine

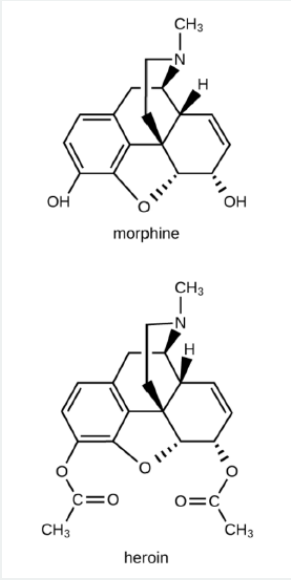
High levels of dopamine are therefore available to stimulate the pleasure centers of the brain. The enhancement of dopamine action is thought to be responsible for cocaine's "high" and its addictive properties. After the binge, dopamine is depleted in less than an hour. This leaves the user in a pleasureless state and (often) craving more cocaine.

Cocaine is used as the salt cocaine hydrochloride and in the form of broken lumps of the free (unneutralized) base, which is called *crack cocaine*.

$$\underset{\text{Cocaine (freebase)}}{C_{17}H_{21}O_4N} + HCl \longrightarrow \underset{\text{Cocaine hydrochloride}}{C_{17}H_{21}O_4NH^+Cl^-}$$

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.

Morphine and Heroin



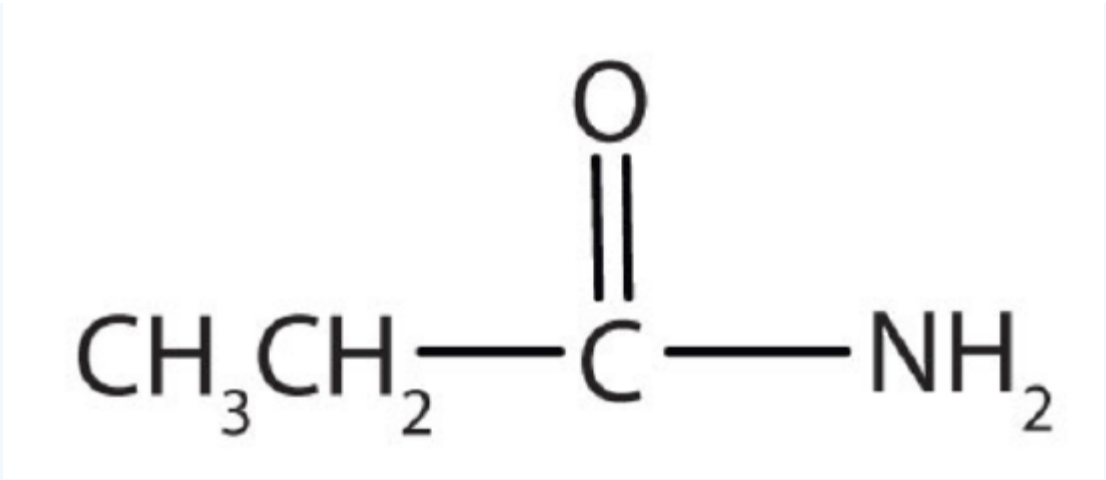
Morphine, a strong narcotic used to relieve pain, contains two hydroxyl functional groups, located at the bottom of the molecule in this structural formula. Changing one of these hydroxyl groups to a methyl ether group forms codeine, a less potent drug used as a local anesthetic. If both hydroxyl groups are converted to esters of acetic acid, the powerfully addictive drug heroin results (Figure 9.9.4).

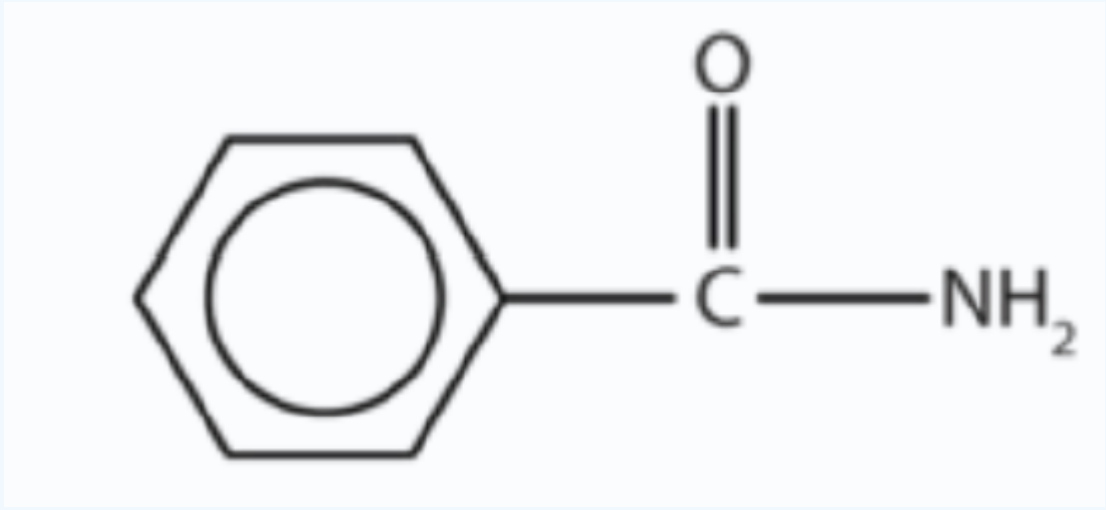


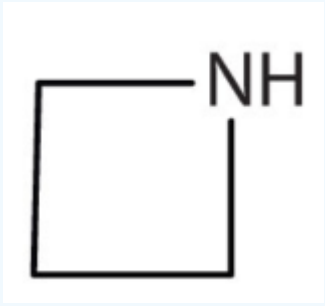
Figure 9.9.4 Poppies can be used in the production of opium, a plant latex that contains morphine from which other opiates, such as heroin, can be synthesized. (credit: Karen Roe)

Example 9.9.1: Amines and Amides

Identify whether each compound is an amide or an amine.

a. 

b. 

c. 

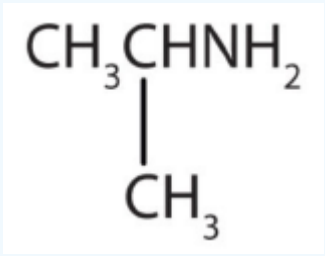
Solutions

a. The compound has the $CONH_2$ functional group so it is an amide.

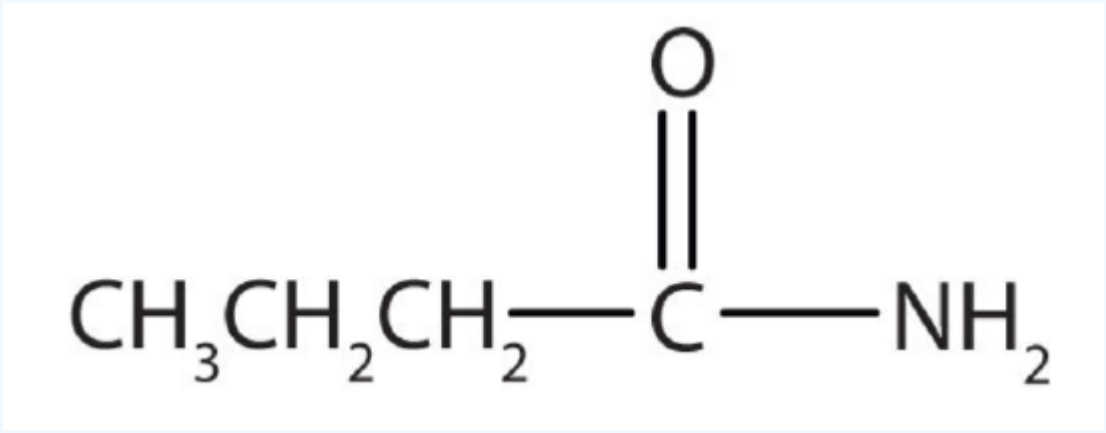
b. The compound has the $CONH_2$ functional group so it is an amide.

c. The compound has the NH functional group so it is an amine.

Exercise 9.9.1

a. 

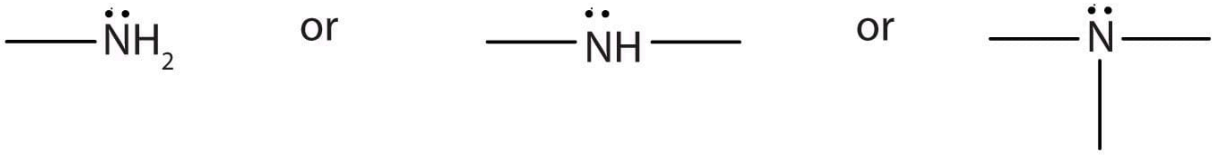
b. $CH_3CH_2CH_2CH_2CH_2CH_2NH_2$

c. 

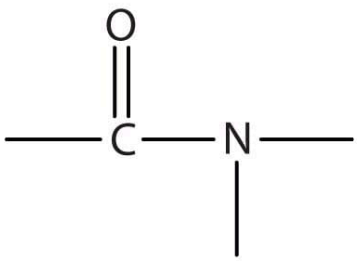
Answer available at the end of this section.

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 named by naming the alkyl groups attached to the nitrogen atom, followed by the suffix *-amine*.
- Amides have a general structure in which a nitrogen atom is bonded to a carbonyl carbon atom.



(Figure 9.9.5) Amide

- Like amines, various nomenclature rules may be used to name amides, but all include use of the class-specific suffix *-amide*:

- Heterocyclic amines are cyclic compounds with one or more nitrogen atoms in the ring.

Contributors and Attributions

Marisa Alviar-Agnew (Sacramento City College)

Libretext: The Basics of GOB Chemistry (Ball et al.)

OpenSTAX

Wikipedia

Answers

Exercise 9.9.1

a. amine b. amine c. amide

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10: POLYMERS

10.1: Polymerization - Making Big Ones Out of Little Ones
10.2: Polyethylene - From the Battle of Britain to Bread Bags
10.3: Addition Polymerization - One + One + One + ... Gives One!
10.4: Rubber and Other Elastomers
10.5: Condensation Polymers
10.6: Properties of Polymers
10.7: Plastics and the Environment

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10.1: Polymerization - Making Big Ones Out of Little Ones

Learning Objectives

- Define the terms *monomer* and *polymer*.
- Know the different types of natural polymers.

A **polymer** is a large molecule, or macromolecule, composed of many repeated subunits.The term "polymer" derives from the Greek word *polus (*meaning "many, much") and m*eros* (meaning "part"), and refers to a molecule whose structure is composed of multiple repeating units, from which originates a characteristic of high relative molecular mass and attendant properties. As shown schematically in Figure 10.1.1.

Due to their broad range of properties, both synthetic and natural polymers play essential and ubiquitous roles in everyday life. Polymers range from familiar synthetic plastics such as polystyrene to natural biopolymers such as DNA and proteins that are fundamental to biological structure and function. Polymers, both natural and synthetic, are created via polymerization of many small molecules, known as monomers. Their consequently large molecular mass relative to small molecule compounds produces unique physical properties, including toughness, viscoelasticity, and a tendency to form glasses and semicrystalline structures rather than crystals. The terms polymer and resin are often synonymous with plastic.

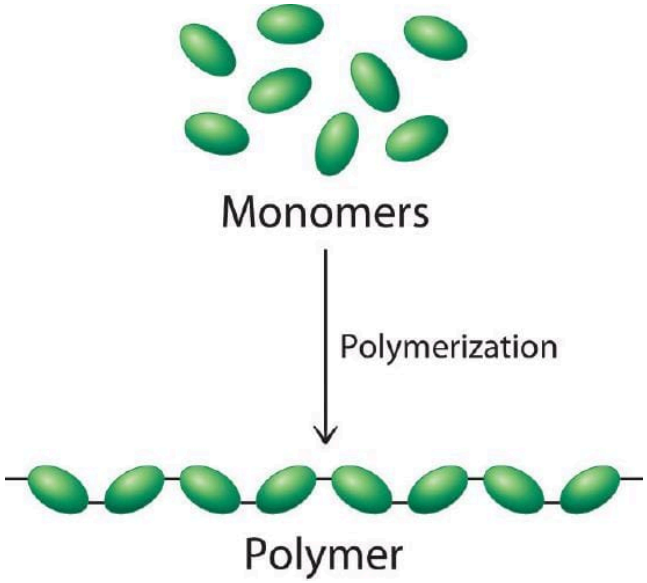
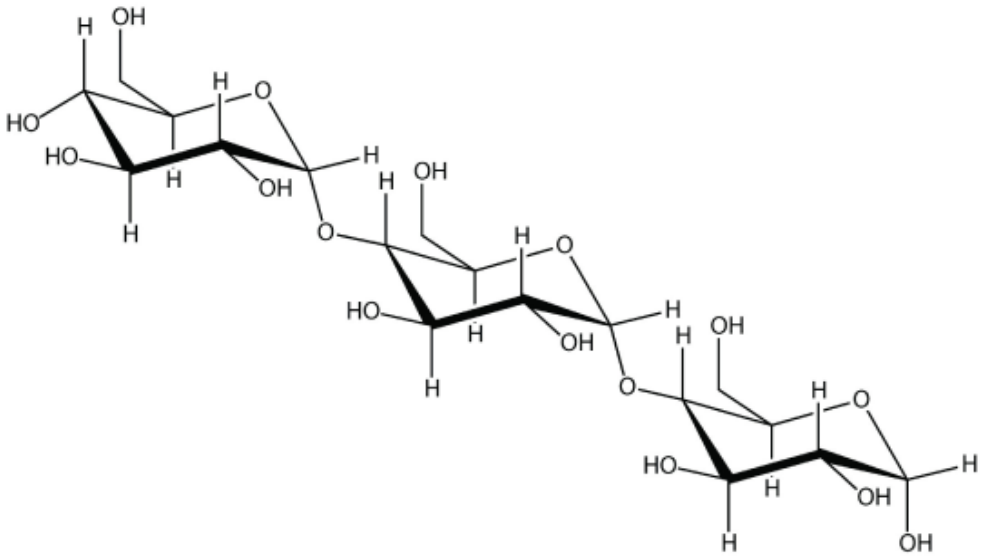


Figure 10.1.1 *Polymer formation during a polymerization reaction, a large number of monomers become connected by covalent bonds to form a single long molecule, a polymer.*

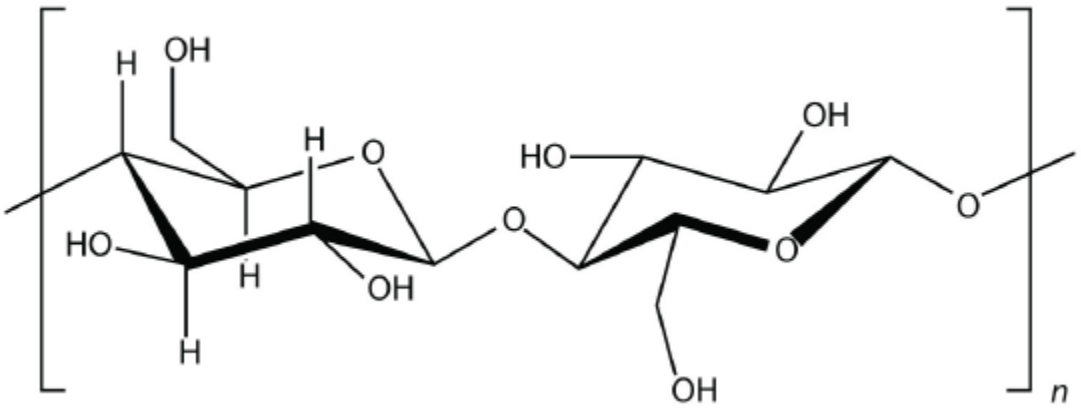
Natural Polymers

Some very important biological materials are polymers. Of the three major food groups, polymers are represented in two: proteins and carbohydrates. **Proteins** are polymers of amino acids, which are monomers that have an amine functional group and a carboxylic acid functional group. Proteins play a crucial role in living organisms.

Linking hundreds of glucose molecules together makes a relatively common material known as *starch*:



Starch is an important source of energy in the human diet. Note how individual glucose units are joined together. They can also be joined together in another way, like this:



This polymer is known as *cellulose*. **Cellulose** is a major component in the cell walls of plants. Curiously, despite the similarity in the building blocks, some animals (such as humans) cannot digest cellulose; those animals that can digest cellulose typically rely on symbiotic bacteria in the digestive tract for the actual digestion. Animals do not have the proper enzymes to break apart the glucose units in cellulose, so it passes through the digestive tract and is considered *dietary fiber*.

Deoxyribonucleic acid* (*DNA*) and *ribonucleic acid* (*RNA*)** are also polymers, composed of long, three-part chains consisting of phosphate groups, sugars with 5 C atoms (ribose or deoxyribose), and N-containing rings referred to as bases. Each combination of the three parts is called a nucleotide; DNA and RNA are essentially polymers of nucleotides that have rather complicated but intriguing structures (F***igure 10.1.2 - Nucleotides). DNA is the fundamental material in chromosomes and is directly responsible for heredity, while RNA is an essential substance in protein synthesis.

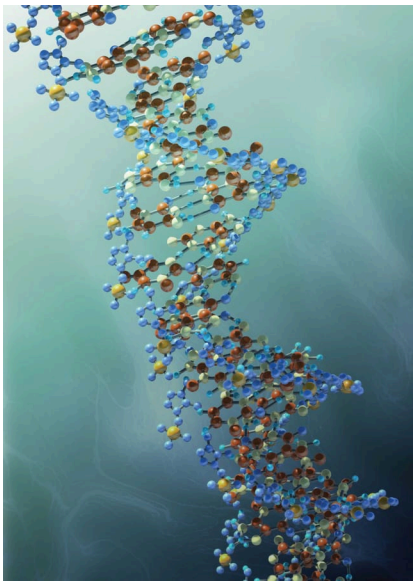


Figure 10.1.2 *Nucleotides © Thinkstock*

The DNA in our cells is a polymer of nucleotides, each of which is composed of a phosphate group, a sugar, and a N-containing base

The above mentioned biopolymers (polymers produced by living organisms) are discussed further in Chapter 16.

Celluloid: Billiard Balls

Celluloids are a class of compounds created from nitrocellulose (partially nitrated cellulose) and camphor, with added dyes and other agents. Generally considered the first thermoplastic, it was first created as Parkesinein (by Alexander Parkes of Birmingham England) in 1856 and as Xylonite in 1869. In the 1860s, an American, John Wesley Hyatt, acquired Parkes's patent and began experimenting with cellulose nitrate with the intention of manufacturing billiard balls, which until that time were made from ivory. In the 1870s the modified plastic was registered as "celluloid".

The main use was in movie and photography film industries, which used only celluloid film stock prior to the adoption of acetate safety film in the 1950s. Celluloid is highly flammable, difficult and expensive to produce and no longer widely used; its most common uses today are in table tennis balls, musical instruments, and guitar picks.

Bakelite (sometimes spelled **Baekelite**) or **polyoxybenzylmethylenglycolanhydride** was the first plastic made from synthetic components. It is a thermosetting phenol formaldehyde resin, formed from a condensation reaction of phenol with formaldehyde. It was developed by the Belgian-American chemist Leo Baekeland in Yonkers, New York, in 1907.

Bakelite was patented on December 7, 1909. The creation of a synthetic plastic was revolutionary for its electrical non conductivity and heat-resistant properties in electrical insulators, radio and telephone casings and such diverse products as kitchenware, jewelry, pipe stems, children's toys, and firearms.

Polymers

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 10.1.2 *Polymers Crash Course*

Summary

- Polymers are giant molecules that consist of long chains of units called monomers connected by covalent bonds.
- Polymerization is the process of linking monomers together to form a polymer.
- Plastic is the general term for polymers made from synthetic materials.
- Several important biological polymers include proteins, starch, cellulose, DNA and RNA.

Contributors and Attributions

- Joshua Halpern, Scott Sinex and Scott Johnson
- TextMap: Beginning Chemistry (Ball et al.)

- Marisa Alviar-Agnew (Sacramento City College)

- Wikipedia

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10.2: Polyethylene - From the Battle of Britain to Bread Bags

Learning Objectives

- List the different types of polyethylene.
- Differentiate between thermolastic and thermosetting polymers.

Polyethylene was first synthesized by the German chemist Hans von Pechmann, who prepared it by accident in 1898. Industrial production of low-density polyethylene (LDPE) began in 1939 in England. Because polyethylene was found to have very low-loss properties at very high frequency radio waves, commercial distribution in Britain was suspended on the outbreak of World War II in order to produce insulation for UHF (ultra high frequency) and SHF (super high frequency) cables of radar sets.

Polyethylene or **polythene** is the most common plastic. As of 2017, over 100 million tonnes of polyethylene resins are produced annually, accounting for 34% of the total plastics market. Its primary use is in packaging (plastic bags, plastic films, geomembranes, containers including bottles, etc.). Many kinds of polyethylene are known, with most having the chemical formula $(C_2H_4)_n$. PE is usually a mixture of similar polymers of ethylene with various values of *n*.

Polymers based on skeletons with only carbon are all synthetic. Let's begin by looking at polyethylene Figure 10.2.1 . It is the simplest polymer, consisting of random-length (but generally very long) chains made up of two-carbon units.

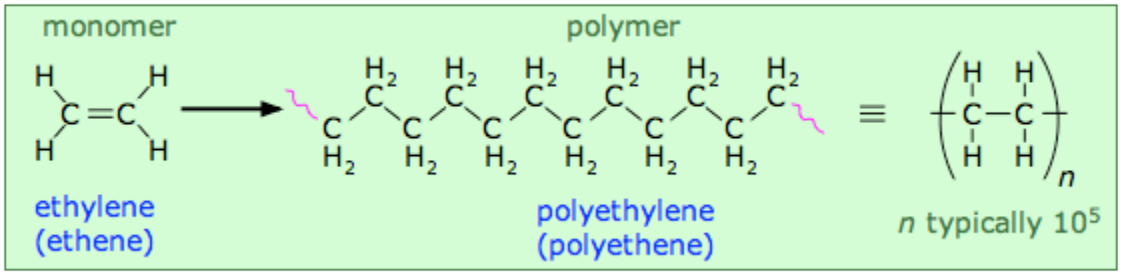


Figure 10.2.1 *Polyethylene*.

You will notice some "fuzziness" in the way that the polyethylene structures are represented above. The squiggly lines at the ends of the long structure indicate that the same pattern extends indefinitely. The more compact notation on the right shows the minimal repeating unit enclosed in brackets overprinted with a dash; this means the same thing and is the preferred way of depicting polymer structures.

Types of Polyethylene

Most of synthetic polymers are formed from ethylene. The relative lengths of the chains and any branches control the properties of polyethylene. The most important polymer grades with regard to volume are High density polyethylene (HDPE) Low density polyethylene (LDPE), and Linear low density polyethylene (LLDPE).

HDPE (High density polyethylene) is defined by a density of greater or equal to 0.941 g/cm^3. HDPE has a low degree of branching. The mostly linear molecules pack together well, so intermolecular forces are stronger than in highly branched polymers. HDPE has high tensile strength. It is used in products and packaging such as milk jugs, detergent bottles, butter tubs, garbage containers, and water pipes. One-third of all toys are manufactured from HDPE. In 2007, the global HDPE consumption reached a volume of more than 30 million tons.

LDPE (Low density polyethylene) is defined by a density range of 0.910–0.940 g/cm^3. LDPE has a high degree of short- and long-chain branching, which means that the chains do not pack into the crystal structure as well. It has, therefore, less strong intermolecular forces as the instantaneous-dipole induced-dipole attraction is less. This results in a lower tensile strength and increased ductility. The high degree of branching with long chains gives molten LDPE unique and desirable flow properties. LDPE is used for both rigid containers and plastic film applications such as plastic bags and film wrap. In 2013, the global LDPE market

had a volume of almost US$33 billion.

LLDPE (Linear low density polyethylene) is defined by a density range of 0.915–0.925 g/cm^3. LLDPE is a substantially linear polymer with significant numbers of short branches. LLDPE has higher tensile strength than LDPE, and it exhibits higher impact and puncture resistance than LDPE. Lower thickness (gauge) films can be blown, compared with LDPE, with better environmental stress-cracking resistance, but is not as easy to process. LLDPE is used in packaging, particularly film for bags and sheets. Lower thickness may be used compared to LDPE. It is used for cable coverings, toys, lids, buckets, containers, and pipe. While other applications are available, LLDPE is used predominantly in film applications due to its toughness, flexibility, and relative transparency. Product examples range from agricultural films, Saran wrap, and bubble wrap, to multilayer and composite films. In 2013, the world LLDPE market reached a volume of US$40 billion.

Figure 10.2.2 A pill box presented to a technician at Imperial Chemical Industries (ICI) in Northwich, Englandin 1936 made from the first pound of polyethylene.

Polyethylene Production

Video 10.2.1 *The commercial production of Polyethylene (polyethene). from the Royal Society of Chemistry*

Answer available at the end of this section.

Thermoplastic and Thermosetting Polymers

Polymers can be classified by their physical response to heating. Polyethylene is a thermoplastic; however, it can become a thermoset plastic when modified (such as cross-linked polyethylene). **Thermoplastics** are plastics that soften when heated and become firm again when cooled. This is the more popular type of plastic because the heating and cooling may be repeated and the thermoplastic may be reformed.

Thermosets are plastics that soften when heated and can be molded, but harden permanently. They will decompose when reheated. An example is Bakelite, which is used in toasters, handles for pots and pans, dishes, electrical outlets and billiard balls.

Summary

Polyethylene is the long chain polymer formed from ethylene (ethene) monomers.

Polyethylene can be classified as HDPE, LDPE, and LLDPE based on how close the polymer chains pack together affecting its density.

Polymers can be classified as thermoplastics (can be reformed after repeated heating) or thermosets (harden permanently) based on their physical response to heating.

Contributors and Attributions

- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook
- Charles Ophardt, Professor Emeritus, Elmhurst College; Virtual Chembook
- Wikipedia

Answers

Polyethylene Production

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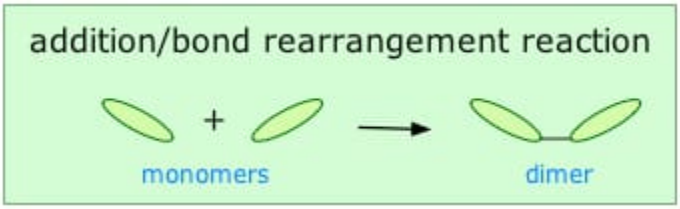
10.3: Addition Polymerization - One + One + One + ... Gives One!

Learning Objectives

- Define addition polymerization.
- Draw the structure of a polymer from its monomer.
- Know the uses/applications of common polymers.

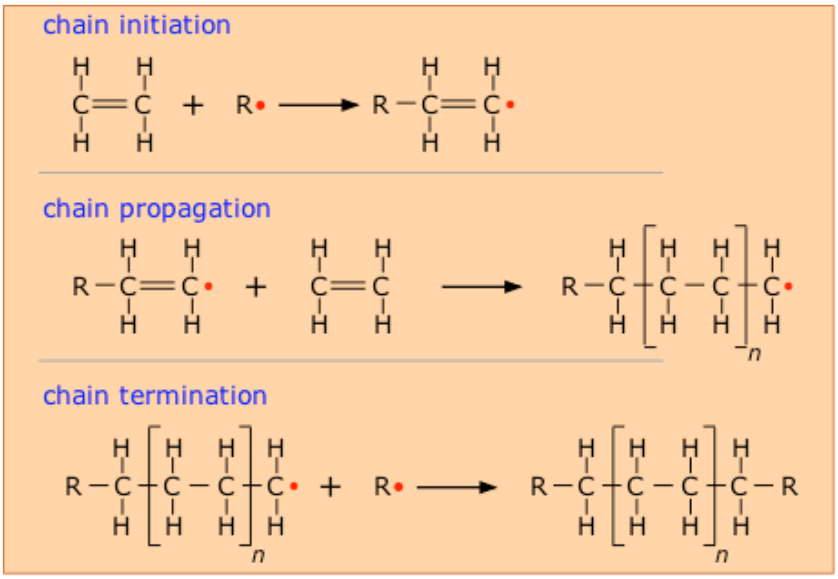
Addition polymerization and condensation polymerization are two modes of polymerization reactions in the formation of polymers. In addition polymerization, the monomer molecules bond to each other without the loss of any other atoms. Addition polymers from alkene monomers or substituted alkene monomers are the biggest groups of polymers in this class. Ring opening polymerization can occur without the loss of any small molecules. Whereas, in condensation polymerization (Section 10.5) two different monomers combine with the loss of a small molecule, usually water. Most polyesters and polyamides (nylon) are in this class of polymers.

Addition or *chain-growth* polymerization involves the rearrangement of bonds within the monomer in such a way that the monomers link up directly with each other:



In order to make this happen, a chemically active molecule (called an *initiator*) is needed to start what is known as a *chain reaction*. The manufacture of polyethylene is a very common example of such a process. It employs a *free-radical* initiator that donates its unpaired electron to the monomer, making the latter highly reactive and able to form a bond with another monomer at this site.

In theory, only a single chain-initiation process needs to take place, and the chain-propagation step then repeats itself indefinitely, but in practice multiple initiation steps are required, and eventually two radicals react (*chain termination*) to bring the polymerization to a halt.



As with all polymerizations, chains having a range of molecular weights are produced, and this range can be altered by controlling the pressure and temperature of the process.

Polypropylene

Polypropylene (**PP**), also known as **polypropene**, is a thermoplastic polymer used in a wide variety of applications. It is produced via chain-growth polymerization from the monomer propylene.Phillips Petroleum chemists J. Paul Hogan and Robert Banks first polymerized propylene in 1951. Propylene was first polymerized to a crystalline isotactic polymer by Giulio Natta as well as by the German chemist Karl Rehn in March 1954. Polypropylene is used alone or as a copolymer, usually with with ethylene. These polymers have an exceptionally wide range of uses — rope, binder covers, plastic bottles, staple yarns, non-woven fabrics, electric kettles. When uncolored, it is translucent but not transparent. Its resistance to fatigue makes it useful for food containers and their lids, and flip-top lids on bottled products such as ketchup.

After polyethylene, polypropylene is the most profitable plastic with revenues expected to exceed US$145 billion by 2019. The sales of this material are forecast to grow at a rate of 5.8% per year until 2021. Polypropylene is produced by the chain-growth polymerization of propylene:

Polypropylène.png

Polystyrene

Polystyrene was discovered in 1839 by Eduard Simon, an apothecary from Berlin.In 1941, Dow Chemical invented a Styrofoam process. Polystyrene is transparent but rather brittle, and yellows under uv light. Widely used for inexpensive packaging materials and "take-out trays", foam "packaging peanuts", CD cases, foam-walled drink cups, and other thin-walled and moldable parts.

Expanded polystyrene (EPS) is a rigid and tough, closed-cell foam with a normal density range of 11 to 32 kg/m^3. It is usually white and made of pre-expanded polystyrene beads. EPS is used for food containers, molded sheets for building insulation, and packing material either as solid blocks formed to accommodate the item being protected or as loose-fill "peanuts" cushioning fragile items inside boxes. EPS is colloquially called "styrofoam" in the United States and Canada, an incorrectly applied genericization of Dow Chemical's brand of *extruded* polystyrene.

Polystyrene results when styrene monomers interconnect. In the polymerisation, the carbon–carbon π bond of the vinyl group is broken and a new carbon–carbon σ bond is formed, attaching to the carbon of another styrene monomer to the chain.

Polystyrene formation.PNG

Polyvinyl Chloride

PVC was accidentally synthesized in 1872 by German chemist Eugen Baumann.. The polymer appeared as a white solid inside a flask of vinyl chloride that had been left exposed to sunlight. **Polyvinyl chloride** (**PVC**) is the world's third-most widely produced synthetic plastic polymer, after polyethylene and polypropylene. About 40 million tonnes are produced per year. Polyvinyl chloride is one of the world's most widely used polymers. By itself it is quite rigid and used in construction materials such as pipes, house siding, flooring. Addition of plasticizers make it soft and flexible for use in upholstery, electrical insulation, shower curtains and waterproof fabrics. There is some effort being made to phase out this polymer owing to environmental concerns.

Polytetrafluorehtylene (PTFE): The Nonstick Coating

Polytetrafluoroethylene (**PTFE**) is a synthetic fluoropolymer of tetrafluoroethylene that has numerous applications. The best-known brand name of PTFE-based formulas is **Teflon** (Figure 10.3.1) Aldehydby Chemours. Chemours is a spin-off of DuPont, which originally discovered the compound in 1938. This highly-crystalline fluorocarbon is exceptionally inert to chemicals and solvents. Water and oils do not wet it, which accounts for its use in cooking ware and other anti-stick applications, including personal care products.

These properties — non-adhesion to other materials, non-wetability, and very low coefficient of friction ("slipperyness") — have their origin in the highly electronegative nature of fluorine whose atoms partly shield the carbon chain. Fluorine's outer electrons are so strongly attracted to its nucleus that they are less available to participate in London (dispersion force) interactions.

Figure 10.3.1 Advertisement of the Happy Pan, a Teflon-coated pan from the 1960s. Source: Wikipedia

Some common addition polymers are listed in Tables 10.3.1 and 10.3.2. 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 10.3.1 Some Addition Polymers.

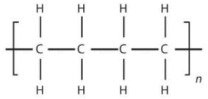
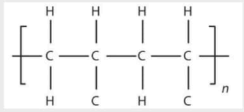
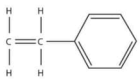
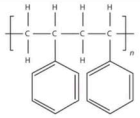
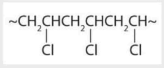
Monomer	Polymer	Polymer Name [Trade Name(s)]	Some Uses
 $CH_2{=}CH_2$	 ~$CH_2CH_2CH_2CH_2CH_2CH_2$~	polyethylene	plastic bags, bottles, toys, electrical insulation
 $CH_2{=}CHCH_3$		polypropylene	carpeting, bottles, luggage, exercise clothing
		polystyrene	"take-out trays", foam "packaging peanuts", CD cases, foam-walled drink cups, and other thin-walled and moldable parts.
$CH_2{=}CHCl$		polyvinyl chloride	bags for intravenous solutions, pipes, tubing, floor coverings
$CF_2{=}CF_2$	~$CF_2CF_2CF_2CF_2CF_2CF_2$~	polytetrafluoroethylene (Teflon)	Non-stick coating for cooking utensils, chemically-resistant specialty plastic parts, Gore-Tex

Figure 10.3.2

Table 10.3.2 Other Polymers and their Uses.

Monomer	Polymer Name	Trade Name(s)	Uses
$H_2C{=}CCl_2$	polyvinylidene dichloride	Saran	Clinging food wrap

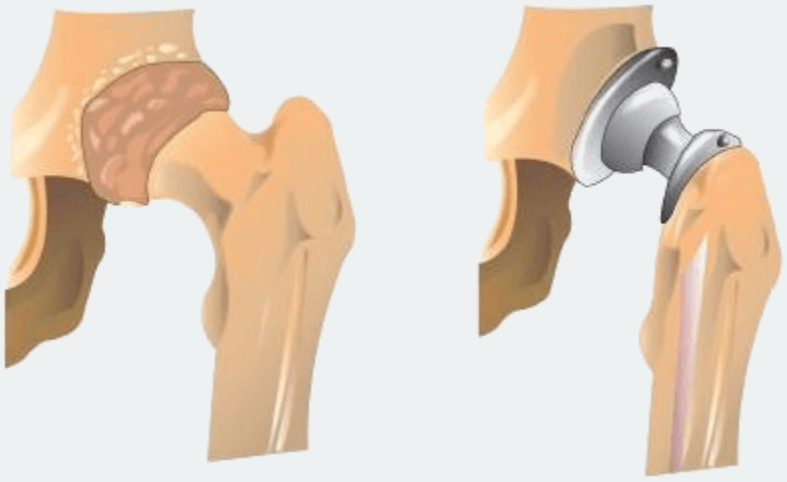
Monomer	Polymer Name	Trade Name(s)	Uses
$H_2C=CH(CN)$	polyacrylonitrile	Orlon, Acrilan, Creslan	Fibers for textiles, carpets, upholstery
$H_2C=CH(OCOCH_3)$	polyvinyl acetate		Elmer's glue - Silly Putty Demo
$H_2C=CH(OH)$	polyvinyl alcohol		Ghostbusters Demo
$H_2C=C(CH_3)COOCH_3$	polymethyl methacrylate	Plexiglass, Lucite	Stiff, clear, plastic sheets, blocks, tubing, and other shapes
$H_2C=CH-C(CH_3)=CH_2$	polyisoprene	natural or some synthetic rubber	applications similar to natural rubber
$H_2C=CH-CH=CH_2$	polybutadiene	polybutadiene synthetic rubber	select synthetic rubber applications
$H_2C=CH-CCl=CH_2$	polychloroprene	Neoprene	chemically-resistant rubber

Processing Polymers

Molding is the process of manufacturing by shaping liquid or pliable raw material using a rigid frame called a mold or matrix. This itself may have been made using a pattern or model of the final object. **Compression molding** is a forming process in which a plastic material is placed directly into a heated metal mold then is softened by the heat and therefore forced to conform to the shape of the mold, as the mold closes. **Transfer molding** (BrE moulding) is a manufacturing process where casting material is forced into a mold. Transfer molding is different from compression molding in that the mold is enclosed [Hayward] rather than open to the fill plunger resulting in higher dimensional tolerances and less environmental impact.

Injection moulding is a manufacturing process for producing parts by injecting molten material into a mould. Injection moulding can be performed with a host of materials mainly including metals (for which the process is called die-casting), glasses, elastomers, confections, and most commonly thermoplastic and thermosetting polymers. **Extrusion** is a process used to create objects of a fixed cross-sectional profile. A material is pushed through a die of the desired cross-section. **Drawing** is a similar process, which uses the tensile strength of the material to pull it through the die. This limits the amount of change which can be performed in one step, so it is limited to simpler shapes, and multiple stages are usually needed. Drawing is the main way to produce wire. Metal bars and tubes are also often drawn.

Medical Uses of Polymers



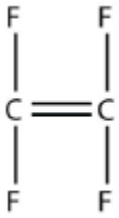
An interesting use of polymers is the replacement of diseased, worn out, or missing parts in the body. For example, about a 250,000 hip joints and 500,000 knees are replaced in US hospitals each year. The artificial ball-and-socket hip joints are made of a special steel (the ball) and plastic (the socket). People crippled by arthritis or injuries gain freedom of movement and relief from pain. Patients with heart and circulatory problems can be helped by replacing worn out heart valves with parts based on synthetic polymers. These are only a few of the many biomedical uses of polymers.

Figure 10.3.2: *Hip Joint Replacement. Synthetic polymers are an important part of a hip joint replacement. The hip is much like a ball-and-socket joint, and total hip replacements mimic this with a metal ball that fits in a plastic cup.*

Figure

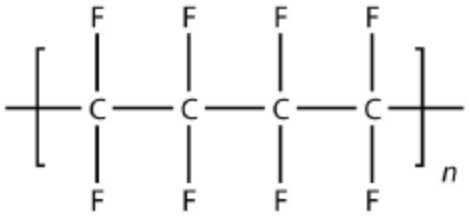
Example 10.3.1

Draw the polymer that results from the polymerization of tetrafluoroethylene.



Solution

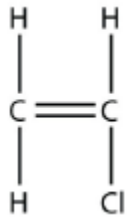
In the case of this monomer, the double bond opens up and joins to other monomers, just as with ethylene. The polymer that is made has this structure:



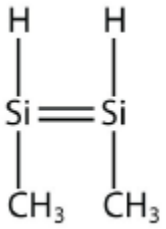
Exercise 10.3.1

Draw the polymer that results from the polymerization of the following monomers:

a.

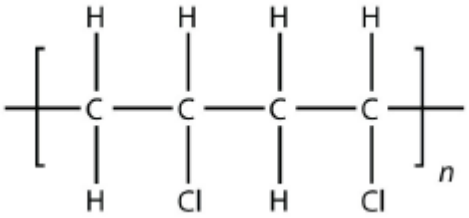


b.

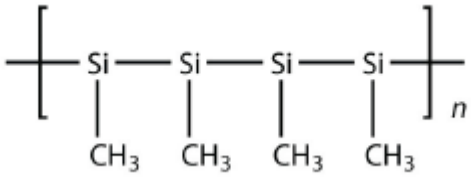


Answers

a.



b.



Summary

- Addition polymerization is when the monomer molecules bond to each other without the loss of any other atoms.
- Examples of addition polymers include polyethylene, polypropylene, polystyrene, polyvinylchloride, polytetrafluoroethylene, etc.
- Many objects in daily use from packing, wrapping, and building materials include half of all polymers synthesized. Other uses include textiles, many electronic appliance casings, CD's, automobile parts, and many others are made from polymers.

Contributors and Attributions

- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook

- TextMap: Beginning Chemistry (Ball et al.)
- Libretext: The Basics of GOB Chemistry (Ball et al.)

- Marisa Alviar-Agnew (Sacramento City College)

- Charles Ophardt (Professor Emeritus, Elmhurst College); Virtual Chembook

- Wikipedia

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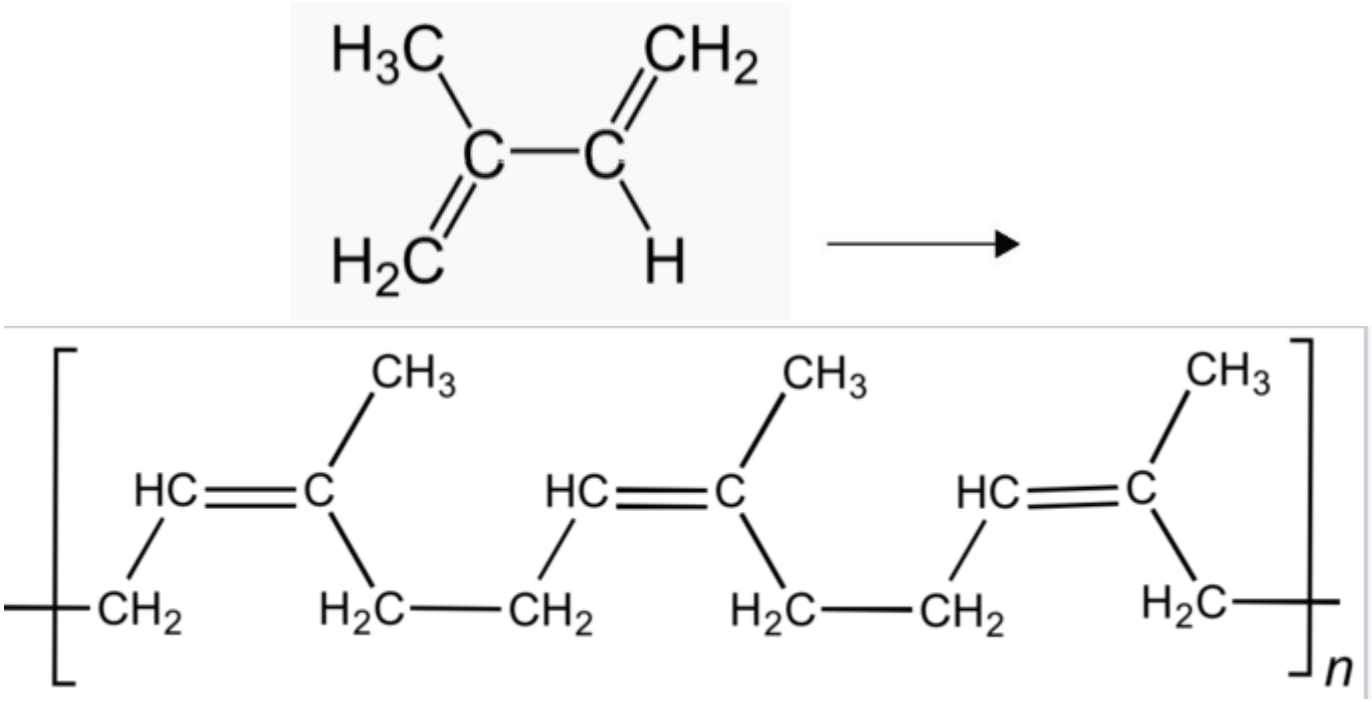
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10.4: Rubber and Other Elastomers

Learning Objectives

- Know the properties of rubber.
- Describe the process of vulcanization.

Natural rubber, also called **India rubber** or ***caoutchouc***, as initially produced, consists of polymers of the organic compound isoprene, with minor impurities of other organic compounds, plus water. Thailand and Indonesia are two of the leading rubber producers. Forms of polyisoprene that are used as natural rubbers are classified as elastomers.



Isoprene Polyisoprene (rubber)

Currently, rubber is harvested mainly in the form of the latex from the rubber tree or others. The latex is a sticky, milky colloid drawn off by making incisions in the bark and collecting the fluid in vessels in a process called "tapping". The latex then is refined into rubber ready for commercial processing. In major areas, latex is allowed to coagulate in the collection cup. The coagulated lumps are collected and processed into dry forms for marketing.

Natural rubber is used extensively in many applications and products, either alone or in combination with other materials. In most of its useful forms, it has a large stretch ratio and high resilience, and is extremely waterproof.

Vulcanization

In 1832–1834 Nathaniel Hayward and Friedrich Ludersdorf discovered that rubber treated with sulfur lost its stickiness. It is likely Hayward shared his discovery with Charles Goodyear, possibly inspiring him to make the discovery of vulcanization. Thomas Hancock (1786–1865), a scientist and engineer, was the first to patent vulcanization of rubber. He was awarded a British patent on May 21, 1845. Three weeks later, on June 15, 1845, Charles Goodyear was awarded a patent in the United States. It was Hancock's friend William Brockedon who coined term 'vulcanization'. Goodyear claimed that he had discovered vulcanization earlier, in 1839.

Sulfur vulcanization is a chemical process for converting natural rubber or related polymers into more durable materials by heating them with sulfur or other equivalent curatives or accelerators. Sulfur forms cross-links (bridges) between sections of polymer chain which results in increased rigidity and durability, as well as other changes in the mechanical and electronic properties of the material. A vast array of products are made with vulcanized rubber, including tires, shoe soles, hoses, and conveyor belts. The term *vulcanization* is derived from Vulcan, the Roman god of fire.

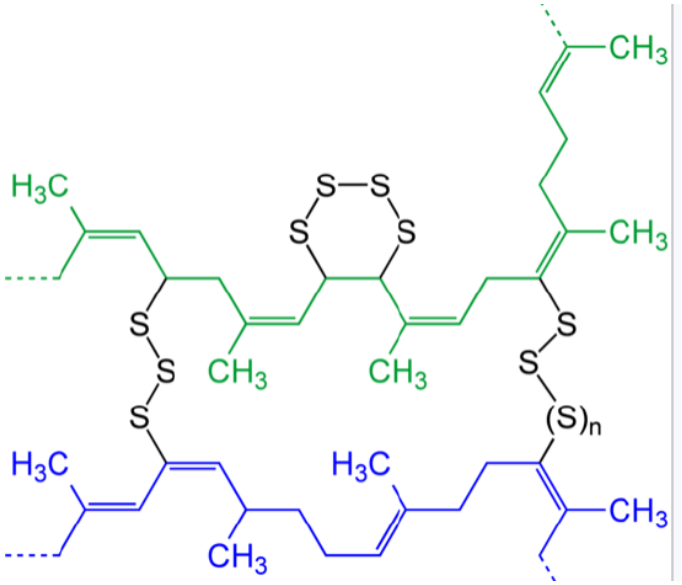


Figure \(\ **PageIndex*{1}*\)** General representation of the chemical structure of vulcanized natural rubber showing the crosslinking of two polymer chains (**blue** and **green**) with sulfur (n = 0, 1, 2, 3 ...).

Synthetic Rubber

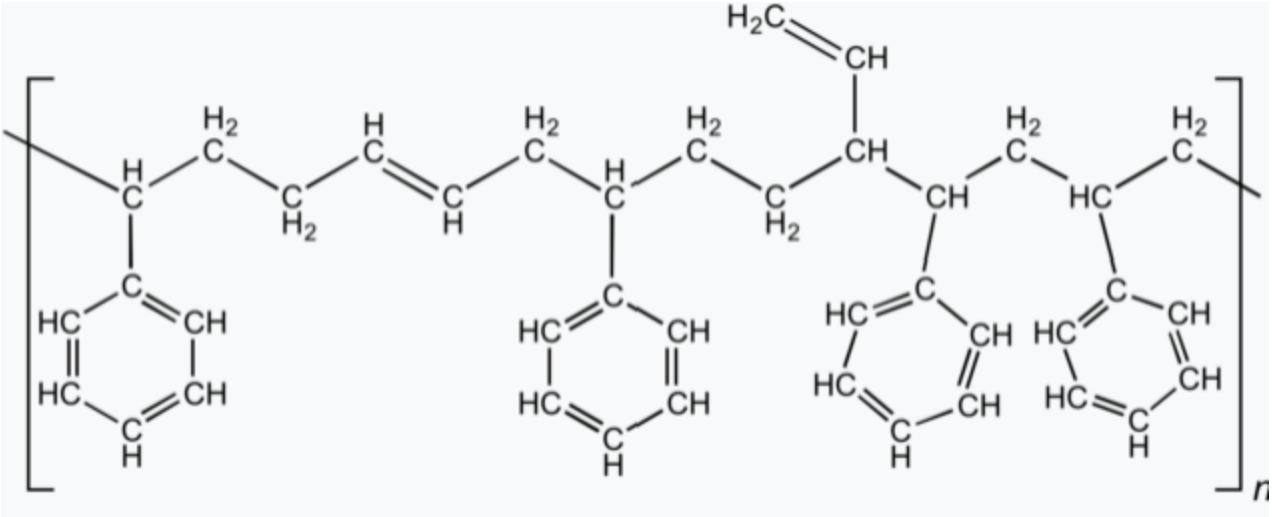
The expanded use of bicycles, and particularly their pneumatic tires, starting in the 1880s, created increased demand for rubber. In 1909 a team headed by Fritz Hofmann, working at the Bayer laboratory in Germany, succeeded in polymerizing isoprene, the first synthetic rubber. A synthetic rubber is any artifiical elastomer. These are mainly polymers synthesized from petroleum by products.

Polybutadiene rubber is a polymer formed from the polymerization of the monomer 1,3-butadiene. Polybutadiene has a high resistance to wear and is used especially in the manufacture of tires, which consumes about 70% of the production. Another 25% is used as an additive to improve the toughness (impact resistance) of plastics such as polystyrene and acrylonitrile butadiene styrene (ABS). Polybutadiene rubber accounted for about a quarter of total global consumption of synthetic rubbers in 2012. It is also used to manufacture golf balls, various elastic objects and to coat or encapsulate electronic assemblies, offering high electrical resistivity.

Neoprene (also **polychloroprene** or **pc-rubber**) is a family of synthetic rubbers that are produced by polymerization of chloroprene. Neoprene exhibits good chemical stability and maintains flexibility over a wide temperature range. Neoprene is sold either as solid rubber or in latex form and is used in a wide variety of applications, such as laptop sleeves, orthopaedic braces (wrist, knee, etc.), electrical insulation, liquid and sheet applied elastomeric membranes or flashings, and automotive fan belts.Neoprene is produced by free-radical polymerization of chloroprene. In commercial production, this polymer is prepared by free radical emulsion polymerization. Polymerization is initiated using potassium persulfate. Bifunctional nucleophiles, metal oxides (e.g. zinc oxide), and thioureas are used to crosslink individual polymer strands.

Free radical production of neoprene.png

Styrene-butadiene or **styrene-butadiene rubber** (**SBR**) describe families of synthetic rubbers derived from styrene and butadiene (the version developed by Goodyear is called **Neolite**). These materials have good abrasion resistance and good aging stability when protected by additives. In 2012, more than 5.4 million tonnes of SBR were processed worldwide. About 50% of car tires are made from various types of SBR.



It is a commodity material which competes with natural rubber. The elastomer is used widely in pneumatic tires. Other uses include shoe heels and soles, gaskets, and even chewing gum.

Polymers in Paints

Polymers are one of the key components of modern paints that function as binders. The binder is the film-forming component of paint. It is the only component that is always present among all the various types of formulations. The binder imparts properties such as gloss, durability, flexibility, and toughness. Binders include synthetic or natural resins such as alkyds, acrylics, vinyl-acrylics, vinyl acetate/ethylene (VAE), polyurethanes, polyesters, melamine resins, epoxy, or siloxanes or oils.

Summary

The many uses of natural rubber has led to development and manufacture of synthetic rubber.

Sulfur vulcanization is a chemical process for converting natural rubber or related polymers into more durable materials by heating them with sulfur or other equivalent curatives or accelerators.

Three examples of synthetic rubber used in various applications are polybutadiene, polychloroprene (Neoprene), and styrene-butadiene rubber (SBR)

Contributors and Attributions

Marisa Alviar-Agnew (Sacramento City College)

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10.5: Condensation Polymers

Learning Objectives

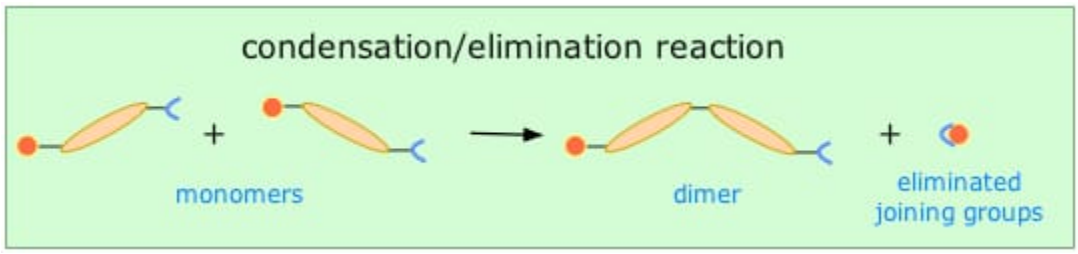
- Know the difference between addition and condensation polymerization.
- Know the properties and uses of common synthetic condensation polymers.

A large number of important and useful polymeric materials are not formed by addition polymerizaiton, but proceed instead by conventional functional group transformations of polyfunctional reactants. These polymerizations often (but not always) occur with loss of a small byproduct, such as water, and generally (but not always) combine two different components in an alternating structure. The polyester Dacron and the polyamide Nylon 66, shown here, are two examples of synthetic condensation polymers, also known as step-growth polymers. In contrast to addition polymerizaion, most of which grow by carbon-carbon bond formation, step-growth polymers generally grow by carbon-heteroatom bond formation (C-O & C-N in Dacron & Nylon respectively). Although polymers of this kind might be considered to be alternating copolymers, the repeating monomeric unit is usually defined as a combined moiety.

Examples of naturally occurring condensation polymers are cellulose, starch, the polypeptide chains of proteins, and poly(β-hydroxybutyric acid), a polyester synthesized in large quantity by certain soil and water bacteria.

Nylon and Other Polyamides

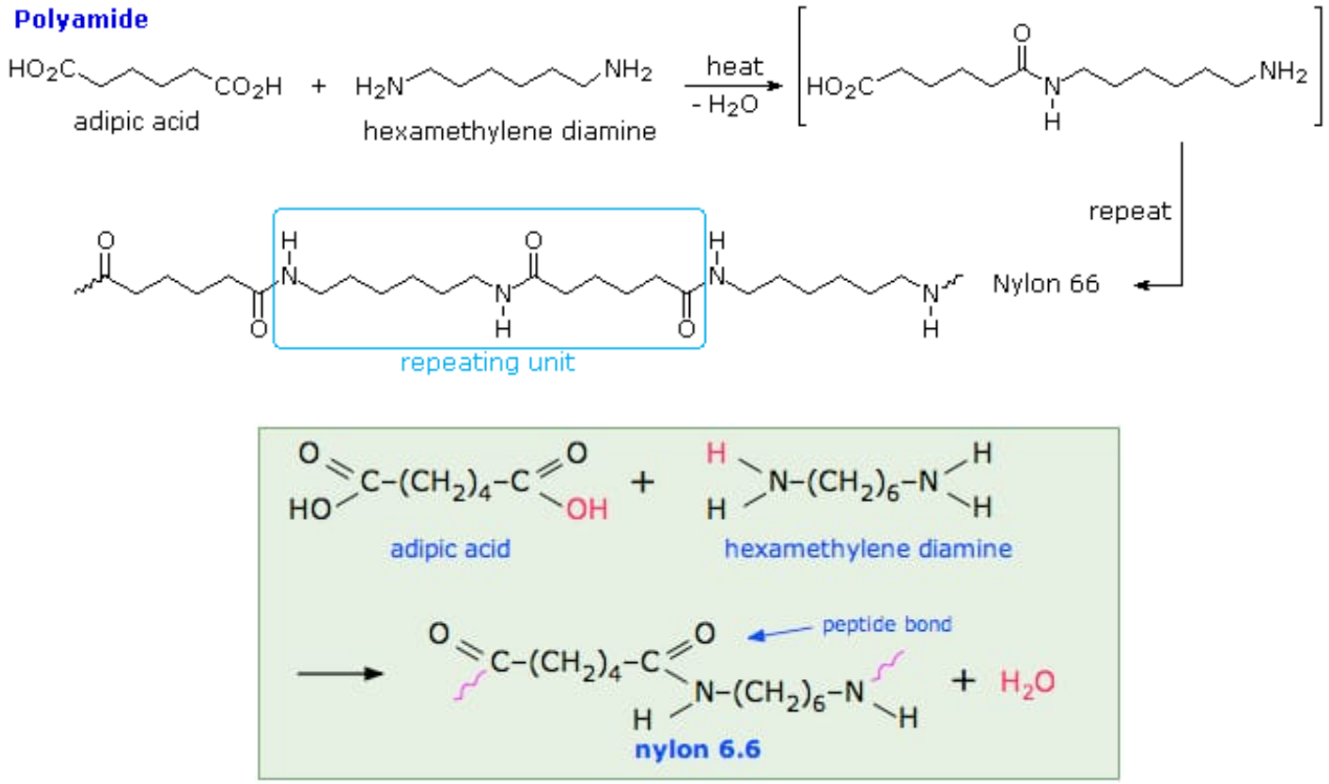
Condensation polymerization (also known as *step-growth*) requires that the monomers possess two or more kinds of functional groups that are able to react with each other in such a way that parts of these groups combine to form a small molecule (often H_2O) which is eliminated from the two pieces. The now-empty bonding positions on the two monomers can then join together .



One important class of condensation polymers are polyamides. They arise from the reaction of carboxylic acid and an amine. Examples include nylons and proteins.

When prepared from diamines and dicarboxylic acids, e.g. the production of nylon 66, the polymerization produces two molecules of water per repeat unit:

$$n\ H_2N\text{-}X\text{-}NH_2 + n\ HO_2C\text{-}Y\text{-}CO_2H \rightarrow [HN\text{-}X\text{-}NHC(O)\text{-}Y\text{-}C(O)]_n + 2n\ H_2O$$



Note that the monomeric units that make up the polymer are not identical with the starting components.

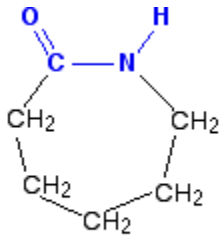
Nylon is a thermoplastic silky material that can be melt-processed into fibers, films, or shapes.[:2] It is made of repeating units linked by amide links similar to the peptide bonds in proteins. Nylon polymers can be mixed with a wide variety of additives to achieve many different property variations. Nylon polymers have found significant commercial applications in fabric and fibers (apparel, flooring and rubber reinforcement), in shapes (molded parts for cars, electrical equipment, etc.), and in films (mostly for food packaging).

Figure 10.5.1 Wallace H.Carothers

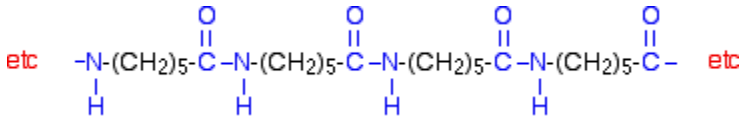
Nylon was the first commercially successful synthetic thermoplastic polymer. DuPont began its research project in 1927. The first example of nylon (nylon 6,6) was produced using diamines on February 28, 1935, by Wallace Hume Carothers (Figure 10.5.1) at DuPont's research facility at the DuPont Experimental Station. In response to Carothers' work, Paul Schlack at IG Farben developed nylon 6, a different molecule based on caprolactam, on January 29, 1938.[:10]

Nylon was first used commercially in a nylon-bristled toothbrush in 1938, followed more famously in women's stockings or "nylons" which were shown at the 1939 New York World's Fair and first sold commercially in 1940. During World War II, almost all nylon production was diverted to the military for use in parachutesand parachute cord. Wartime uses of nylon and other plastics greatly increased the market for the new materials.

Other polyamides of practical use include nylon 6 and kevlar. Nylon-6 is made from a monomer called caprolactam.



Notice that this already contains an amide link. When this molecule polymerizes, the ring opens, and the molecules join up in a continuous chain. Nylon 6 fibers are tough, possessing high tensile strength, as well as elasticity and lustre. They are wrinkleproof and highly resistant to abrasion and chemicals such as acids and alkalis. The fibers can absorb up to 2.4% of water, although this lowers tensile strength.



Kevlar is similar in structure to nylon-6,6 except that instead of the amide links joining chains of carbon atoms together, they join benzene rings. The two monomers are benzene-1,4-dicarboxylic acid and 1,4-diaminobenzene.

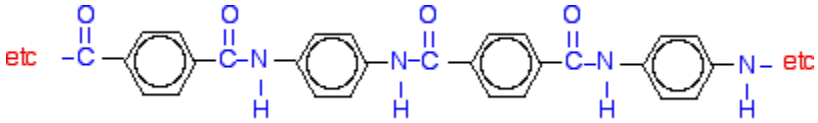


benzene-1,4-dicarboxylic acid



1,4-diaminobenzene

If you line these up and remove water between the -COOH and -NH_2 groups in the same way as we did with nylon-6,6, you get the structure of Kevlar:

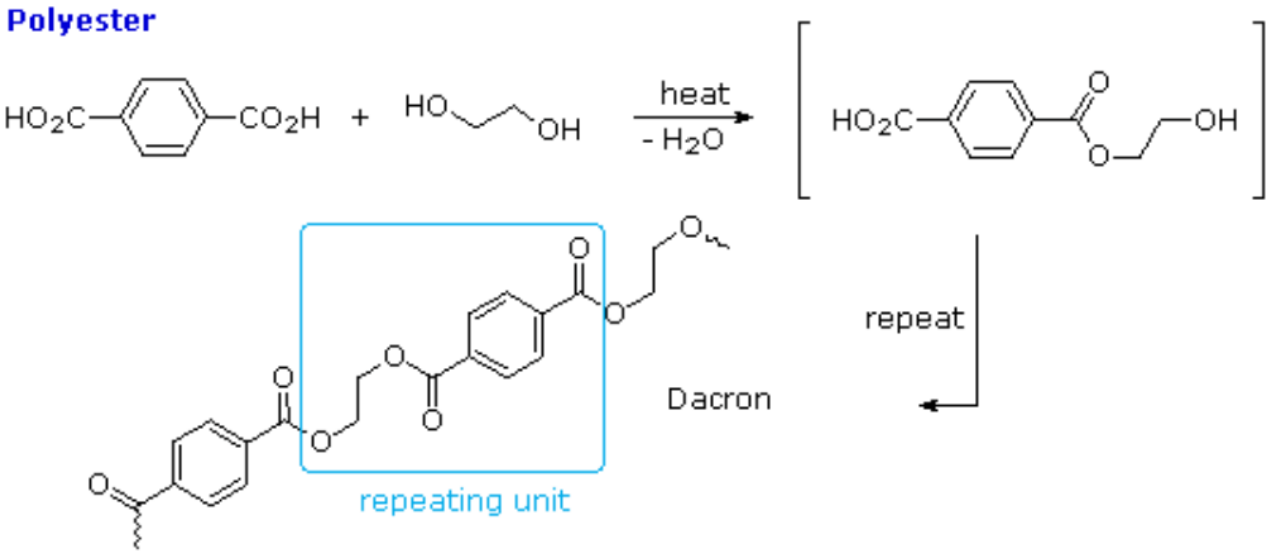


Kevlar is a very strong material - about five times as strong as steel, weight for weight. It is used in bulletproof vests, in composites for boat construction, in lightweight mountaineering ropes, and for lightweight skis and racquets - amongst many other things.

Polyethylene Terephthalate and Other Polyesters

One important class of condensation polymers are polyesters. They arise from the reaction of carboxylic acid and an alcohol. Examples include polyesters, e.g. polyethyleneterephthalate:

$$n\ HO\text{-}X\text{-}OH + n\ HO_2C\text{-}Y\text{-}CO_2H \rightarrow [O\text{-}X\text{-}O_2C\text{-}Y\text{-}C(O)]_n + (3n\text{-}2)\ H_2O$$



Polyethylene terephthalate (sometimes written poly(ethylene terephthalate)), commonly abbreviated **PET**, **PETE**, or the obsolete PETP or PET-P, is the most common thermoplastic polymer resin of the polyester family and is used in fibres for clothing, containers for liquids and foods, thermoforming for manufacturing, and in combination with glass fibre for engineering resins.

It may also be referred to by the brand names **Terylene** in the UK, **Lavsan** in Russia and the former Soviet Union, and **Dacron** in the US.

The majority of the world's PET production is for synthetic fibres (in excess of 60%), with bottle production accounting for about 30% of global demand. In the context of textile applications, PET is referred to by its common name, polyester, whereas the acronym *PET* is generally used in relation to packaging. Polyester makes up about 18% of world polymer production and is the fourth-most-produced polymer after polyethylene (PE), polypropylene (PP) and polyvinyl chloride (PVC).

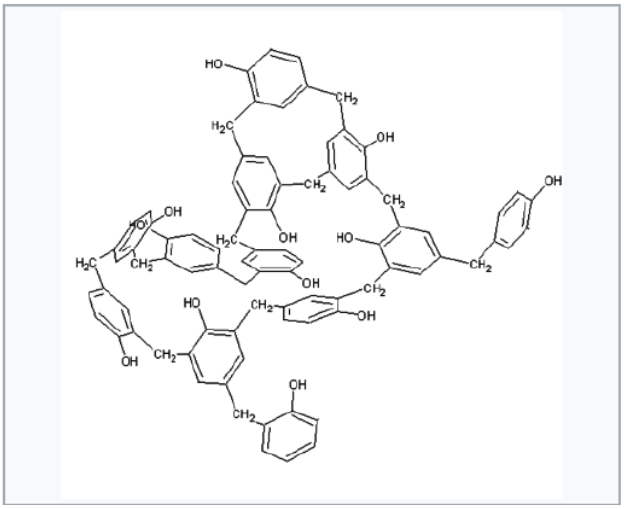
Phenol-Formaldehyde and Related Resins

Bakelite was patented on December 7, 1909. The creation of a synthetic plastic was revolutionary for its electrical nonconductivity and heat-resistant properties in electrical insulators, radio and telephone casings and such diverse products as kitchenware, jewelry, pipe stems, children's toys, and firearms.

In recent years the "retro" appeal of old Bakelite products has made them collectible.

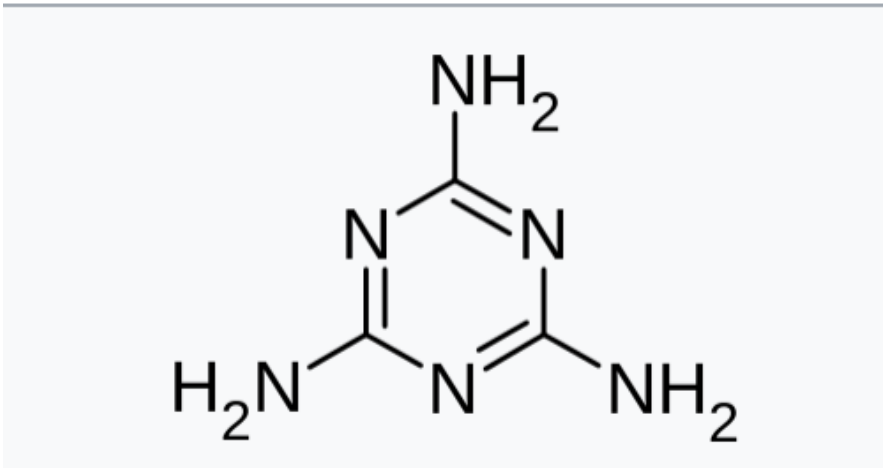
Bakelite was designated a National Historic Chemical Landmark on November 9, 1993, by the American Chemical Society in recognition of its significance as the world's first synthetic plastic.

Bakelite



Melamine /ˈmɛləmiːn/ (About this soundlisten) is an organic compound with the formula $C_3H_6N_6$. This white solid is a trimer of cyanamide, with a 1,3,5-triazine skeleton. Like cyanamide, it contains 67% nitrogen by mass, and its derivatives have fire retardant properties due to its release of nitrogen gas when burned or charred. Melamine can be combined with formaldehyde and other agents to produce melamine resins. Such resins are characteristically durable thermosetting plastic used in high pressure decorative laminates such as Formica, melamine dinnerware, laminate flooring, and dry erase boards. Melamine foam is used as insulation, soundproofing material and in polymeric cleaning products, such as Magic Eraser.

Melamine



Other Condensation Polymers

Polycarbonates (**PC**) are a group of thermoplastic polymers containing carbonate groups in their chemical structures. Polycarbonates used in engineering are strong, tough materials, and some grades are optically transparent. They are easily worked, molded, and thermoformed. Because of these properties, polycarbonates find many applications. Polycarbonates received their name because they are polymers containing carbonate groups (–O–(C=O)–O–). A balance of useful features, including temperature resistance, impact resistance and optical properties, positions polycarbonates between commodity plastics and engineering plastics.

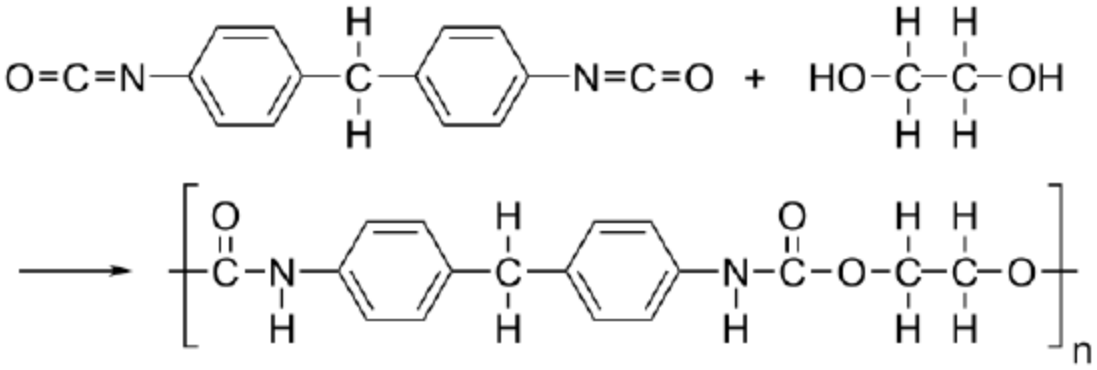
The main polycarbonate material is produced by the reaction of bisphenol A (BPA) and phosgene $COCl_2$. The overall reaction can be written as follows:

Polycarbonatsynthese.svg

Polycarbonate is mainly used for electronic applications that capitalize on its collective safety features. Being a good electrical insulator and having heat-resistant and flame-retardant properties. The second largest consumer of polycarbonates is the construction industry, e.g. for domelights, flat or curved glazing, and sound walls, which all use extruded flat solid or multiwall sheet, or corrugated sheet. A major application of polycarbonate is the production of Compact Discs, DVDs, and Blu-ray Discs.

Polyurethane (**PUR** and **PU**) is a polymer composed of organic units joined by carbamate (urethane) links. While most polyurethanes are thermosetting polymers that do not melt when heated, thermoplastic polyurethanes are also available.

Polyurethanes are in the class of compounds called **reaction polymers**, which include epoxies, unsaturated polyesters, and phenolics. Polyurethanes are produced by reacting an isocyanate containing two or more isocyanate groups per molecule ($R–(N=C=O)_n$) with a polyol containing on average two or more hydroxyl groups per molecule ($R'–(OH)_n$) in the presence of a catalyst or by activation with ultraviolet light.



Polyurethanes are used in the manufacture of high-resilience foam seating, rigid foam insulation panels, microcellular foam seals and gaskets, durable elastomeric wheels and tires (such as roller coaster, escalator, shopping cart, elevator, and skateboard wheels), automotive suspension bushings, electrical potting compounds, high performance adhesives, surface coatings and surface sealants, synthetic fibers (e.g., Spandex), carpet underlay, hard-plastic parts (e.g., for electronic instruments), condoms, and hoses.

Figure 10.5.2 A polyurethane foam sponge.

Health and Safety

Fully reacted polyurethane polymer is chemically inert. No exposure limits have been established in the U.S. by OSHA (Occupational Safety and Health Administration) or ACGIH (American Conference of Governmental Industrial Hygienists). It is not regulated by OSHA for carcinogenicity.

Figure 10.5.3 *Open-flame test. Top, untreated polyurethane foam burns vigorously. Bottom, with fire-retardant treatment.*

Polyurethane polymer is a combustible solid and can be ignited if exposed to an open flame. Decomposition from fire can produce significant amounts of carbon monoxide and hydrogen cyanide, in addition to nitrogen oxides, isocyanates, and other toxic products.Because of the flammability of the material, it has to be treated with flame retardants (at least in case of furniture), almost all of which are considered harmful. California later issued Technical Bulletin 117 2013 which allowed most polyurethane foam to pass flammability tests without the use of flame retardants. Green Science Policy Institute states: "Although the new standard can be met without flame retardants, it does NOT ban their use. Consumers who wish to reduce household exposure to flame retardants can look for a TB117-2013 tag on furniture, and verify with retailers that products do not contain flame retardants."

Liquid resin blends and isocyanates may contain hazardous or regulated components. Isocyanates are known skin and respiratory sensitizers. Additionally, amines, glycols, and phosphate present in spray polyurethane foams present risks.

Exposure to chemicals that may be emitted during or after application of polyurethane spray foam (such as isocyanates) are harmful to human health and therefore special precautions are required during and after this process.

In the United States, additional health and safety information can be found through organizations such as the Polyurethane Manufacturers Association (PMA) and the Center for the Polyurethanes Industry (CPI), as well as from polyurethane system and raw material manufacturers. Regulatory information can be found in the Code of Federal Regulations Title 21 (Food and Drugs) and Title 40 (Protection of the Environment). In Europe, health and safety information is available from ISOPA, the European Diisocyanate and Polyol Producers Association.

Epoxy is either any of the basic components or the cured end products of **epoxy resins**, as well as a colloquial name for the epoxide functional group. Epoxy resins, also known as **polyepoxides**, are a class of reactive prepolymers and polymers which contain epoxide groups.

Epoxy resins may be reacted (cross-linked) either with themselves through catalytic homopolymerisation, or with a wide range of co-reactants including polyfunctional amines, acids (and acid anhydrides), phenols, alcohols and thiols (usually called mercaptans). These co-reactants are often referred to as hardeners or curatives, and the cross-linking reaction is commonly

referred to as curing. The structure of bisphenol-A diglycidyl ether epoxy resin is shown below: *n* denotes the number of polymerized subunits and is typically in the range from 0 to 25

Figure 10.5.4 *Bisphenol-A diglycidyl ether epoxy.*

Reaction of polyepoxides with themselves or with polyfunctional hardeners forms a thermosetting polymer, often with favorable mechanical properties and high thermal and chemical resistance. Epoxy has a wide range of applications, including metal coatings, use in electronics/electrical components/LEDs, high tension electrical insulators, paint brush manufacturing, fiber-reinforced plastic materials and structural adhesives. Epoxy is sometimes used as a glue (see image at right).

Figure 10.5.5 A 5-minute epoxy glue.

Composite Materials

A **composite material** (also called a **composition material** or shortened to **composite,** which is the common name) is a material made from two or more constituent materials with significantly different physical or chemical properties that, when combined, produce a material with characteristics different from the individual components. Composite materials are generally used for buildings, bridges, and structures such as boat hulls, swimming pool panels, racing car bodies, shower stalls, bathtubs, storage tanks, imitation granite and cultured marble sinks and countertops.

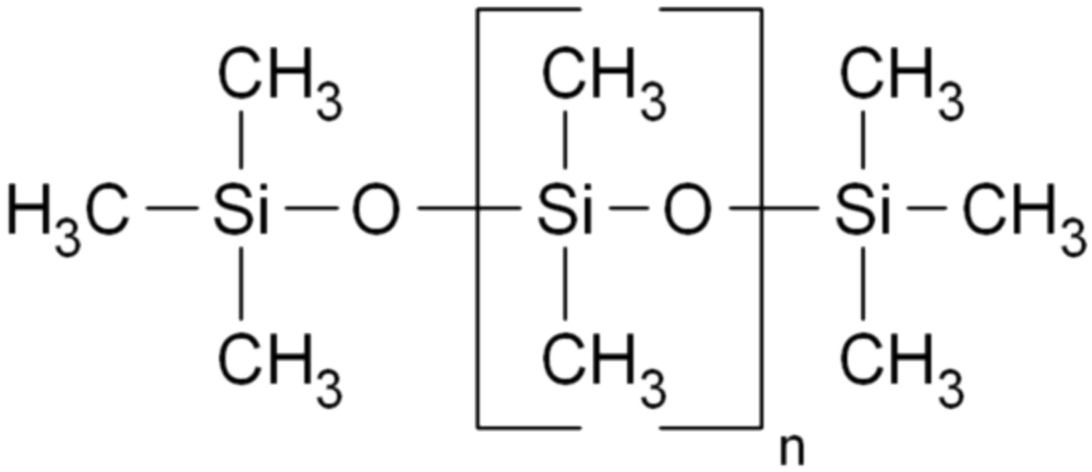
Composites are made up of individual materials referred to as constituent materials. There are two main categories of constituent materials: **matrix** (binder) and **reinforcement**. At least one portion of each type is required. The matrix material surrounds and supports the reinforcement materials by maintaining their relative positions. The reinforcements impart their special mechanical and physical properties to enhance the matrix properties. A synergism produces material properties unavailable from the individual constituent materials, while the wide variety of matrix and strengthening materials allows the designer of the product or structure to choose an optimum combination. Many commercially produced composites use a polymer matrix material often called a resin solution. There are many different polymers available depending upon the starting raw ingredients. There are several broad categories, each with numerous variations. The most common are known as polyester, vinyl ester, epoxy, phenolic, polyimide, polyamide, polypropylene, PEEK (polyether ether ketone), and others. Common fibres used for reinforcement include glass fibres, carbon fibres, cellulose (wood/paper fibre and straw) and high strength polymers for example aramid. Silicon carbide fibers are used for some high temperature applications.

One of the most common and familiar composite is fibreglass, in which small glass fibre are embedded within a polymeric material (normally an epoxy or polyester). The glass e is relatively strong and stiff (but also brittle), whereas the polymer is ductile (but also weak and flexible). Thus the resulting fibreglass is relatively stiff, strong, flexible, and ductile.

Figure 10.5.6 *Glass reinforcements used for fiberglass are supplied in different physical forms, microspheres, chopped or woven.*

Silicones

Silicones, also known as **polysiloxanes**, are polymers that include any synthetic compound made up of repeating units of siloxane. Silicones consist of an inorganic silicon-oxygen backbone chain (···–Si–O–Si–O–Si–O–···) with organic side groups attached to the silicon atoms. Silicones have in general the chemical formula $[R_2SiO]_n$, where R is an organic group such as an alkyl (methyl, ethyl) or phenyl group. A silicone polymer tha consist of repeated units of dimethyl silicone is shown below.



They are typically heat-resistant and either liquid or rubber-like. Silicones are used in many products. Ullmann's Encyclopedia of Industrial Chemistry lists the following major categories of application: Electrical (e.g., insulation), electronics (e.g., coatings), household (e.g., sealants and cooking utensils), automobile (e.g., gaskets), aeroplane (e.g., seals), office machines (e.g., keyboard pads), medicine and dentistry (e.g., tooth impression molds), textiles and paper (e.g., coatings). For these applications, an estimated 400,000 tonnes of silicones were produced in 1991.

Figure 10.5.7 *Soup ladle and pasta ladle made of silicone.*

Silicone vs Silicon

Silicone is often confused with silicon, but they are distinct substances. Silicon is a chemical element, a hard dark-grey semiconducting metalloid which in its crystalline form is used to make integrated circuits ("electronic chips") and solar cells. Silicones are compounds that contain silicon, carbon, hydrogen, oxygen, and perhaps other kinds of atoms as well, and have very different physical and chemical properties.

Summary

- Condensation polymerization (also known as *step-growth*) requires that the monomers possess two or more kinds of functional groups that are able to react with each other in such a way that parts of these groups combine to form a small molecule (often H_2O) which is eliminated from the two pieces. The now-empty bonding positions on the two monomers can then join together .
- Examples of natural condensation polymers include cellulose, starch, and polypeptide chains of proteins.
- Several synthetic condensation polymers discussed include nylon, kevlar, polyester, Bakelite, Melamine, polycarbonates, polyurethanes, epoxies.
- Synthetic condensation polymers have a wide array of household, industrial, commercial, and medical uses and applications.

Contributors and Attributions

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10.6: Properties of Polymers

Learning Objectives

- Know the properties of polymers based on their molecular and intermolecular structures.
- Know the relationship between degree of crystallinity to physical properties of polymers.

The physical properties of a polymer such as its strength and flexibility depend on:

- *chain length* - in general, the longer the chains the stronger the polymer;
- *side groups* - polar side groups (including those that lead to hydrogen bonding) give stronger attraction between polymer chains, making the polymer stronger;
- *branching* - straight, unbranched chains can pack together more closely than highly branched chains, giving polymers that have higher density, are more crystalline and therefore stronger;
- *cross-linking* - if polymer chains are linked together extensively by covalent bonds, the polymer is harder and more difficult to melt.

Crystalline and Amorphous Polymers

When applied to polymers, the term *crystalline* has a somewhat ambiguous usage. A synthetic polymer may be loosely described as crystalline if it contains regions of three-dimensional ordering on atomic (rather than macromolecular) length scales, usually arising from intramolecular folding and/or stacking of adjacent chains. Synthetic polymers may consist of both crystalline and amorphous regions; the degree of crystallinity may be expressed in terms of a weight fraction or volume fraction of crystalline material. Few synthetic polymers are entirely crystalline. The crystallinity of polymers is characterized by their degree of crystallinity, ranging from zero for a completely non-crystalline polymer to one for a theoretical completely crystalline polymer. Polymers with microcrystalline regions are generally tougher (can be bent more without breaking) and more impact-resistant than totally amorphous polymers.Polymers with a degree of crystallinity approaching zero or one will tend to be transparent, while polymers with intermediate degrees of crystallinity will tend to be opaque due to light scattering by crystalline or glassy regions. For many polymers, reduced crystallinity may also be associated with increased transparency.

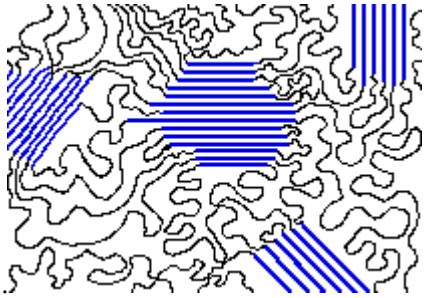


Figure 10.6.1 *The crystalline parts of this polymer are shown in blue.*

Depending on the degree of crystallinity, there will be a higher temperature, the *melting point* t_m , at which the crystalline regions come apart and the material becomes a viscous liquid. Such liquids can easily be injected into molds to manufacture objects of various shapes, or extruded into sheets or fibers. Other polymers (generally those that are highly cross-linked) do not melt at all; these are known as *thermosets*. If they are to be made into molded objects, the polymerization reaction must take place within the molds — a far more complicated process. About 20% of the commercially-produced polymers are thermosets; the remainder are thermoplastics.

The Glass Transition Temperature

In some polymers (known as *thermoplastics*) there is a fairly definite softening point that is observed when the thermal kinetic

energy becomes high enough to allow internal rotation to occur within the bonds and to allow the individual molecules to slide independently of their neighbors, thus rendering them more flexible and deformable. This defines the *glass transition temperature* t_g . Hard plastics like polystyrene and poly(methyl methacrylate) are used well below their glass transition temperatures, i.e., when they are in their glassy state. Their T_g values are well above room temperature, both at around 100 °C (212 °F). Rubber elastomers like polyisoprene and polyisobutylene are used above their T_g, that is, in the rubbery state, where they are soft and flexible.

Fiber Formation

Bill Pittendreigh, DuPont, and other individuals and corporations worked diligently during the first few months of World War II to find a way to replace Asian silk and hemp with nylon in parachutes. It was also used to make tires, tents, ropes, ponchos, and other military supplies. It was even used in the production of a high-grade paper for U.S. currency. At the outset of the war, cotton accounted for more than 80% of all fibers used and manufactured, and wool fibers accounted for nearly all of the rest. By August 1945, manufactured fibers had taken a market share of 25%, at the expense of n. After the war, e of shortages of both silk and nylon, nylon parachute material was sometimes repurposed to make dresses.Nylon 6 and 66 fibers are used in carpet manufacture. Nylon is one kind of fibers used in tire cord. Herman E. Schroeder pioneered application of nylon in tires.

Figure 10.6.2 Blue nylon fabric ball gown *by Emma Domb, Science History Institute.*

Fabrics woven or knitted from polyester thread or yarn are used extensively in apparel and home furnishings, from shirts and pants to jackets and hats, bed sheets, blankets, upholstered ure and computer mouse mats. Industrial polyester fibers, yarns and ropes are used in car tire reinforcements, fabrics for conveyor belts, safety belts, coated fabrics and plastic reinforcements with high-energy absorption. Polyester fiber is used as cushioning and insulating material in pillows, comforters and upholstery padding. Polyester fabrics are highly stain-resistant—in fact, the only class of dyes which *can* be used to alter the color of polyester fabric are what are known as disperse dyes.

Figure 10.6.3 *Stretching polyester fabric.*

Acrylic fibers are synthetic fibers made from a polymer (polyacrylonitrile) with an average molecular weight of ~100,000, about 1900 monomer units. For a fiber to be called "acrylic" in the US, the polymer must contain at least 85% acrylonitrile monomer. Typical comonomers are vinyl acetate or methyl acrylate. DuPont created the first acrylic fibers in 1941 and trademarked them under the name **Orlon**. It was first developed in the mid-1940s but was not produced in large quantities until the 1950s. Strong and warm, acrylic fiber is often used for sweaters and tracksuits and as linings for boots and gloves, as well as in furnishing fabrics and carpets. It is manufactured as a filament, then cut into short staple lengths similar to wool hairs, and spun into yarn.

Modacrylic is a modified acrylic fiber that contains at least 35% and at most 85% acrylonitrile monomer. The comonomers vinyl chloride, vinylidene chloride or vinyl bromide used in modacrylic give the fiber flame retardant properties. End-uses of modacrylic include faux fur, wigs, hair extensions and protective clothing.

Microfiber (or **microfibre**) is synthetic fiber finer than one denier or decitex/thread, having a diameter of less than ten micrometres. This is smaller than the diameter of a strand of silk (which is approximately one denier), which is itself about 1/5 the diameter of a human hair.

Figure 10.6.4 *Close-up view of microfiber (left) and microfiber household cloth (right).*

The most common types of microfibers are made from polyesters, polyamides (e.g., nylon, Kevlar, Nomex, trogamide), or a conjugation of polyester, polyamide, and polypropylene. Microfiber is used to make mats, knits, and weaves for apparel, upholstery, industrial filters, and cleaning products. The shape, size, and combinations of synthetic fibers are selected for specific characteristics, including softness, toughness, absorption, water repellency, electrostatics, and filtering capabilities.

Environmental and Safety Issues

Microfiber textiles tend to be flammable if manufactured from hydrocarbons (polyester) or carbohydrates (cellulose) and emit toxic gases when burning, more so if aromatic (PET, PS, ABS) or treated with halogenatedflame retardants and azo dyes. Their polyester and nylon stock are made from petrochemicals, which are not a renewable resource and are not biodegradable. However, if made out of polypropylene, they are recyclable (Prolen).

For most cleaning applications they are designed for repeated use rather than being discarded after use. An exception to this is the precise cleaning of optical components where a wet cloth is drawn once across the object and must not be used again as the debris collected are now embedded in the cloth and may scratch the optical surface.

Microfiber that is made from petrochemicals includes polyester and nylon which are not biodegradable. However, microfiber made from polypropylene can be recyclable. Microfiber products may also have the potential of entering the oceanic water supply and food chain similar to other microplastics. Synthetic clothing made of microfibers that are washed can release materials and travel to local wastewater treatment plants, contributing to plastic pollution in water. Fibers retained in wastewater treatment sludge (biosolids) that are land-applied can persist in soils.

There are environmental concerns about this product entering the oceanic food chain similar to other microplastics. A study by the clothing brand Patagonia and University of California, Santa Barbara, found that when synthetic jackets made of microfibers are washed, on average 1.7 grams (0.060 oz) of microfibers are released from the washing machine. These microfibers then travel to local wastewater treatment plants, where up to 40% of them enter into rivers, lakes, and oceans where they contribute to the overall plastic pollution. Microfibers account for 85% of man-made debris found on shorelines worldwide.

However, no pesticides are used for producing synthetic fibers (in comparison to cotton). If these products are made of polypropylene yarn, the yarn is dope-dyed; i.e. no water is used for dyeing (as with cotton, where thousands of liters of water become contaminated).

Summary

- The physical properties of a polymer such as its strength and flexibility depend on chain length, side groups present, branching, and cross-linking.
- Synthetic polymers may consist of both crystalline (more ordered, crystal-like) and amorphous (less ordered) regions; the degree of crystallinity may be expressed in terms of a weight fraction or volume fraction of crystalline material.
- The crystallinity of polymers is characterized by their degree of crystallinity, ranging from zero for a completely non-crystalline polymer to one for a theoretical completely crystalline polymer. Polymers with microcrystalline regions are generally tougher (can be bent more without breaking) and more impact-resistant than totally amorphous polymers.
- Due to their chemical structure, nylon, polyester, and acrylic fibers have physical properties that are comparable or even superior to natural fibers Thus, many of these fibers have a variety of uses and have replaced natural fibers in various products.

Contributors and Attributions

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10.7: Plastics and the Environment

Learning Objectives

- Know the problems associated with plastics.
- Identify the type of polymer associated with each recycling number.
- Know the different plastic recycling processes.

Problems with Plastics

Due to their low cost, ease of manufacture, versatility, and imperviousness to water, plastics are used in a multitude of products of different scale, including paper clips and spacecraft. They have prevailed over traditional materials, such as wood, stone, horn and bone, leather, metal, glass, and ceramic, in some products previously left to natural materials. However, there are numerous problems encountered with plastic use.

Small-molecule release

Many kinds of polymers contain small molecules — either unreacted monomers, or substances specifically added (plasticizers, uv absorbers, flame retardants, etc.) to modify their properties. Many of these smaller molecules are able to diffuse through the material and be released into any liquid or air in contact with the plastic — and eventually into the aquatic environment. Those that are used for building materials (in mobile homes, for example) can build up in closed environments and contribute to indoor air pollution.

Residual monomer

Formation of long polymer chains is a complicated and somewhat random process that is never perfectly stoichiometric. It is therefore not uncommon for some unreacted monomer to remain in the finished product. Some of these monomers, such as formaldehyde, styrene (from polystyrene, including polystyrene foam food take-out containers), vinyl chloride, and bisphenol-A (from polycarbonates) are known carcinogens. Although there is little evidence that the small quantities that diffuse into the air or leach out into fluids pose a quantifiable health risk, people are understandably reluctant to tolerate these exposures, and public policy is gradually beginning to regulate them.

Perfluorooctanoic acid (PFOA), the monomer from which Teflon is made, has been the subject of a 2004 lawsuit against a DuPont factory that contaminated groundwater. Small amounts of PFOA have been detected in gaseous emissions from hot fluorocarbon products.

Decomposition products

Most commonly-used polymers are not readily biodegradable, particularly under the anaerobic conditions of most landfills. And what decomposition does occur will combine with rainwater to form *leachates* that can contaminate nearby streams and groundwater supplies. Partial photodecomposition, initiated by exposure to sunlight, is a more likely long-term fate for exposed plastics, resulting in tiny broken-up fragments. Many of these materials are less dense than seawater, and once they enter the oceans through coastal sewage outfalls or from marine vessel wastes, they tend to remain there indefinitely.

Open burning of polymeric materials containing chlorine (polyvinyl chloride, for example) is known to release compounds such as dioxins that persist in the environment. Incineration under the right conditions can effectively eliminate this hazard. Disposed products containing **fluorocarbons** (Teflon-coated ware, some personal-care, waterproofing and anti-stick materials) break down into perfluorooctane sulfonate which has been shown to damage aquatic animals.

Hazards to animals

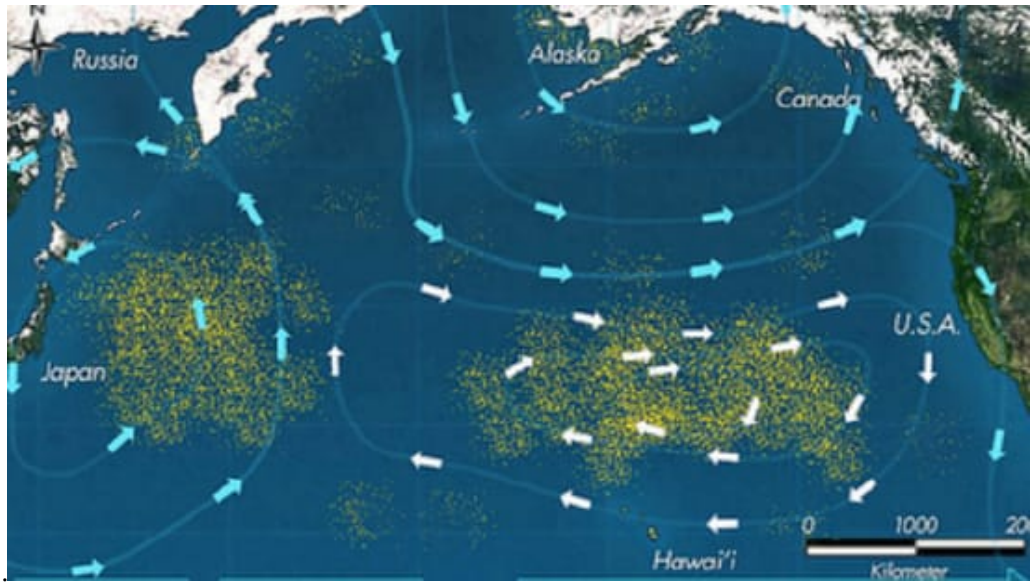
There are two general types of hazards that polymers can introduce into the aquatic environment. One of these relates to the release of small molecules that act as hormone disrupters as described above. It is well established that small aquatic animals such as fish are being seriously affected by such substances in many rivers and estuarine systems, but details of the sources and identities of these molecules have not been identified. One confounding factor is the release of sewage water containing human birth-control drugs (which have a feminizing effect on sexual development) into many waterways.

The other hazard relates to pieces of plastic waste that aquatic animals mistake for food or become entangled in (Figure 10.7.1) .



Figure 10.7.1 A p*lastic bag (probably mistaken for a jellyfish, the sea turtle's only food) cannot be regurgitated and leads to intestinal blockage and a slow death (left) remains of an albatross that mistook bits of plastic junk for food (right).*

These dangers occur throughout the ocean, but are greatly accentuated in regions known as gyres. These are regions of the ocean in which a combination of ocean currents drives permanent vortices that tend to collect and concentrate floating materials. The most notorious of these are the Great Pacific Gyres that have accumulated astounding quantities of plastic waste.



Recycling

The huge quantity (one estimate is 10^8 metric tons per year) of plastic materials produced for consumer and industrial use has created a gigantic problem of what to do with plastic waste which is difficult to incinerate safely and which, being largely non-biodegradable, threatens to overwhelm the capacity of landfills. An additional consideration is that *de novo* production most of the major polymers consumes non-renewable hydrocarbon resources.



Figure 10.7.2 Plastic water bottles present a special recycling problem because of their widespread use in away-from-home locations.

Plastics recycling has become a major industry, greatly aided by enlightened trash management policies in the major developed nations. However, it is plagued with some special problems of its own:

- Recycling is only profitable when there is a market for the regenerated material. Such markets vary with the economic cycle (they practically disappeared during the recession that commenced in 2008.)
- The energy-related costs of collecting and transporting plastic waste, and especially of processing it for re-use, are frequently the deciding factor in assessing the practicability of recycling.
- Collection of plastic wastes from diverse sources and locations and their transport to processing centers consumes energy and presents numerous operational problems.
- Most recycling processes are optimized for particular classes of polymers. The diversity of plastic types necessitates their

separation into different waste streams — usually requiring manual (i.e., low-cost) labor. This in turn encourages shipment of these wastes to low-wage countries, thus reducing the availability of recycled materials in the countries in which the plastics originated.

Some of the major recycling processes include

- Thermal decomposition processes that can accommodate mixed kinds of plastics and render them into fuel oil, but the large inputs of energy they require have been a problem.
- A very small number of condensation polymers can be depolymerized so that the monomers can be recovered and re-used.
- Thermopolymers can be melted and pelletized, but those of widely differing types must be treated separately to avoid incompatability problems.
- Thermosets are usually shredded and used as filler material in recycled thermopolymers.

Other processes

A process has also been developed in which many kinds of plastic can be used as a carbon source in the recycling of

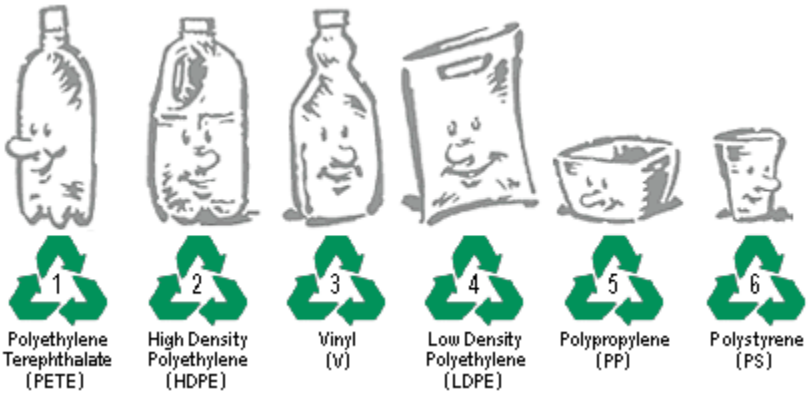
scrap steel. There is also a possibility of mixed recycling of different plastics, which does not require their separation. It is called compatibilization and requires use of special chemical bridging agents compatibilizers. It can help to keep the quality of recycled material and to skip often expensive and inefficient preliminary scanning of waste plastics streams and their separation/purification.

Figure 10.7.3 *Plastic or other polymer compatibilization.*

Recycled Plastics

Seven groups of plastic polymers, each with specific properties, are used worldwide for packaging applications (see Table 10.7.1). Each group of plastic polymer can be identified by its plastic identification code (PIC), usually a number or a letter abbreviation. For instance, low-density polyethylene can be identified by the number "4" or the letters "LDPE". The PIC appears inside a three-chasing-arrow recycling symbol. The symbol is used to indicate whether the plastic can be recycled into new products.

The PIC was introduced by the Society of the Plastics Industry, Inc., to provide a uniform system for the identification of various polymer types and to help recycling companies separate various plastics for reprocessing. Manufacturers of plastic products are required to use PIC labels in some countries/regions and can voluntarily mark their products with the PIC where there are no requirements. Consumers can identify the plastic types based on the codes usually found at the base or at the side of the plastic products, including food/chemical packaging and containers.



Not all categories are accepted by all local recycling authorities, so residents need to be informed about which kinds should be placed in recycling containers and which should be combined with ordinary trash.

Table 10.7.1 *The Major Groups of Plastic Polymers. Source: Wikipedia*

Plastic identification code	Type of plastic polymer	Properties	Common packaging applications	Melting temperatures (°C)

Symbol Resin Code 01 PET.svg	Polyethylene terephthalate(PET, PETE)	Clarity, strength, toughness, barrier to gas and moisture.	Soft drink, water and salad dressing bottles; peanut butter and jam jars; ice cream cone lids; small consumer electronics	Tm = 250
Symbol Resin Code 02 PE-HD.svg	High-density polyethylene(HDPE)	Stiffness, strength, toughness, resistance to moisture, permeability to gas	Water pipes, Gas & Fire Pipelines, Electrical & Communications conduit, hula hoop rings, five gallon buckets, milk, juice and water bottles; grocery bags, some shampoo/toiletry bottles	Tm = 130
Symbol Resin Code 03 PVC.svg	Polyvinyl chloride(PVC)	Versatility, ease of blending, strength, toughness.	Blister packaging for non-food items; cling films for non-food use. May be used for food packaging with the addition of the plasticisers needed to make natively rigid PVC flexible. Non-packaging uses are electrical cable insulation; rigid piping; vinyl records.	Tm = 240
Symbol Resin Code 04 PE-LD.svg	Low-density polyethylene(LDPE)	Ease of processing, strength, toughness, flexibility, ease of sealing, barrier to moisture	Frozen food bags; squeezable bottles, e.g. honey, mustard; cling films; flexible container lids	Tm = 120
Symbol Resin Code 05 PP.svg	Polypropylene(PP)	Strength, toughness, resistance to heat, chemicals, grease and oil, versatile, barrier to moisture.	Reusable microwaveable ware; kitchenware; yogurt containers; margarine tubs; microwaveable disposable take-away containers; disposable cups; soft drink bottle caps; plates.	Tm = 173
Symbol Resin Code 06 PS.svg	Polystyrene(PS)	Versatility, clarity, easily formed	Egg cartons; packing peanuts; disposable cups, plates, trays and cutlery; disposable take-away containers	Tm = 240
Symbol Resin Code 07 O.svg	Other (often polycarbonateor ABS)	Dependent on polymers or combination of polymers	Beverage bottles, baby milk bottles. Non-packaging uses for polycarbonate, compact discs, "unbreakable" glazing, electronic apparatus housing, lenses (including sunglasses), prescription glasses, automotive headlamps, riot shields, instrument panels.	Polycarbonate: Tm = 225

Tire Recycling

The large number of rubber tires that are disposed of, together with the increasing reluctance of landfills to accept them, has stimulated considerable innovation in the re-use of this material, especially in the construction industry.

Plastics and Fire Hazards

The term *fire (or flame)-retardant* as applied to organic (i.e., containing carbon) materials, is intended to refer to *reduced* fire hazard, as all will burn under certain circumstances. Fabric flammability is an important textile issue, especially for stage drapery that will be used in a public space such as a school, theatre or special event venue. In the United States, Federal regulations require that drapery fabrics used in such spaces be certified as flame or fire-retardant. For draperies and other fabrics used in public places, this is known as the NFPA 701 Test, which follows standards developed by the National Fire Protection Association (NFPA). Although all fabrics will burn, some are naturally more resistant to fire than others. Those that are more flammable can have their fire resistance drastically improved by treatment with fire-retardant chemicals. Inherently flame-retardant fabrics such as polyester are commonly used for flame retardant curtain fabrics.

The deaths in fiery crashes of race car drivers Fireball Roberts at Charlotte, and Eddie Sachs and Dave MacDonald at Indianapolis in 1964 led to the use of flame-resistant ics such as Nomex. Nomex and related aramid polymers are related to nylon, but have aromatic backbones, and hence are more rigid and more durable. Nomex is an example of a *meta* variant of the aramids (Kevlar is a *para* aramid). Unlike Kevlar, Nomex strands cannot align during filament polymerization and has less strength. However, it has excellent thermal, chemical, and radiation resistance for a polymer material.

A Nomex hood is a common piece of racing and firefighting equipment. It is placed on the head on top of a firefighter's face mask. The hood protects the portions of the head not covered by the helmet and face mask from the intense heat of the fire.

Figure 10.7.4 A firefighter in Toronto, Canada wears a Nomex hood in 2007.

Wildland firefighters wear Nomex shirts and trousers as part of their personal protective equipment during wildfire suppression activities.

Racing car drivers wear driving suits constructed of Nomex and or other fire retardant materials, along with Nomex gloves, long underwear, balaclavas, socks, helmet lining and shoes, to protect them in the event of a fire.

Military pilots and aircrew wear flight suits made of over 92 percent Nomex to protect them from the possibility of cockpit fires and other mishaps. Recently, troops riding in ground vehicles have also begun wearing Nomex. Kevlar thread is often used to hold the fabric together at seams.

Military tank drivers also typically use Nomex hoods as protection against fire.

Plasticizers and Pollution

Plasticizers (UK: **plasticisers**) or **dispersants** are additives that increase the plasticity or decrease the viscosity of a material. These substances are compounded into certain types of plastics to render them more flexible by lowering the glass transition temperature. They accomplish this by taking up space between the polymer chains and acting as lubricants to enable the chains to more readily slip over each other. Many (but not all) are small enough to be diffusible and a potential source of health problems.

Polyvinyl chloride polymers are one of the most widely-plasticized types, and the odors often associated with flexible vinyl materials such as garden hoses, waterbeds, cheap shower curtains, raincoats and upholstery are testament to their ability to migrate into the environment.

The well-known "new car smell" is largely due to plasticizer release from upholstery and internal trim.

According to 2014 data, the total global market for plasticizers was 8.4 million metric tonnes including 1.3 million metric tonnes in Europe.

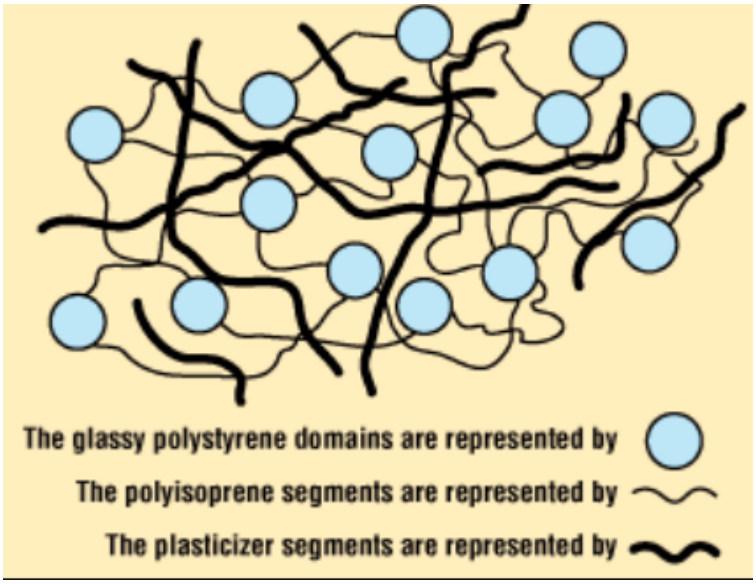


Figure 10.7.5 Shares of global plasticizer consumption in 2014 (8 million metric tons).

Substantial concerns have been expressed over the safety of some plasticizers, especially because some low molecular weight ortho-phthalates have been classified as potential endocrine disruptors with some developmental toxicity reported.

Summary

- Plastics are found everywhere due to its low cost, versatility, ease of use etc.
- Plastics pose a threat to the environment due to residual or degradation products that contribute to air and water pollution.
- Plastics hazards to animals and marine life as these living creatures mistake them for food.
- Plastic polymers are classified into seven groups for recycling purposes.

Contributors and Attributions

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11: NUCLEAR CHEMISTRY

11.1: Natural Radioactivity

11.2: Nuclear Equations

11.3: Half-Life and Radioisotopic Dating

11.4: Artificial Transmutation

11.5: Uses of Radioisotopes

11.6: Penetrating Power of Radiation

11.7: Energy from the Nucleus

11.8: Nuclear Bombs

11.9: Uses and Consequences of Nuclear Energy

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11.1: Natural Radioactivity

Learning Objectives

- Know the different sources of background radiation.
- Describe the biological impact of ionizing radiation
- List common sources of radiation exposure in the US.

Background Radiation

We are all exposed to a small amount of radiation in our daily lives. This **background radiation** comes from naturally occurring sources and from human-produced radiation. Exposure to x-rays and nuclear medicine isotopes, ground sources, and cosmic radiation account for almost half of the background exposure of the average American. Radon gas, formed from the decay of uranium and thorium isotopes, is responsible for a little over half the total amount of background radiation. See the table below for background sources.

Table 11.1.1 *Sources of Background Radiation*

radon	54%
consumer products	3%
nuclear medicine	4%
cosmic radiation	8%
terrestrial	8%
internal	11%
x-rays	11%
other	1%

The Problem of Radon

For many people, one of the largest sources of exposure to radiation is from radon gas (Rn-222). Radon-222 is an α emitter with a half–life of 3.82 days. It is one of the products of the radioactive decay series of U-238, which is found in trace amounts in soil and rocks. The radon gas that is produced slowly escapes from the ground and gradually seeps into homes and other structures above. Since it is about eight times more dense than air, radon gas accumulates in basements and lower floors, and slowly diffuses throughout buildings (Figure 11.1.1).

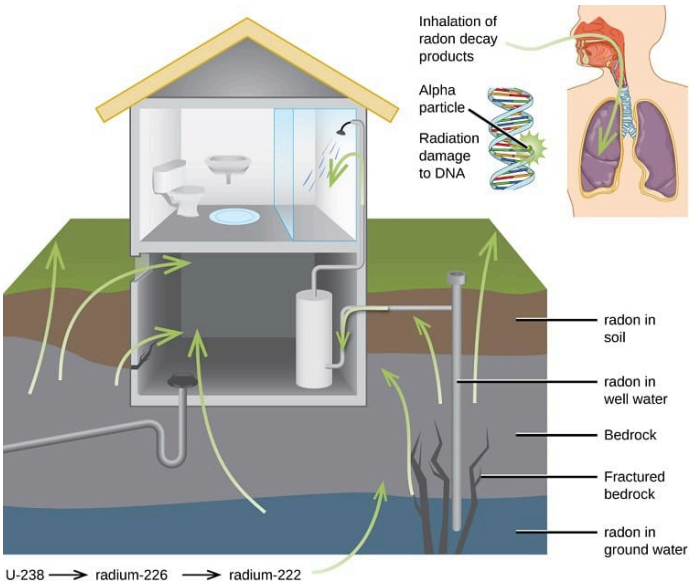


Figure 11.1.1: Radon-222 seeps into houses and other buildings from rocks that contain uranium-238, a radon emitter. The radon enters through cracks in concrete foundations and basement floors, stone or porous cinderblock foundations, and openings for water and gas pipes.

Radon is found in buildings across the country, with amounts depending on where you live. The average concentration of radon inside houses in the US (1.25 pCi/L) is about three times the levels found in outside air, and about one in six houses have radon levels high enough that remediation efforts to reduce the radon concentration are recommended. Exposure to radon increases one's risk of getting cancer (especially lung cancer), and high radon levels can be as bad for health as smoking a carton of cigarettes a day. Radon is the number one cause of lung cancer in nonsmokers and the second leading cause of lung cancer overall. Radon exposure is believed to cause over 20,000 deaths in the US per year.

Measuring Radiation Exposure

Several different devices are used to detect and measure radiation, including Geiger counters, scintillation counters (scintillators), and radiation dosimeters (Figure 11.1.2). Probably the best-known radiation instrument, the Geiger counter (also called the Geiger-Müller counter) detects and measures radiation. Radiation causes the ionization of the gas in a Geiger-Müller tube. The rate of ionization is proportional to the amount of radiation. A scintillation counter contains a scintillator—a material that emits light (luminesces) when excited by ionizing radiation—and a sensor that converts the light into an electric signal. Radiation dosimeters also measure ionizing radiation and are often used to determine personal radiation exposure. Commonly used types are electronic, film badge, thermoluminescent, and quartz fiber dosimeters.

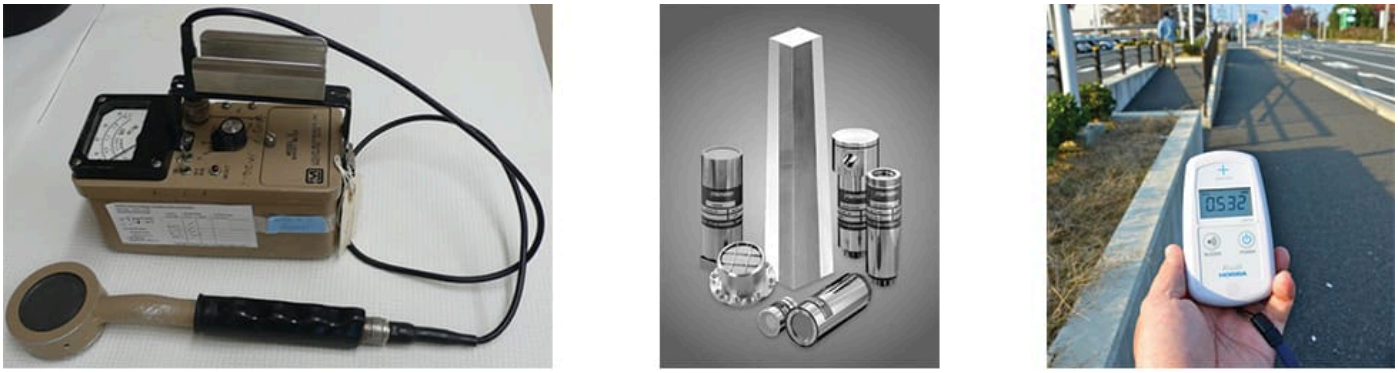


Figure 11.1.2: Devices such as (a) Geiger counters, (b) scintillators, and (c) dosimeters can be used to measure radiation. (credit c: modification of work by "osaMu"/Wikimedia commons).

Radiation Damage to Cells

The increased use of radioisotopes has led to increased concerns over the effects of these materials on biological systems (such as humans). All radioactive nuclides emit high-energy particles or electromagnetic waves. When this radiation encounters living cells, it can cause heating, break chemical bonds, or ionize molecules. The most serious biological damage results when these radioactive emissions fragment or ionize molecules. For example, alpha and beta particles emitted from nuclear decay reactions possess much higher energies than ordinary chemical bond energies. When these particles strike and penetrate matter, they produce ions and molecular fragments that are extremely reactive. The damage this does to biomolecules in living organisms can cause serious malfunctions in normal cell processes, taxing the organism's repair mechanisms and possibly causing illness or even death (Figure 11.1.3).

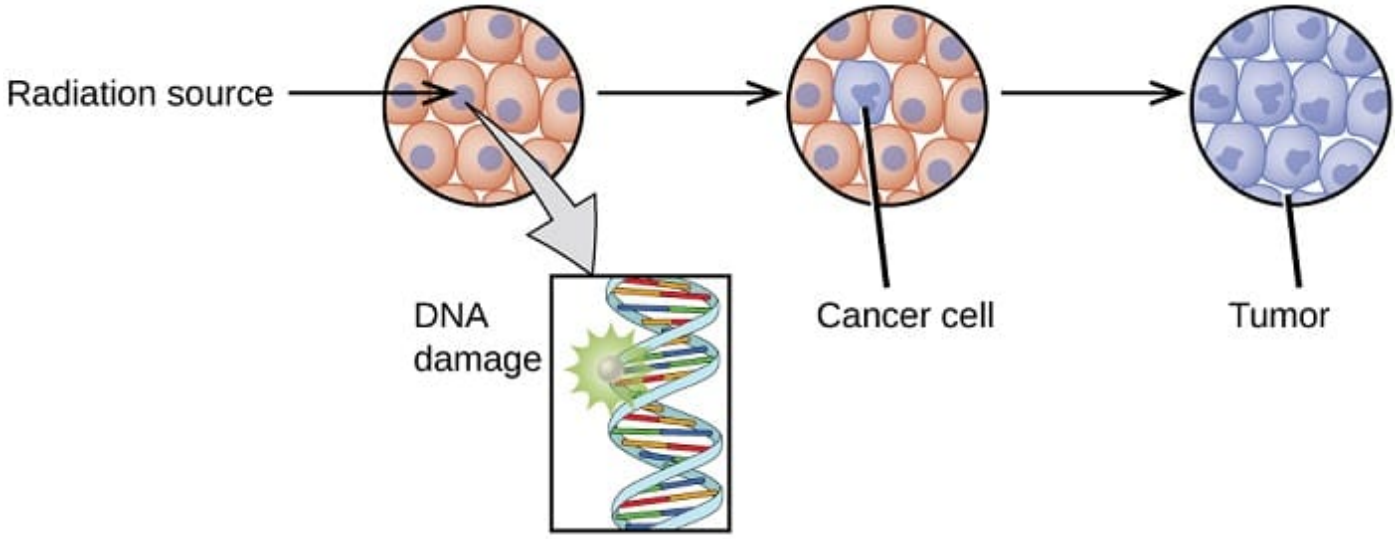


Figure 11.1.3: Radiation can harm biological systems by damaging the DNA of cells. If this damage is not properly repaired, the cells may divide in an uncontrolled manner and cause cancer.

Radiation can harm either the whole body (somatic damage) or eggs and sperm (genetic damage). Its effects are more pronounced in cells that reproduce rapidly, such as the stomach lining, hair follicles, bone marrow, and embryos. This is why patients undergoing radiation therapy often feel nauseous or sick to their stomach, lose hair, have bone aches, and so on, and why particular care must be taken when undergoing radiation therapy during pregnancy.

Ionizing vs. Nonionizing Radiation

There is a large difference in the magnitude of the biological effects of nonionizing radiation (for example, light and microwaves) and ionizing radiation, emissions energetic enough to knock electrons out of molecules (for example, α and β particles, γ rays, X-rays, and high-energy ultraviolet radiation) (Figure 11.1.4).

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Figure 11.1.4: Lower frequency, lower-energy electromagnetic radiation is nonionizing, and higher frequency, higher-energy electromagnetic radiation is ionizing.

Energy absorbed from nonionizing radiation speeds up the movement of atoms and molecules, which is equivalent to heating the sample. Although biological systems are sensitive to heat (as we might know from touching a hot stove or spending a day at the beach in the sun), a large amount of nonionizing radiation is necessary before dangerous levels are reached. Ionizing radiation, however, may cause much more severe damage by breaking bonds or removing electrons in biological molecules, disrupting their structure and function. The damage can also be done indirectly, by first ionizing H_2O (the most abundant molecule in living organisms), which forms a H_2O^+ ion that reacts with water, forming a hydronium ion and a hydroxyl radical:

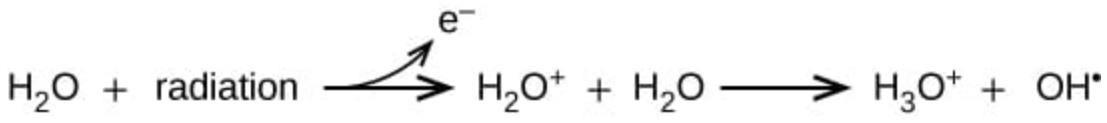


Figure 11.1.5.

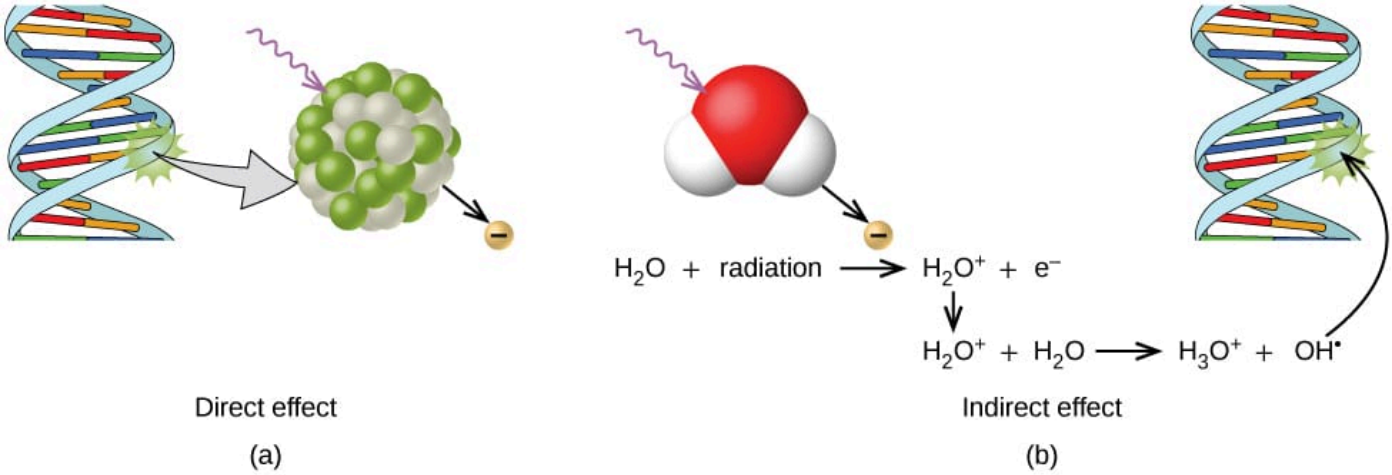


Figure 11.1.5: Ionizing radiation can (a) directly damage a biomolecule by ionizing it or breaking its bonds, or (b) create an H_2O^+ ion, which reacts with H_2O to form a hydroxyl radical, which in turn reacts with the biomolecule, causing damage indirectly.

Effects of Long-term Radiation Exposure on the Human Body

The effects of radiation depend on the type, energy, and location of the radiation source, and the length of exposure. As shown in Figure 11.1.6, the average person is exposed to background radiation, including cosmic rays from the sun and radon from uranium in the ground; radiation from medical exposure, including CAT scans, radioisotope tests, X-rays, and so on; and small amounts of radiation from other human activities, such as airplane flights (which are bombarded by increased numbers of cosmic rays in the upper atmosphere), radioactivity from consumer products, and a variety of radionuclides that enter our bodies when we breathe (for example, carbon-14) or through the food chain (for example, potassium-40, strontium-90, and iodine-131).

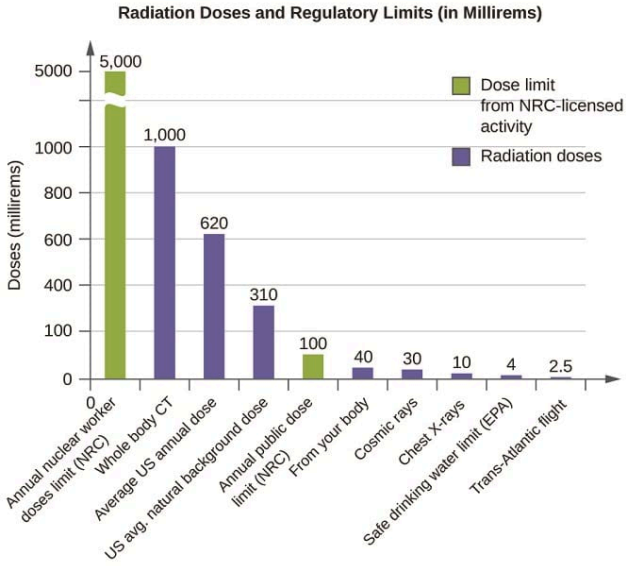


Figure 11.1.6 The total annual radiation exposure for a person in the US is about 620 mrem. The various sources and their relative amounts are shown in this bar graph. (source: U.S. Nuclear Regulatory Commission).

A short-term, sudden dose of a large amount of radiation can cause a wide range of health effects, from changes in blood chemistry to death. Short-term exposure to tens of rems of radiation will likely cause very noticeable symptoms or illness; a

dose of about 500 rems is estimated to have a 50% probability of causing the death of the victim within 30 days of exposure. Exposure to radioactive emissions has a cumulative effect on the body during a person's lifetime, which is another reason why it is important to avoid any unnecessary exposure to radiation. Health effects of short-term exposure to radiation are shown in Table 11.1.2.

Table 11.1.2 *Health Effects of Radiation*

Exposure (rem)	Health Effect	Time to Onset (without treatment)
5–10	changes in blood chemistry	—
50	nausea	hours
55	fatigue	—
70	vomiting	—
75	hair loss	2–3 weeks
90	diarrhea	—
100	hemorrhage	—
400	possible death	within 2 months
1000	destruction of intestinal lining	—
	internal bleeding	—
	death	1–2 weeks
2000	damage to central nervous system	—
	loss of consciousness;	minutes
	death	hours to days

It is impossible to avoid some exposure to ionizing radiation. We are constantly exposed to background radiation from a variety of natural sources, including cosmic radiation, rocks, medical procedures, consumer products, and even our own atoms. We can minimize our exposure by blocking or shielding the radiation, moving farther from the source, and limiting the time of exposure.

Summary

- Background radiation is defined and different sources of background radiation are listed.
- We are constantly exposed to radiation from a variety of naturally occurring and human-produced sources.
- Various devices, including Geiger counters, scintillators, and dosimeters, are used to detect and measure radiation, and monitor radiation exposure.
- Ionizing radiation is the most harmful because it can ionize molecules or break chemical bonds, which damages the molecule and causes malfunctions in cell processes. It can also create reactive hydroxyl radicals that damage biological molecules and disrupt physiological processes.

Contributors and Attributions

-

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11.2: Nuclear Equations

Learning Objectives

- Identify common particles and energies involved in nuclear reactions.
- Write and balance nuclear equations.

Changes of nuclei that result in changes in their atomic numbers, mass numbers, or energy states are nuclear reactions. To describe a nuclear reaction, we use an equation that identifies the nuclides involved in the reaction, their mass numbers and atomic numbers, and the other particles involved in the reaction.

Types of Particles in Nuclear Reactions

Many entities can be involved in nuclear reactions. The most common are protons, neutrons, alpha particles, beta particles, positrons, and gamma rays, as shown in Table 11.2.1.

Table 11.2.1 A Summary of the Names, Symbols, Representations, and Descriptions of the Most Common Particles in Nuclear Reactions.

Name	Symbol(s)	Representation	Description
Alpha particle	^4_2He or $^4_2\alpha$		(High-energy) helium nuclei consisting of two protons and two neutrons
Beta particle	^0_1e or $^0_{-1}\beta$		(High-energy) electrons
Positron	$^0_{+1}\text{e}$ or $^0_{+1}\beta$		Particles with the same mass as an electron but with 1 unit of positive charge
Proton	^1_1H or ^1_1p		Nuclei of hydrogen atoms
Neutron	^1_0n		Particles with a mass approximately equal to that of a proton but with no charge
Gamma ray	γ		Very high-energy electromagnetic radiation

Balancing Nuclear Reactions

A balanced chemical reaction equation reflects the fact that during a chemical reaction, bonds break and form, and atoms are rearranged, but the total numbers of atoms of each element are conserved and do not change. A balanced nuclear reaction equation indicates that there is a rearrangement during a nuclear reaction, but of subatomic particles rather than atoms. Nuclear reactions also follow conservation laws, and they are balanced in two ways:

1. The sum of the mass numbers of the reactants equals the sum of the mass numbers of the products.
2. The sum of the charges of the reactants equals the sum of the charges of the products.

If the atomic number and the mass number of all but one of the particles in a nuclear reaction are known, we can identify the particle by balancing the reaction. For instance, we could determine that $^{17}_8\text{O}$ is a product of the nuclear reaction of $^{14}_7\text{N}$ and ^4_2He if we knew that a proton, ^1_1H, was one of the two products. Example 11.2.1 shows how we can identify a nuclide by balancing the nuclear reaction.

Nuclear Decay Processes

Radioactive decay involves the emission of a particle and/or energy as one atom changes into another. In most instances, the atom changes its identity to become a new element. There are four different types of emissions that occur.

Alpha Emission

Alpha (α) **decay** involves the release of helium ions from the nucleus of an atom. This ion consists of two protons and two neutrons and has a $2+$ charge. Release of an α-particle produces a new atom that has an atomic number two less than the original atom and an atomic weight that is four less. A typical alpha decay reaction is the conversion of uranium-238 to thorium:

$$^{238}_{92}\mathrm{U} \rightarrow {}^{234}_{90}\mathrm{Th} + {}^{4}_{2}\alpha^{+}$$

We see a decrease of two in the atomic number (uranium to thorium) and a decrease of four in the atomic weight (238 to 234). Usually the emission is not written with atomic number and weight indicated since it is a common particle whose properties should be memorized. Quite often the alpha emission is accompanied by gamma (γ) radiation, a form of energy release. Many of the largest elements in the periodic table are alpha-emitters.

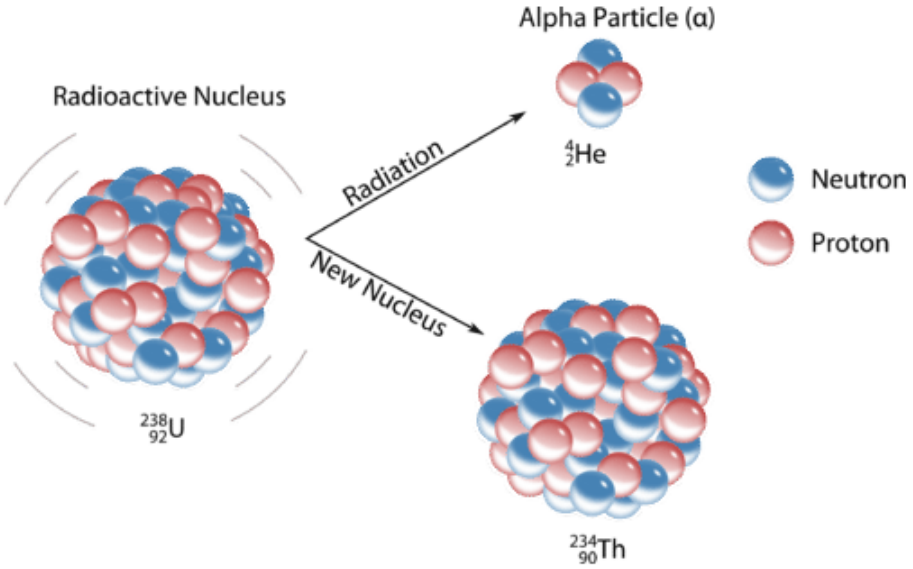


Figure 11.2.1 *Emission of an alpha particle from the nucleus.*

Chemists often use the names **parent isotope** and **daughter isotope** to represent the original atom and the product other than the alpha particle. In the previous example,

$$^{238}_{92}\mathrm{U}$$

is the parent isotope, and

$$^{234}_{90}\mathrm{Th}$$

is the daughter isotope. When one element changes into another in this manner, it undergoes **radioactive decay**.

Example 11.2.1

Write the nuclear equation that represents the radioactive decay of radon-222 by alpha particle emission and identify the daughter isotope.

Solution

Radon has an atomic number of 86, so the parent isotope is represented as

$$^{222}_{86}\mathrm{Rn}$$

We represent the alpha particle as

$$^{4}_{2}\mathrm{He}$$

Use subtraction (222 – 4 = 218 and 86 – 2 = 84) to identify the daughter isotope as polonium:

$$^{222}_{86}\mathrm{Rn} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{218}_{84}\mathrm{Th}$$

Exercise 11.2.1

Write the nuclear equation that represents radioactive decay of polonium-208 by alpha particle emission and identify the daughter isotope.

Answer available at the end of this section.

Beta Emission

Beta (β) **decay** is a more complicated process. Unlike the α-emission, which simply expels a particle, the β-emission involves the transformation of a neutron in the nucleus to a proton and an electron. The electron is then ejected from the nucleus. In the process,the atomic number increases by one while the atomic weight stays the same. As is the case with α-emissions, β -emissions are often accompanied by γ-radiation.

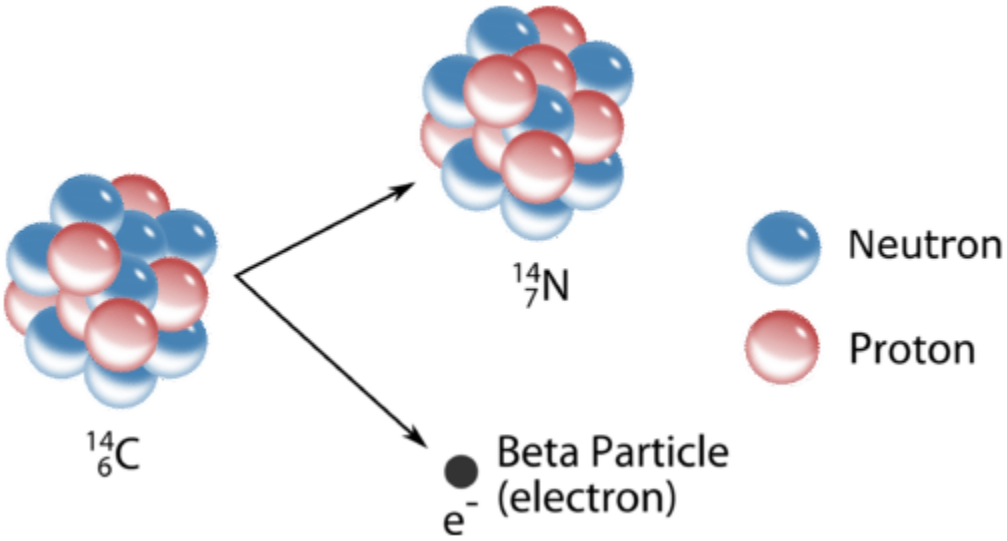


Figure 11.2.2 *Beta emission.*

A typical beta decay process involves carbon-14, often used in radioactive dating techniques. The reaction forms nitrogen-14 and an electron:

$$^{14}_{6}\mathrm{C} \rightarrow {}^{14}_{7}\mathrm{N} + {}^{0}_{-1}\mathrm{e}$$

Again, the beta emission is usually simply indicated by the Greek letter β; memorization of the process is necessary in order to follow nuclear calculations in which the Greek letter β appears without further notation.

Example 11.2.2

Write the nuclear equation that represents the radioactive decay of boron-12 by beta particle emission and identify the daughter isotope. A gamma ray is emitted simultaneously with the beta particle.

Solution

The parent isotope is $^{4}_{2}\mathrm{He}$

while one of the products is $^{0}_{-1}\mathrm{e}$

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 carbon-12.

Exercise 11.2.2

Write the nuclear equation that represents the radioactive decay of rubidium-87 by beta particle emission and identify the daughter isotope.

Answer available at the end of this section.

Gamma Emission

Gamma (γ) **radiation** is simply energy. It may be released by itself or more commonly in association with other radiation events. There is no change of atomic number of atomic weight in a simple γ-emission. Often, an isotope may produce γ-radiation as a result of a transition in a metastable isotope. This type of isotope may just "settle", with a shifting of particles in the nucleus. The composition of the atom is not altered, but the nucleus could be considered more "comfortable" after the shift. This shift increases the stability of the isotope from the energetically unstable (or "metastable") isotope to a more stable form of the nucleus. Gamma (γ) emission can occur virtually instantaneously, as it does in the alpha decay of uranium-238 to thorium-234, where the asterisk denotes an excited state:

$$^{238}_{92}\mathrm{U} \rightarrow \underbrace{^{234}_{90}\mathrm{Th}^{*}}_{\substack{\text{excited}\\ \text{nuclear}\\ \text{state}}} + {}^{4}_{2}\alpha \xrightarrow{\text{relaxation}} {}^{234}_{90}\mathrm{Th} + {}^{0}_{0}\gamma \tag{11.2.1}$$

If we disregard the decay event that created the excited nucleus, then

$$^{234}_{88}\mathrm{Th}^{*} \rightarrow {}^{234}_{88}\mathrm{Th} + {}^{0}_{0}\gamma \tag{11.2.2}$$

or more generally,

$$^{A}_{Z}\mathrm{X}^{*} \rightarrow {}^{A}_{Z}\mathrm{X} + {}^{0}_{0}\gamma \tag{11.2.3}$$

Gamma emission can also occur after a significant delay. For example, technetium-99*m* has a half-life of about 6 hours before emitting a γ ray to form technetium-99 (the *m* is for metastable). Because γ rays are energy, their emission does not affect either the mass number or the atomic number of the daughter nuclide. Gamma-ray emission is therefore the only kind of radiation that does not necessarily involve the conversion of one element to another, although it is almost always observed in conjunction with some other nuclear decay reaction.

Positron Emission

A **positron** is a positive electron (a form of antimatter). This rare type of emission occurs when a proton is converted to a neutron and a positron in the nucleus, with ejection of the positron. The atomic number will decrease by one while the atomic weight does not change. A positron is often designated by β^+.

Carbon-11 emits a positron to become boron-11:

$$^{11}_{6}\mathrm{C} \rightarrow {}^{11}_{5}\mathrm{B} + {}^{0}_{+1}\beta$$

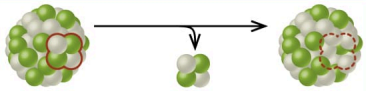
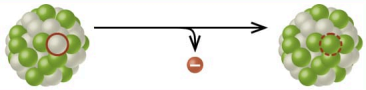
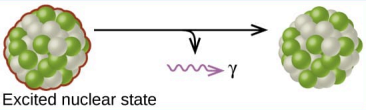
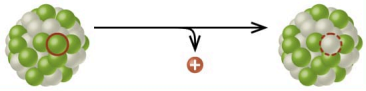
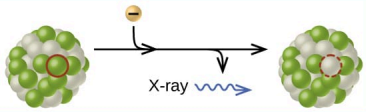
Electron Capture

An alternate way for a nuclide to increase its neutron to proton ratio is by a phenomenon called electron capture. In electron capture, an electron from an inner orbital is captured by the nucleus of the atom and combined with a proton to form a neutron. For example, silver-106 undergoes electron capture to become palladium-106.

$$^{106}_{47}\mathrm{Ag} + {}^{0}_{-1}\mathrm{e} \rightarrow {}^{106}_{46}\mathrm{Pd}$$

Note that the overall result of electron capture is identical to positron emission. The atomic number decreases by one while the mass number remains the same.

Table 11.2.2 Different Types of Decay and Changes in Atomic and Mass Numbers.

Type	Nuclear equation	Representation	Change in mass/atomic numbers
Alpha decay	${}^{A}_{Z}\mathrm{X} \quad {}^{4}_{2}\mathrm{He} + {}^{A-4}_{Z-2}\mathrm{Y}$		A: decrease by 4 Z: decrease by 2
Beta decay	${}^{A}_{Z}\mathrm{X} \quad {}^{0}_{-1}\mathrm{e} + {}^{A}_{Z+1}\mathrm{Y}$		A: unchanged Z: increase by 1
Gamma decay	${}^{A}_{Z}\mathrm{X} \quad {}^{0}_{0}\gamma + {}^{A}_{Z}\mathrm{Y}$		A: unchanged Z: unchanged
Positron emission	${}^{A}_{Z}\mathrm{X} \quad {}^{0}_{+1}\mathrm{e} + {}^{A}_{Y-1}\mathrm{Y}$		A: unchanged Z: decrease by 1
Electron capture	${}^{A}_{Z}\mathrm{X} \quad {}^{0}_{-1}\mathrm{e} + {}^{A}_{Y-1}\mathrm{Y}$		A: unchanged Z: decrease by 1

Following are the equations of several nuclear reactions that have important roles in the history of nuclear chemistry:

- The first naturally occurring unstable element that was isolated, polonium, was discovered by the Polish scientist Marie Curie and her husband Pierre in 1898. It decays, emitting α particles:

$$^{212}_{84}\mathrm{Po} \longrightarrow {}^{208}_{82}\mathrm{Pb} + {}^{4}_{2}\mathrm{He}$$

- The first nuclide to be prepared by artificial means was an isotope of oxygen, ^{17}O. It was made by Ernest Rutherford in 1919 by bombarding nitrogen atoms with α particles:

$$^{14}_{7}\mathrm{N} + {}^{4}_{2}\alpha \longrightarrow {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{H}$$

- James Chadwick discovered the neutron in 1932, as a previously unknown neutral particle produced along with ^{12}C by the nuclear reaction between ^{9}Be and ^{4}He:

$$^{9}_{4}\mathrm{Be} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{12}_{6}\mathrm{C} + {}^{1}_{0}\mathrm{n}$$

- The first element to be prepared that does not occur naturally on the earth, technetium, was created by bombardment of

molybdenum by deuterons (heavy hydrogen, ${}^{2}_{1}\mathrm{H}$), by Emilio Segre and Carlo Perrier in 1937:

$$ {}^{2}_{1}\mathrm{H} + {}^{97}_{42}\mathrm{Mo} \longrightarrow 2{}^{1}_{0}\mathrm{n} + {}^{97}_{43}\mathrm{Tc} $$

- The first controlled nuclear chain reaction was carried out in a reactor at the University of Chicago in 1942. One of the many reactions involved was:

$$ {}^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{87}_{35}\mathrm{Br} + {}^{146}_{57}\mathrm{La} + 3{}^{1}_{0}\mathrm{n} $$

Summary

- Nuclei can undergo reactions that change their number of protons, number of neutrons, or energy state.
- Many different particles can be involved in nuclear reactions. The most common are protons, neutrons, positrons (which are positively charged electrons), electrons, alpha (α) particles (which are high-energy helium nuclei), beta (β) particles (which are high-energy electrons), and gamma (γ) rays (which compose high-energy electromagnetic radiation).
- As with chemical reactions, nuclear reactions are always balanced. When a nuclear reaction occurs, the total mass (number) and the total charge remain unchanged.

Contributors and Attributions

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- Marisa Alviar-Agnew (Sacramento City College)

Answers

Exercise 11.2.1

$$ {}^{208}_{80}\mathrm{Po} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{204}_{82}\mathrm{Pb} $$

$${}^{204}_{82}\mathrm{Pb}$$

Exercise 11.2.2

$$ {}^{87}_{37}\mathrm{Rb} \rightarrow {}^{87}_{38}\mathrm{Sr} + {}^{0}_{-1}\mathrm{e} $$

$${}^{87}_{38}\mathrm{Sr}$$

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11.3: Half-Life and Radioisotopic Dating

Learning Objectives

- Define *half-life*.
- Determine the amount of radioactive substance remaining after a given number of half-lives.
- Define a radioactive decay series.

Whether or not a given isotope is radioactive is a characteristic of that particular isotope. Some isotopes are stable indefinitely, while others are radioactive and decay through a characteristic form of emission. As time passes, less and less of the radioactive isotope will be present, and the level of radioactivity decreases. An interesting and useful aspect of radioactive decay is **half life**. which is the amount of time it takes for one-half of a radioactive isotope to decay. The half-life of a specific radioactive isotope is constant; it is unaffected by conditions and is independent of the initial amount of that isotope.

For example, cobalt-60, an isotope that emits gamma rays used to treat cancer, has a half-life of 5.27 years (Figure 11.3.1). In a given cobalt-60 source, since half of the $^{60}_{27}\text{Co}$ nuclei decay every 5.27 years, both the amount of material and the intensity of the radiation emitted is cut in half every 5.27 years. (Note that for a given substance, the intensity of radiation that it produces is directly proportional to the rate of decay of the substance and the amount of the substance.) This is as expected for a process following first-order kinetics. Thus, a cobalt-60 source that is used for cancer treatment must be replaced regularly to continue to be effective.

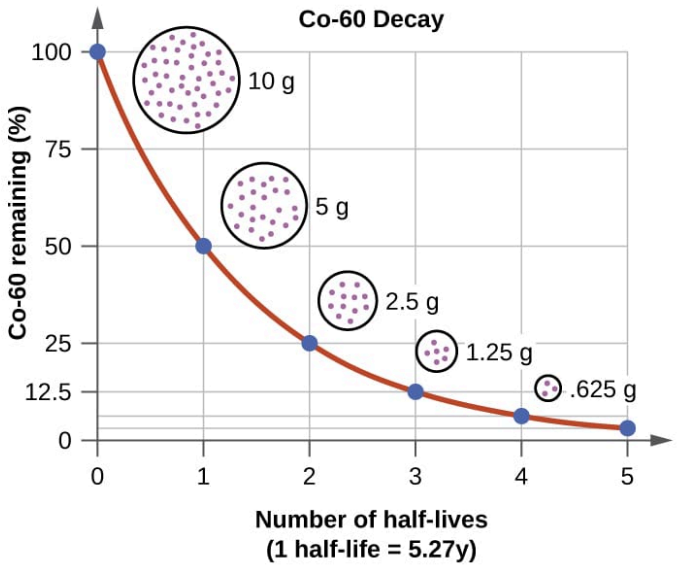


Figure 11.3.1 For cobalt-60, which has a half-life of 5.27 years, 50% remains after 5.27 years (one half-life), 25% remains after 10.54 years (two half-lives), 12.5% remains after 15.81 years (three half-lives), and so on.

We can determine the amount of a radioactive isotope remaining after a given number half-lives by using the following expression:

$$amount\ \ remaining\ =\ initial\ amount \times \left(\frac{1}{2}\right)^{n}$$

where *n* is the number of half-lives. This expression works even if the number of half-lives is not a whole number.

Example 11.3.1:

The half-life of fluorine-20 is 11.0 s. If a sample initially contains 5.00 g of fluorine-20, how much remains after 44.0 s?

Solution

If we compare the time that has passed to the isotope's half-life, we note that 44.0 s is exactly 4 half-lives, so using the previous expression, *n* = 4. Substituting and solving results in the following:

$$amount\ remaining = 5.00g \times \left(\frac{1}{2}\right)^4$$
$$amount\ remaining = 5.00g \times \left(\frac{1}{16}\right)$$
$$amount\ remaining = 0.313g$$

Less than one-third of a gram of fluorine-20 remains.

Exercise 11.3.1

The half-life of titanium-44 is 60.0 y. A sample of titanium contains 0.600 g of titanium-44. How much remains after 240.0 y?

Answer available at the end of this section.

Example 11.3.2

If there are 60 grams of Np-240 present, how much Np-240 will remain after 4 hours? (Np-240 has a half-life of 1 hour)

Solution

Np-240 with a half life of only 1 hour.

Amount of Np-240 present	Amount of time passed
60 g	0 (this is the amount before any time has passed)
30 g	1 hour (1 half-life)
15 g	2 hours (2 half-lives)
7.5 g	3 hours
3.75 g	4 hours

After 4 hours, only $3.75\ \text{g}$ of our original $60\ \text{g}$ sample would remain the radioactive isotope Np-240.

Exercise 11.3.2

A sample of Ac-225 originally contained 80 grams and after 50 days only 2.55 grams of the original Ac-225 remain. What is the half life of Ac-225?

Answer

10 days.

The half-lives of many radioactive isotopes have been determined and they have been found to range from extremely long half-lives of 10 billion years to extremely short half-lives of fractions of a second. For example: the half-life of $^{209}_{83}\text{Bi}$ is 1.9×10^{19} years; $^{239}_{94}\text{Ra}$ is 24,000 years; $^{222}_{86}\text{Rn}$ is 3.82 days; and element-111 (Rg for roentgenium) is 1.5×10^{-3} seconds. The table below illustrates half-lives for several selected elements.

Table 11.3.1*: Table of Selected Half-lives*

Element	Mass Number (A)	Half-life	Element	Mass Number (A)	Half Life
Uranium	238	4.5 Billion years	Californium	251	800 years
Neptunium	240	1 hour	Nobelium	254	3 seconds
Plutonium	243	5 hours	Carbon	14	5730 years
Americium	245	25 minutes	Carbon	16	740 milliseconds

Uranium Decay Series

The naturally occurring radioactive isotopes of the heaviest elements fall into chains of successive disintegrations, or decays, and all the species in one chain constitute a radioactive family, or radioactive decay series. Three of these series include most of the naturally radioactive elements of the periodic table. They are the uranium series, the actinide series, and the thorium series. (Figure 11.3.2). In all three series, the end-product is a stable isotope of lead.

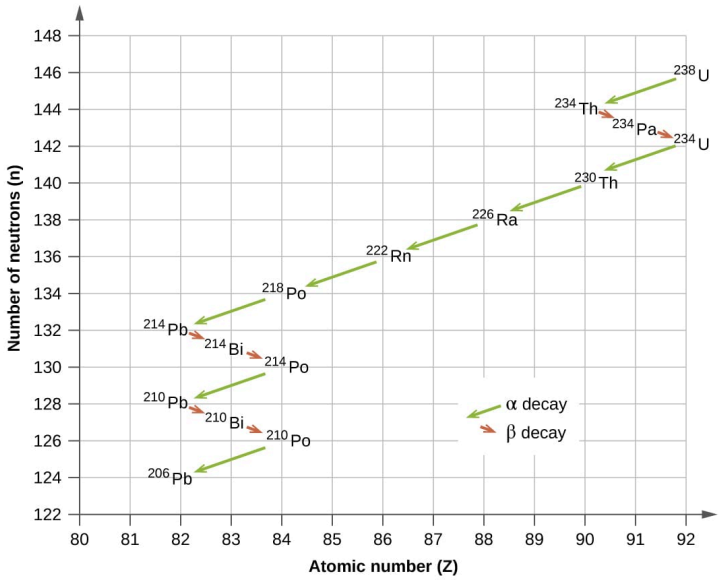


Figure 11.3.2 Uranium-238 undergoes a radioactive decay series consisting of 14 separate steps before producing stable lead-206. This series consists of eight α decays and six β decays.

Radioactive Dating

Radioactive dating *is a process by which the approximate age of an object is determined through the use of certain radioactive nuclides*. For example, carbon-14 has a half-life of 5,730 years and is used to measure the age of organic material. The ratio of carbon-14 to carbon-12 in living things remains constant while the organism is alive because fresh carbon-14 is entering the organism whenever it consumes nutrients. When the organism dies, this consumption stops, and no new carbon-14 is added to the organism. As time goes by, the ratio of carbon-14 to carbon-12 in the organism gradually declines, because carbon-14 radioactively decays while carbon-12 is stable. Analysis of this ratio allows archaeologists to estimate the age of organisms that were alive many thousands of years ago. For example, with the half-life of $^{14}_{6}\mathrm{C}$ 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.

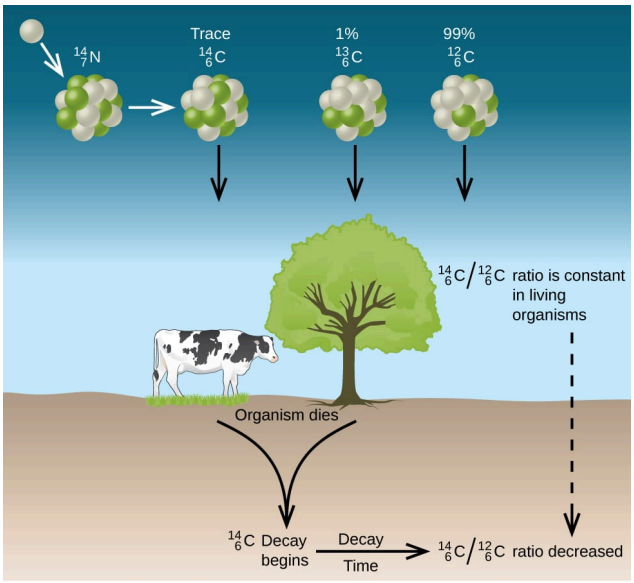


Figure 11.3.3: Along with stable carbon-12, radioactive carbon-14 is taken in by plants and animals, and remains at a constant level within them while they are alive. After death, the C-14 decays and the C-14:C-12 ratio in the remains decreases. Comparing this ratio to the C-14:C-12 ratio in living organisms allows us to determine how long ago the organism lived (and died). (CC-BY 4.0; OpenStax).

C-14 dating does have limitations. For example, a sample can be C-14 dating if it is approximately 100 to 50,000 years old. Before or after this range, there is too little of the isotope to be detected. Substances must have obtained C-14 from the atmosphere. For this reason, aquatic samples cannot be effectively C-14 dated. Lastly, accuracy of C-14 dating has been affected by atmosphere nuclear weapons testing. Fission bombs ignite to produce more C-14 artificially. Samples tested during and after this period must be checked against another method of dating (isotopic or tree rings).

To calculate the age of a substance using isotopic dating, use the equation below:

$$\text{how old (time)} = n \times t_{1/2}$$

where n is the number of half-lives and $t_{1/2}$ is the half-life (in time).

Example 11.3.3

How long will it take for 18.0 grams of Ra-226 to decay to leave a total of 2.25 grams? Ra-226 has a half-life of 1600 years.

Solution

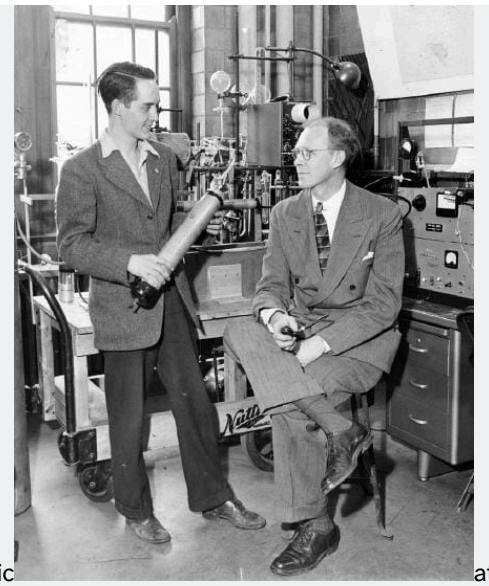
18.0g ⇒ 9.0g ⇒ 4.5g ⇒ 2.25g, this is three half-lives

$$\text{how old (time)} = 3 \times 1600\,years$$

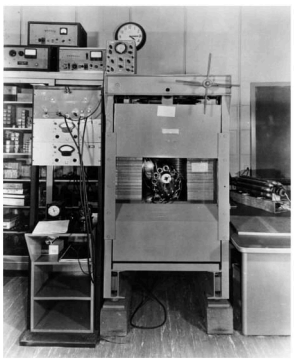
This decay process takes 4800 years to occur.

Willard Libby

A National Historic Chemical Landmark -American Chemical Society



Dedicated at the University of Chicago on October 10, 2016.



Libby's anti-coincidence counter. The circular arrangement of Geiger counters (center) detected radiation in samples while the thick metal shields on all sides were designed to reduce background radiation.
University of Chicago Photographic Archive, apf1-03874, Special Collections Research Center, University of Chicago Library.

In 1946, Willard Libby proposed an innovative method for dating organic materials by measuring their content of carbon-14, a newly discovered radioactive isotope of carbon. Known as radiocarbon dating, this method provides objective age estimates for carbon-based objects that originated from living organisms. The “radiocarbon revolution” made possible by Libby’s discovery greatly benefited the fields of archaeology and geology by allowing practitioners to develop more precise historical chronologies across geography and cultures.

Willard F. Libby (right), the physical chemist who conceived of radiocarbon dating, with graduate student Ernest Anderson.

University of Chicago Photographic Archive, apf1-03868, Special Collections Research Center, University of Chicago Library.

Go to Link below for more details

www.acs.org/content/acs/en/education/whatischemistry/landmarks/radiocarbon-dating.html

Radioactive Dating Using Nuclides Other than Carbon-14

Radioactive dating can also use other radioactive nuclides with longer half-lives to date older events. An ingenious application of half-life studies established a new science of determining ages of materials by half-life calculations. For geological dating, the

decay of U-238 can be used. The half-life of U-238 is 4.5×10^9 years. The end product of the decay of U-238 is Pb-206. After one half-life, a 1.00 gram sample of uranium will have decayed to 0.50 grams of U-238 and 0.43 grams of Pb-206. By comparing the amount of U-238 to the amount of Pb-206 in a sample of uranium mineral, the age of the mineral can be estimated. Present day estimates for the age of the Earth's crust from this method is at 4 billion years. This radioactivity approach can be used to detecting fake wine vintages too.

Isotopes with shorter half-lives are used to date more recent samples. For example, tritium ($t_{1/2}$ =12.3 years) can date samples within an age range of 1-100 years. Chemists and geologists use tritium dating to determine the age of water (ocean and fresh). In addition, tritium dating can be useful in determining the age of wines and brandies.

K-40 decays by positron emission and electron capture to form Ar-40 with a half-life of 1.25 billion years. If a rock sample is crushed and the amount of Ar-40 gas that escapes is measured, determination of the Ar-40:K-40 ratio yields the age of the rock. Other methods, such as rubidium-strontium dating (Rb-87 decays into Sr-87 with a half-life of 48.8 billion years), operate on the same principle. To estimate the lower limit for the earth's age, scientists determine the age of various rocks and minerals, making the assumption that the earth is older than the oldest rocks and minerals in its crust. As of 2014, the oldest known rocks on earth are the Jack Hills zircons from Australia, found by uranium-lead dating to be almost 4.4 billion years old.

Summary

- Natural radioactive processes are characterized by a half-life, the time it takes for half of the material to decay radioactively.
- The amount of material left over after a certain number of half-lives can be determined using the following expression:

$$amount\ \ remaining\ =\ initial\ amount \times \left(\frac{1}{2}\right)^n$$

  where *n* is the number of half-lives.

- C-14 dating procedures have been used to determine the age of organic artifacts. Its half-life is approximately 5700 years.

Contributors and Attributions

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-
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- Elizabeth R. Gordon (Furman University)
- American Chemical Society-Chemical Landmarks

Answers

Exercise 11.3.1

0.0375 g

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11.4: Artificial Transmutation

Learning Objective

- Describe the synthesis of transuranium nuclides.

After the discovery of radioactivity, the field of nuclear chemistry was created and developed rapidly during the early twentieth century. A slew of new discoveries in the 1930s and 1940s, along with World War II, combined to usher in the Nuclear Age in the mid-twentieth century. Science learned how to create new substances, and certain isotopes of certain elements were found to possess the capacity to produce unprecedented amounts of energy, with the potential to cause tremendous damage during war, as well as produce enormous amounts of power for society's needs during peace.

Synthesis of Nuclides

Nuclear transmutation is the conversion of one nuclide into another. It can occur by the radioactive decay of a nucleus, or the reaction of a nucleus with another particle. The first manmade nucleus was produced in Ernest Rutherford's laboratory in 1919 by a transmutation reaction, the bombardment of one type of nuclei with other nuclei or with neutrons. Rutherford bombarded nitrogen atoms with high-speed α particles from a natural radioactive isotope of radium and observed protons resulting from the reaction:

$$^{14}_{7}\mathrm{N} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{H}$$

The $^{17}_{8}\mathrm{O}$ and $^{1}_{1}\mathrm{H}$ nuclei that are produced are stable, so no further (nuclear) changes occur.

To reach the kinetic energies necessary to produce transmutation reactions, devices called particle accelerators are used. These devices use magnetic and electric fields to increase the speeds of nuclear particles. In all accelerators, the particles move in a vacuum to avoid collisions with gas molecules. When neutrons are required for transmutation reactions, they are usually obtained from radioactive decay reactions or from various nuclear reactions occurring in nuclear reactors. The Chemistry in Everyday Life feature that follows discusses a famous particle accelerator that made worldwide news.

CERN Particle Accelerator

Located near Geneva, the CERN ("Conseil Européen pour la Recherche Nucléaire," or European Council for Nuclear Research) Laboratory is the world's premier center for the investigations of the fundamental particles that make up matter. It contains the 27-kilometer (17 mile) long, circular Large Hadron Collider (LHC), the largest particle accelerator in the world (Figure 11.4.1). 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 11.4.1: A small section of the LHC is shown with workers traveling along it. (credit: Christophe Delaere)

In 2012, CERN announced that experiments at the LHC showed the first observations of the Higgs boson, an elementary particle that helps explain the origin of mass in fundamental particles. This long-anticipated discovery made worldwide news and resulted in the awarding of the 2013 Nobel Prize in Physics to François Englert and Peter Higgs, who had predicted the existence of this particle almost 50 years previously.

Prior to 1940, the heaviest-known element was uranium, whose atomic number is 92. Now, many artificial elements have been synthesized and isolated, including several on such a large scale that they have had a profound effect on society. One of these—element 93, neptunium (Np)—was first made in 1940 by McMillan and Abelson by bombarding uranium-238 with neutrons. The reaction creates unstable uranium-239, with a half-life of 23.5 minutes, which then decays into neptunium-239. Neptunium-239 is also radioactive, with a half-life of 2.36 days, and it decays into plutonium-239. The nuclear reactions are:

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{239}_{92}\mathrm{U} \tag{11.4.1}$$

$$^{239}_{92}\mathrm{U} \longrightarrow {}^{239}_{93}\mathrm{Np} + {}^{0}_{-1}\mathrm{e} \quad t_{\frac{1}{2}} \qquad \text{half-life} = 23.5\ \text{min} \tag{11.4.2}$$

$$^{239}_{93}\mathrm{Np} \longrightarrow {}^{239}_{94}\mathrm{Pu} + {}^{0}_{-1}\mathrm{e} \quad t_{\frac{1}{2}} \qquad \text{half-life} = 2.36\ \text{days} \tag{11.4.3}$$

Plutonium is now mostly formed in nuclear reactors as a byproduct during the decay of uranium. Some of the neutrons that are released during U-235 decay combine with U-238 nuclei to form uranium-239; this undergoes β decay to form neptunium-239, which in turn undergoes β decay to form plutonium-239 as illustrated in the preceding three equations. It is possible to summarize these equations as:

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{239}_{92}\mathrm{U} \xrightarrow{\beta^-} {}^{239}_{93}\mathrm{Np} \xrightarrow{\beta^-} {}^{239}_{94}\mathrm{Pu}$$

Heavier isotopes of plutonium—Pu-240, Pu-241, and Pu-242—are also produced when lighter plutonium nuclei capture neutrons. Some of this highly radioactive plutonium is used to produce military weapons, and the rest presents a serious storage problem because they have half-lives from thousands to hundreds of thousands of years.

Although they have not been prepared in the same quantity as plutonium, many other synthetic nuclei have been produced. Nuclear medicine has developed from the ability to convert atoms of one type into other types of atoms. Radioactive isotopes of several dozen elements are currently used for medical applications. The radiation produced by their decay is used to image or treat various organs or portions of the body, among other uses.

The elements beyond element 92 (uranium) are called transuranium elements. As of this writing, 22 transuranium elements have been produced and officially recognized by IUPAC; several other elements have formation claims that are waiting for approval. Some of these elements are shown in Table 11.4.1.

Table 11.4.1 *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	$^{242}_{96}\mathrm{Cm} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{245}_{98}\mathrm{Cf} + {}^{1}_{0}\mathrm{n}$
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	$^{206}_{82}\mathrm{Pb} + {}^{54}_{24}\mathrm{Cr} \longrightarrow {}^{257}_{106}\mathrm{Sg} + 3\,{}^{1}_{0}\mathrm{n}$ $^{249}_{98}\mathrm{Cf} + {}^{18}_{8}\mathrm{O} \longrightarrow {}^{263}_{106}\mathrm{Sg} + 4\,{}^{1}_{0}\mathrm{n}$
meitnerium	Mt	107	$^{209}_{83}\mathrm{Bi} + {}^{58}_{26}\mathrm{Fe} \longrightarrow {}^{266}_{109}\mathrm{Mt} + {}^{1}_{0}\mathrm{n}$

Summary

- It is possible to produce new atoms by bombarding other atoms with nuclei or high-speed particles.
- The products of transmutation reactions can be stable or radioactive.
- A number of artificial elements, including technetium, astatine, and the transuranium elements, have been produced in this way.

Contributors and Attributions

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11.5: Uses of Radioisotopes

Learning Objectives

- Understand how radiation is used in agriculture and various industries.
- Understand the difference between diagnostic and therapeutic radiation.

Radioactive isotopes have the same chemical properties as stable isotopes of the same element, but they emit radiation, which can be detected. If we replace one (or more) atom(s) with radioisotope(s) in a compound, we can track them by monitoring their radioactive emissions. This type of compound is called a radioactive tracer (or radioactive label). Radioisotopes are used to follow the paths of biochemical reactions or to determine how a substance is distributed within an organism.

Radioisotopes in Industry and Agriculture

Radioisotopes (radioactive isotopes or radionuclides or radioactive nulcides) are used in two major ways: either for their radiation alone (irradiation, nuclear batteries) or for the combination of chemical properties and their radiation (tracers, biopharmaceuticals).

Tracer Applications

Radioactive isotopes are effective tracers because their radioactivity is easy to detect. A **tracer** is a substance that can be used to follow the pathway of that substance through some structure. For instance, leaks in underground water pipes can be discovered by running some **tritium (H-3)**-containing water through the pipes and then using a Geiger counter to locate any radioactive tritium subsequently present in the ground around the pipes. (Recall that tritium is a radioactive isotope of hydrogen.)

Tracers are used in diverse ways to study the mechanisms of chemical reactions in plants and animals. These include labeling fertilizers in studies of nutrient uptake by plants and crop growth, investigations of digestive and milk-producing processes in cows, and studies on the growth and metabolism of animals and plants.

For example, the radioisotope **C-14** was used to elucidate the details of how photosynthesis occurs. The overall reaction is:

$$6\,\mathrm{CO_2}(g) + 6\,\mathrm{H_2O}(l) \longrightarrow \mathrm{C_6H_{12}O_6}(s) + 6\,\mathrm{O_2}(g),$$

but the process is much more complex, proceeding through a series of steps in which various organic compounds are produced. In studies of the pathway of this reaction, plants were exposed to CO_2 containing a high concentration of ${}^{14}_{6}\mathrm{C}$. At regular intervals, the plants were analyzed to determine which organic compounds contained carbon-14 and how much of each compound was present. From the time sequence in which the compounds appeared and the amount of each present at given time intervals, scientists learned more about the pathway of the reaction.

Phosphorus-32 is used in plant sciences for tracking a plant's uptake of fertilizer from the roots to the leaves. The phosphorus-32-labelled fertilizer is given to the plant hydroponically or via water in the soil and the usage of the phosphorus can be mapped from the emitted beta radiation. The information gathered by mapping the fertilizer uptake show how the plant takes up and uses the phosphorus from fertilizer.

Irradiation of Food and Mail

Co-60 (gamma source) and x-rays are use to irradiate many foods in the United States. Ionizing radiation can be used to kill food borne illnesses like salmonella and e coli. Irradiating food can also prolong shelf-life, delay ripening, and destroy insects. In addition, gamma/x-ray can sterilize foods making refrigeration unnecessary. Often, sterilized food is served to hospital patients who have impaired immune systems.

In the United States, irradiation of food is regulated by the FDA (Food and Drug Administration). Foods that have been irradiated must display the symbol called the radura on their packaging. Some foods that could display this symbol are: meats (beef, pork,

chicken), shrimp, lobster, fruits, vegetables, shellfish, and spices. Contrary to the belief of some people, irradiation of food *does not* make the food itself radioactive.



Figure 11.5.1 The preservation of strawberries with Ionizing Radiation.

In the fall of 2001, anthrax laced letters *(*Figure 11.5.2) were sent to various new agencies and two United States senators. Anthrax is an infectious disease caused by bacteria. It exists naturally in some soils and can be isolated in a laboratory.

Figure 11.5.2 Anthrax-laced letter that was sent to Senator Tom Daschle. Image taken from: https://upload.wikimedia.org/wikiped...hle_letter.jpg

To combat this form of bioterrorism, the United States Postal Service(USPS)and the Federal Bureau of Investigation (FBI) installed x-ray generators to irradiate suspicious looking mail sent to some governmental facilities. X-rays will kill the majority of this bacteria and some viruses as well. Once irradiated, mail (packages and letters) might change in color, texture, and smell. This ionizing radiation chemically alters the composition of the mail's paper component. The x-rays do not leave the mail radioactive.

Smoke Detectors

Americium-241, an α emitter with a half-life of 458 years, is used in tiny amounts in ionization-type smoke detectors (Figure 11.5.3). The α emissions from Am-241 ionize the air between two electrode plates in the ionizing chamber. A battery supplies a potential that causes movement of the ions, thus creating a small electric current. When smoke enters the chamber, the movement of the ions is impeded, reducing the conductivity of the air. This causes a marked drop in the current, triggering an alarm.

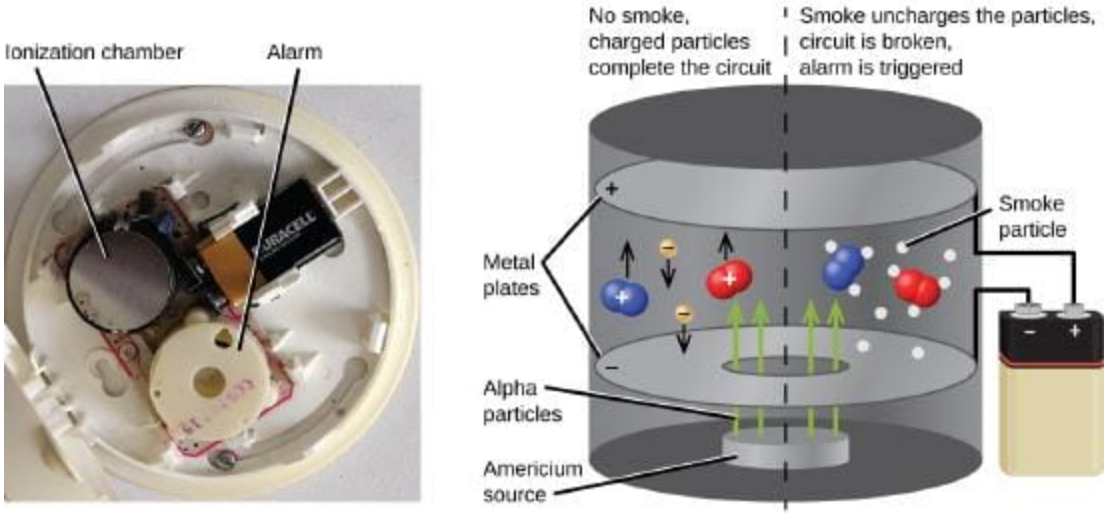


Figure 11.5.3 Inside a smoke detector, Am-241 emits α particles that ionize the air, creating a small electric current. During a fire, smoke particles impede the flow of ions, reducing the current and triggering an alarm. (credit a: modification of work by "Muffet"/Wikimedia Commons)

Other Applications

Commercial applications of radioactive materials are equally diverse . They include determining the thickness of films, paper, and thin metal sheets by exploiting the penetration power of various types of radiation(Figure 11.5.4). Flaws in metals used for structural purposes can be detected using high-energy gamma rays from cobalt-60 in a fashion similar to the way X-rays are used to examine the human body. In one form of pest control, flies are controlled by sterilizing male flies with γ radiation so that females breeding with them do not produce offspring.

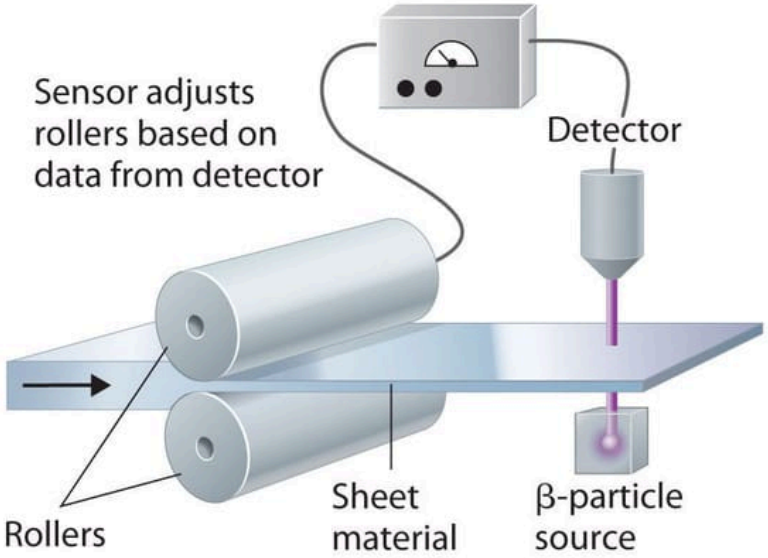


Figure 11.5.4 Using radiation to control the thickness of a material. Because the amount of radiation absorbed by a material is proportional to its thickness, radiation can be used to control the thickness of plastic film, tin foil, or paper. As shown, a beta emitter is placed on one side of the material being produced and a detector on the other. An increase in the amount of radiation that reaches the detector indicates a decrease in the thickness of the material and vice versa. The output of the detector can thus be used to control the thickness of the material.

Radioisotopes in Medicine

Radioactive tracers are also used in many medical applications, including both diagnosis and treatment. They are used to measure engine wear, analyze the geological formation around oil wells, and much more.

Radioisotopes have revolutionized medical practice, where they are used extensively. Over 10 million nuclear medicine procedures and more than 100 million nuclear medicine tests are performed annually in the United States.

Diagnostic Medical Applications

Diagnostic medical applications involve testing for a disease or condition. In nuclear medicine, this could involve using PET scans, or isotopic studies. The radiation involved for each of these types of tools will vary in mrem or mSv amounts.

PET Scanning

Positron Emission Tomography or PET scan is a type of nuclear medicine imaging. Depending on the area of the body being imaged, a radioactive isotope is either injected into a vein, swallowed by mouth, or inhaled as a gas. When the radioisotope is collected in the appropriate area of the body, the gamma ray emissions are detected by a PET scanner (often called a gamma camera) which works together with a computer to generate special pictures, providing details on both the structure and function of various organs. Watch this informational video on how this technique works.

PET Scan

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 11.5.1 *PET scans: What to expect.*

PET scans are used to:

- Detect cancer
- Determine the amount of cancer spread
- Assess the effectiveness of treatment plans
- Determine blood flow to the heart muscle
- Determine the effects of a heart attack
- Evaluate brain abnormalities such as tumors and memory disorders
- Map brain and heart function

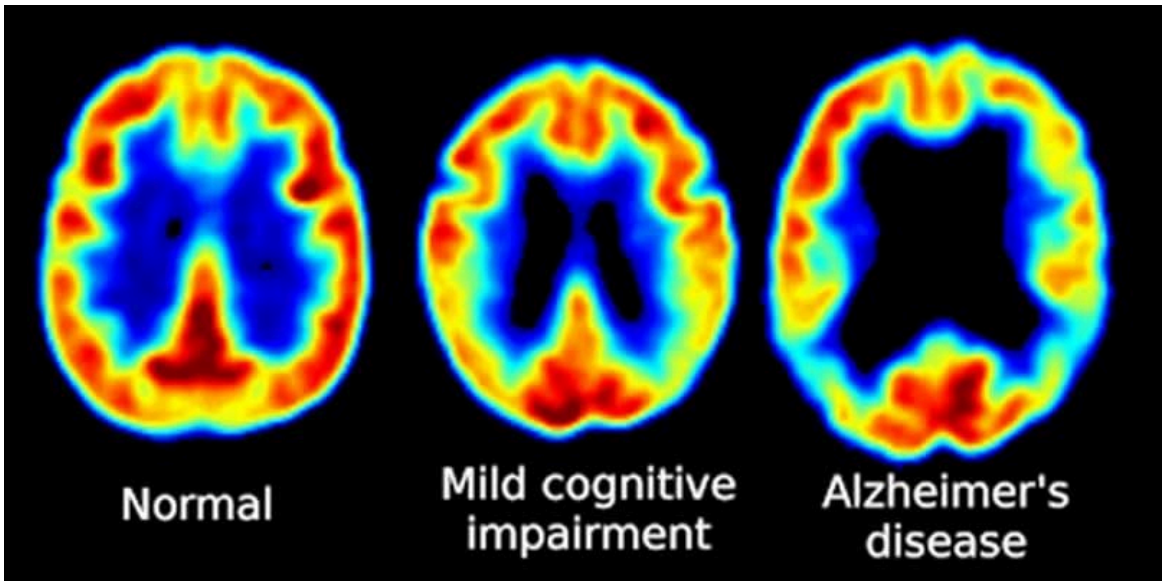


Figure 11.5.5 Mild cognitive impairment (MCI) is a state between normal ageing and dementia, where someone's mind is functioning less well than would be expected for their age. This image is for illustrative purposes only. (Public Domain; Center For Functional Imaging, Lawrence Berkeley National Laboratory. Alzheimer's Disease Neuroimaging Initiative (ADNI).

PET Scanning, is used to image the physiological aspects of the body rather than the anatomy (Figures 11.5.5 and 11.5.6). It images the function of the body rather than the form, such as where tagged molecules go and how they are used. For instance, if you were to image the brain of a deceased person, nothing would show up on a PET scan opposed to a CAT scan, as the brain is no longer functional. Pet Scanning is very useful in imaging tumors, which can be done when patients are injected with certain tracers. Often times PET scanners are used in collaboration with CAT scanners to create a composite image that shows both the function and form of the body. The animation below is a whole-body PET scan using the radioisotope of ^{18}F ($t_{1/2}$ = 110 min). Using this tracer, doctors can determine if cancer has metastasized by looking at the metabolic activity of glucose.

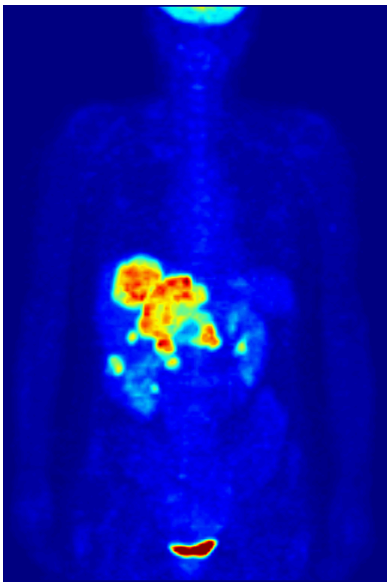


Figure 11.5.6 A whole body analysis by a PET scan. (Public Domain; Jens Maus, http://jens-maus.de/)

Other Isotopic Tests

Radioisotopes have revolutionized medical practice, where they are used extensively. Over 10 million nuclear medicine procedures and more than 100 million nuclear medicine tests are performed annually in the United States. Four typical examples of radioactive tracers used in medicine are technetium-99 ($^{99}_{43}\mathrm{Tc}$), thallium-201 ($^{201}_{81}\mathrm{Tl}$), iodine-131 ($^{131}_{53}\mathrm{I}$), and sodium-24 ($^{24}_{11}\mathrm{Na}$). Damaged tissues in the heart, liver, and lungs absorb certain compounds of technetium-99 preferentially. After it is injected, the

location of the technetium compound, and hence the damaged tissue, can be determined by detecting the γ rays emitted by the Tc-99 isotope. Thallium-201 (Figure 11.5.7) becomes concentrated in healthy heart tissue, so the two isotopes, Tc-99 and Tl-201, are used together to study heart tissue. Iodine-131 concentrates in the thyroid gland, the liver, and some parts of the brain. It can therefore be used to monitor goiter and treat thyroid conditions, such as Grave's disease, as well as liver and brain tumors. Salt solutions containing compounds of sodium-24 are injected into the bloodstream to help locate obstructions to the flow of blood.

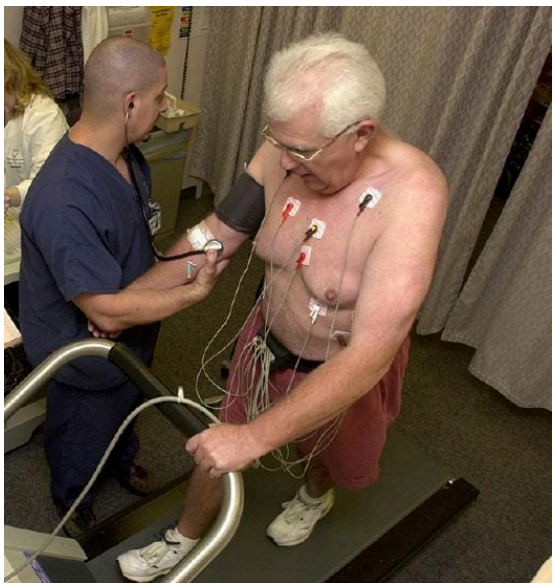


Figure 11.5.7 Administering thallium-201 to a patient and subsequently performing a stress test offer medical professionals an opportunity to visually analyze heart function and blood flow. (credit: modification of work by "BlueOctane"/Wikimedia Commons)

Small doses of I-131 (too small to kill cells) are used for purposes of imaging the thyroid. Once the iodine is concentrated in the thyroid, the patient lays down on a sheet of film and the radiation from the I-131 makes a picture of the thyroid on the film. The half-life of iodine-131 is approximately 8 days so after a few weeks, virtually all of the radioactive iodine is out of the patient's system. During that time, they are advised that they will set off radiation detectors in airports and will need to get special permission to fly on commercial flights.

Some isotopes that are used to diagnose diseases are shown in Table 11.5.1. All of these nuclear isotopes release one form of ionizing radiation (either/add particle or ray). In addition, each isotopic application would involve a specific amount of mrem/mSv radiation.

Table 11.5.1 Selected Radioisotopes Used in Diagnostic Nuclear Medicine

Symbol-mass	Half-Life ($t_{1/2}$)	Application
Xe-133	5.27 days	Lung imaging
H-3	12.26 years	Analyzing total body water
Tl-201	73 hours	Stress tests for heart problems
Fe-59	44.5 days	Detection of anemia
Gd-153	242 days	Analyzing bone density
Cr-51	27.8 days	Determining blood volume
C-11	20.4 minutes	Brain scans
Tc-99m	6.0 hours	Heart, lung, kidney, bone marrow, brain, or bone marrow imaging
Pu-238	86 years	Powering pacemakers
I-131	8.0 days	Imaging Thyroid

Symbol-mass	Half-Life ($t_{1/2}$)	Application
The “m” in Tc-99m stands for “metastable,” indicating that this is an unstable, high-energy state of Tc-99. Metastable isotopes emit γ radiation to rid themselves of excess energy and become (more) stable.		

Keep in mind that x-rays, CT scans, PET scans, and isotopic studies involve ionizing radiation. In contrast, MRI (magnetic resonance imaging) and ultrasounds do not utilize ionizing forms of radiation.

Therapeutic Radiation

There are many techniques used to treat cancer. Surgery can be used to remove cancerous tumors inside or on the body. With chemotherapy, ingested or injected chemicals are used to kill rapidly dividing cells (cancerous and noncancerous). Other cancer treatment methods include immunotherapy, stem cell replacement, hormone therapy, and targeted therapy.

Radiation therapy and Chemotherapy: Two different treatment procedures

Patients diagnosed with cancer might be required to do chemotherapy or radiation therapy. Sometimes, both of these methods are used for a patient. In this picture, a female patient is receiving chemotherapy through an IV. She is participating in cooling therapy while receiving her treatment. By placing her hands and feet in cooling devices, this will lower her chances of losing her finger and toenails. Cold cap therapy is also now available for chemotherapy patients. Wearing this type of device could enable a patient to keep his/her hair during chemotherapy.



Figure 11.5.8 *(CC BY 2.0; Jenny Mealing)*.

Current therapeutic radiation applications involve the use of gamma, x-rays, or protons. Recently, some research facilities are investigating the use of alpha and beta tagged molecules to kill cancer cells. These radioisotopes will first locate a cancer related molecule on a tumor cell. Then, the alpha or beta tagged species will inject its radiation into the tumor. Sr-89 (beta emitter) and Ra-223 (alpha emitter) have been used in clinical research trials of certain types of bone cancers.

Radiation Therapy is used as a treatment to control malignant cells within cancer patients. Oncologists (specialists that deal with cancer) utilize radiation frequently to help slow or cure the spread of cancer within individuals. Radiation is specifically applied to malignant tumors in order to shrink them in size. Medical professionals, mainly radiation oncologists, administer a variety of dosages to patient, contingent to the patients current health, as well as other treatments such as chemotherapy, success of surgery, etc.

External Beam Therapy (Photon and Proton Therapy)

External Beam Therapy (EBT) is a method of delivering a high energy beam of radiation to the precise location of a patient's tumor. These beams can destroy cancer cells and with careful planning, NOT kill surrounding cells. The concept is to have several beams of radiation, each of which is sub-lethal, enter the body from different directions. The only place in the body where the beam would be lethal is at the point where all the beams intersect. Before the EBT process, the patient is three-dimensionally mapped using CT scans and x-rays. The patient receives small tattoos to allow the therapist to line up the beams exactly. Alignment lasers are used to precisely locate the target. The radiation beam is usually generated with a linear accelerator. The video below illustrates the basic preparation and administration of external beam therapy.

Radiation Therapy

YouTube Video

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Video 11.5.2 *Targeting cancer - Radiation therapy treatment process.*

Photon EBT utilizes either x-ray or gamma rays. An x-ray source would require a linear accelerator to produce high energy electrons. In contrast, a gamma source incorporates a radioactive isotope (like Co-60). Keep in mind both of these technologies use ionizing radiation. As a result, cancer patients must be monitored throughout their life to ensure they do not develop other cancers, like leukemia. EBT is used to treat the following diseases as well as others:

- Breast cancer
- Colorectal cancer
- Head and neck cancer
- Lung cancer
- Prostate cancer

The majority of radiation patients receive photon EBT. The smaller size of this machine makes this therapy an option for all sizes of hospitals and cancer treatment centers. Photon EBT equipment costs approximately three million dollars. The size and the price of this technology enables smaller facilities to keep their patients closer to home during treatment

Another method of radiation treatment involving protons is not as commonly used in the United States. **Photon therapy** requires a cyclotron to generate proton beams (recall, a proton is an ionized H-1 isotope). Unlike x-ray or gamma rays (photon therapy), protons are extremely heavy.

At this time, research facilities are working on miniaturizing proton generators. An ideal technology would reduce the cost from hundreds of millions of dollars to about twenty to thirty million per device. This would make proton therapy more available and convenient for patients.

Proton Therapy vs Radiation Therapy

YouTube Video

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Video11.5.3 *Proton therapy versus radiation therapy*

There are many advantages to choosing proton therapy over photon therapy. Unlike photon radiation, proton beams will only penetrate to the depth of the tumor and not pass through the entire body. This reduces the overall toxicity dose. In addition, fewer treatments are required for proton therapy patients than photon therapy.Unfortunately, proton therapy is more expensive than photon therapy and less common. Once approved by a facility and medical insurance, a patient may have to move temporarily to a larger city to receive treatment. Some forms of cancer have never been clinically treated with proton therapy (namely, breast cancer). Patients desiring proton therapy might not be able to receive type of therapy due to lack of research.

Brachtherapy

Brachytherapy involves placing ionizing pellets(seeds) or rods directly at the tumor. Photons (in the form of x-ray or gamma ray) are produced inside the body and will penetrate throughout this particular area localizing the radiation. Pellets are surgically implanted while rods can be temporarily inserted to produce radiation internally. With pellets/seeds, the patient will remain radioactive as long as these devices remain inside the body. People undergoing this type of radiotherapy need to be aware of their constant emission of radiation. Radiation that is administered through rods connected to a photon device will disperse energy immediately and not leave the patient radioactive.

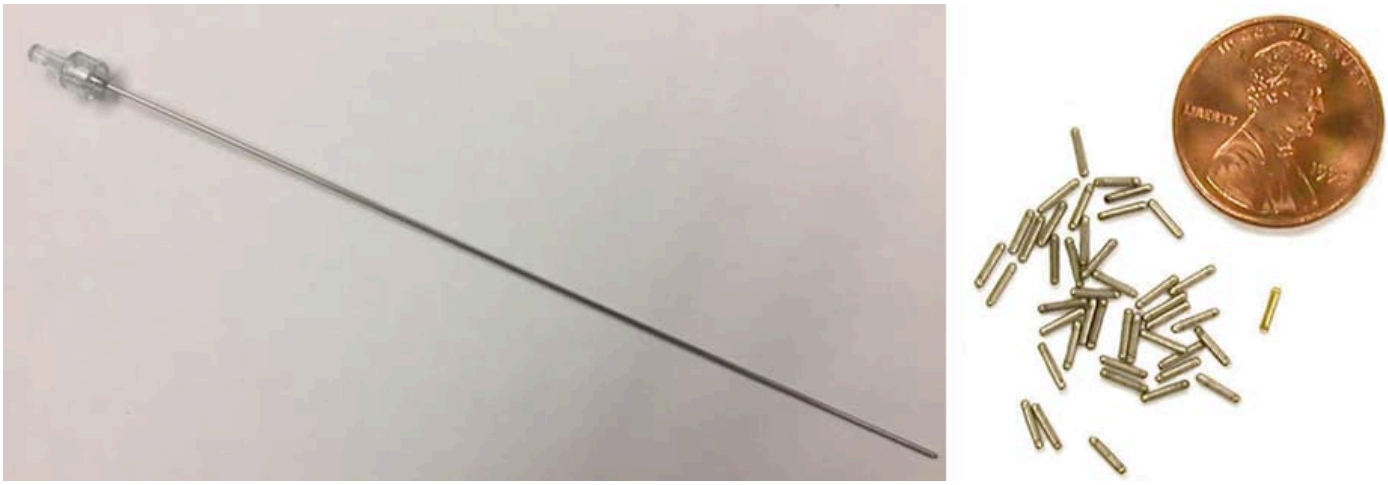


Figure 11.5.9 The picture on the left shows a brachytherapy rod. This device would be connected to a gamma source and connected inside a human body. The second images shows radioactive pellets or seeds that can be surgically implanted near a tumor. Note how small the pellets are when compared to an American penny. Image taken from: https://c1.staticflickr.com/8/7254/7...74d83b7058.jpg

Brachytherapy is widely used in the treatment of cancers involving reproductive organs. Because the radiation is isolated internally, patients are less likely to experience side effects when receiving this type of treatment. Cancers that have been treated with brachytherapy are shown below:

- Prostate
- Breast

- Esophageal
- Lung
- Uterine
- Anal/Rectal
- Sarcomas
- Head and neck

Table 11.5.2 list commonly used radionuclides for brachtherapy.

Table 11.5.2 Commonly Used Radiation Sources (radionuclides) for Brachytherapy.

Radionuclide	Type	Half-life
Cesium-131 (^{131}Cs)	Electron Capture, ε	9.7 days
Cesium-137 (^{137}Cs)	β^-- particles, γ-rays	30.17 years
Cobalt-60 (^{60}Co)	β^-- particles, γ-rays	5.26 years
Iridium-192 (^{192}Ir)	γ-rays	73.8 days
Iodine-125 (^{125}I)	Electron Capture, ε	59.6 days
Palladium-103 (^{103}Pd)	Electron Capture, ε	17.0 days
Ruthenium-106 (^{106}Ru)	β^-- particles	1.02 years
Radium-226 (^{226}Ra)	β^-- particles	1599 years

Side Effects of Radiation Therapy

Patients receiving radiation therapy can experience a variety of side effects. For example, sterility could occur if reproductive organs are irradiated. Skin that has been irradiated can appear dry and feel itchy. Some patients will loose sensation in the irradiated area. Radiation can affect the production of white and red blood cells. A reduction of white blood cells results in immunity disorders. Red blood cell lose causes anemia. Gastrointestinal issues such as diarrhea and nausea are common during radiation therapy. Some patients will lose hair as well. Lastly, dry mouth and tooth decay are prevalent during radiation treatments.

Medications are available to alleviate symptoms of radiation therapy. Narcotics can be prescribed to help alleviate intense pain. Prescription medications like zofran (Figure 11.5.10) and phenergan can help with nausea. Special mouthwashes have been formulated to reduce dry mouth and cavities.



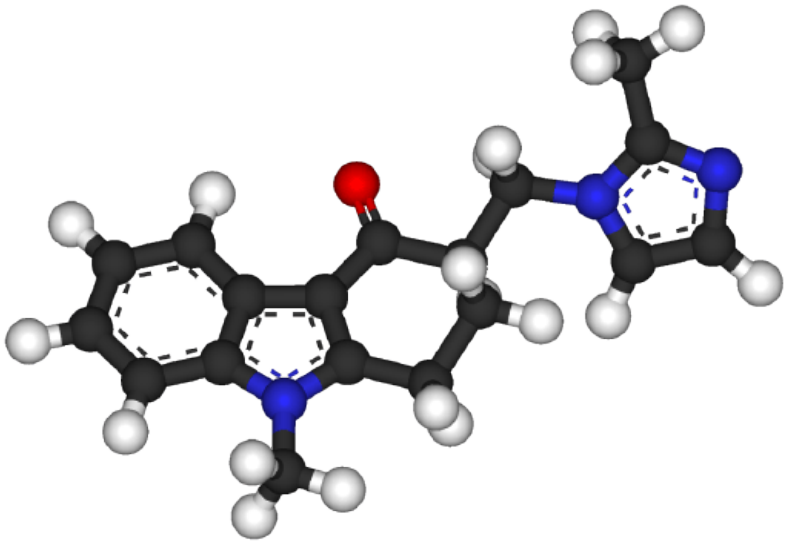


Figure 11.5.10(left) *Zofran is a medication used to prevent nausea and vomiting caused by cancer chemotherapy, radiation therapy, or surgery. (right) A vial of Zofran 4 mg containing ondansetron for intravenous injection. This medicine is a controlled substance and is used for nausea. Images used with permision (left: Public domain; Fvasconcellos and right: CC BY 3.0; Intropin)*

Hair loss is a side effect of radiation, but only locally

Radiation therapy can cause hair loss, but hair is only lost in the area being treated. For instance, radiation to your head may cause you to lose some or all the hair on your head (even eyebrows and lashes), but if you get treatment to your hip, you won't lose the hair on your head.

Summary

- Compounds known as radioactive tracers can be used to follow reactions, track the distribution of a substance, diagnose and treat medical conditions, and much more.
- Other radioactive substances are helpful for controlling pests, visualizing structures, providing fire warnings, and for many other applications.
- Hundreds of millions of nuclear medicine tests and procedures, using a wide variety of radioisotopes with relatively short half-lives, are performed every year in the US.

- Radiation therapy uses high-energy radiation to kill cancer cells by damaging their DNA. The radiation used for this treatment may be delivered externally or internally.

Contributors and Attributions

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11.6: Penetrating Power of Radiation

Learning Objective

- Compare qualitatively the ionizing and penetration power of alpha particles (α), beta particles (β), and gamma rays (γ).

With all the radiation from natural and man-made sources, we should quite reasonably be concerned about how all the radiation might affect our health. The damage to living systems is done by radioactive emissions when the particles or rays strike tissue, cells, or molecules and alter them. These interactions can alter molecular structure and function; cells no longer carry out their proper function and molecules, such as DNA, no longer carry the appropriate information. Large amounts of radiation are very dangerous, even deadly. In most cases, radiation will damage a single (or very small number) of cells by breaking the cell wall or otherwise preventing a cell from reproducing.

The ability of radiation to damage molecules is analyzed in terms of what is called **ionizing power**. When a radiation particle interacts with atoms, the interaction can cause the atom to lose electrons and thus become ionized. The greater the likelihood that damage will occur by an interaction is the ionizing power of the radiation.

Much of the threat from radiation is involved with the ease or difficulty of protecting oneself from the particles. How thick of wall do you need to hide behind to be safe? The ability of each type of radiation to pass through matter is expressed in terms of **penetration power.** The more material the radiation can pass through, the greater the penetration power and the more dangerous they are. In general, the greater mass present the greater the ionizing power and the lower the penetration power.

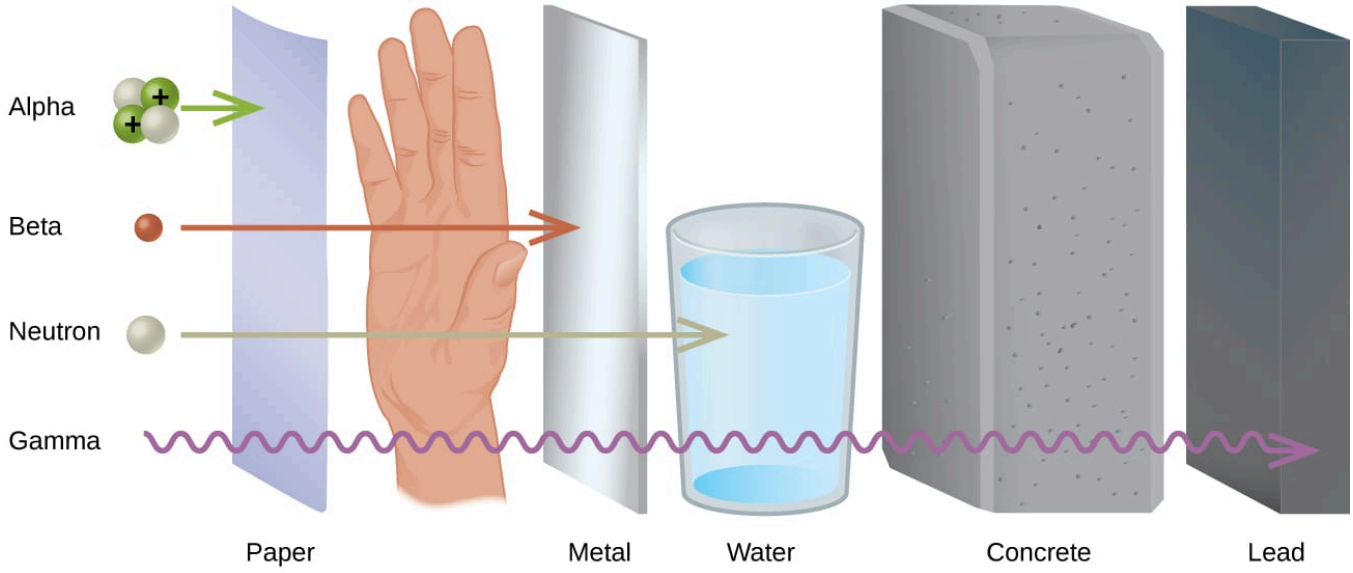


Figure 11.6.1: The ability of different types of radiation to pass through material is shown. From least to most penetrating, they are alpha < beta < neutron < gamma. (CC BY-SA 4.0; OpenStax).

Comparing only the three common types of ionizing radiation, **alpha particles** have the greatest mass. Because of the large mass of the alpha particle, it has the highest ionizing power and the greatest ability to damage tissue. That same large size of alpha particles, however, makes them less able to penetrate matter. Alpha particles have the least penetration power and can be stopped by a thick sheet of paper or even a layer of clothes. They are also stopped by the outer layer of dead skin on people. This may seem to remove the threat from alpha particles but only from external sources. In a situation like a nuclear explosion or some sort of nuclear accident where radioactive emitters are spread around in the environment, the emitters can be inhaled or taken in with food or water and once the alpha emitter is inside you, you have no protection at all.

Beta particles are much smaller than alpha particles and therefore, have much less ionizing power (less ability to damage tissue), but their small size gives them much greater penetration power. Most resources say that beta particles can be stopped by a one-quarter inch thick sheet of aluminum. Once again, however, the greatest danger occurs when the beta emitting source gets inside

of you.

Gamma rays are not particles but a high energy form of electromagnetic radiation (like x-rays except more powerful). Gamma rays are energy that has no mass or charge. Gamma rays have tremendous penetration power and require several inches of dense material (like lead) to shield them. Gamma rays may pass all the way through a human body without striking anything. They are considered to have the least ionizing power and the greatest penetration power.

A comparison of Alpha particles, beta particles and gamma rays is given in Table $11.6.1$.

Table $11.6.1$ *Comparison of Penetrating Power,Ionizing Power and Shielding of Alpha and Beta Particles, and Gamma Rays.*

Particle	Symbol	Mass	Penetrating Power	Ionizing Power	Shielding
Alpha	α	4amu	Very Low	Very High	Paper Skin
Beta	β	$1/2000\text{amu}$	Intermediate	Intermediate	Aluminum
Gamma	γ	0 (energy only)	Very High	Very Low	2 inches lead

The safest amount of radiation to the human body is zero. It isn't possible to be exposed to no ionizing radiation so the next best goal is to be exposed to as little as possible. The two best ways to minimize exposure is to limit time of exposure and to increase distance from the source.

Summary

- Types of radiation differ in their ability to penetrate material and damage tissue, with alpha particles the least penetrating but potentially most damaging and gamma rays the most penetrating.
- The two best ways to minimize exposure is to limit time of exposure and to increase distance from the source.

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11.7: Energy from the Nucleus

Learning Objectives

- Explain where nuclear energy comes from.
- Describe the difference between fission and fusion.
- Know key examples of nuclear fission and nuclear fusion.

A combination of radiochemistry and radiation chemistry is used to study nuclear reactions such as fission and fusion. Some early evidence for nuclear fission was the formation of a short-lived radioisotope of barium which was isolated from neutron irradiated uranium (^{139}Ba, with a half-life of 83 minutes and ^{140}Ba, with a half-life of 12.8 days, are major fission products of uranium). **Nuclear fission** is the splitting of an atomic nucleus. In nuclear weapons and reactors, neutrons hit unstable nuclei to form smaller atoms. **Nuclear Fusion** is the bringing together of two atomic nuclei to form a larger atom. Figure 11.7.1 illustrates the difference between nuclear fission and nuclear fusion.

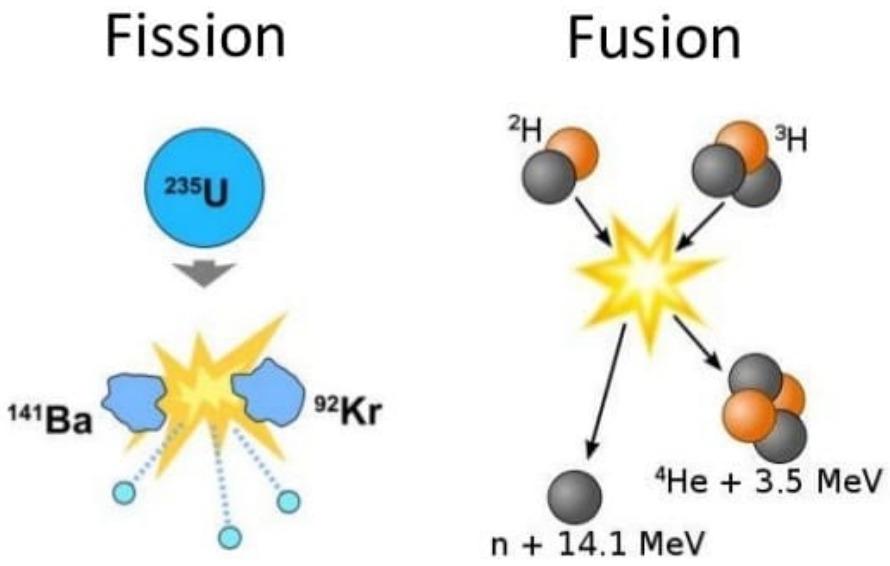


Figure 11.7.1 Nuclear fission occurs with one large nuclear is split into two or more smaller nuclei (left) . Nuclear fusion happens when two small nuclei combine to make a larger nucleus (right) .

Einstein and the Equivalence of Mass and Energy

Nuclear changes occur with a simultaneous release of energy. Where does this energy come from? If we could precisely measure the masses of the reactants and products of a nuclear reaction, we would notice that the amount of mass drops slightly in the conversion from reactants to products. Consider the following nuclear equation, in which the molar mass of each species is indicated to four decimal places:

$$^{235}_{235.0439}\mathrm{U} \rightarrow ^{139}_{138.9088}\mathrm{Ba} + ^{94}_{93.9343}\mathrm{Kr} + ^{2^1}_{2\times 1.0087}\mathrm{n}$$

If we compare the mass of the reactant (235.0439) to the masses of the products (sum=234.8605) we notice a mass difference of -0.1834 g or -0.0001834 kg. Where did this mass go?

According to Albert Einstein's theory of relativity, energy (*E*) and mass (*m*) are related by the following equation:

$$E = mc^2$$

where *c* is the speed of light, or

$$c = 3.00 \times 10^8\, m/s$$

In the course of the chemical reaction for uranium, the mass difference is converted to energy, which is given off by the reaction:

$$E = (-0.0001834\, kg)(3.00 \times 10^8\, m/s)^2 = -1.65 \times 10^{13} J = -1.65 \times 10^{10} kJ$$

(For the units to work out, mass must be expressed in units of kilograms.) That is, 16.5 billion kJ of energy is given off every time 1 mol of uranium-235 undergoes this nuclear reaction. This is an extraordinary amount of energy. Compare it to combustion reactions of hydrocarbons, which give off about 650kJ/mol of energy for every CH_2 unit in the hydrocarbon-on the order of *hundreds* of kilojoules per mole. Nuclear reactions give off *billions* of kilojoules per mole.

If this energy could be properly harvested, it would be a significant source of energy for our society. **Nuclear energy** involves the controlled harvesting of energy from fission reactions. The reaction can be controlled because the fission of uranium-235 (and a few other isotopes, such as plutonium-239) can be artificially initiated by injecting a neutron into a uranium nucleus. The overall nuclear equation, with energy included as a product, is then as follows:

$$^{235}\mathrm{U} + {}^{1}\mathrm{n} \rightarrow {}^{139}\mathrm{Ba} + {}^{94}\mathrm{Kr} + 3\,{}^{1}\mathrm{n}$$

Thus by the careful addition of extra neutrons into a sample of uranium, we can control the fission process and obtain energy that can be used for other purposes. (Artificial or induced radioactivity, in which neutrons are injected into a sample of matter that subsequently cause fission, was first demonstrated in 1934 by Irène Joliot-Curie and Frédéric Joliot, the daughter and son-in-law of Marie Curie.)

Binding Energy

The forces that bind nucleons together in an atomic nucleus are much greater than those that bind an electron to an atom through electrostatic attraction. This is evident by the relative sizes of the atomic nucleus and the atom (10^{-15} and 10^{-10}m, respectively). The energy required to pry a nucleon from the nucleus is therefore much larger than that required to remove (or ionize) an electron in an atom. In general, all nuclear changes involve large amounts of energy per particle undergoing the reaction. This has numerous practical applications.

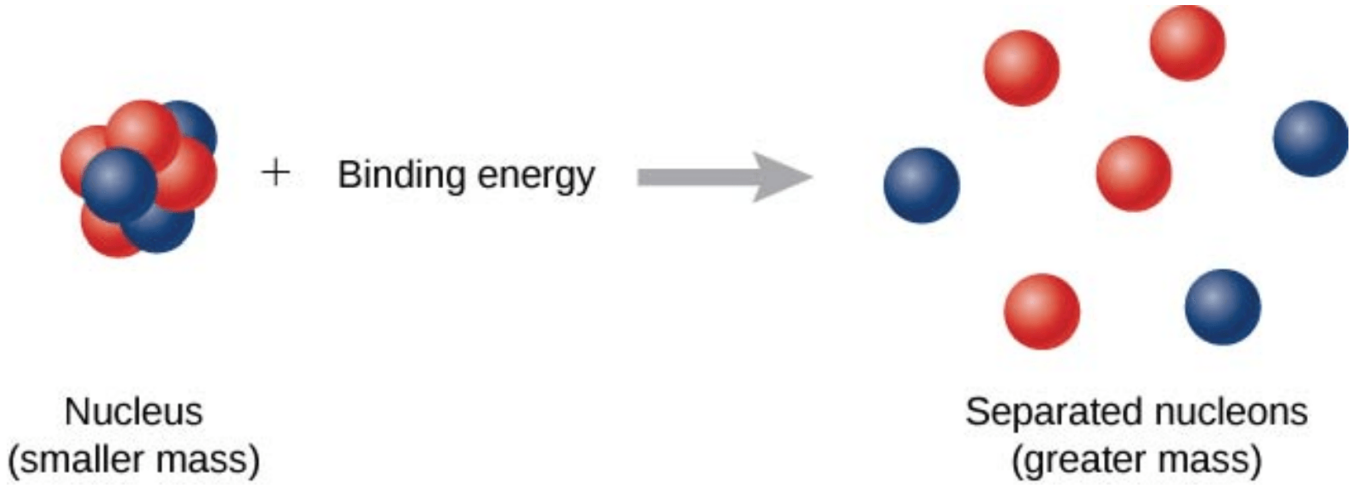


Figure 11.7.2*The binding energy is the energy required to break a nucleus into its constituent protons and neutrons. A system of separated nucleons has a greater mass than a system of bound nucleons.*

As shown in figure 11.7.2, energy is put into the system to break apart the nucleus. The amount of energy required is called the total **binding energy** (BE), E_b. The binding energy is equal to the amount of energy released in forming the nucleus, and is therefore given by

$$E_b = (\Delta m)c^2. \tag{11.7.1}$$

In nuclear physics, one of the most important experimental quantities is the *binding energy per nucleon (BEN)*, which is defined by

$$BEN = \frac{E_b}{A} \tag{11.7.2}$$

This quantity is the average energy required to remove an individual nucleon (proton or neutron) from a nucleus—analogous to the ionization energy of an electron in an atom. If the BEN is relatively large, the nucleus is relatively stable. BEN values are estimated from nuclear scattering experiments.

Figure 11.7.3 shows the relative binding energies for various isotopes. Of these elements, fission requires heavy, unstable nuclei. This means selected atoms would have low binding energies and would have large atomic masses. Nuclei that are larger than Fe-56 may undergo fission. Uranium-238 and uranium-235 both have lower binding energies with heavy masses-.

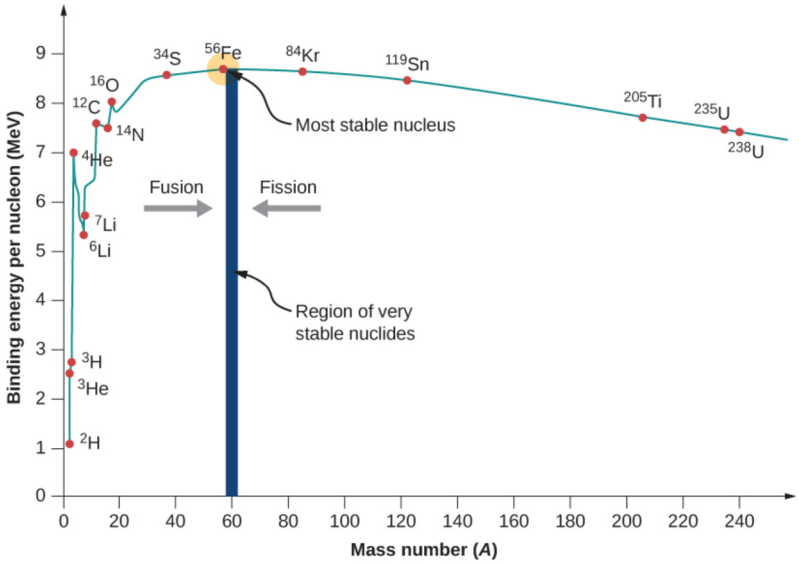


Figure 11.7.3 In this graph of binding energy per nucleon for stable nuclei, the BEN is greatest for nuclei with a mass near ^{56}Fe. Therefore, fusion of nuclei with mass numbers much less than that of Fe, and fission of nuclei with mass numbers greater than that of Fe, are exothermic processes. (CC BY. OpenStax).

These two isotopes would be suitable for splitting based on these requirements. Of these two isotopes, only uranium-235 is readily fissionable. This is due to odd neutron count contributing to additional instability. Another fissionable isotope not shown in Figure 11.7.3 is plutonium-239. This is a synthetic isotope produced by transmutation and decay reactions. Like uranium-235, it has low binding energy, high mass, and an odd number of neutrons. U-235 and Pu-239 are used in atomic bombs (fission based) and nuclear reactors.

Positively charged centers of atoms make nuclear fusion extremely difficult. For this reason, smaller atoms are suitable for fusion reactions. In addition, these particular isotopes need to have low binding energies in order to undergo fusion. Atoms that possess these two qualities are H-2 and H-3. For fusion to occur, extreme temperatures are required to fuse these deuterium and tritium together.

As we will see, the BEN-versus-*A* graph implies that nuclei divided or combined release an enormous amount of energy. This is the basis for a wide range of phenomena, from the production of electricity at a nuclear power plant to sunlight.

Nuclear Fission

In both fission and fusion, large amounts of energy are given off in the form of heat, light, and gamma radiation. Italian physicist, Enrico Fermi, performed the first fission reaction in 1934. He was unaware that he had split a uranium atom into two smaller nuclei. Nuclear fission of heavy elements was discovered on December 17, 1938 by German Otto Hahn and his assistant Fritz Strassmann, and explained theoretically in January 1939 by Lise Meitner (Figure 11.7.4) and her nephew Otto Robert Frisch. Frisch named the process "fission" by analogy with biological fission of living cells.

Figure 11.7.4 *Austrian physicist, Lise Meitner of U-238.*

Image take from: https://upload.wikimedia.org/wikiped...ner12crop2.J

Since then, fission has been observed in many other isotopes, including most actinide isotopes that have an odd number of neutrons. A typical nuclear fission reaction is shown in Figure 11.7.5.

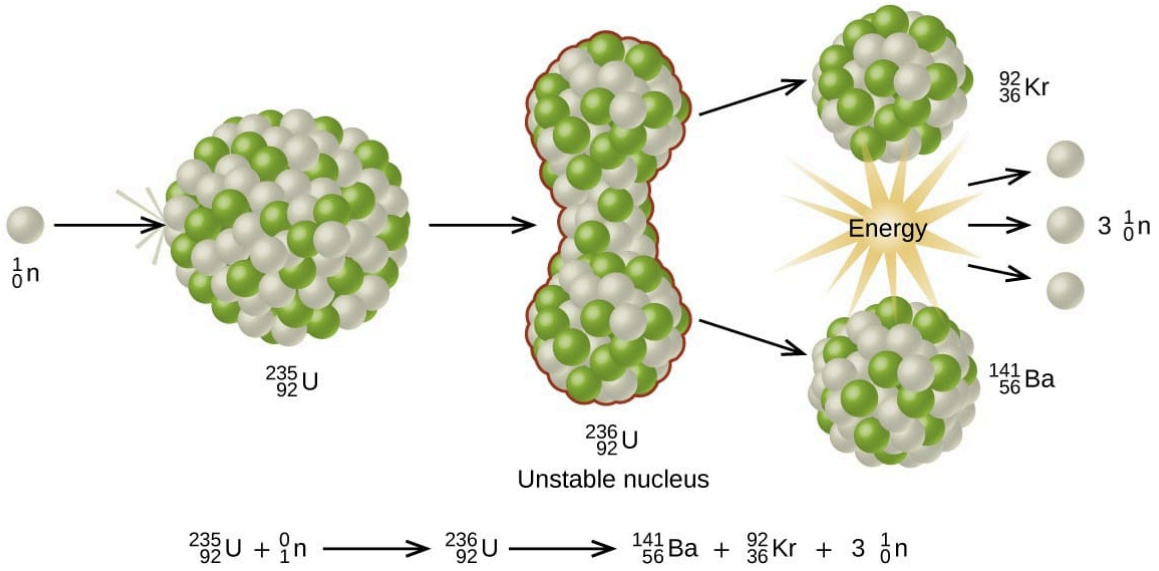


Figure 11.7.5 When a slow neutron hits a fissionable U-235 nucleus, it is absorbed and forms an unstable U-236 nucleus. The U-236 nucleus then rapidly breaks apart into two smaller nuclei (in this case, Ba-141 and Kr-92) along with several neutrons (usually two or three), and releases a very large amount of energy.

Among the products of Meitner, Hahn, and Strassman's fission reaction were barium, krypton, lanthanum, and cerium, all of which have nuclei that are more stable than uranium-235. Since then, hundreds of different isotopes have been observed among the products of fissionable substances.

Fission has been used in nuclear weapons and powers all nuclear reactors. Approximately fifty-five countries worldwide possess fission technology in the form of research or energy reactors. Less than ten of these countries have fission weapons.

A tremendous amount of energy is produced by the fission of heavy elements. For instance, when one mole of U-235 undergoes fission, the products weigh about 0.2 grams less than the reactants; this "lost" mass is converted into a very large amount of energy, about 1.8×10^{10} kJ per mole of U-235. Nuclear fission reactions produce incredibly large amounts of energy compared to chemical reactions. The fission of 1 kilogram of uranium-235, for example, produces about 2.5 million times as much energy as is produced by burning 1 kilogram of coal.

Nuclear Chain Reaction

As described earlier, when undergoing fission U-235 produces two "medium-sized" nuclei, and two or three neutrons. These neutrons may then cause the fission of other uranium-235 atoms, which in turn provide more neutrons that can cause fission of even more nuclei, and so on. If this occurs, we have a nuclear chain reaction (Figure 11.7.6). On the other hand, if too many neutrons escape the bulk material without interacting with a nucleus, then no chain reaction will occur.

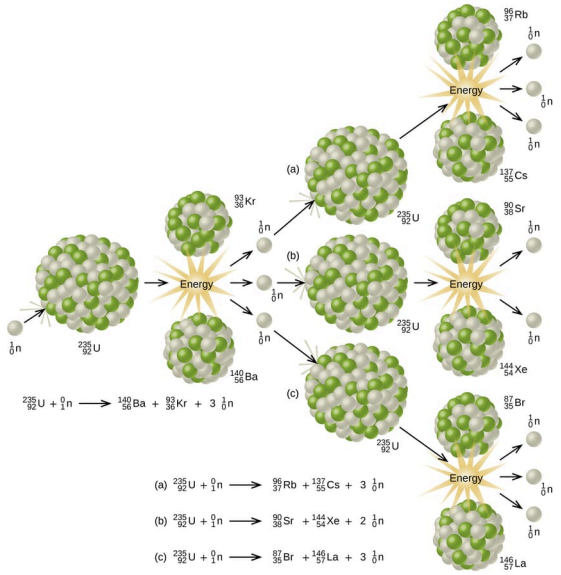


Figure 11.7.6 The fission of a large nucleus, such as U-235, produces two or three neutrons, each of which is capable of causing fission of another nucleus by the reactions shown. If this process continues, a nuclear chain reaction occurs.

Material that can sustain a nuclear fission chain reaction is said to be fissile or fissionable. (Technically, fissile material can undergo fission with neutrons of any energy, whereas fissionable material requires high-energy neutrons.) Nuclear fission becomes self-sustaining when the number of neutrons produced by fission equals or exceeds the number of neutrons absorbed by splitting nuclei plus the number that escape into the surroundings. The amount of a fissionable material that will support a self-sustaining chain reaction is a critical mass. An amount of fissionable material that cannot sustain a chain reaction is a subcritical mass. An amount of material in which there is an increasing rate of fission is known as a supercritical mass. The critical mass depends on the type of material: its purity, the temperature, the shape of the sample, and how the neutron reactions are controlled (Figure 11.7.7).

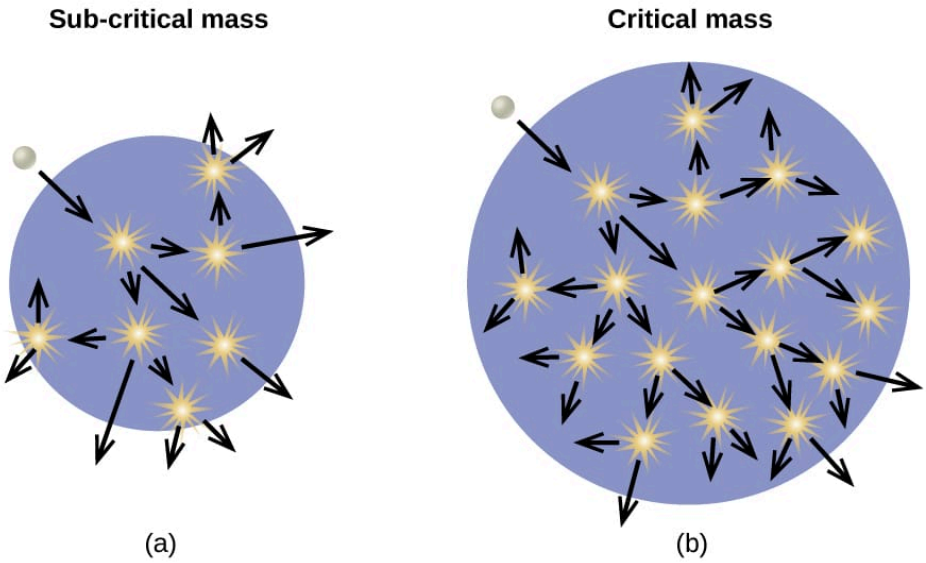


Figure 11.7.7 (a) In a subcritical mass, the fissile material is too small and allows too many neutrons to escape the material, so a chain reaction does not occur. (b) In a critical mass, a large enough number of neutrons in the fissile material induce fission to create a chain reaction.

Thermonuclear Reactions

Thermonuclear fusion is a way to achieve nuclear fusion by using extremely high temperatures. There are two forms of thermonuclear fusion: *uncontrolled*, in which the resulting energy is released in an uncontrolled manner, as it is in thermonuclear

weapons ("hydrogen bombs") and in most stars; and *controlled*, where the fusion reactions take place in an environment allowing some or all of the energy released to be harnessed for constructive purposes. The discussion below is limited to the fusion process that powers the sun and the stars.

The prime energy producer in the sun is the fusion of hydrogen to form helium, which occurs at a solar-core temperature of 14 million kelvin. The net result is the fusion of four protons into one alpha particle, with the release of two positrons, two neutrinos (which changes two of the protons into neutrons), and energy (Figure 11.7.8).

This is a net reaction of a more complicated series of events:

$$4\,{}^{1}_{1}\mathrm{H} \longrightarrow {}^{4}_{2}\mathrm{He} + 2\,{}^{1}_{0}\mathrm{n}$$

A helium nucleus has a mass that is 0.7% less than that of four hydrogen nuclei; this lost mass is converted into energy during the fusion. This reaction produces about 3.6×10^{11} kJ of energy per mole of ${}^{4}_{2}\mathrm{He}$ produced. This is somewhat larger than the energy produced by the nuclear fission of one mole of U-235 (1.8×10^{10} kJ), and over 3 million times larger than the energy produced by the (chemical) combustion of one mole of octane (5471 kJ).

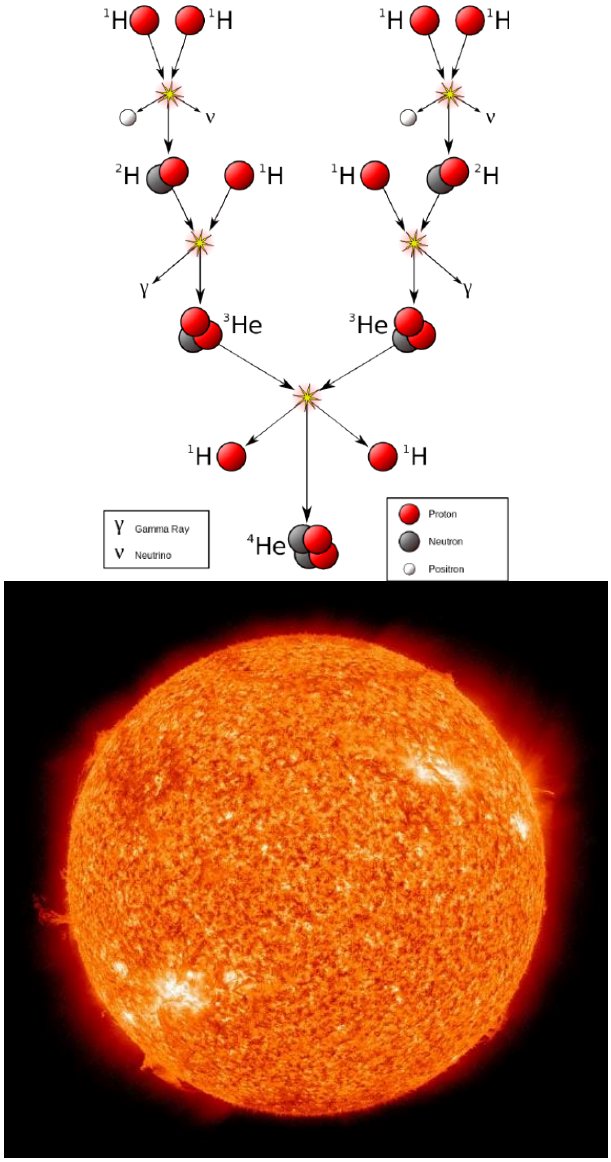


Figure 11.7.8 Nuclear fusion producing helium (left). The Sun is a main-sequence star, and thus generates its energy by nuclear fusion of hydrogen nuclei into helium (right).

Summary

- Nuclear energy comes from tiny mass changes in nuclei as radioactive processes occur.
- In fission, large nuclei break apart and release energy; in fusion, small nuclei merge together and release energy.
- The continues process whereby neutrons produced from the initial fission of a large nucleus like U-235 cause further fission of another nucleus.
- In a critical mass, a large enough number of neutrons in the fissile material induce fission to create a chain reaction.
- The most important fusion process in nature is the one that powers the stars. The net result is the fusion of four protons into one alpha particle, with the release of two positrons, two neutrinos (which changes two of the protons into neutrons), and energy

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- TextMap: Beginning Chemistry (Ball et al.)

- Marisa Alviar-Agnew (Sacramento City College)

- Wikipedia

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11.8: Nuclear Bombs

Learning Objectives

- Describe the key features of an atomic bomb.
- Define nuclear fallout.

World war two brought about many advances in weaponry. The Nazis used the immense science ability of their newly conquered countries to attempt to create super weapons to keep the new territory. The weapons included new tanks like the feared Tiger Tank, or the highly advanced Luftwaffe air force. However, the one weapon the Nazi's really wanted to hold was the atomic bomb. The problem that the Nazi's began to have though was that many of the great minds they once had left the country and came to the United States. Also, in the end Allied troops got to Hitler and his scientists just before they could complete any atomic bombs. The U.S. also wanted to create an atom bomb, and for the same reasons. The Manhattan Project was started to form this new weapon.

The Manhattan Project was successful in the United States because of the vast resources that could be pulled together for the project. The great minds worked under the University of Chicago football field to try and create fission. A plant in Tennessee had the sole purpose of producing enough uranium for atomic bomb testing. Finally, New Mexico was the epicenter of the whole operation. This is where the bombs were constructed and tested. The resources needed were immense. There had to be enough fuel for the bomb, and everything required to make it. There had to be housing and food for all the scientists. Maybe most importantly, there had to be enough money to support the project. The Unites States was able to effectively use all of these resources, while the Germans did not have the resources, and didn't use them as effectively. Finally, after years of hard work an atomic bomb test took place of July 16, 1945. The bomb was held together in some parts by just tape, yet it was a huge success. The problem was that the war in Europe was already over, so President Truman had to decide whether or not to use the bomb on Japan.

The war in the Pacific was a lot different than the war in Europe. In Europe, you landed once and fought your way through to Berlin to defeat the Nazi's. However, in the Pacific Japan controlled hundreds of Islands before you got to the mainland. The invasion would have cost huge amounts of American lives and resources. As a result, when the bomb had a successful test President Truman said he hardly hesitated to approve of the usage of the atomic bomb on Japan.

The first atomic bomb was dropped on Hiroshima on August 6, 1945 by the Enola Gay. The bomb destroyed the city, killing almost 100,000 people. The city of Hiroshima was essentially leveled. Following this attack, on August 9, 1945 another atomic bomb was dropped on Nagasaki. The same effects were felt in this city. The United States was ready to drop another atomic bomb in the third week of August, 3 more in September, and 3 more in October if necessary. However, on August 15 Japan surrendered to the allies and World War Two was officially over.



Figure 11.8.1 (left) Hiroshima before the atomic bomb (right) Hiroshima after the atomic bomb

The Workings of the Atomic Bomb

A crucial feature of the fission of uranium without which an atom bomb is impossible is that fission *produces more neutrons than it consumes*. As can be seen from Eqs. (1), for every neutron captured by a $^{235}_{92}\mathrm{U}$ nucleus, between two and four neutrons are produced. Suppose now that we have a very large sample of the pure $^{235}_{92}\mathrm{U}$ isotope and a stray neutron enters this sample. As soon as it hits a $^{235}_{92}\mathrm{U}$ nucleus, fission will take place and about three neutrons will be produced. These in turn will fission three more $^{235}\mathrm{U}$ nuclei, producing a total of nine neutrons. A third repetition will produce 27 neutrons. a fourth 81. and so on. This process (which is called a *chain reaction*) escalates very rapidly. Within a few microseconds a very large number of nuclei fission, with the release of a tremendous amount of energy, and an atomic explosion results.

$$
{}^{235}_{92}\mathrm{U} + {}^{1}_{0}n \longrightarrow \left[{}^{236}_{92}\mathrm{U}\right] \begin{cases} \longrightarrow {}^{140}_{56}\mathrm{Ba} + {}^{93}_{36}\mathrm{Kr} + 3{}^{1}_{0}n \\ \longrightarrow {}^{144}_{55}\mathrm{Cs} + {}^{90}_{37}\mathrm{Rb} + 2{}^{1}_{0}n \\ \longrightarrow {}^{144}_{54}\mathrm{Xe} + {}^{90}_{38}\mathrm{Sr} + 2{}^{1}_{0}n \\ \longrightarrow {}^{146}_{57}\mathrm{La} + {}^{87}_{35}\mathrm{Br} + 3{}^{1}_{0}n \\ \longrightarrow {}^{160}_{62}\mathrm{Sm} + {}^{72}_{30}\mathrm{Zn} + 4{}^{1}_{0}n \end{cases}
$$

There are two reasons why a normal sample of uranium metal does not spontaneously explode in this way. In the first place natural uranium consists mainly of the isotope $^{238}_{92}\mathrm{U}$, while the fissionable isotope $^{235}_{92}\mathrm{U}$ comprises only 0.7 percent of the total. Most of the neutrons produced in a given fission process are captured by $^{238}_{92}\mathrm{U}$ nuclei without any further production of neutrons. The escalation of the fission process thus becomes impossible. However, even a sample of pure $^{235}\mathrm{U}$ will not always explode spontaneously. If it is sufficiently small, many of the neutrons will escape into the surroundings without causing further fission. The sample must exceed a **critical mass** before an explosion results. In an atomic bomb several pieces of fissionable material, all of which are below the critical mass, are held sufficiently far apart for no chain reaction to occur. When these are suddenly

brought together, an atomic explosion results immediately.

Two types of atomic bombs were developed concurrently during the war: a relatively simple and a more complex . The gun-type design proved impractical to use with , and therefore a simpler gun-type called was developed that used , an that makes up only 0.7 percent of natural . Chemically identical to the most common isotope, , and with almost the same mass, it proved difficult to separate the two.

In parallel with the work on uranium was an effort to produce , which was discovered at the in 1940. After the feasibility of the world's first artificial nuclear reactor, the , was demonstrated in 1942 at the in the , the Project designed the at Oak Ridge and the production reactors at the in , in which uranium was irradiated and into plutonium. The plutonium was then chemically separated from the uranium, using the . The plutonium implosion-type weapon was developed in a concerted design and development effort by the Los Alamos Laboratory.

Isotopic Enrichment

A great deal of the five years of the Manhattan Project was spent in separating the 0.7 percent of ^{235}U from the more abundant ^{238}U. Most of this work was performed at the at . This was done by preparing the gaseous compound UF_6 and allowing it to effuse through a porous screen. Each effusion resulted in a gas which was slightly richer in the lighter isotope. Repeating this process eventually produced a compound rich enough in ^{235}U for the purposes of bomb manufacture.

Synthesis of Plutonium

In parallel with the work on uranium was an effort to produce , which was discovered at the in 1940. Only the first bomb dropped on Japan used uranium. The second bomb used the artificial element *plutonium*, produced by the neutron bombardment of ^{238}U:

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{239}_{94}\mathrm{Pu} + 2\,{}^{0}_{-1}\beta$$

Fission of Pu-239 occurs in much the same way as for U-235, giving a variety of products; for example,

$$^{239}_{94}\mathrm{Pu} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{90}_{38}\mathrm{Pu} + {}^{147}_{56}\mathrm{Ba} + 3\,{}^{1}_{0}\mathrm{n}$$

Again this is a highly exothermic reaction yielding about the same energy per mole (20 000 GJ mol^{-1}) as ^{235}U.

This immense amount of energy released is the reason why plutonium and uranium were used. By comparison, 1 ton of TNT yields about 4 GJ mol^{-1} of energy. This means that the atomic bombs had about 5,000 times more energy than 1 ton of TNT, that is a huge amount of energy, and explains why the bomb was so effective and destructive.

Nuclear Explosion

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 11.8.1 *Nuclear explosion power comparison.*

Although the Fat Man atomic bomb was extremely powerful and destructive, it is not even close to the power of subsequent nuclear bombs. The atomic age was set forth by the United States on those two fateful days in August. In the subsequent years many other countries harnessed the power of nuclear weapons, including Russia, China, Britain, and France. The "high point" of

the atomic age came with the explosion of the *Tsar Bomba* by Russia. This bomb was equal to 50 megatons of TNT, or 2,500 times more powerful than the Fat Man bomb. It was said that when the bomb was detonated the shock wave in the ground could be felt over 600 miles away (the bomb wasn't even detonated on the ground either, but rather in mid air!). The advance and use of nuclear weapons seemed to be growing at an extraordinarily fast pace. However, countries stepped up and signed various treaties, including the Nuclear Non-Proliferation Treaty, to stop the increase in nuclear weapons and hopefully the use of any more in the future.

Bomb Construction

At Los Alamos, New Mexico, J. Robert Oppenheimer, and his research group were given the task of assembling and testing the fission bomb. Both types of fuel that were manufactured (U-235 and Pu-239) would be placed separately into two different bomb designs. The smaller of the two bombs would contain U-235 and was code-named "Little Boy." The larger bomb, which housed Pu-239, was named "Fat Man." Of the two, only the Pu-239 bomb would be tested before it was dropped in wartime.

The basic design of the U-235 bomb is shown in the figure below. To prevent the spontaneous detonation of an atomic bomb, the fissile U-235 is kept in a subcritical configuration. It is then rapidly assembled into a supercritical mass using conventional explosives. Once the bomb has achieved this mass, any neutron introduced into it will be likely to initiate a chain reaction. The mechanism for "Little Boy" was a gun that fired one subcritical piece of U-235 into another to form a supercritical mass (Figure 11.8.2). The pieces had to be assembled within a time less than the average time between appearances of spontaneous neutrons from either U-235 or cosmic radiation. A conventional explosive in an artillery barrel could fire the U-235 mass at speeds of a few millimeters per second, fast enough to prevent a fizzle caused by a spontaneous neutron setting off a premature chain reaction.

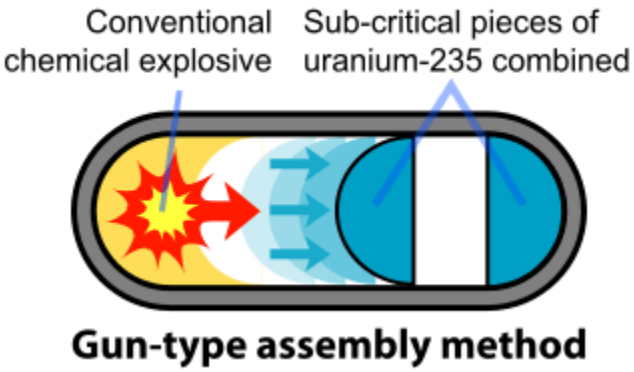


Figure 11.8.2: Little Boy: Gun-Type Device. (Public Domain).

Originally, the gun-type mechanism was planned for both the U-235 and Pu-239 weapons. However, a problem arose with the Pu-239 bomb that required a different assembly mechanism because of the small amount of Pu-240 that is produced with the Pu-239 in the reactor. Pu-240 emits large numbers of neutrons spontaneously: 1,030 neutrons per gram per second compared with 0.0004 neutrons per gram per second for U-235. Even at a concentration of 1% Pu-240 in the fissile Pu-239, the required mass of Pu emits 52,000 neutrons per second or one neutron every 20 microseconds. Thus, it is very probable that a neutron from Pu-240 will initiate a premature chain reaction during the critical last 100 microseconds of the critical mass in a gun-type assembly. This problem was discovered in mid-1944, well after the start of the construction of the massive Hanford plutonium production facilities.

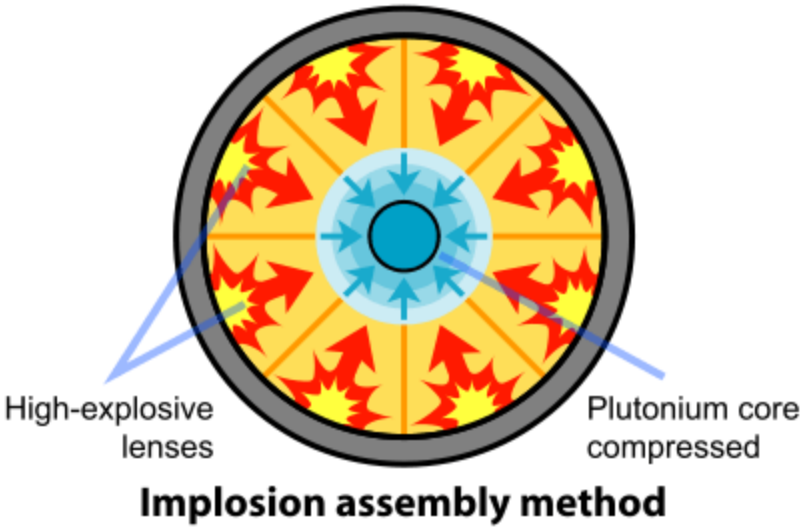


Figure 11.8.3: Fat Man: Implosion-type bomb. (Public Domain).

The removal of the Pu-240 was impractical. So the scientists and engineers looked for a faster method of assembling the plutonium. A mechanism based on implosion provided the solution to this problem. In this design, the fissile material is shaped into a single sphere with a mass slightly less than critical (Figure 11.8.3). Layers of carefully shaped high explosives surround the sphere. When the explosives are detonated, the force of the shock wave compresses the fissile material into a smaller volume, forming a supercritical mass. This method of assembly is much faster than the gun-type mechanism and thus eliminates the problems resulting from spontaneous neutron emission of Pu-240. The spherical mass resulted in a pumpkin-shaped weapon called "Fat Man".

Example 11.8.1

Watch the from the 23-minute mark through the 32-minute mark of the third installment of the History Channel's Manhattan Project and answer the questions below.

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

1. What were the problems with the two different types of fuel that were to be used in the fission weapons?
2. What was the configuration or set-up of the Pu-239 bomb?
3. The combination of electromagnetic separation and gaseous diffusion enriched enough U-235 to produce how many bombs?
4. Why was the U-235 bomb never tested?
5. When was the construction of the U-235 completed?
6. How much did Truman know about the nuclear bombs when FDR was alive?
7. Who was selected to pilot the plane for the nuclear weapons?
8. What island would serve as a base to house the nuclear bombs before delivering them to their targets?

In July 1945, the United States had enough fissile material for one uranium and two plutonium weapons. The scientists and engineers felt confident that the gun-type assembly mechanism for Little Boy would function properly. Besides, they did not have the material for a test device. They were less confident about the implosion mechanism on the plutonium weapon and felt that a test was necessary. On July 16, 1945, the first nuclear device, known as "The Gadget", was placed on a 100-foot tower and successfully detonated in the Alamogordo Desert, 200 miles south of Los Alamos (Figure 11.8.4).

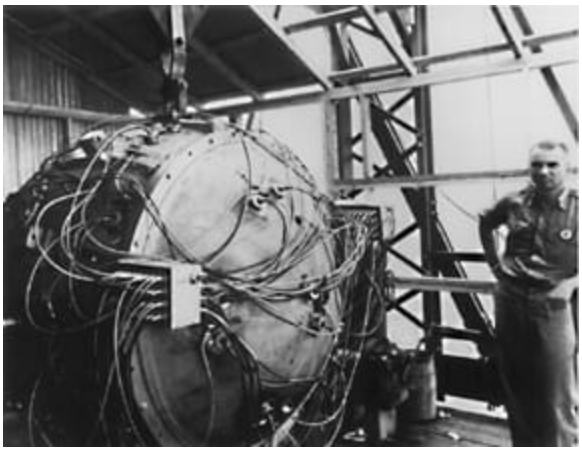


Figure 11.8.4: The Gadget at the Trinity Test Site, 1945. Courtesy of the U.S. Department of Defense

As the war with Japan continued and a costly allied invasion loomed as a real possibility, President Truman approved the use of nuclear weapons against selected Japanese targets. The U.S. Army Air Force received orders to use these weapons anytime after August 3, 1945. On August 6, "Little Boy" was dropped on Hiroshima (Figure 11.8.5).



Figure 11.8.5: Little Boy - The only U-235 weapons constructed during WWII. Courtesy of the U.S. Department of Defense

Little Boy was a uranium weapon containing 141.4 pounds of fissionable material containing 82.7% U-235. Only about two pounds fissioned, releasing an energy equivalent to 15-16,000 tons of TNT. The immediate effects of the blast killed an estimated 70,000 people, and by the end of 1945 an additional 20,000 to 70,000 deaths occurred, many due to lack of adequate medical resources.

Three days later, "Fat Man" destroyed a large part of Nagasaki (Figure 11.8.6). Fat Man contained 13.6 pounds of Pu-239, of which only 2 pounds underwent fission. The explosive yield was equivalent to about 22,000 tons of TNT. Fat man resulted in 35,000 immediate deaths. By the end of 1945, at least 70,000 people perished in this event.



Figure 11.8.6***:*** *Fat Man – One of many Pu-239 nuclear weapons constructed during WWII. Courtesy of the U.S. Department of Defense*

Example 11.8.2

Start the video below at the 23:20 mark and stop it at the 29-minute setting. Then, answer the questions below:

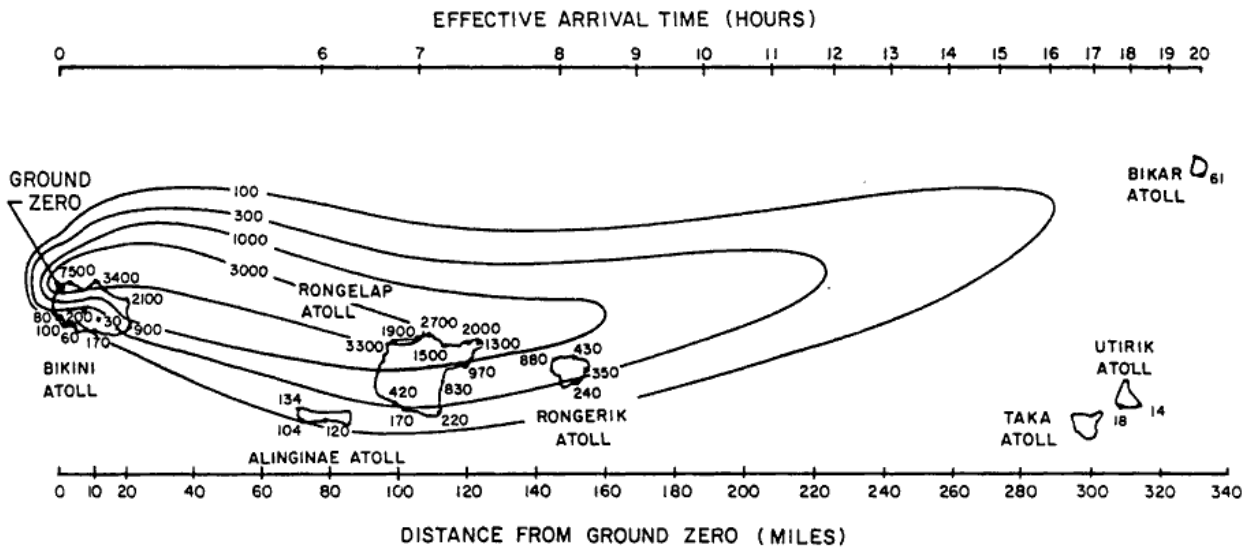
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View this YouTube Video online

9. When and where was the first nuclear bomb tested?
10. Was the bomb placed on the ground?
11. What were scientists afraid the first nuclear bomb would do?
12. What did Edward Teller (father of the fusion bomb) apply to his skin before the bomb was ignited? Why did he do this?
13. What did the bomb do to the tower and the surrounding sand?
14. In the photograph, where did General Grove focus his attention?

Nuclear Fallout

Nuclear fallout refers to the radioactive material that "falls out" of the atmosphere after a nuclear explosion (reactor or bomb). It consists of dust and radioactive particles that can contaminate an area with radioactivity and pose a huge health hazard to biological organisms. It can contaminate the animal food chain which can have drastic effects on the affected region. Weather has a huge impact on fallout, wind currents can spread radioactive fallout either over a large area, such as in the case of *Castle Bravo*, or not.



alt

Figure 11.8.2: The 450 km (280 mi) fallout plume from 15 Mt shot Castle Bravo, 1954. (Pubic Domain; United States Department of Energy via Wikipedia)

In regards to nuclear reactions, fission produces more fallout products that fusion. Intense heat of the latter type of reactions reduces the amount and type of radioisotopes produced. Although more powerful, fusion is a "cleaner" type of nuclear reaction. By increasing the fission component of a fusion weapon, bombs can be designed to generate more fallout products.Of the different types of isotopes that fission produces, the most worrisome are Sr-90, Cs-137,and I-131. The first of these isotopes has a half-life of 28.8 years and decays by gamma and beta emission. Once ingested or inhaled, Sr-90 deposits in teeth, bone,and bone marrow. Sr-90 exposure can lead to bone cancer and/or leukemia. Cs-137 ($t_{1/2}$ = 30.17 years) emits beta and gamma radiation. This ionizing radiation deposits in soft tissues of the body. In addition, this particular radioisotope is water soluble and can easily contaminant food and water supplies. I-131 had a half-life over 8.1 days and undergoes gamma/beta decay. Once this fallout product enters the body, it attacks the thyroid gland. Extensive damage could affect heart rate, blood pressure, body temperature, and childhood growth. In addition, I-131 exposure could result in thyroid cancer.

Nuclear Fallout

Watch the fallout video and then answer the questions below:

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

Summary

- In an atomic bomb several pieces of fissionable material are held sufficiently far apart for no chain reaction to occur. When these are suddenly brought together, the critical mass is reached and an atomic explosion results immediately.
- The two fission bombs assembled at Los Alamos, New Mexico, by J. Robert Oppenheimer, and his research group were manufactured with two types of fuel namely, U-235 and Pu-239.
  - The smaller of the two bombs would contain U-235 and was code-named "Little Boy." This bomb was dropped in Hirsohima, Japan on Aug.6, 1945.
  - The larger bomb, which housed Pu-239, was named "Fat Man." This bomb was dropped in Nagazaki, Japan on Aug.9,

1945.

- Nuclear fallout refers to the radioactive material that "falls out" of the atmosphere after a nuclear explosion (reactor or bomb).

Contributors and Attributions

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11.9: Uses and Consequences of Nuclear Energy

Learning Objective

- Know the benefits and consequences of nuclear energy.

Nuclear Power Generation

The generation of electricity is critical for operation of businesses, health care delivery, schools, homes, and other areas requiring the use of electrical power. According to 2011 statistics, coal is used for 42% of the total power generated, with natural gas being employed for another 25%. Nuclear power plants are employed in about 19% of the cases, with renewable energy sources supplying the last 13%. All of these fuels are used to heat water to generate steam. The steam then turns a turbine to generate electricity.

Nuclear power plants use the energy from nuclear fission to produce electricity. **U-235** is the preferred nuclear fuel because when its atoms are split (fissioned), they not only emit heat and high energy radiation but also enough neutrons to maintain a chain reaction and provide energy to power a nuclear power plant. Uranium is found in rocks all over the world but is relatively rare and the supply is finite making it a nonrenewable energy source.

Uranium usually occurs in combination with small amounts of other elements and once it is mined, the U-235 must be extracted and processed before it can be used as a fuel in a nuclear power plant to generate electricity. The processed uranium is formed into fuel rods and then bundled into fuel assemblies. Fuel assemblies are stored onsite until they are needed by the reactor operators. At this stage, the uranium is only mildly radioactive, and essentially all radiation is contained within the metal tubes. When needed, the fuel is loaded into a reactor core (Figure $11.9.1$). Typically, about one third of the reactor core (40 to 90 fuel assemblies) is changed out every 12 to 24 months.

The most common type of reactors are the **pressurized water reactors** (PWR) (Figure $11.9.1$) in which water is pumped through the reactor core and heated by the fission process. The water is kept under high pressure inside the reactor so it does not boil. The heated water from the reactor passes through tubes inside the steam generator where the heat is transferred to water flowing around the tubes in the steam generator. The water in the steam generator boils and turns to steam. The steam is piped to the turbines. The force of the expanding steam drives the turbines, which spin a magnet in coil of wire – the generator– to produce electricity.

After passing through the turbines, the steam is converted back to water by circulating it around tubes carrying cooling water in the condenser. The condensed steam – now water – is returned to the steam generators to repeat the cycle.

The three water systems (condenser, steam generator, and reactor) are separate from each other and are not permitted to mix. Water in the reactor is radioactive and is contained within the containment structure whereas water in the steam generator and condenser is nonradioactive.

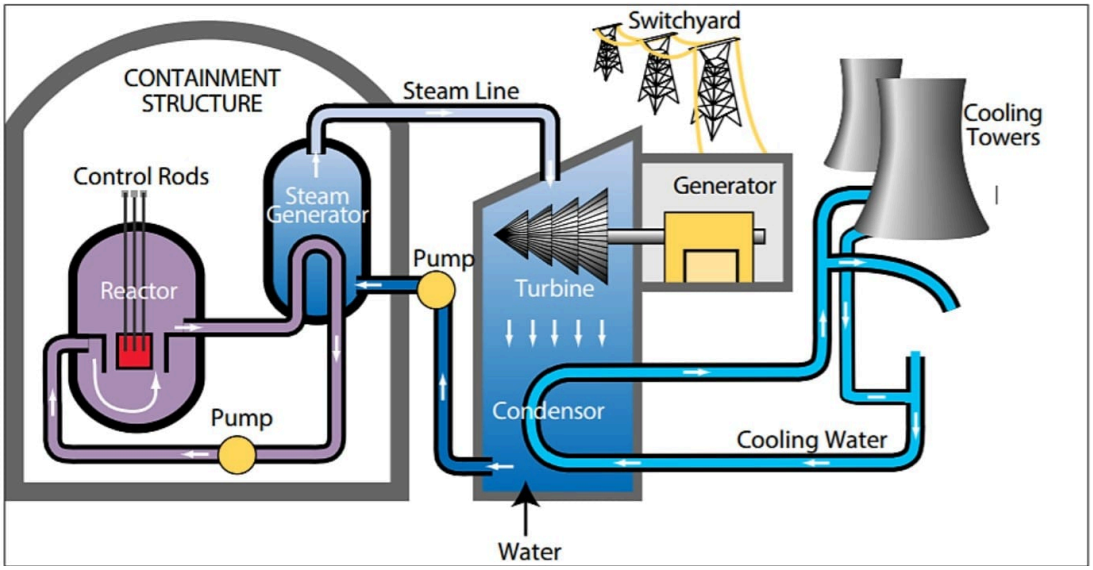


Figure 11.9.1**:** *A schematic diagram of a pressurized water reactor (PWR), the most common type of nuclear reactor. Diagram from Tennessee Valley Authority (public domain). www.tva.com*

Benefits of Nuclear Energy

By using fission, nuclear power plants generate electricity without emitting air pollutants like those emitted by fossil fuel-fired power plants. This means that financial costs related to chronic health problems caused by air pollutants such as particulate material, carbon monoxide, nitrogen oxides and ozone among others are significantly reduced. In addition nuclear reactors do not produce carbon dioxide while operating which means that nuclear energy does not contribute to the global warming problem.

Another benefit of nuclear energy over fossil fuels especially coal is that uranium generates far more power per unit weight or volume. This means that less of it needs to be mined and consequently the damage to the landscapes is less especially when compared to the damage that results from coal mining such as mountaintop removal.

Nuclear power is also used to propel ships. The turbine can be connected to a propeller system. The rotating turbine shaft will turn the propeller to move the ship.



Figure 11.9.2 *Nuclear submarine.*

The Drawbacks of Nuclear Energy

The main environmental concern related to nuclear power is the creation of radioactive wastes such as uranium mill tailings, spent (used) reactor fuel, and other radioactive wastes. These materials can remain radioactive and dangerous to human health for thousands of years. Radioactive wastes are classified as low-level and high-level. By volume, most of the waste related to the nuclear power industry has a relatively low-level of radioactivity. **Uranium mill tailings** contain the radioactive element radium, which decays to produce **radon**, a radioactive gas. Most uranium mill tailings are placed near the processing facility or mill where they come from. Uranium mill tailings are covered with a barrier of material such as clay to prevent radon from escaping into the atmosphere, and they are then covered by a layer of soil, rocks, or other materials to prevent erosion of the sealing barrier.

Spent fuel rods contain a variety of products, consisting of unstable nuclei ranging in atomic number from 25 to 60, some transuranium elements, including plutonium and americium, and unreacted uranium isotopes. The unstable nuclei and the transuranium isotopes give the spent fuel a dangerously high level of radioactivity. The long-lived isotopes require thousands of years to decay to a safe level. The ultimate fate of the nuclear reactor as a significant source of energy in the United States probably rests on whether or not a politically and scientifically satisfactory technique for processing and storing the components of spent fuel rods can be developed.

The other types of **low-level radioactive waste** are the tools, protective clothing, wiping cloths, and other disposable items that get contaminated with small amounts of radioactive dust or particles at nuclear fuel processing facilities and power plants. These materials are subject to special regulations that govern their handling, storage, and disposal so they will not come in contact with the outside environment.

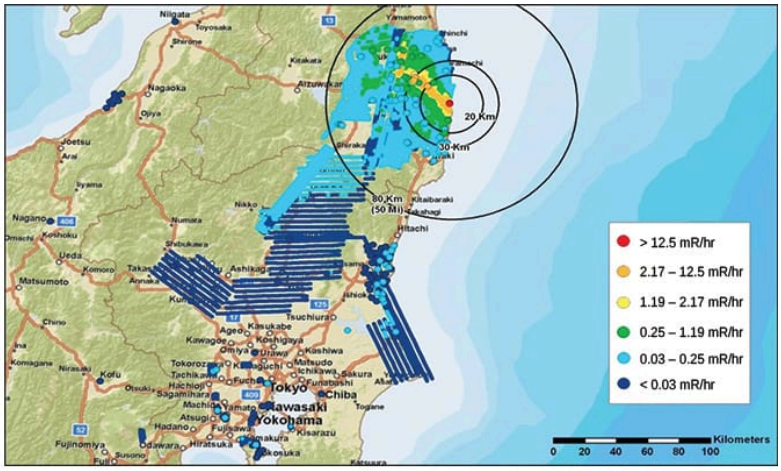
High-level radioactive waste consists of spent nuclear reactor fuel (i.e., fuel that is no longer useful for producing electricity). The spent reactor fuel is in a solid form consisting of small fuel pellets in long metal tubes called rods. Spent reactor fuel assemblies are initially stored in specially designed pools of water, where the water cools the fuel and acts as a radiation shield. Spent reactor fuel assemblies can also be stored in specially designed dry storage containers. An increasing number of reactor operators now store their older spent fuel in dry storage facilities using special outdoor concrete or steel containers with air cooling. There is currently no permanent disposal facility in the United States for high-level nuclear waste.

When a nuclear reactor stops operating, it must be **decommissioned**. This involves safely removing the reactor and all equipment that has become radioactive from service and reducing radioactivity to a level that permits other uses of the property. The U.S. Nuclear Regulatory Commission has strict rules governing nuclear power plant decommissioning that involve cleanup of radioactively contaminated plant systems and structures, and removal of the radioactive fuel.

A **nuclear meltdown**, or uncontrolled nuclear reaction in a nuclear reactor, can potentially result in widespread contamination of air and water. Some serious nuclear and radiation accidents have occurred worldwide. The most severe accident was the Chernobyl accident of 1986 in the then Soviet Union (now Ukraine) which killed 31 people directly and sickened or caused cancer in thousands more. The Fukushima Daiichi nuclear disaster (2011) in Japan (Figure 11.9.3) was caused by a 9.0 magnitude earthquake that shut down power supply and a tsunami that flooded the plant's emergency power supply. This resulted in the release of radioactivity although it did not directly result in any deaths at the time of the disaster. Another nuclear accident was the Three Mile Island accident (1979) in Pennsylvania, USA. This accident resulted in a near disastrous core meltdown that was due to a combination of human error and mechanical failure but did not result in any deaths and no cancers or otherwise have been found in follow up studies of this accident. While there are potentially devastating consequences to a nuclear meltdown, the likelihood of one occurring is extremely small. After every meltdown, including the 2011 Fukushima Daiichi disaster, new international regulations were put in place to prevent such an event from occurring again.



(a)



(b)

Figure 11.9.3 (a) After the accident, contaminated waste had to be removed, and (b) an evacuation zone was set up around the plant in areas that received heavy doses of radioactive fallout. (credit a: modification of work by "Live Action Hero"/Flickr)

The processes for mining and refining uranium ore and making reactor fuel require large amounts of energy. Nuclear power plants have large amounts of metal and concrete, which also require large amounts of energy to manufacture. If fossil fuels are used for mining and refining uranium ore or in constructing the nuclear plant, then the emissions from burning those fuels could be associated with the electricity that nuclear power plants generate.

Nuclear Reactor Design and Operation

YouTube Video

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Video 11.9.1 *The design and safe operation of a nuclear reactor.*

Summary

- The importance of nuclear power in generating electricity is described.
- The operation of a nuclear power plant is described.
- The drawbacks of nuclear energy is described.

Contributors and Attributions

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12: CHEMISTRY OF EARTH

12.1: Spaceship Earth- Structure and Composition
12.2: Silicates and the Shapes of Things
12.3: Metals and Ores
12.4: Earth's Dwindling Resources

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12.1: Spaceship Earth- Structure and Composition

Learning Objective

- Describe the chemical composition and structure of Earth.

The layers found inside Earth are divided by composition into core, mantle, and crust or by mechanical properties into lithosphere and asthenosphere. Scientists use information from earthquakes and computer modeling to learn about Earth's interior.

THE EARTH'S LAYERS

The layers scientists recognize are pictured in Figure 12.1.1.

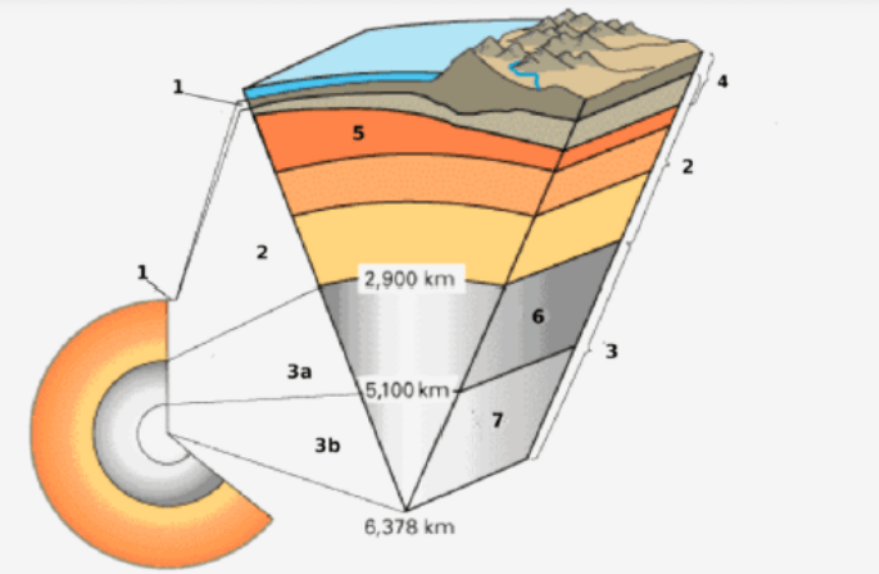


Figure 12.1.1 *A cross section of Earth showing the following layers: (1) crust (2) mantle (3a) outer core (3b) inner core (4) lithosphere (5) asthenosphere (6) outer core (7) inner core.*

Core, mantle, and crust are divisions based on chemical composition:

Crust: The Earth's surface is the crust. Generally speaking, the crust is predominately silicon oxide and aluminum oxide. Continental crust is thicker and less dense than oceanic crust. Earth's crust varies in thickness from less than 5 km (under mid-ocean spreading ridges) to more than 70 km (beneath the highest mountain range).

Mantle: The next layer down chemically is the mantle. The mantle has an ultramafic composition – it contains more iron, magnesium, less aluminum and somewhat less silicon than the crust. The mantle is roughly 2,900 km thick. In terms of volume, the mantle is the largest of earth's three chemical layers.

Core:The final layer is the core, which is mostly iron and nickel. The core is about 3,500 km thick.

Table 12.1.1 summarizes the chemical layers of the earth.

Table 12.1.1 *Chemical Layers of Earth.*

Crust	Mantle	Core
composition: high Si, Al, & O	*composition:* moderate Si, high Mg & Fe	*composition:* Fe & Ni

thickness: 5 to 70 km	*thickness:* 2,900 km	*thickness:* 3,500 km

Table 12.1.2 provides the elemental composition of the Earth's crust.

Table 12.1.2 The Elements of Earth's Crust. Source: Wikipedia

Most Abundant Elements of Earth's Crust	Approximate % by weight
O	46.6
Si	27.7
Al	8.1
Fe	5.0
Ca	3.6
Na	2.8
K	2.6
Mg	1.5

Lithosphere and asthenosphere are divisions based on mechanical properties:

1. The lithosphere is composed of both the crust and the portion of the upper mantle that behaves as a brittle, rigid solid.
2. The asthenosphere is partially molten upper mantle material that behaves plastically and can flow.

Compositional and Mechanical Layers of the Earth

https://www.khanacademy.org/science/cosmology-and-astronomy/earth-history-topic/plate-techtonics/v/compositional-and-mechanical-layers-of-the-earth

Video 12.1.1 *A comparison of the compositional and mechanical layers of the earth.*

Crust and Lithosphere

Earth's outer surface is its crust; a cold, thin, brittle outer shell made of rock. The crust is very thin, relative to the radius of the planet. There are two very different types of crust, each with its own distinctive physical and chemical properties, which are summarized in Table 12.1.3.

Table 12.1.3 The Physical and Chemical Properties of Oceanic and Continental Crust.

Crust	Thickness	Density	Composition	Rock types
Oceanic	5-12 km (3-8 mi)	3.0 g/cm^3	Mafic	Basalt and gabbr
Continental	Avg. 35 km (22 mi)	2.7 g/cm^3	Felsic	All types

Oceanic crust is composed of mafic magma that erupts on the seafloor to create basalt lava flows or cools deeper down to create the intrusive igneous rock gabbro (Figure 12.1.2).



Figure 12.1.2 Gabbro

Sediments, primarily muds and the shells of tiny sea creatures, coat the sea floor. Sediment is thickest near the shore where it comes off the continents in rivers and on wind currents.

Continental crust is made up of many different types of igneous, metamorphic, and sedimentary rocks. The average composition is granite, which is much less dense than the mafic rocks of the oceanic crust (Figure 12.1.3). Because it is thick and has relatively low density, continental crust rises higher on the mantle than oceanic crust, which sinks into the mantle to form basins. When filled with water, these basins form the planet's oceans.



Figure 12.1.3 *The granite from Missouri is more than 1 billion years old.*

The **lithosphere** is the outermost mechanical layer, which behaves as a brittle, rigid solid. The lithosphere is about 100 kilometers thick. Look at Figure 12.1.1. Can you find where the crust and the lithosphere are located? How are they different from each other?

The definition of the lithosphere is based on how earth materials behave, so it includes the crust and the uppermost mantle, which are both brittle. Since it is rigid and brittle, when stresses act on the lithosphere, it breaks. This is what we experience as an earthquake.

Mantle

The two most important things about the mantle are: (1) it is made of solid rock, and (2) it is hot. Scientists know that the mantle is made of rock based on evidence from seismic waves, heat flow, and meteorites.

The properties fit the ultramafic rock peridotite, which is made of the iron- and magnesium-rich silicate minerals (Figure 12.1.4). Peridotite is rarely found at Earth's surface.

Scientists know that the mantle is extremely hot because of the heat flowing outward from it and because of its physical properties.



Figure 12.1.4 *Peridotite is formed of crystals of olivine (green) and pyroxene (black).*

Core

At the planet's center lies a dense metallic core. Scientists know that the core is metal because:

1. The density of Earth's surface layers is much less than the overall density of the planet, as calculated from the planet's rotation. If the surface layers are less dense than average, then the interior must be denser than average. Calculations indicate that the core is about 85% iron metal with nickel metal making up much of the remaining 15%.
2. Metallic meteorites are thought to be representative of the core. The 85% iron/15% nickel calculation above is also seen in metallic meteorites (Figure 12.1.5).



Figure 12.1.5 *An iron meteorite is the closest thing to the Earth's core that we can hold in our hands.*

If Earth's core were not metal, the planet would not have a magnetic field. Metals such as iron are magnetic, but rock, which makes up the mantle and crust, is not.

Summary

- The core, mantle, and crust are divisions of Earth based on chemical composition.
- The lithosphere and asthenosphere are divisions of Earth based on mechanical properties.
- The three most abundant elements of Earth's crust are oxygen (46.6% by weight), silicon (27.7%), and aluminum (8.1%).

Contributors

Libretext: Fundamentals of Geology (Schulte)

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Wikipedia

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12.2: Silicates and the Shapes of Things

Learning Objective

- Describe different types of silicate based minerals.

The silicates are the largest, the most interesting and the most complicated class of minerals than any other minerals. Approximately 30% of all minerals are silicates and some geologists estimate that 90% of the Earth's crust is made up of silicates, SiO_4^{4-} based material. Thus, oxygen and silicon are the two most abundant elements in the earth's crust.

The building block of all of these minerals is the **silica tetrahedron**, a combination of four oxygen atoms and one silicon atom. As we've seen, it's called a tetrahedron because planes drawn through the oxygen atoms form a shape with 4 surfaces (Figure 12.2.1). Since the silicon ion has a charge of 4 and each of the four oxygen ions has a charge of –2, the silica tetrahedron has a net charge of –4.

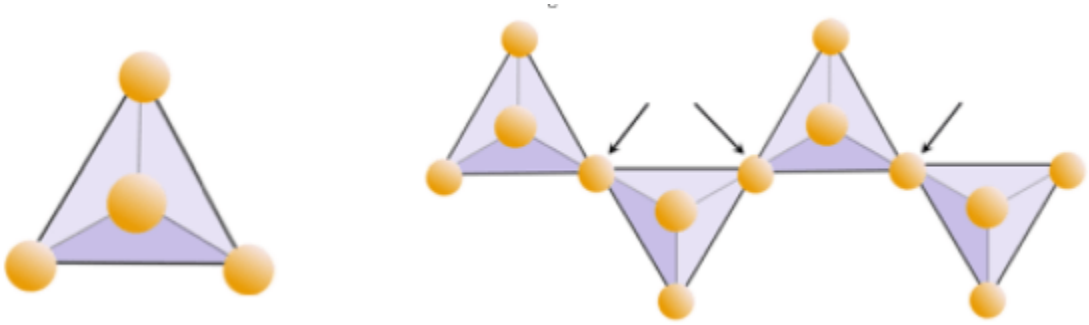
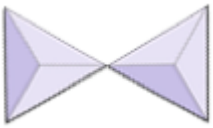
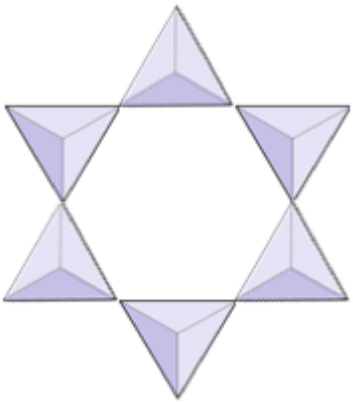
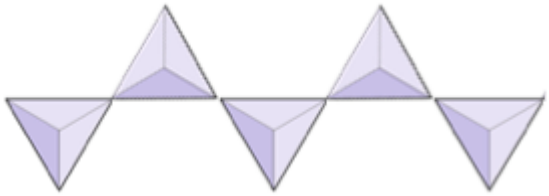
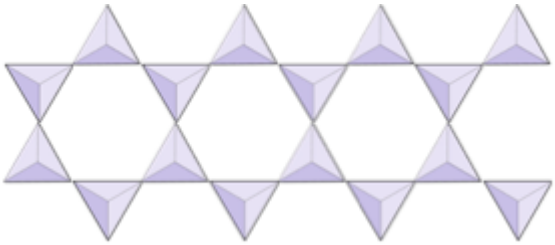
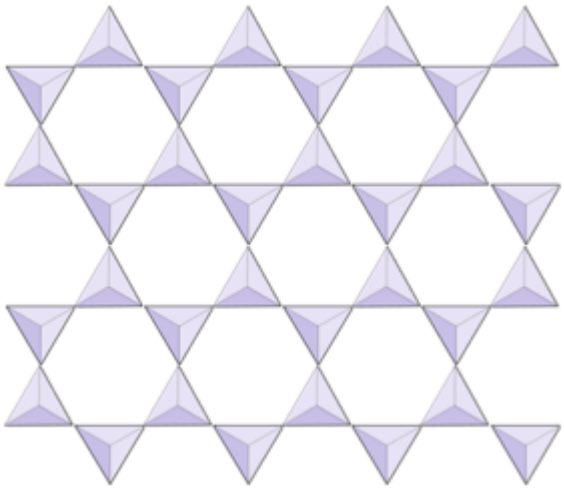


Figure 12.2.1 *A single silica tetrahedron (left) with four oxygen ions per silicon ion (SiO_4). Part of a single chain of tetrahedra (right), where the oxygen atoms at the adjoining corners are shared between two tetrahedra (arrows). For a very long chain the resulting ratio of silicon to oxygen is 1 to 3 (SiO_3).*

In silicate minerals, these tetrahedra are arranged and linked together in a variety of ways, from single units to complex frameworks (Table 12.2.1).

Table 12.2.1 *Silicate Mineral Configurations (The triangles represent silica tetrahedra).*

Tetrahedron Configuration Picture	Tetrahedron Configuration Name	Example Minerals
	Isolated (nesosilicates)	Olivine, garnet, zircon, kyanite
	Pairs (sorosilicates)	Epidote, zoisite
	Rings (cyclosilicates)	Tourmaline
	Single chains (inosilicates)	Pyroxenes, wollastonite
	Double chains (inosilicates)	Amphiboles

	Sheets (phyllosilicates)	Micas, clay minerals, serpentine, chlorite
3-dimensional structure	Framework (tectosilicates)	Feldspars, quartz, zeolite

In the extreme case, the tetrahedra are arranged in a regular, orderly fashion forming a three-dimensional network. **Quartz** is such a structure (Figure 12.2.2), and its formula is SiO_2. If silica in the molten state is cooled very slowly it crystallizes at the freezing point. But if molten silica is cooled more rapidly, the resulting solid is a disorderly arrangement which is called **glass**, often also called *quartz*.

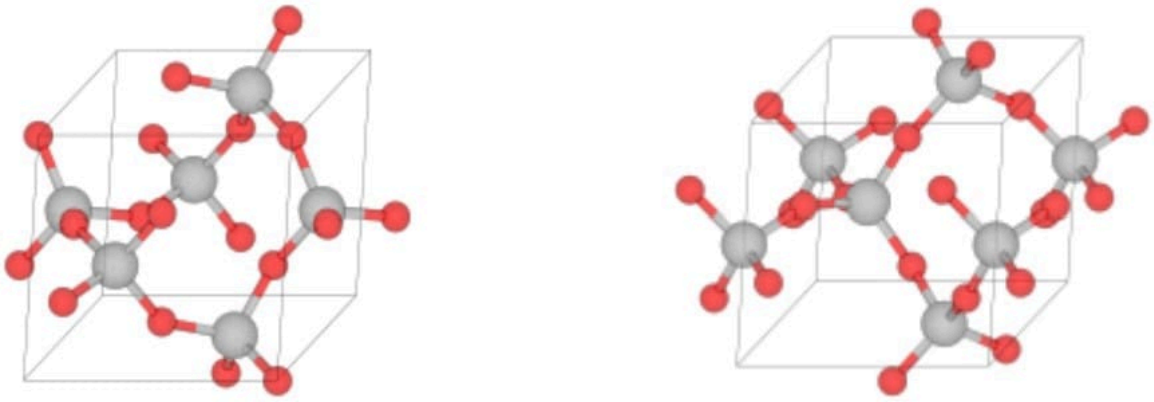


Figure 12.2.2 Crystal structure of alpha (left) and beta (right) quartz. The red balls are oxygen and gray are silicon.

Note:

Silicates are extremely important materials, both natural (such as granite, gravel, and garnet) and artificial (such as Portland cement, ceramics, glass, and waterglass), for all sorts of technological and artistic activities. Source: Wikipedia

Glasses

Glass is a non-crystalline, often transparent amorphous solid, that has widespread practical, technological, and decorative use in, for example, window panes, tableware, optics, and optoelectronics. The most familiar, and historically the oldest, types of manufactured glass are "silicate glasses" based on the chemical compound silica (silicon dioxide, or quartz), the primary constituent of sand. The term *glass*, in popular usage, is often used to refer only to this type of material, which is familiar from use as window glass and glass bottles. Of the many silica-based glasses that exist, ordinary glazing and container glass is formed from a specific type called soda-lime glass, composed of approximately 75% silicon dioxide (SiO_2), sodium oxide (Na_2O) from sodium carbonate (Na_2CO_3), calcium oxide (CaO), also called lime, and several minor additives.

Table 12.2.2 list the more common types of silicate glasses and their ingredients, properties, and applications. Figure 12.2.3 are examples of silicate glasses.

Table 12.2.2 Common Types of Silicate Glasses.

Type and Properties	Key Ingredients	Applications
Fused quartz has very low thermal expansion and excellent resistance to thermal shock, being able to survive immersion in water while red hot, resists high temperatures (1000–1500 °C) and chemical weathering, and is very hard.	Chemically pure silica (silicon dioxide)	Used for high-temperature applications such as furnace tubes, lighting tubes, melting crucibles, etc.
Soda-lime-silica glass is transparent, easily formed, and most suitable for window glass and tableware.[68] However, it has a high thermal expansion and poor resistance to heat.	(Na_2O) + lime (CaO) + magnesia (MgO) + alumina (Al_2O_3) account for over 75% of manufactured glass, containing about 70 to 74% silica by weight	Typically used for windows, bottles, light bulbs, and jars.[
Sodium borosilicate glasses have fairly low coefficients of thermal expansion (7740 Pyrex CTE is 3.25×10^{-6}/°C[69] as compared to about 9×10^{-6}/°C for a typical soda-lime glass[70]). They are, therefore, less subject to stress caused by thermal expansion and thus less vulnerable to cracking from thermal shock.	5–13% boron trioxide (B_2O_3)	Commonly used for e.g. labware (e.g. Pyrex, Duran), household cookware, and sealed beam car head lamps.[
Lead-oxide glass, crystal glass, lead glass has high density which results in a high electron density, and hence high refractive index, making the look of glassware more brilliant and causing noticeably more specular reflection and increased optical dispersion.[61][72] Lead glass has a high elasticity, making the glassware more workable and giving rise to a clear "ring" sound when struck.	silica + lead oxide (PbO) + potassium oxide (K_2O) + soda (Na_2O) + zinc oxide (ZnO) + alumina	Used for tableware, art objects, optical glass.
Aluminosilicate glass tends to be more difficult to melt and shape compared to borosilicate compositions, but has excellent thermal resistance and durability.	alumina and silica	Extensively used for fiberglass, used for making glass-reinforced plastics (boats, fishing rods, etc.), top-of-stove cookware, and halogen bulb glass.
Germanium-oxide glass is an extremely clear glass. Light loses only 5% of its intensity through 1 km of glass fiber.	alumina + germanium dioxide (GeO_2).	Used for fiber-optic waveguides in communication networks.
Colored glass is clear glass with oxides added .	Different oxide additives produce the different colors in glass: turquoise (copper(II) oxide),[121] purple (manganese dioxide), red (cadmium sulfide), blue (cobalt oxide) and green (Iron(II) oxide and chromium(III) oxide).	Used for tableware and decorative glassware.



a. b. c.

Figure 12.2.3 *Examples of silicate glasses: a. Pyrex measuring cup, b. red glass bottle with yellow glass overlay, and c. four-color Roman glass bowl, manufactured circa 1st century B.C..*

Asbestos

Asbestos is the name applied to six naturally occurring minerals that are mined from the earth. The different types of asbestos are:

- Amosite
- Chrysotile
- Tremolite
- ActinoliteUnlink
- Anthophyllite
- Crocidolite

Of these six, three are used more commonly. **Chrysotile** (white) is the most common, but it is not unusual to encounter**. Amosite** (brown / off-white), or **Crocidolite** (blue) as well. Asbestos are noncombustable fibrous material, and they have been used for terminal insulation material, brake linings, construction material, and filters. When mixed with cement, it reinforce the mechanical strength of concrete. It decomposes due to loss of water, and forms forsterite and silica at high temperature.

Ceramics

A **ceramic** is a solid material comprising an inorganic compound of metal, non-metal or ionic and covalent bonds. Common examples are earthenware, porcelain, and brick.

Varying crystallinity and electron composition in the ionic and covalent bonds cause most ceramic materials to be good thermal and electrical insulators (extensively researched in ceramic engineering). With such a large range of possible options for the composition/structure of a ceramic (e.g. nearly all of the elements, nearly all types of bonding, and all levels of crystallinity), the breadth of the subject is vast, and identifiable attributes (e.g. hardness, toughness, electrical conductivity, etc.) are difficult to specify for the group as a whole. General properties such as high melting temperature, high hardness, poor conductivity, high moduli of elasticity, chemical resistance and low ductility are the norm,[1] with known exceptions to each of these rules (e.g. piezoelectric ceramics, glass transition temperature, superconductive ceramics, etc.).

Cement and Concrete

A **cement** is a binder, a substance used for construction that sets, hardens, and adheres to other materials to bind them together.

Cement is seldom used on its own, but rather to bind sand and gravel (aggregate) together. Cement mixed with fine aggregate produces mortar for masonry, or with sand and gravel, produces concrete. Cement is the most widely used material in existence and is only behind water as the planet's most-consumed resource.[1]

Cements used in construction are usually inorganic, often lime or calcium silicate based.

Concrete is a composite material composed of fine and coarse aggregate bonded together with a fluid cement (cement paste) that hardens over time—most frequently in the past a lime-based cement binder, such as lime putty, but sometimes with other hydraulic cements, such as a calcium aluminate cement or with Portland cement to form **Portland cement concrete** (for its visual resemblance to Portland stone).[2][3] Many other non-cementitious types of concrete exist with different methods of binding aggregate together, including asphalt concrete with a bitumen binder, which is frequently used for road surfaces, and polymer concretes that use polymers as a binder.

Summary

- The silicates are the largest, the most interesting and the most complicated class of minerals than any other minerals. Approximately 90% of the Earth's crust is made up of silicates, SiO_4^{4-} based material.
- Silicates are extremely important materials, both natural (such as granite, gravel, and garnet) and artificial (such as Portland cement, ceramics, glass, and waterglass), for all sorts of technological and artistic activities

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- Libretext: Inorganic Chemistry
- Wikipedia

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12.3: Metals and Ores

Learning Objectives

- Identify important metals and describe their extraction from their main ores.
- List different metals, their uses, and their alloys.
- Describe the environmental impact of metal production.

Most metals are found as types of rock in the Earth's crust. These ores contain sufficient minerals with important elements including metals that can be economically extracted from the rock. Metal ores are generally oxides, sulfides, silicates (Table 12.3.1) or "native" metals (such as native copper) that are not commonly concentrated in the Earth's crust, or "noble" metals (not usually forming compounds) such as gold (Figure 12.3.1). The ores must be processed to extract the metals of interest from the waste rock and from the ore minerals.



Figure 12.3.1: Three Common Ores. (left) Iron ore, (middle) Manganese ore – psilomelane, and (right) Lead ore – galena and anglesite.

Alloys

An **alloy** is a mixture composed of two or more elements, at least one of which is a metal. You are probably familiar with some alloys of copper (such as brass and bronze) and iron (steel) . Alloys can be one of two general types. In one type, called a **substitutional alloy**, the various atoms simply replace each other in the crystal structure. In another type, called an **interstitial alloy**, the smaller atoms such as carbon fit in between the larger atoms in the crystal packing arrangement.

Steels are a very important class of alloys. The many types of steels are primarily composed of iron, with various amounts of the elements carbon, chromium, manganese, nickel, molybdenum, and boron. Steels are widely used in building construction because of their strength, hardness, and resistance to corrosion. Most large modern structures like skyscrapers and stadiums are supported by a steel skeleton (see figure below).



Figure 12.3.2: The Willis Tower (formerly called the Sears Tower) in Chicago was once the tallest building in the world and is still the tallest in the Western Hemisphere. The use of steel columns makes it possible to build taller, stronger, and lighter buildings.

Copper,Brass, and Bronze

Copper is a chemical element with the symbol **Cu** (from Latin:) and atomic number 29. It is a soft, malleable, and ductile metal with very high thermal and electrical conductivity. A freshly exposed surface of pure copper has a pinkish-orange color. Copper is used as a conductor of heat and electricity and as a building material.

Copper is one of the few metals that can occur in nature in a directly usable metallic form (native metals). This led to very early human use in several regions, from c. 8000 BC. Thousands of years later, it was the first metal to be smelted from sulfide ores, c. 5000 BC, the first metal to be cast into a shape in a mold, c. 4000 BC and the first metal to be purposefully alloyed with another metal, tin, to create bronze, c. 3500 BC.

Most commercial ores are sulfides, especially chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4) and, to a lesser extent, covellite (CuS) and chalcocite (Cu_2S).

Cu_2S, is converted into oxides:

$$2\ Cu_2S + 3\ O_2 \rightarrow 2\ Cu_2O + 2\ SO_2$$

The cuprous oxide is then converted to copper upon heating:

$$2\ Cu_2O \rightarrow 4\ Cu + O_2$$

Copper is a constituent of various metal alloys, such as sterling silver used in jewelry, cupronickel used to make marine hardware and coins, and constantan used in strain gauges and thermocouples for temperature measurement. Bronze, an alloy of copper and tin has been in use since ancient times. The Bronze Age saw the increased use of metals rather than stone for weapons, tools, and decorative objects. Brass, an alloy of copper and zinc, is widely used in musical instruments like the trumpet and trombone. Alloys are commonly used in manufactured items because the properties of these metal mixtures are often superior to a pure metal. Bronze is harder than copper and more easily cast. Brass is very malleable and its acoustic properties make it useful for musical instruments (Figure 12.3.1).



Figure 12.3.3 A bronze helmet and a trumpet made of brass. Copper alloys are widely used in the production of coinage; seen here are two examples - post-1964 American dimes, which are composed of the alloy cupronickel and a pre-1968 Canadian dime, which is composed of an alloy of 80 percent silver and 20 percent copper. (Source: Wikipedia)

Iron and Steel

The early application of iron to the manufacture of tools and weapons was possible because of the wide distribution of iron ores and the ease with which iron compounds in the ores could be reduced by carbon. Iron ore is reduced with coke in a blast furnace (Figure 12.3.1). The blast furnace is loaded with iron ores, usually hematite Fe_2O_3 or magnetite Fe_3O_4, together with coke (coal that has been separately baked to remove volatile components). Air pre-heated to 900 °C is blown through the mixture, in sufficient amount to turn the carbon into carbon monoxide:

$$2\ C + O_2 \rightarrow 2\ CO$$

This reaction raises the temperature to about 2000 °C The carbon monoxide reduces the iron ore to metallic iron[112]

$$Fe_2O_3 + 3\ CO \rightarrow 2\ Fe + 3\ CO_2$$

Some iron in the high-temperature lower region of the furnace reacts directly with the coke:[112]

$$2\ Fe_2O_3 + 3\ C \rightarrow 4\ Fe + 3\ CO_2$$

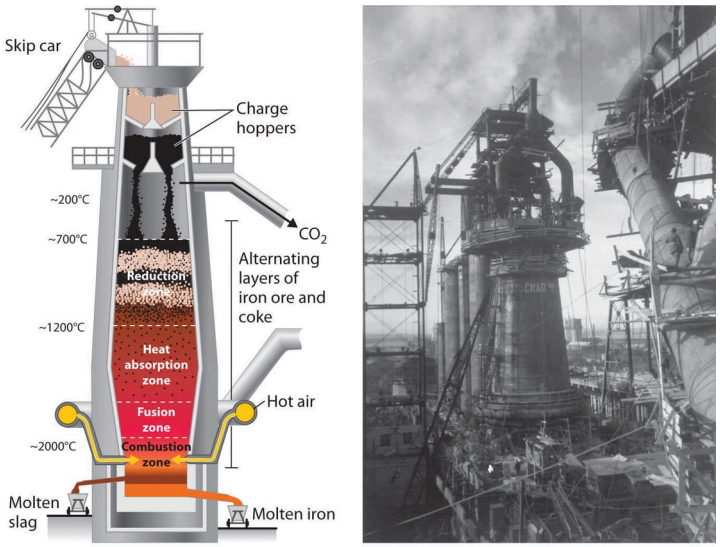


Figure 12.3.4: A Blast Furnace for Converting Iron Oxides to Iron Metal. (a) The furnace is charged with alternating layers of iron ore (largely Fe2O3) and a mixture of coke (C) and limestone (CaCO3). (b) This blast furnace in Magnitogorsk, Russia, was the largest in the world when it was built in 1931.

Much of the iron produced is refined and converted into steel. Steel is made from iron by removing impurities and adding substances such as manganese, chromium, nickel, tungsten, molybdenum, and vanadium to produce alloys with properties that make the material suitable for specific uses. Most steels also contain small but definite percentages of carbon (0.04%–2.5%). However, a large part of the carbon contained in iron must be removed in the manufacture of steel; otherwise, the excess carbon would make the iron brittle. However, there is not just one substance called steel - they are a family of alloys of iron with carbon or various metals.

Impurities in the iron from the Blast Furnace include carbon, sulfur, phosphorus and silicon, which have to be removed.

- **Removal of sulfur**: Sulfur has to be removed first in a separate process. Magnesium powder is blown through the molten iron and the sulfur reacts with it to form magnesium sulfide. This forms a slag on top of the iron and can be removed.

$$Mg + S \rightarrow MgS \tag{12.3.1}$$

- **Removal of carbon:** The still impure molten iron is mixed with scrap iron (from recycling) and oxygen is blown on to the mixture. The oxygen reacts with the remaining impurities to form various oxides. The carbon forms carbon monoxide. Since this is a gas it removes itself from the iron! This carbon monoxide can be cleaned and used as a fuel gas.
- **Removal of other elements:** Elements like phosphorus and silicon react with the oxygen to form acidic oxides. These are removed using quicklime (calcium oxide) which is added to the furnace during the oxygen blow. They react to form compounds such as calcium silicate or calcium phosphate which form a slag on top of the iron.

Cast iron has already been mentioned above. This section deals with the types of iron and steel which are produced as a result of the steel-making process.

- Wrought iron: If all the carbon is removed from the iron to give high purity iron, it is known as wrought iron. Wrought iron is quite soft and easily worked and has little structural strength. It was once used to make decorative gates and railings, but these days mild steel is normally used instead.
- Mild steel: Mild steel is iron containing up to about 0.25% of carbon. The presence of the carbon makes the steel stronger and harder than pure iron. The higher the percentage of carbon, the harder the steel becomes. Mild steel is used for lots of things - nails, wire, car bodies, ship building, girders and bridges amongst others.
- High carbon steel: High carbon steel contains up to about 1.5% of carbon. The presence of the extra carbon makes it very hard, but it also makes it more brittle. High carbon steel is used for cutting tools and masonry nails (nails designed to be driven into concrete blocks or brickwork without bending). High carbon steel tends to fracture rather than bend if mistreated.
- Special steels: These are iron alloyed with other metals (Table 12.3.1).

Table 12.3.1 *Special Steels*

	Iron mixed with	Special properties	Uses include
stainless steel	chromium and nickel	resists corrosion	cutlery, cooking utensils, kitchen sinks, industrial equipment for food and drink processing
titanium steel	titanium	withstands high temperatures	gas turbines, spacecraft
manganese steel	manganese	very hard	rock-breaking machinery, some railway track (e.g. points), military helmets

Steelmaking Animation

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 12.3.1 The process of steelmaking.

Aluminum

Aluminum is too high in the electrochemical series (reactivity series) to extract it from its ore using carbon reduction. The temperatures needed are too high to be economic. Instead, it is extracted by electrolysis. The ore is first converted into pure aluminum oxide by the Bayer Process, and this is then electrolyzed in solution in molten cryolite - another aluminum compound. The aluminum oxide has too high a melting point to electrolyse on its own. The usual aluminum ore is bauxite. Bauxite is essentially an impure aluminum oxide. The major impurities include iron oxides, silicon dioxide and titanium dioxide.

Crushed bauxite is treated with moderately concentrated sodium hydroxide solution. The concentration, temperature and pressure used depend on the source of the bauxite and exactly what form of aluminum oxide it contains. Temperatures are typically from 140°C to 240°C; pressures can be up to about 35 atmospheres. With hot concentrated sodium hydroxide solution, aluminum oxide reacts to give a solution of sodium tetrahydroxoaluminate.

$$Al_2O_3 + 2NaOH + 3H_2O \longrightarrow 2NaAl(OH)_4$$

The sodium tetrahydroxoaluminate solution is cooled, and "seeded" with some previously produced aluminum hydroxide. This provides something for the new aluminum hydroxide to precipitate around.

$$NaAl(OH)_4 \longrightarrow Al(OH)_3 + NaOH$$

Aluminum oxide (sometimes known as alumina) is made by heating the aluminum hydroxide to a temperature of about 1100 - 1200°C.

$$2Al(OH)_3 \longrightarrow Al_2O_3 + 3H_2O$$

The aluminum oxide is electrolyzed in solution in molten cryolite, Na_3AlF_6. Cryolite is another aluminum ore, but is rare and expensive, and most is now made chemically.

Uses of Aluminum

Aluminum is usually alloyed with other elements such as silicon, copper or magnesium. Pure aluminum isn't very strong, and alloying it adds to it strength. Aluminum is especially useful because it

- has a low density;

- is strong when alloyed;
- is a good conductor of electricity;
- has a good appearance;
- resists corrosion because of the strong thin layer of aluminum oxide on its surface. This layer can be strengthened further by anodizing the aluminum.

Anodizing essentially involves etching the aluminum with sodium hydroxide solution to remove the existing oxide layer, and then making the aluminum article the anode in an electrolysis of dilute sulfuric acid. The oxygen given of at the anode reacts with the aluminum surface, to build up a film of oxide up to about 0.02 mm thick. As well as increasing the corrosion resistance of the aluminum, this film is porous at this stage and will also take up dyes. (It is further treated to make it completely non-porous afterwards.) That means that you can make aluminum articles with the colour built into the surface.

Some uses include:

Aluminum is used for	because
aircraft	light, strong, resists corrosion
other transport such as ships' superstructures, container vehicle bodies, tube trains (metro trains)	light, strong, resists corrosion
overhead power cables (with a steel core to strengthen them)	light, resists corrosion, good conductor of electricity
saucepans	light, resists corrosion, good appearance, good conductor of heat

Recycling

Aluminum is an infinitely recyclable material, and it takes up to 95 percent less energy to recycle it than to produce primary aluminum, which also limits emissions, including greenhouse gases. Today, about 75 percent of all aluminum produced in history, nearly a billion tons, is still in use.[6]

The recycling of aluminum generally produces significant cost savings over the production of new aluminum, even when the cost of collection, separation and recycling are taken into account.[7] Over the long term, even larger national savings are made when the reduction in the capital costs associated with landfills, mines, and international shipping of raw aluminum are considered.

Environmental Impact of Steel and Aluminum Production

The impact of steel and aluminum production on the environment can be traced back from the mining of the ores to the production of the final commercial products (i.e. steel and aluminum). The main sources of emissions during the different phases of manufacture include the products of combustion such as nitrous oxide, carbon dioxide, carbon monoxide, and sulfur dioxide and fugitive dust from the operation of equipment. The effect of the different emissions on air quality (i.e. smog formation, greenhouse effect, acid rain etc.) will be discussed in more detail in Chapter 13.

Sulfuric acid is created when water and oxygen interact with sulfur bearing minerals and chemicals in rocks. Many metals become mobile as water becomes more acidic and at high concentrations these metals become toxic to most life forms. There is also production of enormous amounts of wastewater contaminants, hazardous wastes, and solid wastes.

Summary

- Metal ores contain sufficient minerals with important elements including metals that can be economically extracted from the rock. The ores must be processed to extract the metals of interest from the waste rock and from the ore minerals.
- Alloys are mixtures of materials, at least one of which is a metal.
- Bronze alloys were widely used in weapons.
- Brass alloys have long been employed in musical instruments.
- Steel alloys are strong and durable.

- Aluminum alloys are widely used due to its durability, resistance to corrosion, and good conductivity.

Contributors and Attributions

-
- TextMap: General Chemistry: General Chemistry (Petrucci et al.)
- Marisa Alviar-Agnew (Sacramento City College)
- Wikipedia

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12.4: Earth's Dwindling Resources

Learning Objectives

- Describe the composition and classification of solid waste.
- List the 3R's of Garbage and its benefits.

Land Pollution: Solid Wastes

Municipal solid waste (**MSW**), commonly known as **trash** or **garbage** in the United States and **rubbish** in Britain, is a waste type consisting of everyday items that are discarded by the public. "Garbage" can also refer specifically to food waste, as in a garbage disposal; the two are sometimes collected separately. In the European Union, the semantic definition is 'mixed municipal waste,' given waste code 20 03 01 in the European Waste Catalog. Although the waste may originate from a number of sources that has nothing to do with a municipality, the traditional role of municipalities in collecting and managing these kinds of waste have produced the particular etymology 'municipal.'

The composition of municipal solid waste varies greatly from municipality to municipality,[1] and it changes significantly with time. In municipalities which have a well developed waste recycling system, the waste stream mainly consists of intractable wastes such as plastic film and non-recyclable packaging materials. At the start of the 20th century, the majority of domestic waste (53%) in the UK consisted of coal ash from open fires.[2] In developed areas without significant recycling activity it predominantly includes food wastes, market wastes, yard wastes, plastic containers and product packaging materials, and other miscellaneous solid wastes from residential, commercial, institutional, and industrial sources.[3] Most definitions of municipal solid waste do not include industrial wastes, agricultural wastes, medical waste, radioactive waste or sewage sludge.[4] Waste collection is performed by the municipality within a given area. The term *residual waste* relates to waste left from household sources containing materials that have not been separated out or sent for processing.[5] Waste can be classified in several ways but the following list represents a typical classification:

- Biodegradable waste: food and kitchen waste, green waste, paper (most can be recycled, although some difficult to compost plant material may be excluded[6])
- Recyclable materials: paper, cardboard, glass, bottles, jars, tin cans, aluminum cans, aluminium foil, metals, certain plastics, textiles, clothing, tires, batteries, etc.
- Inert waste: construction and demolition waste, dirt, rocks, debris
- Electrical and electronic waste (WEEE) - electrical appliances, light bulbs, washing machines, TVs, computers, screens, mobile phones, alarm clocks, watches, etc.
- Composite wastes: waste clothing, Tetra Pack food and drink cartons, waste plastics such as toys and plastic garden furniture
- Hazardous waste including most paints, chemicals, tires, batteries, light bulbs, electrical appliances, fluorescent lamps, aerosol spray cans, and fertilizers
- Toxic waste including pesticides, herbicides, and fungicides
- Biomedical waste, expired pharmaceutical drugs, etc.

For example, typical municipal solid waste in China is composed of 55.9% food residue, 8.5% paper, 11.2% plastics, 3.2% textiles, 2.9% wood waste, 0.8% rubber, and 18.4% non-combustibles. The breakdown of municipal waste by material is shown below (Figure 12.4.1).

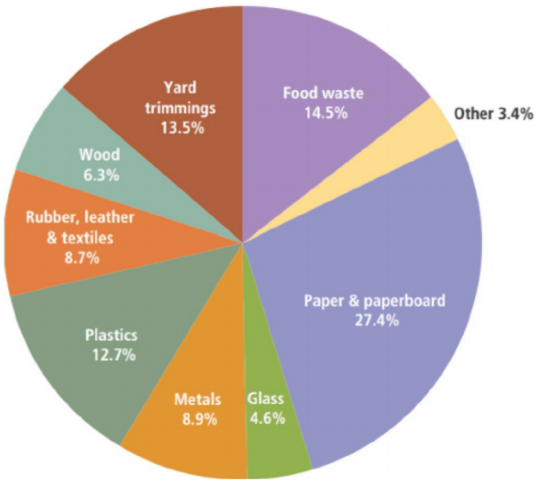


Figure 12.4.1 Total municipal waste generation by material. Source: US EPA

The Three R's of Garbage: Reduce, Reuse and Recyle

Reducing and Reusing Basics

The most effective way to reduce waste is to not create it in the first place. Making a new product requires a lot of materials and energy - raw materials must be extracted from the earth, and the product must be fabricated then transported to wherever it will be sold. As a result, reduction and reuse are the most effective ways you can save natural resources, protect the environment and save money.

Benefits of Reducing and Reusing

- Prevents pollution caused by reducing the need to harvest new raw materials
- Saves energy
- Reduces greenhouse gas emissions that contribute to global climate change
- Helps sustain the environment for future generations
- Saves money
- Reduces the amount of waste that will need to be recycled or sent to landfills and incinerators
- Allows products to be used to their fullest extent

Ideas on How to Reduce and Reuse

- Buy used. You can find everything from clothes to building materials at specialized reuse centers and consignment shops. Often, used items are less expensive and just as good as new.
- Look for products that use less packaging. When manufacturers make their products with less packaging, they use less raw material. This reduces waste and costs. These extra savings can be passed along to the consumer. Buying in bulk, for example, can reduce packaging and save money.
- Buy reusable over disposable items. Look for items that can be reused; the little things can add up. For example, you can bring your own silverware and cup to work, rather than using disposable items.
- Maintain and repair products, like clothing, tires and appliances, so that they won't have to be thrown out and replaced as frequently.
- Borrow, rent or share items that are used infrequently, like party decorations, tools or furniture.

Recycling Basics

Recycling is the process of collecting and processing materials that would otherwise be thrown away as trash and turning them into new products. Recycling can benefit your community and the environment.

Benefits of Recycling

- Reduces the amount of waste sent to landfills and incinerators
- Conserves natural resources such as timber, water and minerals
- Increases economic security by tapping a domestic source of materials
- Prevents pollution by reducing the need to collect new raw materials
- Saves energy
- Supports American manufacturing and conserves valuable resources
- Helps create jobs in the recycling and manufacturing industries in the United States

Recycling Creates Jobs

EPA released significant findings on the economic benefits of the recycling industry with an update to the national Recycling Economic Information (REI) Study in 2016. This study analyzes the numbers of jobs, wages and tax revenues attributed to recycling. The study found that in a single year, recycling and reuse activities in the United States accounted for:

- 757,000 jobs
- $36.6 billion in wages; and
- $6.7 billion in tax revenues.

This equates to 1.57 jobs, $76,000 in wages, and $14,101 in tax revenues for every 1,000 tons of materials recycled.

Summary

- Municipal solid waste (MSW), (i.e. trash or garbage in the United States and rubbish in Britain), is a type of waste consisting of everyday items that are discarded by the public.
- Most definitions of municipal solid waste do not include industrial wastes, agricultural wastes, medical waste, radioactive waste or sewage sludge.
- Typical classification of waste includes biodegradable wastes, recyclable materials, inert waste, electrical and electronic waste, composite wastes, hazardous wastes, toxic waste, and biomedical wastes.
- Reducing, reusing, and recycling solid wastes reduces the amount of waste in landfills and incinerators and promotes safer and cleaner environment.

Contributors and Attributions

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Wikipedia

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13: AIR

13.1: Earth's Atmosphere- Divisions and Composition
13.2: Chemistry of the Atmosphere
13.3: Outdoor Air Pollution
13.4: Automobile Emissions
13.5: Photochemical Smog- Making Haze While the Sun Shines
13.6: Acid Rain- Air Pollution Water Pollution
13.7: Indoor Air Pollution
13.8: Stratospheric Ozone- Earth's Vital Shield
13.9: Carbon Dioxide and Climate Change
13.10: Who Pollutes? Who Pays?

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13.1: Earth's Atmosphere- Divisions and Composition

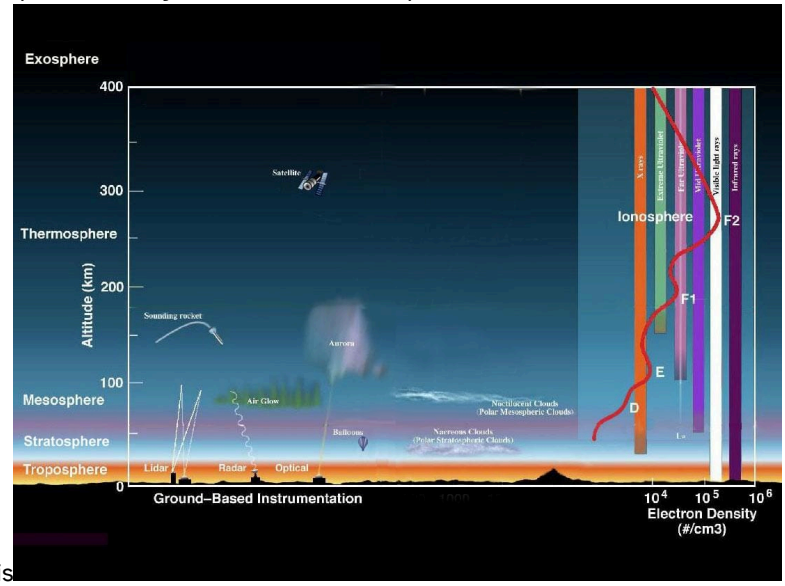
Learning Objectives

- Describe the different layers of the atmosphere.
- Know the composition of air.

The Earth's atmosphere is composed of several layers (Figure 13.1.1). The lowest layer, the troposphere, extends from the Earth's surface up to about 6 miles or 10 kilometers (km) in altitude. Virtually all human activities occur in the troposphere. Mt. Everest, the tallest mountain on the planet, is only about 5.6 miles (9 km) high. The next layer, the stratosphere, continues from 6 miles (10 km) to about 31 miles (50 km). Most commercial airplanes fly in the lower part of the stratosphere.

Most atmospheric ozone is concentrated in a layer in the stratosphere, about 9 to 18 miles (15 to 30 km) above the Earth's surface (see the figure below). Ozone is a molecule that contains three oxygen atoms. At any given time, ozone molecules are constantly formed and destroyed in the stratosphere. The total amount has remained relatively stable during the decades that it has been measured.

The ozone layer in the stratosphere absorbs a portion of the radiation from the sun, preventing it from reaching the planet's surface. Most importantly, it absorbs the portion of UV light called UVB. UVB has been linked to many harmful effects, including skin cancers, cataracts, xand harm to some crops and marine life.

The mesosphere starts just above the stratosphere and extends to 85 kilometers (53 miles) high. Meteors burn up in this layer
The thermosphere starts just above the mesosphere and extends to 600 kilometers (372 miles) high. Aurora and satellites occur in this 

layer. The ionosphere is an abundant layer of electrons and ionized atoms and molecules that stretches from about 48 kilometers (30 miles) above the surface to the edge of space at about 965 km (600 mi), overlapping into the mesosphere and thermosphere. This dynamic region grows and shrinks based on solar conditions and divides further into the sub-regions: D, E and F; based on what wavelength of solar vvradiation is absorbed. The ionosphere is a critical link in the chain of Sun-Earth interactions. This region is what makes radio communications possible. The exosphere is is the upper limit of the atmosphere. It extends from the top of the thermosphere up to 10,000 km (6,200 mi).

Figure 13.1.1 *The Earth's atmosphere* ***Credit:*** *NASA/Goddard*

Composition of the Atmosphere

Except for water vapor, whose atmospheric abundance varies from practically zero up to 4%, the fractions of the major

atmospheric components N_2, O_2, and Ar are remarkably uniform below about 100 km (Table 13.1.1). At greater heights, diffusion becomes the principal transport process, and the lighter gases become relatively more abundant. In addition, photochemical processes result in the formation of new species whose high reactivities would preclude their existence in significant concentrations at the higher pressures found at lower elevations.

The atmospheric gases fall into three abundance categories: major, minor, and trace. Nitrogen, the most abundant component, has accumulated over time as a result of its geochemical inertness; a very small fraction of it passes into the other phases as a result of biological activity and natural fixation by lightning. It is believed that denitrifying bacteria in marine sediments may provide the major route for the return of N_2 to the atmosphere. Oxygen is almost entirely of biological origin, and cycles through the hydrosphere, the biosphere, and sedimentary rocks. Argon consists mainly of Ar^{40} which is a decay product of K^{40} in the mantle and crust.

Table 13.1.1 The Major Components of Clean Dry Air in the Lower Atmosphere

nitrogen	N_2	78.08 %
oxygen	O_2	20.95 %
argon	Ar	0.93 %

The most abundant of the minor gases aside from water vapor is carbon dioxide (Table 13.1.2). Next in abundance are neon and helium. Helium is a decay product of radioactive elements in the earth, but neon and the other inert gases are primordial, and have probably been present in their present relative abundances since the earth's formation. Two of the minor gases, ozone and carbon monoxide, have abundances that vary with time and location. A variable abundance implies an imbalance between the rates of formation and removal. In the case of carbon monoxide, whose major source is anthropogenic (a small amount is produced by biological action), the variance is probably due largely to localized differences in fuel consumption, particularly in internal combustion engines. The nature of the carbon monoxide sink (removal mechanism) is not entirely clear; it may be partly microbial.

Table 13.1.2 The Minor Components of Air in the Lower Atmosphere.

water	H_2O	0-4 %
carbon dioxide	CO_2	325 ppm
neon	Ne	18 ppm
helium	He	5 ppm
methane	CH_4	2 ppm
krypton	Kr	1 ppm
hydrogen	H_2	0.5 ppm
nitrous oxide	N_2O	0.3 ppm
carbon monoxide	CO	0.05-0.2 ppm
ozone	O_3	0.02 - 10 ppm
xenon	Xe	0.08 ppm

Summary

- The layers of the atmosphere include the trophosphere, stratosphere, mesosphere, thermosphere, and exosphere.
- The major components of dry clean air are N_2, O_2, and Ar.
- The most abundant of the minor gases are water vapor and CO_2

Contributors and Attributions

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13.2: Chemistry of the Atmosphere

Learning Objectives

- Describe the nitrogen cycle.
- Describe the oxygen cycle.
- Describe the conditions for temperature inversion.

The mix of gases in the atmosphere forms a complex system organized into layers that together support life on Earth. Although there are numerous gases, as shown in Table 13.1.1, the top four gases make up 99.998 % of the volume of *clean dry air* (unpolluted air that does not contain water vapor). Of this dry composition of the atmosphere **nitrogen**, by far, is the most common (78%). Nitrogen dilutes oxygen and prevents rapid or instantaneous burning at the Earth's surface, as oxygen gas is a necessary reactant of the combustion process. Nitrogen is also needed and used by living things to make proteins, though as nitrogen gas, N_2, it is unavailable to most living things. **Oxygen** is used by all living things to make molecules that are essential for life. It is also essential for aerobic respiration as well as combustion or burning.

Nitrogen Cycle

All life requires nitrogen-compounds, e.g., proteins and nucleic acids. Air, which is 79% nitrogen gas (N_2), is the major reservoir of nitrogen. But most organisms cannot use nitrogen in this form. Figure 13.2.1 illustrates the entire nitrogen cycle. Plants must secure their nitrogen in "fixed" form, i.e., incorporated in compounds such as: nitrate ions (NO_3^-), ammonium ions (NH_4^+) and urea $(NH_2)_2CO$. Animals secure their nitrogen (and all other) compounds from plants (or animals that have fed on plants).

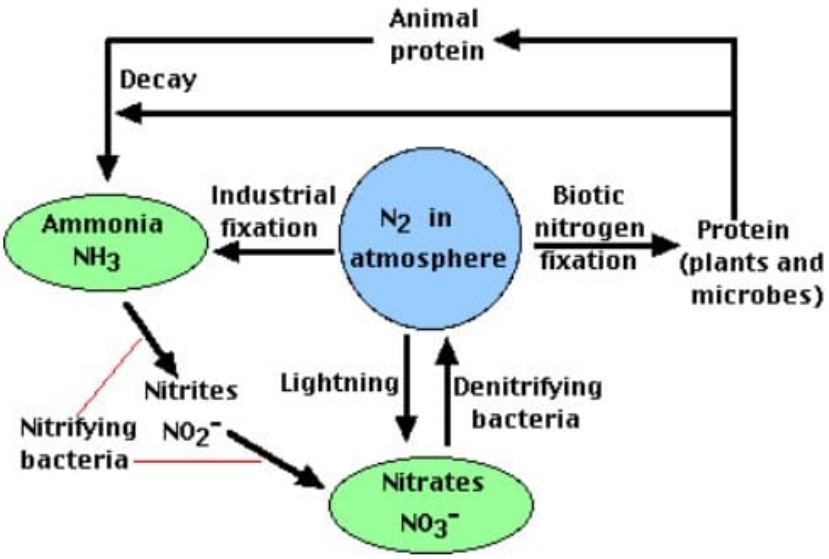


Figure 13.2.1 Nitrogen cycle

Four processes participate in the cycling of nitrogen through the biosphere: (1) nitrogen fixation, (2) decay, (3) nitrification, and (4) denitrification. Microorganisms play major roles in all four of these.

Nitrogen Fixation

The nitrogen molecule (N_2) is quite inert. To break it apart so that its atoms can combine with other atoms requires the input of substantial amounts of energy. Three processes are responsible for most of the nitrogen fixation in the biosphere:

- **atmospheric fixation** by lightning
- **biological fixation** by certain microbes alone or in a symbiotic relationship with some plants and animals
- **industrial fixation**

Atmospheric Fixation

The enormous energy of lightning breaks nitrogen molecules and enables their atoms to combine with oxygen in the air forming nitrogen oxides. These dissolve in rain, forming nitrates, that are carried to the earth. Atmospheric nitrogen fixation probably contributes some 5– 8% of the total nitrogen fixed.

Industrial Fixation

Under great pressure, at a temperature of 600°C, and with the use of a catalyst, atmospheric nitrogen and hydrogen (usually derived from natural gas or petroleum) can be combined to form ammonia (NH3). Ammonia can be used directly as fertilizer, but most of its is further processed to urea and ammonium nitrate (NH4NO3).

Biological Fixation

The ability to fix nitrogen in the soil (Figure $13.2.2$) only in certain bacteria and archaea.

- Some live in a symbiotic relationship with plants of the legume family (e.g., soybeans, alfalfa).
- Some establish symbiotic relationships with plants other than legumes (e.g., alders).
- Some establish symbiotic relationships with animals, e.g., termites and "shipworms" (wood-eating bivalves).
- Some nitrogen-fixing bacteria live free in the soil.
- Nitrogen-fixing cyanobacteria are essential to maintaining the fertility of semi-aquatic environments like rice paddies.

Biological nitrogen fixation requires a complex set of enzymes and a huge expenditure of ATP. Although the first stable product of the process is ammonia, this is quickly incorporated into protein and other organic nitrogen compounds.

Decay

The proteins made by plants enter and pass through food webs just as carbohydrates do. At each trophic level, their metabolism produces organic nitrogen compounds that return to the environment, chiefly in excretions. The final beneficiaries of these materials are microorganisms of decay. They break down the molecules in excretions and dead organisms into **ammonia**.

Nitrification

Ammonia can be taken up directly by plants — usually through their roots. However, most of the ammonia produced by decay is converted into **nitrates**. Until recently this was thought always to be accomplished in two steps:

1. Bacteria of the genus *Nitrosomonas* oxidize $\mathrm{NH_3}$ to **nitrites** ($\mathrm{NO_2^-}$).
2. Bacteria of the genus *Nitrobacter* oxidize the nitrites to **nitrates** ($\mathrm{NO_3^-}$).

These two groups of autotrophic bacteria are called **nitrifying bacteria**. Through their activities (which supply them with all their energy needs), nitrogen is made available to the roots of plants. However, in 2015, two groups reported finding that bacteria in the genus *Nitrospira* were able to carry out both steps: ammonia to nitrite and nitrite to nitrate. This ability is called "comammox" (for complete ammonia oxidation).

In addition, both soil and the ocean contain **archaeal** microbes, assigned to the Crenarchaeota, that convert ammonia to nitrites. They are more abundant than the nitrifying bacteria and may turn out to play an important role in the nitrogen cycle.

Many legumes, in addition to fixing atmospheric nitrogen, also perform nitrification - converting some of their organic nitrogen to nitrites and nitrates. These reach the soil when they shed their leaves.

Denitrification

The three processes above remove nitrogen from the atmosphere and pass it through ecosystems. Denitrification reduces nitrates and nitrites to nitrogen gas, thus replenishing the atmosphere. In the process several intermediates are formed:

- nitric oxide (NO)
- nitrous oxide (N_2O)(a greenhouse gas 300 times as potent as CO_2)
- nitrous acid (HONO)

Once again, bacteria are the agents. They live deep in soil and in aquatic sediments where conditions are anaerobic. They use nitrates as an alternative to oxygen for the final electron acceptor in their respiration.

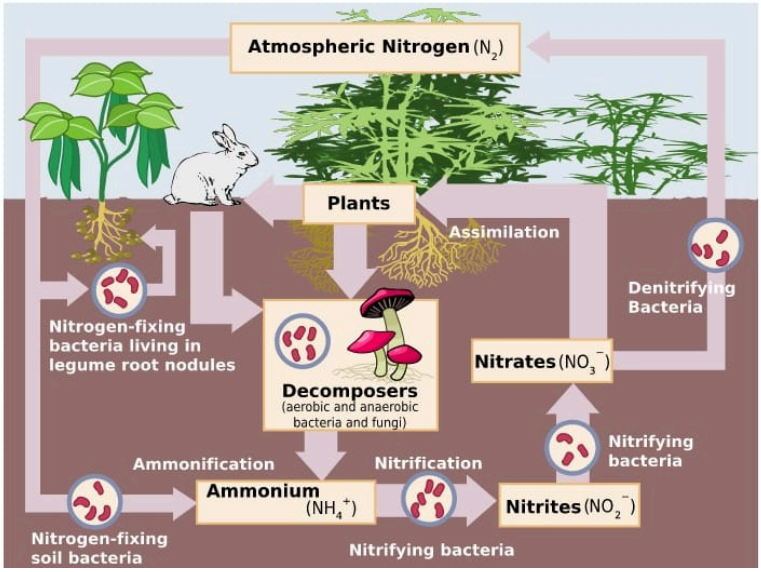


Figure 13.2.2 The role of soil bacteria in the Nitrogen cycle: Nitrogen transitions between various biologically useful forms.

Anammox (anaerobic ammonia oxidation)

Under anaerobic conditions in marine and freshwater sediments, other species of bacteria are able to oxidize ammonia (with NO_2^-) forming nitrogen gas.

$$NH_4^+ + NO_2^- \longrightarrow N_2 + 2\,H_2O$$

The anammox reaction may account for as much as 50% of the denitrification occurring in the oceans. All of these processes participate in closing the nitrogen cycle.

Are the denitrifiers keeping up?

Agriculture may now be responsible for one-half of the nitrogen fixation on earth through the use of fertilizers produced by industrial fixation and the the growing of legumes like soybeans and alfalfa. This is a remarkable influence on a natural cycle. Are the denitrifiers keeping up the nitrogen cycle in balance? Probably not. Certainly, there are examples of nitrogen enrichment in ecosystems. One troubling example: the "blooms" of algae in lakes and rivers as nitrogen fertilizers leach from the soil of adjacent farms (and lawns). The accumulation of dissolved nutrients in a body of water is called **eutrophication**.

Oxygen Cycle

Oxygen is the most abundant element on the earth's crust. The earth's surface is composed of the crust, atmosphere, and hydrosphere. About 50% of the mass of the earth's crust consists of oxygen (combined with other elements, principally silicon). Oxygen occurs as O_2 molecules and, to a limited extent, as O_3 (ozone) molecules in air. It forms about 20% of the mass of the

air. About 89% of water by mass consists of combined oxygen. In combination with carbon, hydrogen, and nitrogen, oxygen is a large part of plants and animals.

Oxygen is a colorless, odorless, and tasteless gas at ordinary temperatures. It is slightly denser than air. Although it is only slightly soluble in water (49 mL of gas dissolves in 1 L at STP), oxygen's solubility is very important to aquatic life.

Oxygen is essential in combustion processes such as the burning of fuels. Plants and animals use the oxygen from the air in respiration (*Figure* 13.2.4*)*. The main way free oxygen is lost from the atmosphere is via and , mechanisms in which life and consume oxygen and release carbon dioxide.

The respiration process is represented as:

$$6\,O_2{}^{+}C_6H_{12}O_6 \longrightarrow 6\,CO_2{}^{+}6H_2O$$

Green plants continually replenish the oxygen in the atmosphere by a process called photosynthesis (*Figure* 13.2.3*)* . The products of photosynthesis may vary, but, in general, the process converts carbon dioxide and water into glucose (a sugar) and oxygen using the energy of light:

$$6\,CO_2(g) + 6\,H_2O(l) \xrightarrow[\text{light}]{\text{chlorophyll}} C_6H_{12}O_6(aq) + 6\,O_2(g) \tag{13.2.1}$$

$$\underset{\text{dioxide}}{\text{carbon}} \qquad \text{water} \qquad \text{glucose} \qquad \text{oxygen} \tag{13.2.2}$$

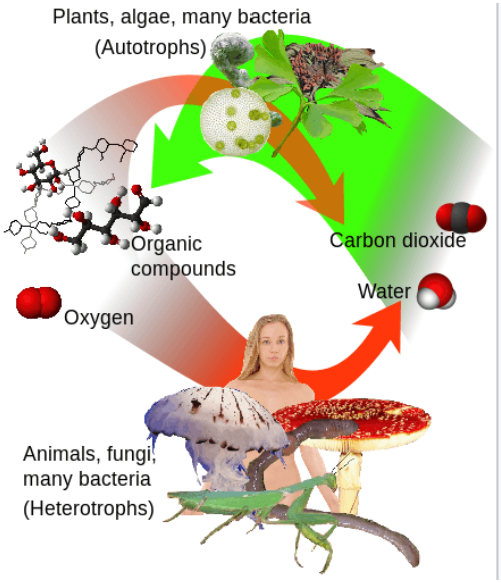


Figure 13.2.3

Overview of and photosynthesis (green) and respiration (red).

Water (at right), together with carbon dioxide (CO_2), form oxygen and organic compounds (at left),

which can be respired to water and (CO_2). Source: Wikipedia

Thus, the oxygen that became carbon dioxide and water by the metabolic processes in plants and animals returns to the atmosphere by photosynthesis. Photosynthesizing organisms include the plant life of the land areas as well as the of the oceans. The tiny marine was discovered in 1986 and accounts for more than half of the photosynthesis of the open ocean.

Oxygen is a key reactant in various oxidation reactions mentioned in section 8.5. Atmospheric free oxygen is also consumed by chemical weathering and surface reactions. An example of surface weathering is formation of rust:

$$\mathbf{4\,FeO + O_2 \longrightarrow 2\,Fe_2O_3}$$

Ozone forms naturally in the upper atmosphere by the action of ultraviolet light from the sun on the oxygen there. Most

atmospheric ozone occurs in the stratosphere, a layer of the atmosphere extending from about 10 to 50 kilometers above the earth's surface. This ozone acts as a barrier to harmful ultraviolet light from the sun by absorbing it via a chemical decomposition reaction:

$$\mathrm{O_3}(g) \xrightarrow{\text{ultraviolet light}} \mathrm{O}(g) + \mathrm{O_2}(g)$$

Temperature Inversions

In meteorology, an **inversion**, also known as a **temperature inversion**, is a deviation from the normal change of an amospheric property with altitude. It almost always refers to an inversion of the thermal lapse rate. Normally, air temperature decreases with an increase in altitude. During an inversion, warmer air is held above cooler air; the normal temperature profile with altitude is inverted.

An inversion traps air pollution, such as smog, close to the ground. An inversion can also suppress convection by acting as a "cap". If this cap is broken for any of several reasons, convection of any moisture present can then erupt into violent thunderstorms Temperature inversion can notoriously result in freezing rain in cold climates.

Summary

- The different forms of nitrogen that can be used in metabolism are produced through the process of nitrogen fixation.
- Bacteria in the soil carry out a process known as denitrification which converts nitrates back to nitrogen gas.
- Oxygen is produced mainly through photosynthesis. An additional source of atmospheric free oxygen comes from , whereby high-energy radiation breaks down atmospheric water and nitrous oxide.
- Oxygen is utilized during cellular respiration and decay. As well as during chemical weathering and various oxidation reactions.
- Temperature inversion is when a layer of cool air is trapped under a layer of warmer air. The cool dense air can trap and accumulate air pollutants.

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- Wikipedia

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13.3: Outdoor Air Pollution

Learning Objectives

- Define air pollution.
- Know the sources and effects of major outdoor pollutants

Air pollution refers to the introduction, into the atmosphere, of substances that have harmful effects on humans, other living organisms, and the environment either as solid particles, liquid droplets or gases. Air pollution can result from natural processes such as dust storms, forest fires, and volcanic eruptions, or from human activities such as biomass burning, vehicular emissions, mining, agriculture, and industrial processes. Improved technology and government policies have helped reduce most types of outdoor air pollution in many industrialized countries including the United States, in recent decades. However, outdoor air quality is still a problem in less industrialized nations, especially in megacities of rapidly industrializing nations such as China and India.

Outdoor pollutants can come from **stationary (point)** sources or **mobile (nonpoint)** sources (Figure 13.3.1). Stationary sources have a fixed location, for example power plant smokestacks, burning, construction sites, farmlands and surface mines among others. Mobile sources of air pollutants move from place to place while emitting pollutants. Examples of mobile sources include vehicles, aircrafts, ships, and trains.

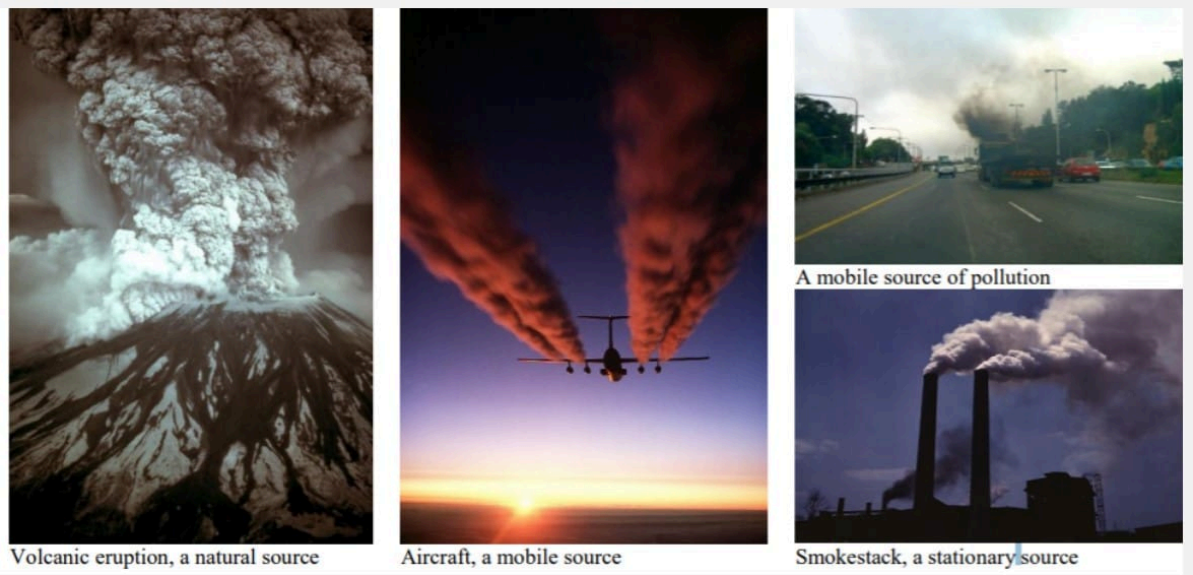


Figure 13.3.1: Images showing various sources of air pollution, including natural and anthropogenic, stationary and mobile. Source: All images obtained from Wiki Commons commons.wikimedia.org/wiki/Air_pollution

Pollutants are categorized into two major types based on how they originated namely primary and secondary pollutants. **Primary pollutants** are those released directly from the source into the air in a harmful form. The primary pollutants that account for nearly all air pollution problems are carbon monoxide (58%), volatile organic compounds (VOCs, 11%), nitrogen oxides (15%), sulfur dioxides (13%), and particulate material (3%). **Secondary pollutants** are produced through reactions between primary pollutants and normal atmospheric compounds. For example, ground-level ozone forms over urban areas through reactions, powered by sunlight, between primary pollutants (oxides of nitrogen) and other atmospheric gases such as VOCs.

Criteria pollutants

Under the Clean Air Act, the Environmental Protection Agency (EPA) establishes air quality standards to protect public health and the environment. EPA has set national air quality standards for six common air pollutants namely: 1) carbon monoxide; 2) ground-level ozone; 3) nitrogen dioxide; 4) Sulfur dioxide; 5) lead; and 6) particulate matter (also known as particle pollution). Of the six pollutants, particle pollution and ground-level ozone are the most widespread health threats. EPA calls these pollutants "criteria"

air pollutants because it regulates them by developing human health-based and/or environmentally-based criteria (science-based guidelines) for setting permissible levels. The set of limits based on human health is called primary standards. Another set of limits intended to prevent environmental and property damage is called secondary standards.

1. **Carbon Monoxide (CO)**: is a colorless, odorless gas emitted from combustion processes, specifically, the incomplete combustion of fuel. Nationally and, particularly in urban areas, the majority of CO emissions to ambient air come from mobile sources. CO can cause harmful health effects by reducing oxygen delivery to the body's organs (like the heart and brain) and tissues. At extremely high levels, CO can cause death.
2. **Ground-level ozone (O_3)**: is a colorless gas with a slightly sweet odor that is not emitted directly into the air, but is created by the interaction of sunlight, heat, oxides of nitrogen (NO_x) and volatile organic compounds (VOCs). Ozone is likely to reach unhealthy levels on hot sunny days in urban environments. Emissions from industrial facilities and electric utilities, motor vehicle exhaust, gasoline vapors, and chemical solvents are some of the major sources of NO_x and VOCs.
3. **Nitrogen dioxide (NO_2)**: is one of a group of highly reactive gasses known as "oxides of nitrogen," or "nitrogen oxides (NO_x)." Other nitrogen oxides include nitrous acid and nitric acid. NO_2 is a yellowish-brown to reddish-brown foul-smelling gas that is a major contributor to smog and acid rain. Nitrogen oxides result when atmospheric nitrogen and oxygen react at the high temperatures created by combustion engines. Most emissions in the U.S. result from combustion in vehicle engines, electrical utility, and industrial combustion.
4. **Sulfur dioxide (SO_2)**: Sulfur dioxide is one of a group of highly reactive gasses known as “oxides of sulfur.” The largest sources of SO_2 emissions are from fossil fuel combustion at power plants (73%) and other industrial facilities (20%). Smaller sources of SO_2 emissions include industrial processes such as extracting metals from their ores, and the burning of high sulfur containing fuels by locomotives, large ships, and non-road equipment.
5. **Lead (Pb)**: is a metal found naturally in the environment as well as in manufactured products. The major sources of lead emissions have historically been from fuels in motor vehicles (such as cars and trucks) and industrial sources. As a result of EPA's regulatory efforts to remove lead from gasoline, emissions of lead from the transportation sector dramatically declined by 95 percent between 1980 and 1999, and levels of lead in the air decreased by 94 percent during that time period. The major sources of lead emissions today are ore and metal processing and piston-engine aircraft operating on leaded aviation gasoline. Today, the highest levels of lead in air are usually found near lead smelters.
6. **Particulate material (PM)**, sometimes known simply as “**particulates**” refers to solid particles and liquid droplets suspended in the air we breathe. Particulate pollution is made up of a variety of components, including acids (nitrates and sulfates), organic chemicals, metals, soil or dust particles, and allergens (pollen and mold spores). The size of the particles in directly linked to their potential for causing health problems. Particles that are 10 micrometers in diameter or smaller generally pass through the throat and nose and enter the lungs. EPA groups these into two types: "**inhalable coarse particles**," with diameters larger than 2.5 micrometers and smaller than 10 micrometers and "**fine particles**," with diameters that are 2.5 micrometers and smaller. How small is 2.5 micrometers? Think about a single hair from your head. The average human hair is about 70 micrometers in diameter – making it 30 times larger than the largest fine particle (Figure 13.3.2). Our respiratory systems are equipped to filter larger particles out of the air once it is inhaled. However, the lungs are vulnerable to both coarse particles (PM_{10}), and fine particles ($PM_{2.5}$). These can slip past the respiratory system's natural defenses and get deep into the lungs and some may even get into the bloodstream. Coarse particles come from road dust while fine particles come from combustion processes.

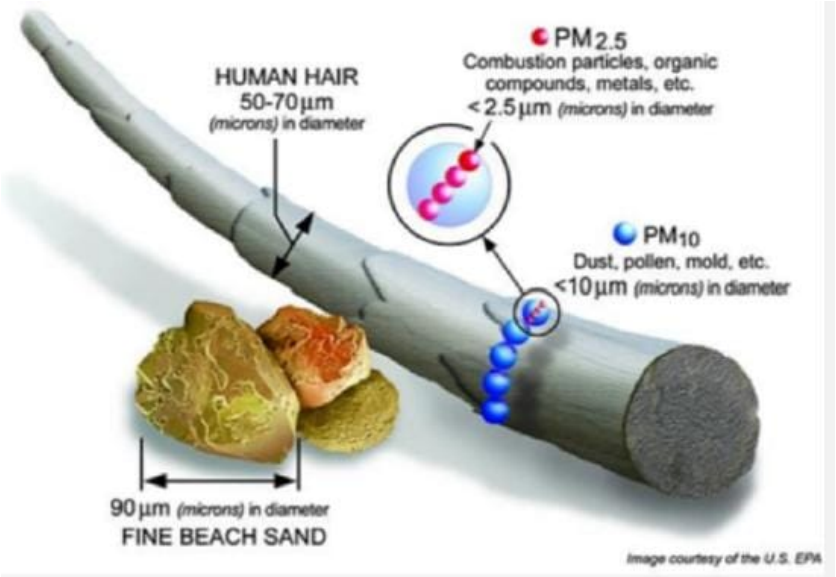


Figure 13.3.2 Graphic showing size comparison of particulate material (PM_{10} and $PM_{2.5}$) compared to fine beach sand and human hair. Source: US EPA http://www.epa.gov/air/particlepollution/basic.html

Volatile Organic Compounds

Volatile organic compounds (VOCs) are carbon-containing chemicals emitted as gases from natural and human-made sources. Natural sources of VOCs include plants, the largest source, and bacteria in the guts of termites and ruminant animals. These compounds are generally oxidized to carbon monoxide and carbon dioxide in the atmosphere. VOCs are of great concern because they are precursors for the formation of ozone, a secondary air pollutant.

A large number of synthetic organic chemicals such as benzene, toluene, formaldehyde, vinyl chloride, chloroform, and phenols are widely used as ingredients in countless household products. Paints, paint strippers, varnishes, many cleaning, disinfecting, cosmetic, degreasing, and hobby products all contain VOCs. Fuels are also made up of organic chemicals. All of these products can release organic compounds while you are using them, and, to some degree, when they are stored. The “new car smell” characteristic of new cars is from a complex mix of dozens of VOC. Also, concentrations of many VOCs are consistently higher indoors (up to ten times higher) than outdoors. They are often held responsible for sick building syndrome, an illness resulting from indoor pollution in which the specific cause is not identified.

Smog

Smog is a mixture of air pollutants (sulfur dioxide, nitrogen oxides, ozone, and particulates) that often form over urban areas as a result of fossil fuel combustion. The term was coined from the terms “smoke” and “fog” referring to a brownish haze that pollutes the air, greatly reducing visibility and making it difficult for some people to breathe (Figure 13.3.3 and 13.3.4). There are two main types of smog: industrial and photochemical smog. **Industrial smog** is produced primarily by the burning of fossil fuels which produces carbon dioxide (from complete combustion), carbon monoxides (from partial combustion), sulfur, and mercury. The sulfur reacts with other chemicals in the atmosphere producing several sulfur compounds including sulfur dioxide. These compounds along with particulate material make up industrial smog. **Photochemical smog** is formed when sunlight drives chemical reactions between primary pollutants from automobiles and normal atmospheric compounds. The product is a mix of over 100 different chemicals with the most abundant being ground-level ozone. This type of smog will be discussed in more detail in section 13.5.



Figure 13.3.3: Smog over Almaty city, Kazakhstan. Photo by Igors Jefimovs. Source: Wikicommons commons.wikimedia.org/wiki/C...dia/File:Smog_ over_Almaty.jpg



Figure 13.3.4: Smog over Santiago in Chile. Source: German Wikipedia commons.wikimedia.org/wiki/C...#/media/File:S antiago30std.jpg

Industrial Smog

Industrial smog or London-type smog is mainly a product of burning large amounts of high sulfur coal. Clean air laws passed in 1956 have greatly reduced smog formation in the United Kingdom; however, in other parts of the world London-type smog is still very prevalent. The main constituent of London-type smog is soot; however, these smogs also contain large quantities of fly ash, sulfur dioxide, sodium chloride and calcium sulfate particles. If concentrations are high enough, sulfur dioxide can react with atmospheric hydroxide to produce sulfuric acid, which will precipitate as acid rain.

$$SO_2 + OH \rightarrow HOSO_2 \tag{13.3.1}$$

$$HOSO_2 + O_2 \rightarrow HO_2 + SO_3 \tag{13.3.2}$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \tag{13.3.3}$$

Concerns about the harmful effects of acid rain have led to strong pressure on industry to minimize the release of SO_2 and NO. For example, coal-burning power plants now use SO_2 "scrubbers," which trap SO_2 by its reaction with lime (CaO) to produce calcium sulfite dihydrate ($CaSO_3 \cdot 2H_2O$; Figure 13.3.5).

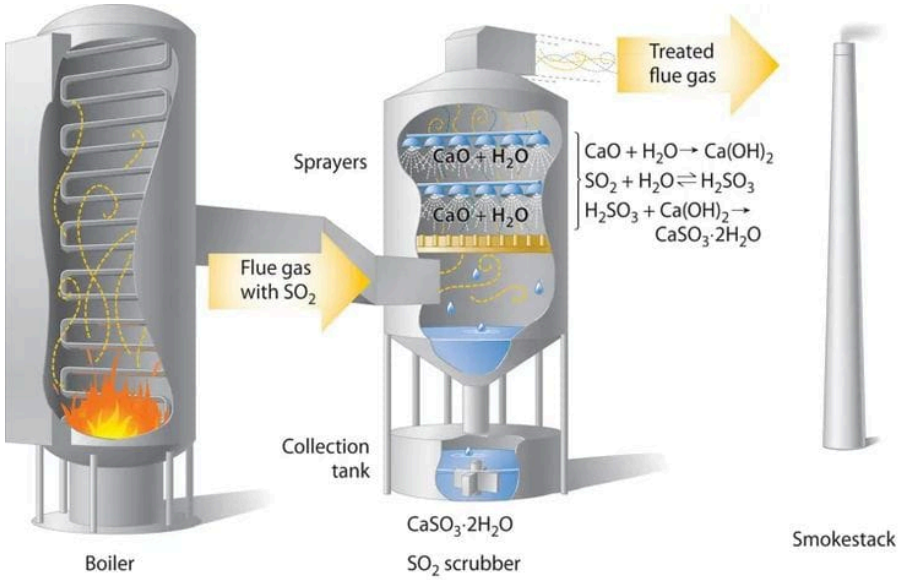


Figure 13.3.5: Schematic Diagram of a Wet Scrubber System. In coal-burning power plants, SO_2 can be removed ("scrubbed") from exhaust gases by its reaction with a lime (CaO) and water spray to produce calcium sulfite dihydrate ($CaSO_3 \cdot 2H_2O$). Removing SO_2 from the gases prevents its conversion to SO_3 and subsequent reaction with rainwater (acid rain). Scrubbing systems are now commonly used to minimize the environmental effects of large-scale fossil fuel combustion.

Toxic pollutants

Toxic air pollutants, also known as hazardous air pollutants, are those pollutants that are known or suspected to cause cancer or other serious health effects, such as reproductive effects or birth defects, or adverse environmental effects. Examples of toxic air pollutants include **benzene**, which is found in gasoline; **perchloroethylene,** which is emitted from some dry cleaning facilities; **methylene chloride**, which is used as a solvent and paint stripper by a number of industries; and others such as dioxin, asbestos, toluene, and metals such as cadmium, mercury, chromium, and lead compounds.

Most air toxics originate from human-made sources, including mobile sources (e.g., cars, trucks, buses) and stationary sources (e.g., factories, refineries, power plants), as well as indoor sources (e.g., some building materials and cleaning solvents). Some air toxics are also released from natural sources such as volcanic eruptions and forest fires. Exposure to air toxics is mainly through breathing but some toxic air pollutants such as mercury can deposit onto soils or surface waters, where they are taken up by plants and ingested by animals and are eventually magnified up through the food chain. Like humans, animals may experience health problems if exposed to sufficiently high quantities of air toxics over time.

Effects of Air Pollution on Human Health

The World Health Organization (WHO) and other international agencies recognize air pollution as a major threat to human health. Numerous scientific studies have linked air pollution to a variety of health problems (Table 13.3.1) including: aggravation of respiratory and cardiovascular diseases; decreased lung function; increased frequency and severity of respiratory symptoms such as difficulty breathing and coughing; increased susceptibility to respiratory infections; effects on the nervous system, including the brain, such as IQ loss and impacts on learning, memory, and behavior; cancer; and premature death. Immediate effects of air pollution may show up after a single exposure or repeated exposures. Other health effects may show up either years after exposure has occurred or only after long or repeated periods of exposure.

Immediate effects of air pollution include irritation of the eyes, nose, and throat, headaches, dizziness, and fatigue. Such immediate effects are usually short-term and treatable. Sometimes the treatment is simply eliminating the person's exposure to the source of the pollution, if it can be identified. Symptoms of some diseases, including asthma, hypersensitivity pneumonitis, and humidifier fever , may also show up soon after exposure to some indoor air pollutants.

Table 13.3.1: Sources and health effects of criteria pollutants

Pollutant	Sources	Health Effects
Ground-level Ozone (O_3)	Secondary pollutant typically formed by chemical reaction of volatile organic compounds (VOCs) and NO_x in the presence of sunlight.	Decreases lung function and causes respiratory symptoms, such as coughing and shortness of breath; aggravates asthma and other lung diseases leading to increased medication use, hospital admissions, emergency department (ED) visits, and premature mortality.
Particulate Matter (PM)	Emitted or formed through chemical reactions; fuel combustion (e.g., burning coal, wood, diesel); industrial processes; agriculture (plowing, field burning); and unpaved roads.	Short-term exposures can aggravate heart or lung diseases leading to respiratory symptoms, increased medication use, hospital admissions, ED visits, and premature mortality; long-term exposures can lead to the development of heart or lung disease and premature mortality.
Lead	Smelters (metal refineries) and other metal industries; combustion of leaded gasoline in piston engine aircraft; waste incinerators; and battery manufacturing.	Damages the developing nervous system, resulting in IQ loss and impacts on learning, memory, and behavior in children. Cardiovascular and renal effects in adults and early effects related to anemia.
Oxides of Nitrogen (NO_x)	Fuel combustion (e.g., electric utilities, industrial boilers, and vehicles) and wood burning.	Aggravate lung diseases leading to respiratory symptoms, hospital admissions, and ED visits; increased susceptibility to respiratory infection.
Carbon Monoxide (CO)	Fuel combustion (especially vehicles), industrial processes, fires, waste combustion, and residential wood burning.	Reduces the amount of oxygen reaching the body's organs and tissues; aggravates heart disease, resulting in chest pain and other symptoms leading to hospital admissions and ED visits.
Sulfur Dioxide (SO_2)	Fuel combustion (especially high-sulfur coal); electric utilities and industrial processes; and natural sources such as volcanoes.	Aggravates asthma and increased respiratory symptoms. Contributes to particle formation with associated health effects.

Source: www.epa.gov

The likelihood of immediate reactions to air pollutants depends on several factors. Age and preexisting medical conditions are two important influences. Some sensitive individuals appear to be at greater risk for air pollution-related health effects, for example, those with pre-existing heart and lung diseases (e.g., heart failure/ischemic heart disease, asthma, emphysema, and chronic bronchitis), diabetics, older adults, and children. In other cases, whether a person reacts to a pollutant depends on individual sensitivity, which varies tremendously from person to person. Some people can become sensitized to biological pollutants after repeated exposures, and it appears that some people can become sensitized to chemical pollutants as well.

Summary

- Air pollution refers to the introduction, into the atmosphere, of substances that have harmful effects on humans, other living organisms, and the environment either as solid particles, liquid droplets or gases.
- Major sources of air pollution are gas emissions from fossil fueled vehicles and their reaction products (CO, NO_x, Ozone) as well as particulate matter, SO_2, and VOCs.
- Examples of toxic air pollutants include benzene, which is found in gasoline; perchloroethylene, which is emitted from some dry cleaning facilities; methylene chloride, which is used as a solvent and paint stripper by a number of industries; and others such as dioxin, asbestos, toluene, and metals such as cadmium, mercury, chromium, and lead compounds.
- Smog is a mixture of air pollutants (sulfur dioxide, nitrogen oxides, ozone, and particulates) that often form over urban areas as a result of fossil fuel combustion. The term was coined from the terms "smoke" and "fog" referring to a brownish haze that pollutes the air, greatly reducing visibility and making it difficult for some people to breathe.
- Numerous scientific studies have linked air pollution to a variety of health problems.

Contributors and Attributions

- Libretext: Introduction to Environmental Science (Zendher et al.)
- TextMap: General CHemistry (Averill and Eldredge)

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- Wikipedia

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13.4: Automobile Emissions

Learning Objective

- Identify the different pollutant gases in automobile emissions.

Exhaust gas or flue gas is emitted as a result of the combustion of fuels such as natural gas, gasoline, petrol, biodiesel blends, diesel fuel, fuel oil, or coal. It is a major component of motor vehicle emissions (and from stationary internal combustion engines), which can also include:

- Crankcase blow-by
- Evaporation of unused gasoline

Motor vehicle emissions contribute to air pollution and are a major ingredient in the creation of smog in some large cities. A 2013 study by MIT indicates that 53,000 early deaths occur per year in the United States alone because of vehicle emissions.

Carbon monoxide and nitrogen oxides are the two main pollutant gases from automobile emissions. Ozone is a result of the reaction between nitrogen oxides and volatile organic compounds (VOCs).

Carbon Monoxide

Carbon Monoxide (CO) is a colorless, odorless gas that can be harmful when inhaled in large amounts. CO is released when something is burned. The greatest sources of CO to outdoor air are cars, trucks and other vehicles or machinery that burn fossil fuels. A variety of items in your home such as unvented kerosene and gas space heaters, leaking chimneys and furnaces, and gas stoves also release CO and can affect air quality indoors.

Harmful effects

Breathing air with a high concentration of CO reduces the amount of oxygen that can be transported in the blood stream to critical organs like the heart and brain.

At very high levels, which are possible indoors or in other enclosed environments, CO can cause dizziness, confusion, unconsciousness and death.

Very high levels of CO are not likely to occur outdoors. However, when CO levels are elevated outdoors, they can be of particular concern for people with some types of heart disease. These people already have a reduced ability for getting oxygenated blood to their hearts in situations where the heart needs more oxygen than usual. They are especially vulnerable to the effects of CO when exercising or under increased stress. In these situations, short-term exposure to elevated CO may result in reduced oxygen to the heart accompanied by chest pain also known as angina.

Nitrogen Oxides

Nitrogen dioxide (NO_2) is one of a group of highly reactive gasses known as "oxides of nitrogen," or "nitrogen oxides (NO_x)." Other nitrogen oxides include nitrous acid and nitric acid. NO_2 is a yellowish-brown to reddish-brown foul-smelling gas that is a major contributor to smog and acid rain. Nitrogen oxides result when atmospheric nitrogen and oxygen react at the high temperatures created by combustion engines. Most emissions in the U.S. result from combustion in vehicle engines, electrical utility, and industrial combustion.

NO_2 primarily gets in the air from the burning of fuel. NO_2 forms from emissions from cars, trucks and buses, power plants, and off-road equipment.

Health effects

Breathing air with a high concentration of NO_2 can irritate airways in the human respiratory system. Such exposures over short periods can aggravate respiratory diseases, particularly asthma, leading to respiratory symptoms (such as coughing, wheezing or difficulty breathing), hospital admissions and visits to emergency rooms. Longer exposures to elevated concentrations of NO_2 may contribute to the development of asthma and potentially increase susceptibility to respiratory infections. People with asthma, as well as children and the elderly are generally at greater risk for the health effects of NO_2.

NO_2 along with other NO_x reacts with other chemicals in the air to form both particulate matter and ozone. Both of these are also harmful when inhaled due to effects on the respiratory system.

Environmental effects

NO_2 and other NO_x interact with water, oxygen and other chemicals in the atmosphere to form acid rain. Acid rain harms sensitive ecosystems such as lakes and forests.

The nitrate particles that result from NO_x make the air hazy and difficult to see though. This affects the many national parks that we visit for the view. NO_x in the atmosphere contributes to nutrient pollution in coastal waters.

Ozone

Ground-level ozone (O_3) is a colorless gas with a slightly sweet odor that is not emitted directly into the air, but is created by the interaction of sunlight, heat, oxides of nitrogen (NO_x) and volatile organic compounds (VOCs). Ozone is likely to reach unhealthy levels on hot sunny days in urban environments. Emissions from industrial facilities and electric utilities, motor vehicle exhaust, gasoline vapors, and chemical solvents are some of the major sources of NO_x and VOCs.

Ozone is a gas composed of three atoms of oxygen (O_3). Ozone occurs both in the Earth's upper atmosphere and at ground level. Ozone can be good or bad, depending on where it is found.

Called stratospheric ozone, good ozone occurs naturally in the upper atmosphere, where it forms a protective layer that shields us from the sun's harmful ultraviolet rays. This beneficial ozone has been partially destroyed by manmade chemicals, causing what is sometimes called a "hole in the ozone." The good news is, this hole is diminishing.

Ozone at ground level is a harmful air pollutant, because of its effects on people and the environment, and it is the main ingredient in “smog."

How does ground-level ozone form?

Tropospheric, or ground level ozone, is not emitted directly into the air, but is created by chemical reactions between oxides of nitrogen (NOx) and volatile organic compounds (VOC). This happens when pollutants emitted by cars, power plants, industrial boilers, refineries, chemical plants, and other sources chemically react in the presence of sunlight.

Ozone is most likely to reach unhealthy levels on hot sunny days in urban environments, but can still reach high levels during colder months. Ozone can also be transported long distances by wind, so even rural areas can experience high ozone levels.

This graphic depicts the formation of ozone from car and factory emissions

Health effects

Ozone in the air we breathe can harm our health especially on hot sunny days when ozone can reach unhealthy levels. People most at risk from breathing air containing ozone include people with asthma, children, older adults, and people who are active outdoors, especially outdoor workers.

Environmental effects

Ozone affects sensitive vegetation and ecosystems, including forests, parks, wildlife refuges and wilderness areas. In particular, ozone harms sensitive vegetation during the growing season.

Summary

- Carbon monoxide and nitrogen oxides are the two main compounds from automobile emissions.
- Ozone but is created by chemical reactions between oxides of nitrogen (NOx) and volatile organic compounds (VOC).
- Different levels of exposure to automobile emissions and ozone can lead to various health problems.

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13.5: Photochemical Smog- Making Haze While the Sun Shines

Learning Objectives

- Describe photochemical smog.
- List different means to address photochemical smog.

Photochemical smog is a type of air pollution due to the reaction of solar radiation with airborne pollutant mixtures of nitrogen oxides (NOx) and volatile organic compounds (hydrocarbons). Smog is a byproduct of modern industrialization. Due to industry and the number of motor vehicles, this is more of a problem in large cities that have a warm, sunny and dry climate.

- **Oxidation**: Photochemical smog is also referred to as oxidizing smog. Oxidation reactions have been defined several ways. In terms of oxygen transfer, oxidation is a gain of oxygen. Oxidation can also be defined as a loss of hydrogen. The most important use of oxidation is described in terms of electron transfer. Oxidation can be described as an increase in oxidation number or loss of electrons. Oxidation numbers represents a distribution of charge. In other words, oxidation numbers represent the charge of the atom if the compound was composed of ions.
- **Reduction**: Reduction can involve the gain of hydrogen or loss of oxygen. Reduction can refer to the gain of electrons, which results in a decrease in oxidation number.

Formation of Photochemical Smog

The different reactions involved in the formation of photochemical smog are given below.

Step 1: People begin driving in the morning, nitrogen is burned or oxidized

$$N_2 + O_2 \rightarrow 2NO$$

- Oxidation number of N_2 is 0. The nitrogen in NO has acquired an oxidation number of +2.

Step 2: After a few hours, NO combines with O_2, in another oxidation reaction

$$2NO + O_2 \rightarrow 2NO_2$$

- The nitrogen in NO has an oxidation number of +2. The nitrogen in NO_2 has an oxidation number of +4.

Step 3: Nitrogen dioxide absorbs light energy, resulting in a reduction reaction

$$NO_2 \rightarrow NO + O$$

- The nitrogen in NO_2 has an oxidation number of +4 and the nitrogen in NO is +2.

Step 4: In sunlight, atomic oxygen combines with oxygen gas to form ozone

$$O + O_2 \rightarrow O_3$$

Step 5: Reaction is temperature and sunlight dependent

$$O_3 + NO \rightleftharpoons NO_2 + O_2$$

Alternative Reactions

NO and NO_2 can also react with the hydrocarbons instead of ozone to form other volatile compounds known as PAN (peroxyacetyl

nitrate) as shown in Figure . The accumulation of ozone and volatile organic compounds along with the energy from the sun forms the brown, photochemical smog seen on hot, sunny days. Panoramic view of Santiago covered by a layer of smog on May 10, 2006. The Metropolitan Region of Santiago facing the driest autumn last 28 years due to lack of rainfall, which coupled with poor air circulation, causes an increase in smog.

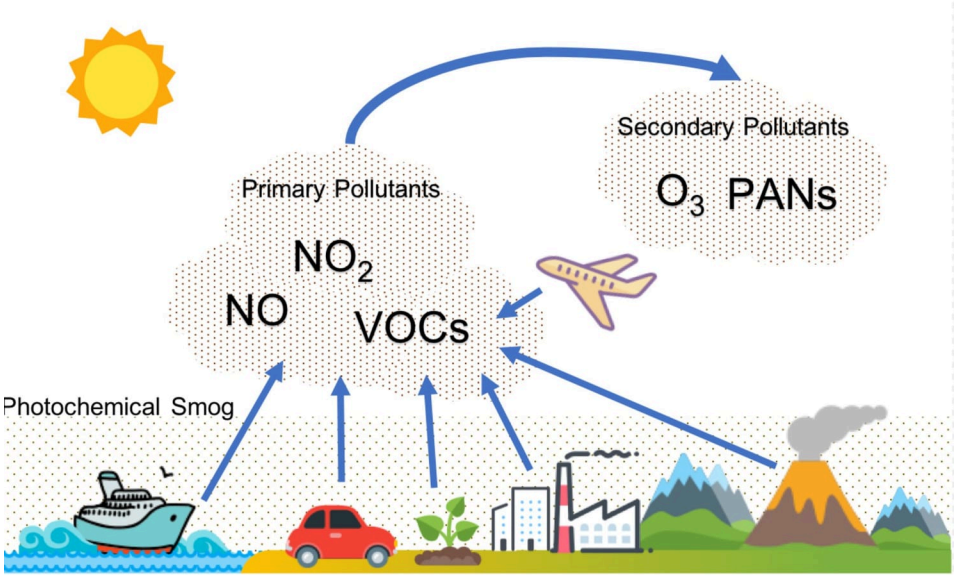


Figure 13.5.1 The photochemical smog formation diagram. Source: Wikipedia

Health Hazards

Because ozone is highly reactive, it has the ability to oxidize and destroy lung tissue. Short term exposures to elevated levels of ozone (above .75 ppm) have been linked to a host of respiratory irritations including coughing, wheezing, substernal soreness, pharyngitis, and dyspnea. Prolonged exposure to the molecule has been proven to cause a permanent reduction in lung function, as well as elevate the risk of developing asthma. Sulfur dioxide is a common component of London smog. Epidemiological studies have linked short term sulfur dioxide exposure to respiratory irritations including coughing, wheezing, and pharyngitis.

Other Harmful Effects of Smog

Plants are harmed by exposure to nitrogen oxides, ozone, and peroxyacetyl nitrate (PAN, see above), all oxidants present in a smoggy atmosphere. PAN is the most harmful of these constituents, damaging younger plant leaves, especially. Ozone exposure causes formation of yellow spots on leaves, a condition called chlorotic stippling. Some plant species, including sword-leaf lettuce, black nightshade, quickweed, and double-fortune tomato, are extremely susceptible to damage by oxidant species in smog and are used as bioindicators of the presence of smog. Costs of crop and orchard damage by smog run into millions of dollars per year in areas prone to this kind of air pollution, such as southern California.

Materials that are adversely affected by smog are generally those that are attacked by oxidants. The best example of such a material is rubber, especially natural rubber, which is attacked by ozone. Indeed, the hardening and cracking of natural rubber has been used as a test for atmospheric ozone.

Visibility-reducing atmospheric aerosol particles are the most common manifestation of the harm done to atmospheric quality by smog. The smog-forming process occurs by the oxidation of organic materials in the atmosphere, and carbon-containing organic materials are the most common constituents of the aerosol particles in an atmosphere afflicted by smog. Conifer trees(pine and cypress) and citrus trees are major contributors to the organic hydrocarbons that are precursors to organic particle formation in smog.

Controlling Photochemical Smog

Every new vehicle sold in the United States must include a catalytic converter to reduce photochemical emissions. Catalytic

converters force CO and incompletely combusted hydrocarbons to react with a metal catalyst, typically platinum, to produce CO_2 and H_2O. Additionally, catalytic converters reduce nitrogen oxides from exhaust gases into O_2 and N_2, eliminating the cycle of ozone formation. Many scientists have suggested that pumping gas at night could reduce photochemical ozone formation by limiting the amount of exposure VOCs have with sunlight.

Preventing Smog with Green Chemistry

Smog is basically a chemical problem, which would indicate that it should be amenable to chemical solutions. Indeed, the practice of green chemistry and the application of the principles of industrial ecology can help to reduce smog. This is due in large part to the fact that a basic premise of green chemistry is to avoid the generation and release of chemical species with the potential to harm the environment. The best way to prevent smog formation is to avoid the release of nitrogen oxides and organic vapors that enable smog to form. At an even more fundamental level, measures can be taken to avoid the use of technologies likely to release such substances, for example, by using alternatives to polluting automobiles for transportation.

The evolution of automotive pollution control devices to reduce smog provides an example of how green chemistry can be used to reduce pollution. The first measures taken to reduce hydrocarbon and nitrogen oxide emissions from automobiles were very much command-and-control and “end-of-pipe” measures. These primitive measures implemented in the early 1970s did reduce emissions, but with a steep penalty in fuel consumption and in driving performance of vehicles. However, over the last three decades, the internal combustion automobile engine has evolved into a highly sophisticated computer-controlled machine that generally performs well, emits few air pollutants, and is highly efficient. (And it would be much more efficient if those drivers who feel that they must drive “sport utility” behemoths would switch to vehicles of a more sensible size.) This change has required an integrated approach involving reformulation of gasoline. The first major change was elimination from gasoline of tetraethyllead, an organometallic compound that poisoned automotive exhaust catalysts (and certainly was not good for people). Gasoline was also reformulated to eliminate excessively volatile hydrocarbons and unsaturated hydrocarbons (those with double bonds between carbon atoms) that are especially reactive in forming photochemical smog.

An even more drastic approach to eliminating smog-forming emissions is the use of electric automobiles that do not burn gasoline. These vehicles certainly do not pollute as they are being driven, but they suffer from the probably unsolvable problem of a very limited range between charges and the need for relatively heavy batteries. However, hybrid automobiles using a small gasoline or diesel engine that provides electricity to drive electric motors propelling the automobile and to recharge relatively smaller batteries can largely remedy the emission and fuel economy problems with automobiles. The internal combustion engine on these vehicles runs only as it is needed to provide power and, in so doing, can run at a relatively uniform speed that provides maximum economy with minimum emissions.

Another approach that is being used on vehicles as large as buses that have convenient and frequent access to refueling stations is the use of fuel cells that can generate electricity directly from the catalytic combination of elemental hydrogen and oxygen, producing only harmless water as a product . There are also catalytic process that can generate hydrogen from liquid fuels, such as methanol, so that vehicles carrying such a fuel can be powered by electricity generated in fuel cells.

Green chemistry can be applied to devices and processes other than automobiles to reduce smog-forming emissions. This is especially true in the area of organic solvents used for parts cleaning and other industrial operations, vapors of which are often released to the atmosphere. The substitution of water with proper additives or even the use of supercritical carbon dioxide fluid can eliminate such emissions.

Summary

- Photochemical smog is a mixture of pollutants that are formed (mostly during the hot summer months) when nitrogen oxides and volatile organic compounds (VOCs) react to sunlight, creating a brown haze above cities.
- Photochemical smog is formed from the reactions of natural and man-made emissions of nitrogen oxides and VOCs.
- Smog is a serious problem in many cities and continues to harm human health and are especially harmful for senior citizens, children, and people with heart and lung conditions such as emphysema, bronchitis, and asthma.
- Catalytic converters in gas powered vehicles help reduce photochemical emissions.
- The practice of green chemistry and the application of the principles of industrial ecology can help to reduce smog.

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- Wikipedia

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13.6: Acid Rain- Air Pollution Water Pollution

Learning Objective

- Describe acid rain and its effects.

Acid rain is a term referring to a mixture of wet and dry deposition (deposited material) from the atmosphere (Figure 13.6.1) containing higher than normal amounts of nitric and sulfuric acids. The precursors, or chemical forerunners, of acid rain formation result from both natural sources, such as volcanoes and decaying vegetation, and man-made sources, primarily emissions of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) resulting from fossil fuel combustion. Acid rain occurs when these gases react in the atmosphere with water, oxygen, and other chemicals to form various acidic compounds. The result is a mild solution of sulfuric acid and nitric acid.

$$SO_2 + HOH \rightarrow H_2SO_3 \tag{13.6.1}$$

$$2NO_2 + HOH \rightarrow HNO_2 + HNO_3 \tag{13.6.2}$$

When sulfur dioxide and nitrogen oxides are released from power plants and other sources, *prevailing winds* blow these compounds across state and national borders, sometimes over hundreds of miles.

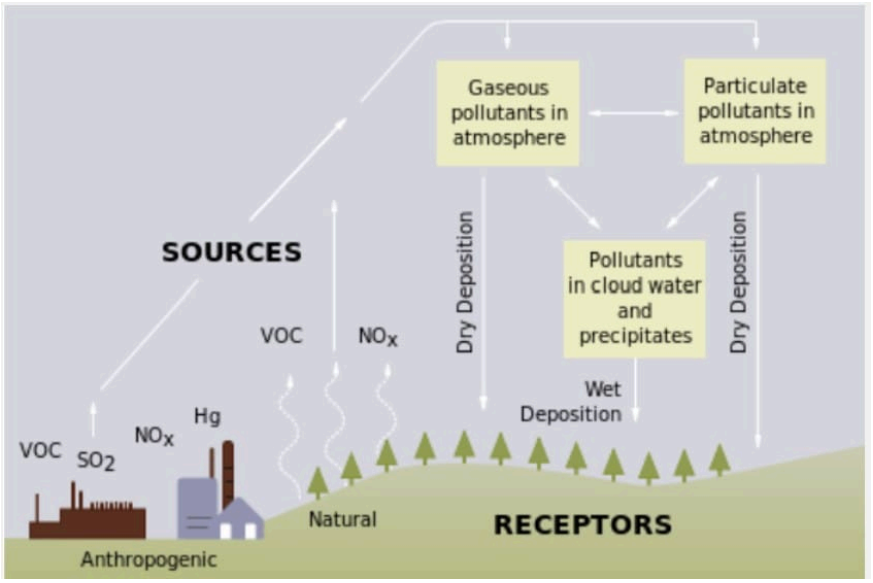


Figure 13.6.1 Processes involved in acid deposition.

Acid rain is measured using a scale called “pH.” The lower a substance’s pH, the more acidic it is. Pure water has a pH of 7.0. However, normal rain is slightly acidic because carbon dioxide (CO_2) dissolves into it forming weak carbonic acid, giving the resulting mixture a pH of approximately 5.6 at typical atmospheric concentrations of CO_2. As of 2000, the most acidic rain falling in the U.S. has a pH of about 4.3.

Effects of Acid Rain

Acid rain causes **acidification** of lakes and streams and contributes to the damage of trees at high elevations (for example, red spruce trees above 2,000 feet) and many sensitive forest soils. In addition, acid rain accelerates the decay of building materials and paints, including irreplaceable buildings, statues, and sculptures that are part of our nation’s cultural heritage. Prior to falling to the earth, sulfur dioxide (SO_2) and nitrogen oxide (NO_x) gases and their particulate matter derivatives—sulfates and nitrates—contribute to visibility degradation and harm public health.

The **ecological** effects of acid rain are most clearly seen in the aquatic, or water, environments, such as streams, lakes, and marshes. Most lakes and streams have a pH between 6 and 8, although some lakes are naturally acidic even without the effects of acid rain. Acid rain primarily affects sensitive bodies of water, which are located in watersheds whose soils have a limited ability to neutralize acidic compounds (called “buffering capacity”). Lakes and streams become acidic (i.e., the pH value goes down) when the water itself and its surrounding soil cannot buffer the acid rain enough to neutralize it. In areas where buffering capacity is low, acid rain releases aluminum from soils into lakes and streams; aluminum is highly toxic to many species of aquatic organisms. Acid rain causes slower growth, injury, or death of forests as shown in Figure 13.6.2. Of course, acid rain is not the only cause of such conditions. Other factors contribute to the overall stress of these areas, including air pollutants, insects, disease, drought, or very cold weather. In most cases, in fact, the impacts of acid rain on trees are due to the combined effects of acid rain and these other environmental stressors.



Figure 13.6.2. Acid rain damage to a forest in the Czech Republic.

Acid rain and the dry deposition of acidic particles contribute to the corrosion of **metals**(such as bronze).

The damage that acid rain does to limestone and marble buildings and sculptures is due to a classic acid–base reaction. Marble and limestone both consist of calcium carbonate ($CaCO_3$), a salt derived from the weak acid H_2CO_3. The reaction of a strong acid with a salt of a weak acid goes to completion. Thus we can write the reaction of limestone or marble with dilute sulfuric acid as follows:

$$CaCO_{3(s)} + H_2SO_{4(aq)} \rightarrow CaSO_{4(s)} + H_2O_{(l)} + CO_{2(g)} \tag{13.6.3}$$

Because $CaSO_4$ is sparingly soluble in water, the net result of this reaction is to dissolve the marble or limestone.

These effects significantly reduce the societal value of buildings, bridges, cultural objects (such as statues, monuments, and tombstones), and cars (Figure 13.6.3).



Figure 13.6.3. A gargoyle that has been damaged by acid rain.

Sulfates and nitrates that form in the atmosphere from sulfur dioxide (SO_2) and nitrogen oxides (NO_x) emissions contribute to **visibility impairment,** meaning we cannot see as far or as clearly through the air. The pollutants that cause acid rain—sulfur dioxide (SO_2) and nitrogen oxides (NO_x)—damage **human health**. These gases interact in the atmosphere to form fine sulfate and nitrate particles that can be transported long distances by winds and inhaled deep into people's lungs. Fine particles can also penetrate indoors. Many scientific studies have identified a relationship between elevated levels of fine particles and increased illness and premature death from heart and lung disorders, such as asthma and bronchitis.

Summary

- Acid rain is a term referring to a mixture of wet and dry deposition (deposited material) from the atmosphere containing higher than normal amounts of nitric and sulfuric acids.
- Acidic rain water in the soil, streams, lakes, and marshes (and other bodies of water) can be harmful to trees, plants, animals, especially aquatic plants and animals.
- Acid rain and the dry deposition of acidic particles contribute to the corrosion of **metals**(such as bronze) and the deterioration of paint and stone (such as marble and limestone).

Contributors and Attributions

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13.7: Indoor Air Pollution

Learning Objectives

- Name the different indoor pollutants and their sources.
- Know the harmful effects of indoor pollutants.

In both developed and developing nations, indoor air pollution poses a greater health risk than outdoor air pollution. According to the World Health Organization (WHO) and other agencies such as the Environmental Protection Agency (EPA), indoor air generally contains higher concentrations of toxic pollutants than outdoor air. Additionally, people generally spend more time indoors than outdoors, hence, the health effects from indoor air pollution in workplaces, schools, and homes are far greater than outdoor. Indoor pollution sources that release gases or particles into the air are the primary cause of indoor air quality problems in homes. Inadequate ventilation can increase indoor pollutant levels by not bringing in enough outdoor air to dilute emissions from indoor sources and by not carrying indoor air pollutants out of the home.

Outdoor air enters and leaves a building by infiltration, natural ventilation, and mechanical ventilation. In infiltration, outdoor air flows into the house through openings, joints, and cracks in walls, floors, and ceilings, and around windows and doors. In natural ventilation, air moves through opened windows and doors. Air movement associated with infiltration and natural ventilation is caused by air temperature differences between indoors and outdoors and by wind. Finally, there are a number of mechanical ventilation devices, from outdoor-vented fans that intermittently remove air from a single room, such as bathrooms and kitchen, to air handling systems that use fans and duct work to continuously remove indoor air and distribute filtered and conditioned outdoor air to strategic points throughout the house. The rate at which outdoor air replaces indoor air is described as the air exchange rate. When there is little infiltration, natural ventilation, or mechanical ventilation, the air exchange rate is low and pollutant levels can increase. High temperature and humidity levels can also increase concentrations of some pollutants.

There are many sources of indoor air pollution in any home (Figure 13.7.1). These include combustion sources such as oil, gas, kerosene, coal, wood, and tobacco products; building materials and furnishings as diverse as deteriorated, asbestos-containing insulation, wet or damp carpet, and cabinetry or furniture made of certain pressed wood products; products for household cleaning and maintenance, personal care, or hobbies; central heating and cooling systems and humidification devices. Pollutants causing indoor air pollution can also originate from outside sources such as radon, pesticides, and outdoor air pollution. Radon is a naturally occurring radioactive gas produced from the decay of uranium in rock. If a building/home is constructed in an area with uranium containing rock, the gas can seep through the foundations and accumulate in basements. Exposure to radon can cause lung cancer.

The relative importance of any single source depends on how much of a given pollutant it emits and how hazardous those emissions are. In some cases, factors such as how old the source is and whether it is properly maintained are significant. For example, an improperly adjusted gas stove can emit significantly more carbon monoxide than one that is properly adjusted. Some sources, such as building materials, furnishings, and household products like air fresheners, release pollutants more or less continuously. Other sources, related to activities carried out in the home, release pollutants intermittently. These include smoking, the use of unvented or malfunctioning stoves, furnaces, or space heaters, the use of solvents in cleaning and hobby activities, the use of paint strippers in redecorating activities, and the use of cleaning products and pesticides in house-keeping. High pollutant concentrations can remain in the air for long periods after some of these activities.

Risks from indoor air pollution differ between less industrialized and industrialized nations. Indoor pollution has a greater impact in less industrialized nations where many people use cheaper sources of fuel such as wood, charcoal, and crop waste among others for cooking and heating, often with little or no ventilation. The most significant indoor pollutant, therefore, is soot and carbon monoxide. In industrialized nations, the primary indoor air health risks are cigarette smoke and radon.

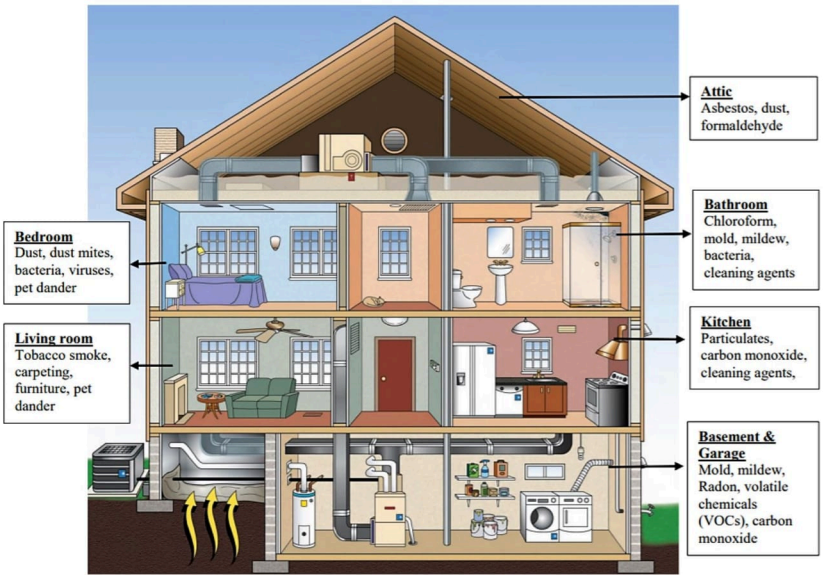


Figure 13.7.1: Sources of indoor air pollution. Image source: EPA http://www.epa.gov/iaq/pdfs/careforyourair.pdf

Combustion Pollutants

Combustion pollutants are gases or particles that come from burning materials. In homes, the major source of combustion pollutants are improperly vented or unvented fuel-burning appliances such as space heaters, wood stoves, gas stoves, water heaters, dryers, and fireplaces. The types and amounts of pollutants produced depends on the type of appliance, how well the appliance is installed, maintained and vented and the kind of fuel it uses. Common combustion pollutants include:

Carbon monoxide (CO) which is a colorless, odorless gas that interferes with the delivery of oxygen throughout the body. Carbon monoxide causes headaches, dizziness, weakness, nausea and even death. Average levels in homes without gas stoves vary from 0.5 to 5 parts per million (ppm). Levels near properly adjusted gas stoves are often 5 to 15 ppm and those near poorly adjusted stoves may be 30 ppm or higher.

Nitrogen dioxide (NO_2) which is a colorless, odorless gas that causes eye, nose and throat irritation, shortness of breath, and an increased risk of respiratory infection. Average level in homes without combustion appliances is about half that of outdoors. In homes with gas stoves, kerosene heaters or un-vented gas space heaters, indoor levels often exceed outdoor levels.

Particulate Matter (PM) which refers to fine particles that forms in smoke when wood or other organic matter burns.

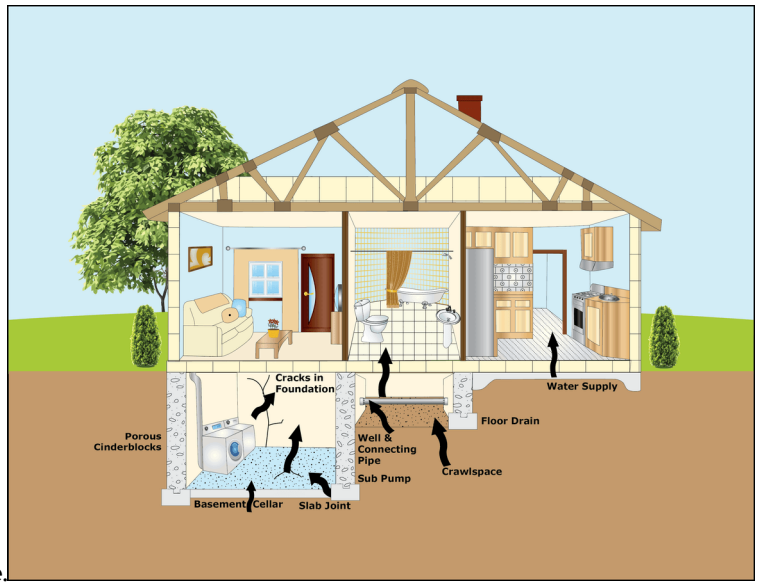
Other pollutants from wood smoke In addition to particle pollution, wood smoke contains several toxic harmful air pollutants including benzene, formaldehyde, acrolein, and polycyclic aromatic hydrocarbons (PAHs).

Secondhand Smoke

Secondhand smoke is a mixture of the smoke given off by the burning of tobacco products, such as cigarettes, cigars or pipes and the smoke exhaled by smokers. Secondhand smoke is also called environmental tobacco smoke (ETS). Exposure to secondhand smoke is sometimes called involuntary or passive smoking. Secondhand smoke, classified by EPA as a Group A carcinogen, contains more than 7,000 substances. Secondhand smoke exposure commonly occurs indoors, particularly in homes and cars. Secondhand smoke can move between rooms of a home and between apartment units. Opening a window or increasing ventilation in a home or car is not protective from secondhand smoke.

Radon

Radon is a radioactive gas that results from the natural decay of uranium and radiumfound in nearly all rocks and soils. Elevated



radon levels have been found in every state. Radon is in the atmosphere and can also be found in ground water. The national average for radon in outdoor air is 0.4 picocuries per liter (pCi/L), while the average for indoor air is 1.3 pCi/L.

Any building can have high levels of radon, including new and old homes, well-sealed and drafty homes, office buildings and schools, and homes with or without basements. Radon gas can get into buildings through cracks in solid floors and walls, construction joints, gaps in suspended floors and around service pipes, cavities inside walls, the water supply and building materials. Testing is the only way to know if your home has elevated radon levels.EPA recommends fixing your home when the radon level is at or above 4 pCi/L.

Figure 13.7.2***:*** *Sources of Radon. Image source: EPA*https://www.epa.gov/radiation/radionuclide-basics-radon

EPA estimates that about 21,000 lung cancer deaths each year in the U.S. are radon-related. Exposure to radon is the second leading cause of lung cancer after smoking. For most people, radon is the single greatest environmental source of radiation exposure. EPA recommends that all homes and schools be tested for radon. For smokers, the risk of lung cancer is heightened due to the combined effects of radon and smoking.

Other Indoor Pollutants

Molds are usually not a problem indoors, unless mold spores land on a wet or damp spot and begin growing. Molds have the potential to cause health problems. Molds produce allergens (substances that can cause allergic reactions) and irritants. Inhaling or touching mold or mold spores may cause allergic reactions in sensitive individuals. Allergic responses include hay fever-type symptoms, such as sneezing, runny nose, red eyes, and skin rash.

Allergic reactions to mold are common. They can be immediate or delayed. Molds can also cause asthma attacks in people with asthma who are allergic to mold. In addition, mold exposure can irritate the eyes, skin, nose, throat, and lungs of both mold-allergic and non-allergic people. Symptoms other than the allergic and irritant types are not commonly reported as a result of inhaling mold.

Volatile organic compounds (VOCs) are emitted as gases from certain solids or liquids. VOCs include a variety of chemicals, some of which may have short- and long-term adverse health effects. Concentrations of many VOCs are consistently higher indoors (up to ten times higher) than outdoors. VOCs are emitted by a wide array of products numbering in the thousands.

Organic chemicals are widely used as ingredients in household products. Paints, varnishes and wax all contain organic solvents, as do many cleaning, disinfecting, cosmetic, degreasing and hobby products. Fuels are made up of organic chemicals. All of these products can release organic compounds while you are using them, and, to some degree, when they are stored.

EPA's Office of Research and Development's "Total Exposure Assessment Methodology (TEAM) Study" (Volumes I through IV, completed in 1985) found levels of about a dozen common organic pollutants to be 2 to 5 times higher inside homes than outside, regardless of whether the homes were located in rural or highly industrial areas. TEAM studies indicated that while people are

using products containing organic chemicals, they can expose themselves and others to very high pollutant levels, and elevated concentrations can persist in the air long after the activity is completed.

VOCs are emitted by a wide array of products used in homes including paints and lacquers, paint strippers, cleaning supplies, varnishes and waxes, pesticides, building materials and furnishings, office equipment, moth repellents, air fresheners, and dry-cleaned clothing. VOCs evaporate into the air when these products are used or sometimes even when they are stored.

Volatile organic compounds irritate the eyes, nose and throat, and cause headaches, nausea, and damage to the liver, kidneys and central nervous system. Some of them can cause cancer.

Asbestos is a mineral fiber that occurs in rock and soil. Because of its fiber strength and heat resistance asbestos has been used in a variety of building construction materials for insulation and as a fire retardant. Asbestos has also been used in a wide range of manufactured goods, mostly in building materials (roofing shingles, ceiling and floor tiles, paper products, and asbestos cement products), friction products (automobile clutch, brake, and transmission parts), heat-resistant fabrics, packaging, gaskets, and coatings.

Asbestos fibers may be released into the air by the disturbance of asbestos-containing material during product use, demolition work, building or home maintenance, repair, and remodeling. In general, exposure may occur only when the asbestos-containing material is disturbed or damaged in some way to release particles and fibers into the air.

Three of the major health effects associated with asbestos exposure are:

· lung cancer

· mesothelioma, a rare form of cancer that is found in the thin lining of the lung, chest and the abdomen and heart

· asbestosis, a serious progressive, long-term, non-cancer disease of the lungs

Improving Your Indoor Air Quality

Take steps to help improve your air quality and reduce your IAQ-related health risks at little or no cost by:

Controlling the sources of pollution: Usually the most effective way to improve indoor air is to eliminate individual sources or reduce their emissions.

Ventilating: Increasing the amount of fresh air brought indoors helps reduce pollutants inside. When weather permits, open windows and doors, or run an air conditioner with the vent control open. Bathroom and kitchen fans that exhaust to the outdoors also increase ventilation and help remove pollutants.

Always ventilate and follow manufacturers' instructions when you use products or appliances that may release pollutants into the indoor air.

Changing filters regularly: Central heaters and air conditioners have filters to trap dust and other pollutants in the air. Make sure to change or clean the filters regularly, following the instructions on the package.

Adjusting humidity: The humidity inside can affect the concentrations of some indoor air pollutants. For example, high humidity keeps the air moist and increases the likelihood of mold.

Keep indoor humidity between 30 and 50 percent. Use a moisture or humidity gauge, available at most hardware stores, to see if the humidity in your home is at a good level. To increase humidity, use a vaporizer or humidifier. To decrease humidity, open the windows if it is not humid outdoors. If it is warm, turn on the air conditioner or adjust the humidity setting on the humid

Get a quick glimpse of some of the most important ways to protect the air in your home by touring the Indoor Air Quality (IAQ) House. Room-by-room, you'll learn about the key pollutants and how to address them.

Interactive Version

https://www.epa.gov/indoor-air-quality-iaq/interactive-tour-indoor-air-quality-demo-house#mainHouse

Text Version

https://www.epa.gov/indoor-air-quality-iaq/text-version-indoor-air-quality-house-tour

Summary

- Indoor pollutants include combustion pollutants (from burning of oil, gas, kerosene, coal, wood, and tobacco products); building materials and furnishings products for household cleaning and maintenance, personal care, or hobbies; central heating and cooling systems and humidification devices.
- Pollutants causing indoor air pollution can also originate from outside sources such as radon, pesticides, and outdoor air pollution.
- Indoor pollutants can cause serious health problems to sensitive groups.
- Several suggestions were provided to improve indoor air quality.

Contributors and Attributions

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US Environmental Protection Agency

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13.8: Stratospheric Ozone- Earth's Vital Shield

Learning Objectives

- Describe the depletion of the ozone layer.
- Explain how chlorine and bromine atoms react with ozone that leads to the depletion of the ozone layer.

The earth's stratospheric ozone layer plays a critical role in absorbing ultraviolet radiation emitted by the sun. In the last thirty years, it has been discovered that stratospheric ozone is depleting as a result of anthropogenic pollutants. There are a number of chemical reactions that can deplete stratospheric ozone; however, some of the most significant of these involves the catalytic destruction of ozone by halogen radicals such as chlorine and bromine.

Introduction

The atmosphere of the Earth is divided into five layers. In order of closest and thickest to farthest and thinnest the layers are listed as follows: troposphere, stratosphere, mesosphere, thermosphere and exosphere. The majority of the ozone in the atmosphere resides in the stratosphere, which extends from six miles above the Earth's surface to 31 miles. Humans rely heavily on the absorption of ultraviolet B rays by the ozone layer because UV-B radiation causes skin cancer and can lead to genetic damage. The ozone layer has historically protected the Earth from the harmful UV rays, although in recent decades this protection has diminished due to stratospheric ozone depletion.

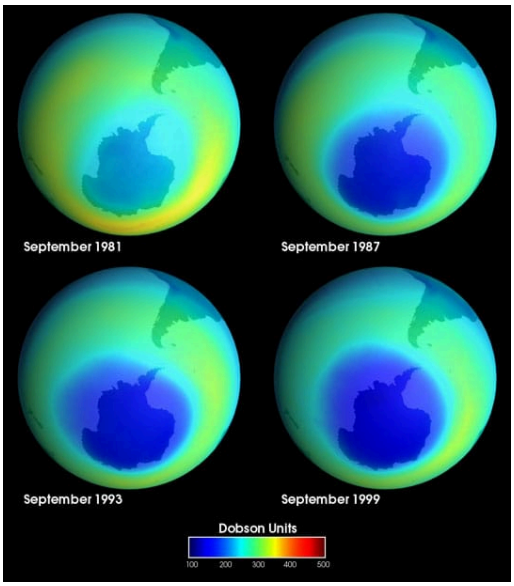


Figure courtesy of NASA.

Ozone depletion is largely a result of man-made substances. Humans have introduced gases and chemicals into the atmosphere that have rapidly depleted the ozone layer in the last century. This depletion makes humans more vulnerable to the UV-B rays which are known to cause skin cancer as well as other genetic deformities. The possibility of ozone depletion was first introduced by scientists in the late 1960's as dreams of super sonic transport began to become a reality. Scientists had long been aware that nitric oxide (NO) can catalytically react with ozone (O_3) to produce O_2 molecules; however, NO molecules produced at ground level have a half life far too short to make it into the stratosphere. It was not until the advent of commercial super sonic jets (which fly in the stratosphere and at an altitude much higher then conventional jets) that the potential for NO to react with stratospheric ozone became a possibility. The threat of ozone depletion from commercial super sonic transport was so great that it is often cited as the main reason why the US federal government pulled support for its development in 1971. Fear of ozone depletion was abated until 1974 when Sherwood Rowland and Mario Molina discovered that chlorofluorocarbons could be photolyzed by high energy photons in the stratosphere. They discovered that this process could releasing chlorine radicals that would catalytically

react with O_3 and destroy the molecule. This process is called the Rowland-Molina theory of O_3 depletion.

The Chapman Cycle

The stratosphere is in a constant cycle with oxygen molecules and their interaction with ultraviolet rays. This process is considered a cycle because of its constant conversion between different molecules of oxygen. The ozone layer is created when ultraviolet rays react with oxygen molecules (O_2) to create ozone (O_3) and atomic oxygen (O). This process is called the *Chapman cycle*.

Step 1: An oxygen molecules is photolyzed by solar radiation, creating two oxygen radicals:

$$h\nu + O_2 \rightarrow 2O^{\cdot}$$

Step 2: Oxygen radicals then react with molecular oxygen to produce ozone:

$$O_2 + O^{\cdot} \rightarrow O_3$$

Step 3: Ozone then reacts with an additional oxygen radical to form molecular oxygen:

$$O_3 + O^{\cdot} \rightarrow 2O_2$$

Step 4: Ozone can also be recycled into molecular oxygen by reacting with a photon:

$$O_3 + h\nu \rightarrow O_2 + O^{\cdot}$$

It is important to keep in mind that ozone is constantly being created and destroyed by the Chapman cycle and that these reactions are natural processes, which have been taking place for millions of years. Because of this, the thickness the ozone layer at any particular time can vary greatly. It is also important to know that O_2 is constantly being introduced into the atmosphere through photosynthesis, so the ozone layer has the capability of regenerating itself.

Chemistry of Ozone Depletion

CFC molecules are made up of chlorine, fluorine and carbon atoms and are extremely stable. This extreme stability allows CFC's to slowly make their way into the stratosphere (most molecules decompose before they can cross into the stratosphere from the troposphere). This prolonged life in the atmosphere allows them to reach great altitudes where photons are more energetic. When the CFC's come into contact with these high energy photons, their individual components are freed from the whole. The following reaction displays how Cl atoms have an ozone destroying cycle:

$$Cl + O_3 \rightarrow ClO + O_2 \qquad \text{(step 1)}$$

$$ClO + O^{\cdot} \rightarrow Cl + O_2 \qquad \text{(step 2)}$$

$$O_3 + O^{\cdot} \rightarrow 2O_2 \qquad \text{(Overall reaction)}$$

Chlorine is able to destroy so much of the ozone because it acts as a catalyst. Chlorine initiates the breakdown of ozone and combines with a freed oxygen to create two oxygen molecules. After each reaction, chlorine begins the destructive cycle again with another ozone molecule. One chlorine atom can thereby destroy thousands of ozone molecules. Because ozone molecules are being broken down they are unable to absorb any ultraviolet light so we experience more intense UV radiation at the earths surface.

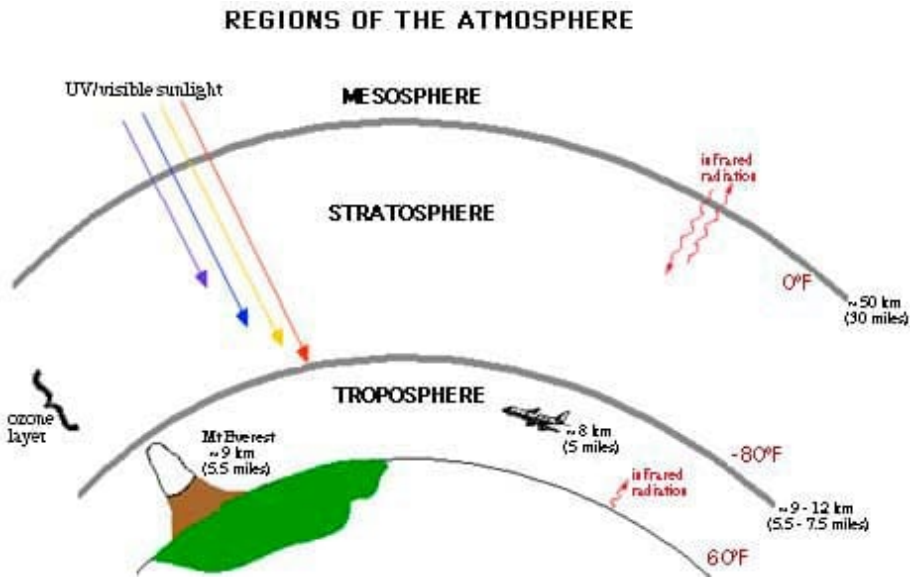


Figure courtesy of NOAA.

From 1985 to 1988, researchers studying atmospheric properties over the south pole continually noticed significantly reduced concentrations of ozone directly over the continent of Antarctica. For three years it was assumed that the ozone data was incorrect and was due to some type of instrument malfunction. In 1988, researchers finally realized their error and concluded that an enormous hole in the ozone layer had indeed developed over Antarctica. Examination of NASA satellite data later showed that the hole had begun to develop in the mid 1970's.

The ozone hole over Antarctica is formed by a slew of unique atmospheric conditions over the continent that combine to create an ideal environment for ozone destruction.

- Because Antarctica is surrounded by water, winds over the continent blow in a unique clockwise direction creating a so called "polar vortex" that effectively contains a single static air mass over the continent. As a result, air over Antarctica does not mix with air in the rest of the earth's atmosphere.
- Antarctica has the coldest winter temperatures on earth, often reaching -110 F. These chilling temperatures result in the formation of polar stratospheric clouds (PSC's) which are a conglomeration of frozen H_2O and HNO_3. Due to their extremely cold temperatures, PSC's form an electrostatic attraction with CFC molecules as well as other halogenated compounds

As spring comes to Antarctica, the PSC's melt in the stratosphere and release all of the halogenated compounds that were previously absorbed to the cloud. In the antarctic summer, high energy photons are able to photolyze the halogenated compounds, freeing halogen radicals that then catalytically destroy O_3. Because Antarctica is constantly surrounded by a polar vortex, radical halogens are not able to be diluted over the entire globe. The ozone hole develops as result of this process.

Resent research suggests that the strength of the polar vortex from any given year is directly correlated to the size of the ozone hole. In years with a strong polar vortex, the ozone hole is seen to expand in diameter, whereas in years with a weaker polar vortex, the ozone hole is noted to shrink

Ozone Depleting Substances

The following substances are listed as ozone depleting substances under Title VI of the United State Clean Air Act:

Table 13.8.1: Ozone Depleting Substances And Their Ozone-Depletion Potential. Taken directly from the Clean Air Act, as of June 2010.

Substance	Ozone- depletion potential
chlorofluorocarbon-11 (CFC–11)	1.0
chlorofluorocarbon-12 (CFC–12)	1.0

Substance	Ozone- depletion potential
chlorofluorocarbon-13 (CFC–13)	1.0
chlorofluorocarbon-111 (CFC–111)	1.0
chlorofluorocarbon-112 (CFC–112)	1.0
chlorofluorocarbon-113 (CFC–113)	0.8
chlorofluorocarbon-114 (CFC–114)	1.0
chlorofluorocarbon-115 (CFC–115)	0.6
chlorofluorocarbon-211 (CFC–211)	1.0
chlorofluorocarbon-212 (CFC–212)	1.0
chlorofluorocarbon-213 (CFC–213)	1.0
chlorofluorocarbon-214 (CFC–214)	1.0
chlorofluorocarbon-215 (CFC–215)	1.0
chlorofluorocarbon-216 (CFC–216)	1.0
chlorofluorocarbon-217 (CFC–217)	1.0
halon-1211	3.0
halon-1301	10.0
halon-2402	6.0
carbon tetrachloride	1.1
methyl chloroform	0.1
hydrochlorofluorocarbon-22 (HCFC–22)	0.05
hydrochlorofluorocarbon-123 (HCFC–123)	0.02
hydrochlorofluorocarbon-124 (HCFC–124)	0.02
hydrochlorofluorocarbon-141(b) (HCFC–141(b))	0.1
hydrochlorofluorocarbon-142(b) (HCFC–142(b))	0.06

Summary

- Any disruption of the balance that results in a higher rate of ozone destruction than ozone creation would result in depletion of ozone.
- Some compounds that release chlorine or bromine when they are exposed to intense UV light in the stratosphere contribute to ozone depletion, and are called ozone-depleting substances (ODS)
- The Montreal Protocol is an international agreement that committed all parties (signatory nations) to a schedule for phasing out the production and use of CFCs and other substances known to be harmful to the ozone layer.

Contributors and Attributions

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13.9: Carbon Dioxide and Climate Change

Learning Objectives

- Define global warming, climate change, the greenhouse effect, and greenhouse gases.
- Discuss strategies for reducing the intensity of the human influence on the greenhouse effect.

Global warming refers to the increase in the average temperature of the Earth's atmosphere due to elevated greenhouse gas concentrations, heightening the greenhouse effect. **Climate change** includes both global warming driven by human-induced emissions of greenhouse gases and the resulting large-scale shifts in weather patterns. Though there have been previous periods of climatic change, since the mid-20th century humans have had an unprecedented impact on Earth's climate system and caused change on a global scale.

The largest driver of warming is the emission of gases that create a greenhouse effect, of which more than 90% are carbon dioxide (CO_2) and methane. Fossil fuel burning (coal, oil, and natural gas) for energy consumption is the main source of these emissions, with additional contributions from agriculture, deforestation, and manufacturing. The human cause of climate change is not disputed by any scientific body of national or international standing. Temperature rise is accelerated or tempered by climate feedbacks, such as loss of sunlight-reflecting snow and ice cover, increased water vapour (a greenhouse gas itself), and changes to land and ocean carbon sinks.

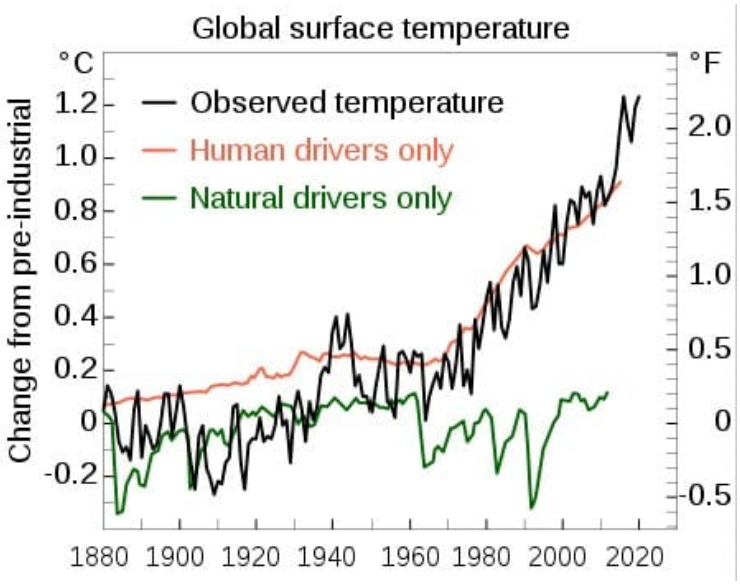


Figure 13.9.1 Observed temperature from NASA versus the 1850-1900 average as a pre-industrial baseline.

The **greenhouse effect** is the process by which radiation from a planet's atmosphere warms the planet's surface to a temperature above what it would be without this atmosphere (Figure 13.9.2). Radiatively active gases (i.e. greenhouse gases) in a planet's atmosphere radiate energy in all directions. Part of this radiation is directed towards the surface, thus warming it. The intensity of downward radiation – that is, the strength of the greenhouse effect – depends on the amount of greenhouse gases that the atmosphere contains. The temperature rises until the intensity of upward radiation from the surface, thus cooling it, balances the downward flow of energy.

Earth's natural greenhouse effect is critical to supporting life and initially was a precursor to life moving out of the ocean onto land. Human activities, mainly the burning of fossil fuels and clear cutting of forests, have increased the greenhouse effect and caused global warming.

The term *greenhouse effect* is a slight misnomer in the sense that physical greenhouses warm via a different mechanism. The greenhouse effect as an atmospheric mechanism functions through radiative heat loss while a traditional greenhouse as a built

structure blocks convective heat loss. The result, however, is an increase in temperature in both cases.

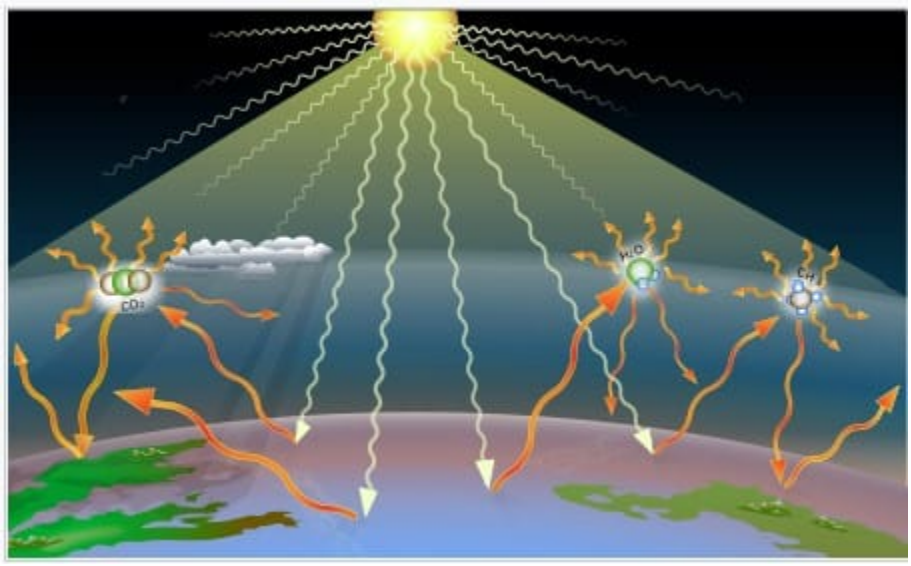


Figure 13.9.2 The greenhouse effect of solar radiation on the Earth's surface caused by emission of greenhouse gases. Source: Wikipedia

Greenhouse Gases and Global Warming

A **greenhouse gas** (sometimes abbreviated **GHG**) is a gas that absorbs and emits radiant energy within the thermal infrared range, causing the greenhouse effect. It's important to realize that **water vapor** (H_2O) is also a greenhouse gas. While humans have little direct impact on water vapor concentrations in the atmosphere, it is still an essential component of the natural greenhouse effect that occurs in our atmosphere. The four major categories of greenhouse gases that have been impacted by humans the most will be discussed in detail below. See Table 13.9.1 for a numeric comparison of these greenhouse gases.

- Carbon dioxide, CO_2
- Methane, CH_4
- Nitrous oxide, N_2O
- Synthetic **fluorinated gases**, including **hydrofluorocarbons** (HFCs), **perfluorocarbons** (PFCs), and **sulfur hexafluoride** (SF_6)

Carbon dioxide (CO_2) is the greenhouse gas responsible for most of the human-caused climate change in our atmosphere. It has the highest concentration in the atmosphere of any of the greenhouse gases that we'll discuss here. Remember that CO_2 is a direct product of both combustion and cellular respiration, causing it to be produced in great quantities both naturally and anthropogenically. Any time biomass or fossil fuels are burned, CO_2 is released. Major anthropogenic sources include: electricity production from coal-fired and natural gas power plants, transportation, and industry (Chapter 4). To get an idea of how CO_2 concentration has changed over time, watch this video compiled by the National Oceanic and Atmospheric Administration (NOAA): http://www.esrl.noaa.gov/gmd/ccgg/trends/history.html. This video contains atmospheric CO_2 concentrations measured directly, dating back to 1958, as well as atmospheric CO_2 concentrations measured indirectly from ice core data, dating back to 800,000 BCE. By 1990, a quantity of over seven billion tons of carbon (equivalent to 26 billion tons of carbon dioxide when the weight of the oxygen atoms are also considered) was being emitted into the atmosphere every year, much of it from industrialized nations. Similar to the action of the naturally existing greenhouse gases, any additional greenhouse gases leads to an increase in the surface temperature of the Earth.

While CO_2 is produced by aerobic cellular respiration, gases such as CH_4 and N_2O are often the products of anaerobic metabolisms. Agriculture is a major contributor to CH_4 emissions. In addition to anaerobic bacteria, methane is also a significant component of natural gas, and is commonly emitted through the mining and use of natural gas and petroleum, in addition to coal

mining. Finally, landfills contribute significantly to CH_4 emissions, as the waste put into the landfill largely undergoes anaerobic decomposition as it is buried under many layers of trash and soil. Natural sources of CH_4 include swamps and wetlands, and volcanoes.

The vast majority of N_2O production by humans comes from agricultural land management. While some N_2O is naturally emitted to the atmosphere from soil as part of the nitrogen cycle, human changes in land management, largely due to agricultural practices, have greatly increased N_2O emissions. Some N_2O is also emitted from transportation and industry.

Due to their relatively high concentrations in the atmosphere compared to synthetic gases, CO_2, CH_4, and N_2O, are responsible for most of the human-caused global climate change over the past century. Figure 13.9.2 shows the increases in all three gases since 1750. Ice core data shows us that the atmospheric CO_2 concentration never exceeded 300 ppm before the industrial revolution. As of early 2015, the current atmospheric CO_2 concentration is 400 ppm.

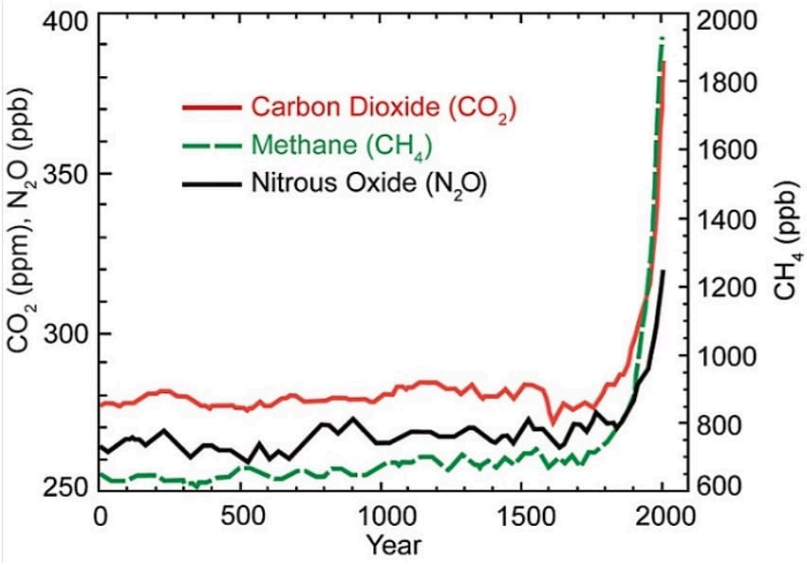


Figure 13.9.2: Increase in greenhouse gas concentrations in the atmosphere over the last 2,000 years. Increases in concentrations of these gases since 1750 are due to human activities in the industrial era. Concentration units are parts per million (ppm) or parts per billion (ppb), indicating the number of molecules of the greenhouse gas per million or billion molecules of air. Source: USGCRP (2009)

One class of greenhouse gas chemicals that has no natural sources is the fluorinated gases. These include HFCs, PFCs, and SF6, among others. Because these are synthetic chemicals that are only created by humans, these gases were essentially non-existent before the industrial revolution. These synthetic gases are used for a wide variety of applications, from refrigerants to semiconductor manufacturing, and propellants to fire retardants. They tend to have a long lifetime in the atmosphere, as seen in Table 13.9.1. Some of these chemicals, as well as the older **chlorofluorocarbons** (CFCs), have been phased out by international environmental legislation under the Montreal Protocol. Due to their long lifespan, many of these now banned CFCs remain in the atmosphere. Newer chemical replacements, such as HFCs, provide many of the same industrial applications, but unfortunately have their own environmental consequences.

Just as greenhouse gases differ in their sources and their residence time in the atmosphere, they also differ in their ability to produce the greenhouse effect. This is measured by the **global warming potential**, or GWP, of each greenhouse gas. The GWP of a greenhouse gas is based on its ability to absorb and scatter energy, as well as its lifetime in the atmosphere. Since CO_2 is the most prevalent greenhouse gas, all other greenhouse gases are measured relative to it. As the reference point, CO_2 always has a GWP of 1. Note the very high GWP values of the synthetic fluorinated gases in Table 13.9.1. This is largely due to their very long residence time in the atmosphere. Also note the higher GWP values for CH_4 and N_2O compared to CO_2.

Table 13.9.1. Comparision of Greenhouse Gases.

Greenhouse gas	Chemical formula or abbreviation	Lifetime in atmosphere	Global warming potential (100-year)
Carbon dioxide	CO_2	Variable	1
Methane	CH_4	12 years	28-36

Nitrous oxide	N_2O	114 years	298
Hydrofluorocarbons	Abbreviation: HFCs	1-270 years	12-14,800
Perfluorocarbons	Abbreviation: PFCs	2,600-50,000 years	7,390
Sulfur hexafluoride	SF6	3,200 years	22,800

Other climate influencers

In addition to greenhouse gases, other manmade changes may be forcing climate change. Increases in near-surface ozone from internal combustion engines, aerosols such as carbon black, mineral dust and aviation-induced exhaust are acting to raise the surface temperature. This primarily occurs due to a decrease in the **albedo** of light-colored surfaces by the darker-colored carbon black, soot, dust, or particulate matter. As you know, it is more comfortable to wear a white shirt on a hot summer day than a black shirt. Why is this? Because the lighter-colored material bounces more solar radiation back toward space than the darker-colored material does, allowing it to stay cooler. The darker-colored material absorbs more solar radiation, increasing its temperature. Just as the white shirt has a higher albedo than the black shirt, light-colored objects in nature (such as snow) have a higher albedo than dark-colored objects (such as soot or dust). As humans increase the amount of carbon black, soot, dust, and particulates in the atmosphere, we decrease the albedo of light-colored surfaces, causing them to absorb more solar radiation and become warmer than they would without human influence. An example of this can be seen in the snow on Figure 13.9.3.



Figure 13.9.3: A photograph of the extreme dust deposition from the deserts of the Colorado Plateau onto the Colorado Rockies snowpack in 2009. Taken from the high point of the Senator Beck Basin in the San Juan Mountains, it captures the extent of the impact of darkening in which the snow albedo dropped to about 30%, more than doubling the absorption of sunlight. Credit: S. McKenzie Skiles, Snow Optics Laboratory, NASA/JPL

Consequences of Climate Change

We will only discuss some of the consequences of climate change in this section, including changes in temperature, precipitation, ocean level, and ocean acidity. There are many more changes that have been seen, and are projected to continue in the future. These include: changes in the amount and distribution of ice and snow, changes in seasonality, ecosystem shift, and habitat changes of plant and animal populations, in addition to others. For more information about these consequence of climate change, visit this site: http://www.epa.gov/climatechange/sci...ors/index.html.

Temperature and precipitation

Temperature and **precipitation** are the two most direct impacts on the Earth's climate due to climate change. By now, you should already understand why an increase in greenhouse gas levels in the atmosphere causes an increase in temperature. But why does

it also impact precipitation patterns? As you already know, water vapor is an important component of the Earth's atmosphere . As the air in the troposphere warms and cools, the amount of water vapor that it holds changes dramatically. Here in Georgia, we have very hot and humid summers. The high summer humidity in this region is possible due to the increased capability warm air has to hold water vapor. Simply put, warmer air can hold more water than cooler air. As air cools, its ability to hold water vapor decreases, and any excess water will leave the air as liquid water. A great example of this is the formation of dew on surfaces overnight. During the day, the temperature is warmer than it is at night, and the air has a relatively high holding capacity for water vapor. When the sun sets, the air cools, decreasing its capacity to hold water vapor. That extra water must go somewhere, and it does that by accumulating on surfaces. Similarly, when warm and cool air fronts collide, the chances for rain and thunderstorms increase. Furthermore, an increase in temperature enhances evaporation occurring at the Earth's surface. This increased evaporation leads to greater concentrations of water vapor in the atmosphere which can lead to increased precipitation.

The change in temperature that we have already seen in the Earth's average atmospheric temperature is relatively small (about1.2 °C, according to Figure 7.5.1). However, as with many of the aspects of climate change, the potential for greater changes increases dramatically as time progresses in the future. This can be seen in Figure 13.9.4, which displays a model of the predicted temperature increase. Notice that these changes occur relatively rapidly, and are not uniform across the globe. What might be some of the reasons for this?

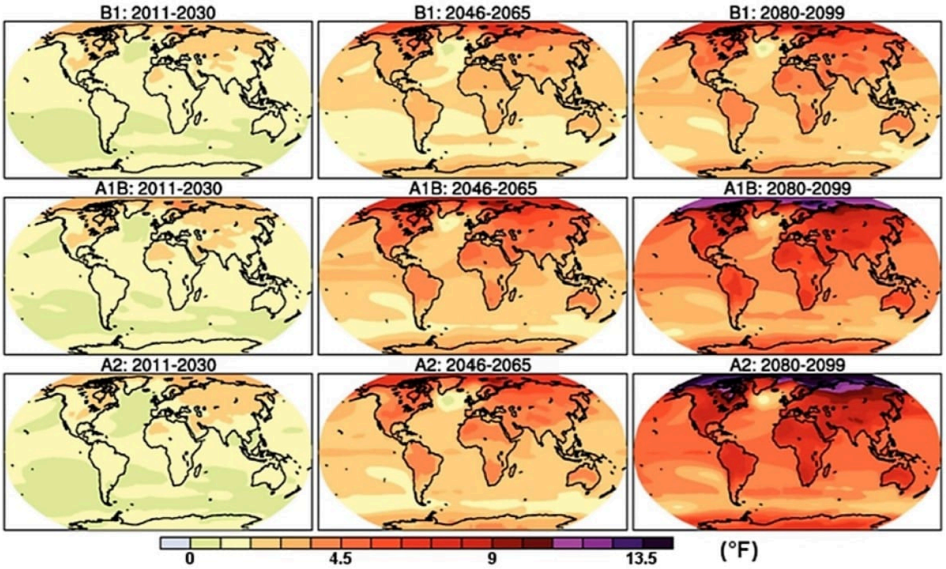


Figure 13.9.4: Projected changes in global average temperatures under three emissions scenarios (rows) for three different time periods (columns). Changes in temperatures are relative to 1961- 1990 averages. The scenarios come from the IPCC Special Report on Emissions Scenarios: B1 is a low emissions scenario, A1B is a medium-high emissions scenario, and A2 is a high emissions scenario. Source: IPCC Working Group I: The Physical Science Basis, 2007.

Changes in precipitation occur due to a variety of factors, including changes in atmospheric water vapor content due to changing temperature, as discussed above. Also at play is the heightened **evaporation** rate of water on Earth's surface under warmer temperatures. More evaporation leads to more precipitation. Finally, shifts in wind patterns impact the distribution of precipitation events. As you can see in Figure 13.9.5, there are some areas of the globe that are expected to have an increase in precipitation, while others are expected to have a dramatic decrease. Some major population centers projected to have a moderate to severe precipitation increase include (population estimates of the metropolitan area given in parentheses): New York, United States (20.1 million); Bogotá, Colombia (12.1 m.); and Manila, Philippines (11.9 m.). What sort of challenges might these cities face in the future as they deal with this change in their climate?

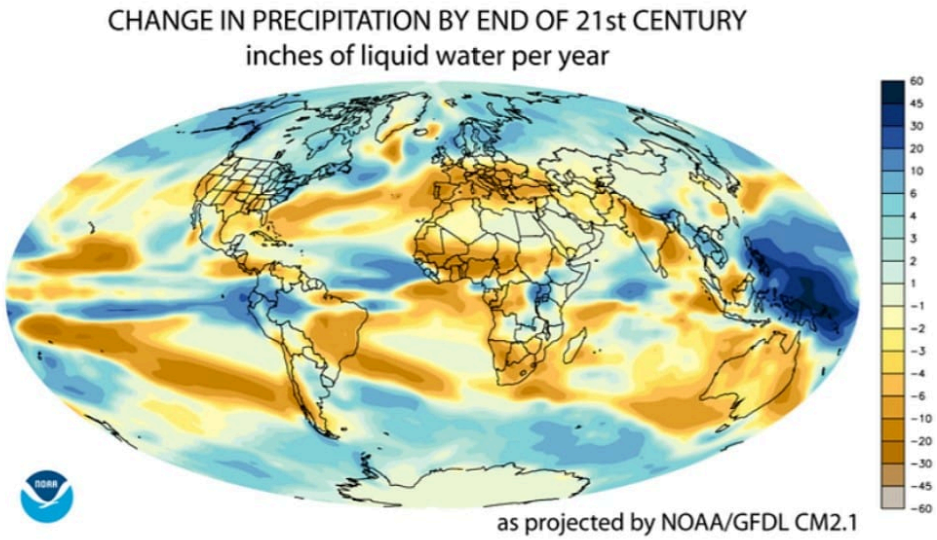


Figure 13.9.5 The plotted precipitation differences were computed as the difference between the 2081 to 2100 20-year averages minus the 1951 to 2000 50-year average. Blue areas project increases in precipitation; brown areas project decreases.

In contrast, many more major metropolitan areas are projected to have a moderate to severe precipitation decrease (droughts) by the end of the 21st century. These include Delhi, India (21.8 m.); Lagos, Nigeria (21 m.); São Paulo, Brazil (20.9 m.); Kolkata, India (14.6 m.); Istanbul, Turkey (14.4 m.); Los Angeles, United States (13.3 m.); Rio de Janeiro, Brazil (12 m.); Paris, France (12 m.); and Lahore, Pakistan (11.3 m.). The largest challenge that these areas are likely to face is a dwindling water supply for drinking and agriculture. See Chapter 8 for more detail on challenges faced by societies to supply clean, reliable water to their populations and farms.

Additional challenges may be felt by all areas of the world with regard to changes in the seasonality or timing of precipitation, as well the form in which precipitation falls (e.g., mist or downpour; rain, ice, or snow). All of these factors affect the availability of soil water for plants, the flow of rivers and streams, and the overall accessibility of water worldwide. Furthermore, scientists predict an increase in the number and severity of storms as climate change progresses. For a full discussion of the potential impacts of this, see the assigned article.

Sea level rise While we know that water continuously cycles around the world, and that the overall quantity of water on Earth will not change due to global climate change, the distribution of this water is changing. In particular, oceans are increasing in volume while land ice stores (such as **glaciers**) are decreasing. This contributes to an increase in sea level worldwide (Figure 13.9.6).

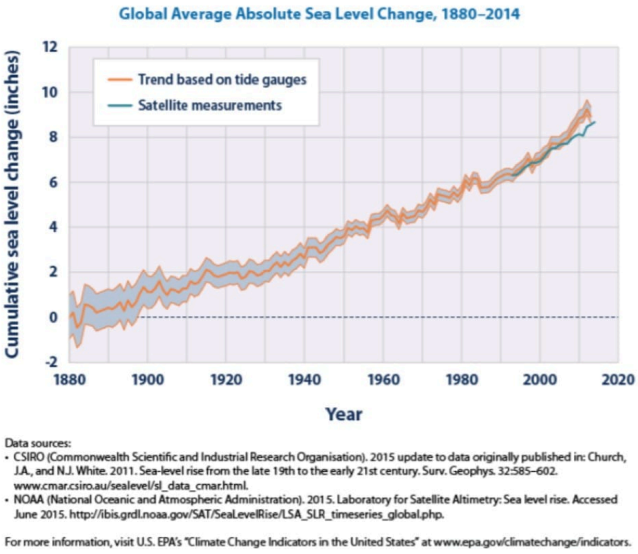


Figure 13.9.6: *This graph shows average absolute cumulative changes in sea level for the world's oceans since 1880, based on a combination of tide gauge measurements and recent satellite measurements. The shaded band shows the likely range of values, based on the number of measurements collected and the precision of the methods used.*

From the data in Figure 13.9.6, we see that sea level has increased at an average of 0.06 inches (0.15 cm) per year over the time period shown above. Most of this rise, however, has occurred within the most recent decades. The rate of increase has gone up to between 0.11 to 0.14 inches (0.28 to 0.36 cm) per year since 1993. There are two forces causing sea level to rise, both caused by climate change. First, the increased global temperature has caused increased ice melting in many regions of the globe. Melting **land ice** (such as the glacier shown in Figure 13.9.7) contributes to sea level rise because water that used to be stored in ice sitting on top of land becomes running water which reaches the ocean through **runoff.** We also observe **sea ice** melting (see http://www.epa.gov/climatechange/sci ence/indicators/index.html for data and figures). Sea ice, such as the ice that covers the arctic regions of the Northern Hemisphere, has no land underneath it. When it melts, the water stays in the same locations, and the overall sea level does not change.



Figure 13.9.7: Glacier Retreat

The second factor that influences sea level rise is a phenomenon called thermal expansion. Due to the physical properties of water, as water warms, its density decreases. A less dense substance will have fewer molecules in a given area than a more dense substance (see Chapter 1 supplemental material). This means that as the overall temperature of the oceans increases due to global climate change, the same amount of water molecules will now occupy a slightly larger volume. This may not seem significant, but considering the 1.3 billion trillion liters (264 billion gallons) of water in the ocean, even a small change in density

can have large effects on sea level as a whole.

Scientists have already documented sea level rise in some areas of the world, including one familiar to most of us: the Southeastern United States. Figure 13.9.8 depicts the measured land area lost due to increasing sea level since 1996. Note that the Southeast (defined here as the Atlantic coast of North Carolina south to Florida) is particularly susceptible to land area loss due to the gently sloping nature of our coastline. Moving northward into the Mid-Atlantic States (defined here as Virginia north to Long Island, New York), coastal habitats tend to have a steeper geography, which protects against some losses.

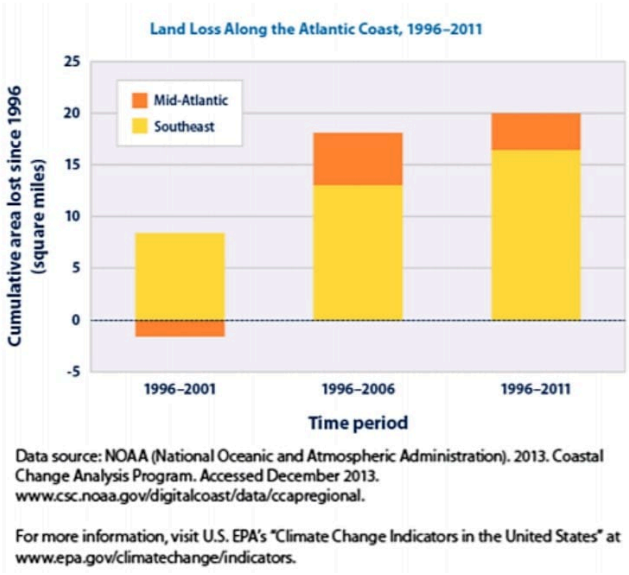


Figure 13.9.8: This graph shows the net amount of land converted to open water along the Atlantic coast during three time periods: 1996–2001, 1996–2006, and 1996–2011. The results are divided into two regions: the Southeast and the Mid-Atlantic. Negative numbers show where land loss is outpaced by the accumulation of new land.

While the ecological effects of sea level rise remain in the United States, we don't project any catastrophic loss of life, property, or livelihood for some time. This is, in part, due to large investments that we have made in infrastructure to protect our cities and farmlands. This is not the case in many areas of the world. For a discussion of the impacts of sea level rise on less industrialized nations of Bangladesh, Maldives, Kiribati, and Fiji, review the required article reading.

Ocean acidification

Dissolved CO_2 is essential for many organisms, including shell-building animals and other organisms that form a hard coating on their exterior (e.g., shellfish, corals, Haptophyte algae). This hard coating is built out of aragonite, a mineral form of the molecule calcium carbonate, $CaCO_3$. These organisms rely on the formation of carbonate ions (see Chapter 1 supplemental material for information on ions), CO_3^{2-}, from dissolved CO_2, through a natural, chemical reaction that occurs. This takes place through a chain-reaction equation, where bicarbonate (HCO_3^-) is formed as an intermediate, and hydrogen ions (H^+) are generated (equations 13.9.1 and 13.9.2).

$$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^- \tag{13.9.1}$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \tag{13.9.2}$$

To have a better visualization of this process, follow along with the interactive graphic at: http://www.whoi.edu/home/oceanus_ima...ification.html.

As you can see, both equations 13.9.1 and 13.9.2 each produce one H^+. This is significant to water chemistry because an increase in H+ concentration means a decrease in the pH of the water. You can see in Figure 13.9.9 that a lower pH means that the liquid is more acidic. As shown in the interactive graphic, an increase in CO_2 in the atmosphere causes additional CO_2 to be dissolved in the ocean. This means that more CO_2 in the atmosphere leads to more acidic ocean environments.

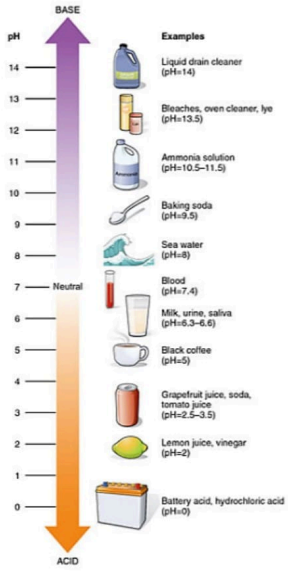


Figure 13.9.9: The pH scale and relative acidity. Illustration from Anatomy & Physiology, Connexions Web site. http://cnx.org/content/col11496/1.6/, Jun 19, 2013.

Unfortunately for shell-building animals, the buildup of H^+ in the more acidic ocean environment blocks the absorption of calcium and CO_3^{2-}, and makes the formation of aragonite more difficult. An aragonite deficit is already being documented in many of the world's oceans, as shown in Figure 13.9.10.

The increasing acidity of the world's oceans is resulting in habitat changes across the globe. This is only expected to worsen as atmospheric CO_2 levels continue to increase. Many organisms, including the corals that are the foundation species of the beautiful coral reefs, are very sensitive to changes in ocean pH. Scientists have documented cases of ecosystem destruction through coral bleaching, caused by the effects of climate change including ocean acidification and increased temperature. For more information, visit the NOAA Coral Reef Conservation Program website: coralreef.noaa.gov/threats/climate/.

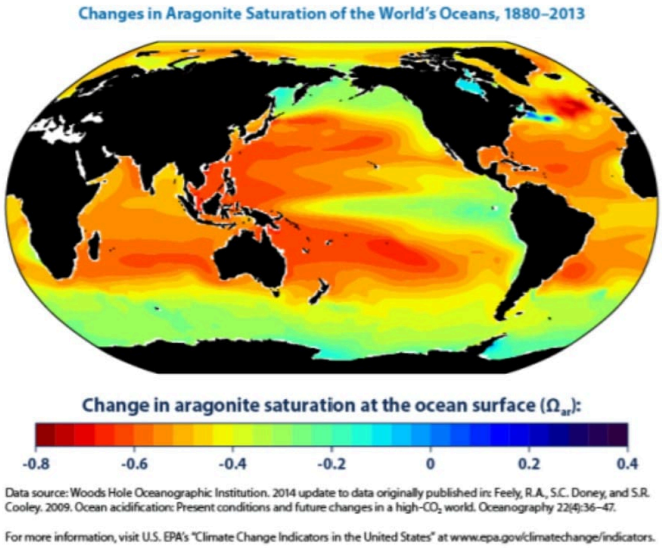


Figure 13.9.10: This map shows changes in the aragonite saturation level of ocean surface waters between the 1880s and the most recent decade (2004–2013). Aragonite is a form of calcium carbonate that many marine animals use to build their skeletons and shells. A negative change represents a decrease in saturation.

Climate Strategies

While the situation surrounding global climate change is in serious need of our attention, it is important to realize that many scientists, leaders, and concerned citizens are making solutions to climate change part of their life's work. The two solutions to the problems caused by climate change are **mitigation** and **adaptation**, and we will likely need a combination of both in order to prosper in the future.

Adaptation strategies

We know that climate change is already occurring, as we can see and feel the effects of it. For this reason, it is essential to also adapt to our changing environment. This means that we must change our behaviors in response to the changing environment around us. Some adaptation strategies are discussed in the required article reading.

Adaption strategies will vary greatly by region, depending on the largest specific impacts in that area. For example, in the city of Delhi, India, a dramatic decrease in rainfall is projected over the next century (Figure 7.6.2). This city will likely need to implement policies and practices relating to conservation of water, for example: rainwater harvesting, water re-use, and increased irrigation efficiency. Rain-limited cities near oceans, such as Los Angeles, California may choose to use desalination to provide drinking water to their citizens. **Desalination** involves taking the salt out of seawater to make it potable (Chapter 14).

Cities with low elevations near oceans may need to implement adaptation strategies to rising sea levels, from seawalls and levees to relocation of citizens. One adaptations strategy gaining use is the creation or conservation of **wetlands**, which provide natural protection against storm surges and flooding.

Mitigation strategies

In general, a strategy to mitigate climate change is one that reduces the amount of greenhouse gases in the atmosphere or prevents additional emissions. Mitigations strategies attempt to "fix" the problems caused by climate change. Governmental regulations regarding fuel efficiency of vehicles is one example of an institutionalized mitigation strategy already in place in the United States and in many other countries around the world. Unlike some other countries, there are no **carbon taxes** or charges on burning fossil fuels in the United States. This is another governmental mitigation strategy that has been shown to be effective in many countries including India, Japan, France, Costa Rica, Canada, and the United Kingdom.

In addition to government measures and incentives, technology can also be harnessed to mitigate climate change. One strategy for this is the use of **carbon capture and sequestration** (CCS). Through CCS, 80-90% of the CO_2 that would have been emitted to the atmosphere from sources such as a coal-fired power plant is instead captured and then stored deep beneath the Earth's surface. The CO_2 is often injected and sequestered hundreds of miles underground into porous rock formations sealed below an impermeable layer, where it is stored permanently (Figure 13.9.11).

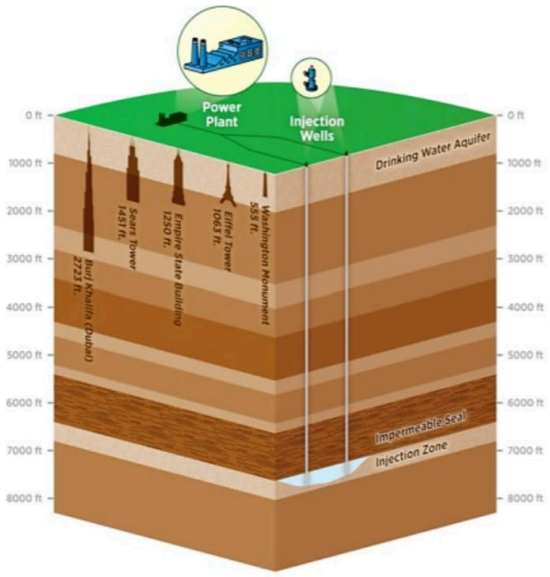


Figure 13.9.11: Carbon capture and sequestration schematic with landmarks shown to scale for depth reference. Source: US EPA.

Scientists are also looking into the use of soils and vegetation for carbon storage potential. Proper management of soil and forest ecosystems has been shown to create additional carbon sinks for atmospheric carbon, reducing the overall atmospheric CO_2 burden. Increasing soil carbon further benefits communities by providing better-quality soil for agriculture and cultivation.

Technologies related to alternative energy sources (Chapter 15) mitigate climate change by providing people with energy not derived from the combustion of fossil fuels. Finally, simple activities such as energy conservation, choosing to walk or bike instead of driving, and disposing of waste properly are activities that, when done by large numbers of people, actively mitigate climate change by preventing carbon emissions.

Take a moment to identify ways that you personally can be involved in the mitigation of or adaptation to climate change. What changes can you make in your own life to prevent excess carbon emissions? Similar to your ecological footprint, which you should have already calculated in lab, you can also calculate your carbon footprint. Use the EPA's carbon footprint calculator to do so, and investigate the Reduce Your Emissions section to find ways to decrease your carbon footprint.

Recommendations from the US Environmental Protection Agency

Figure 13.9.12 list various technologies and approaches that companies and individuals can adapt to reduce greenhouse gases. Technologies related to alternative energy sources mitigate climate change by providing people with energy not derived from the combustion of fossil fuels. Finally, simple activities such as energy conservation, choosing to walk or bike instead of driving, and disposing of waste properly are activities that, when done by large numbers of people, actively mitigate climate change by preventing carbon emissions.

Solutions for Transportation Air Pollution

Sources of air pollution cause: PM = soot = lung problems; CO2 = greenhouse gas = climate change; CO, NOx, SOx, & VOC = smog = asthma and poor air quality/visibility. Solutions provide emission reductions that equal human and environmental health gains.

Figure 13.9.6 *Sources and solutions for transportation air pollution. Image: EPA*

Solutions for transportation air pollution, emission reductions, can lead to cleaner air and better health.

- Catalytic converters in conjunction with unleaded gasoline and low sulfur levels significantly reduce hydrocarbon and nitrogen oxide emissions.
- Fuel standards reduce exposure to pollutants like lead and benzene. Renewable fuels reduce CO_2 emissions.

- Engine technologies like computer controls, variable valve timing, multi-valve engines, turbo charging and gasoline direct injection improve fuel economy and reduce CO_2 emissions.
- Transmission technologies like 7+ speeds, dual clutch transmissions, (DCTs), and continuously variable transmissions (CVTs) improve fuel economy and reduce CO_2 emissions.
- Diesel filters reduce particulate matter from on road and off road diesel engines. Alternative vehicle technologies like plug-in electric vehicles and fuel cells equals zero tailpipe emissions.
- Better transportation planning for passengers and freight reduce emissions and fuel use.

Summary

- Gases that trap heat in the atmosphere are called greenhouse gases.
- The greenhouse effect is the process by which radiation from a planet's atmosphere warms the planet's surface to a temperature above what it would be without this atmosphere.
- Global warming refers to the increase in the average temperature of the Earth’s atmosphere due to elevated greenhouse gas concentrations, heightening the greenhouse effect.
- Climate change includes both global warming driven by human-induced emissions of greenhouse gasesand the resulting large-scale shifts in weather patterns.
- Greenhouse gases differ in their ability to produce the greenhouse effect as measured by the global warming potential, or GWP. A molecule of CH_4 is about 28 times more effective than one of CO_2 at absorbing infrared radiation, while N_2O is 298 times more effective . The synthetic fluorinated gases are evn much higher (in the thousands). This is largely due to their very long residence time in the atmosphere.
- Different technologies and approaches recommended by the US EPA to to reduce human greenhouse emmissions were provided.

Contributors and Attributions

- Marisa Alviar-Agnew (Sacramento City College)

- Libretext: Introduction to Environmental Science (Zendher et al.)
- US EPA
- Wikipedia

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13.10: Who Pollutes? Who Pays?

Learning Objectives

- Know the EPA standards for criteria air pollutants.
- Know the sources, health, and environmental effects of criteria air pollutants.

The Clean Air Act, which was last amended in 1990, requires EPA to set National Ambient Air Quality Standards (40 CFR part 50) for pollutants considered harmful to public health and the environment. The Clean Air Act identifies two types of national ambient air quality standards. ***Primary standards*** provide public health protection, including protecting the health of "sensitive" populations such as asthmatics, children, and the elderly. ***Secondary standards*** provide public welfare protection, including protection against decreased visibility and damage to animals, crops, vegetation, and buildings.

The EPA has set National Ambient Air Quality Standards for six principal pollutants, which are called "criteria" air pollutants. Periodically, the standards are reviewed and may be revised. The current standards are listed in Table 13.10.1. Units of measure for the standards are parts per million (ppm) by volume, parts per billion (ppb) by volume, and micrograms per cubic meter of air ($\mu g/m^3$).

Table 13.10.1 National Ambient Air Quality Standards for Criteria Air Pollutants.

Pollutant [links to historical tables of NAAQS reviews]		Primary/ Secondary	Averaging Time	Level	Form
Carbon Monoxide (CO)		primary	8 hours	9 ppm	Not to be exceeded more than once per year
			1 hour	35 ppm	
Lead (Pb)		primary and secondary	Rolling 3 month average	0.15 $\mu g/m^3$ (1)	Not to be exceeded
Nitrogen Dioxide (NO_2)		primary	1 hour	100 ppb	98th percentile of 1-hour daily maximum concentrations, averaged over 3 years
		primary and secondary	1 year	53 ppb (2)	Annual Mean
Ozone (O_3)		primary and secondary	8 hours	0.070 ppm (3)	Annual fourth-highest daily maximum 8-hour concentration, averaged over 3 years
Particle Pollution (PM)	$PM_{2.5}$	primary	1 year	12.0 $\mu g/m^3$	annual mean, averaged over 3 years
		secondary	1 year	15.0 $\mu g/m^3$	annual mean, averaged over 3 years
		primary and secondary	24 hours	35 $\mu g/m^3$	98th percentile, averaged over 3 years
	PM_{10}	primary and secondary	24 hours	150 $\mu g/m^3$	Not to be exceeded more than once per year on average over 3 years
Sulfur Dioxide (SO_2)		primary	1 hour	75 ppb (4)	99th percentile of 1-hour daily maximum concentrations, averaged over 3 years

Pollutant [links to historical tables of NAAQS reviews]	Primary/ Secondary	Averaging Time	Level	Form
	secondary	3 hours	0.5 ppm	Not to be exceeded more than once per year

(1) In areas designated nonattainment for the Pb standards prior to the promulgation of the current (2008) standards, and for which implementation plans to attain or maintain the current (2008) standards have not been submitted and approved, the previous standards (1.5 µg/m3 as a calendar quarter average) also remain in effect.

(2) The level of the annual NO2 standard is 0.053 ppm. It is shown here in terms of ppb for the purposes of clearer comparison to the 1-hour standard level.

(3) Final rule signed October 1, 2015, and effective December 28, 2015. The previous (2008) O3 standards additionally remain in effect in some areas. Revocation of the previous (2008) O3 standards and transitioning to the current (2015) standards will be addressed in the implementation rule for the current standards.

(4) The previous SO2 standards (0.14 ppm 24-hour and 0.03 ppm annual) will additionally remain in effect in certain areas: (1) any area for which it is not yet 1 year since the effective date of designation under the current (2010) standards, and (2)any area for which an implementation plan providing for attainment of the current (2010) standard has not been submitted and approved and which is designated nonattainment under the previous SO2 standards or is not meeting the requirements of a SIP call under the previous SO2 standards (40 CFR 50.4(3)). A SIP call is an EPA action requiring a state to resubmit all or part of its State Implementation Plan to demonstrate attainment of the required NAAQS.

Table 13.10.2 list the sources and harmful effects of criteria pollutants.

Table 13.10.2 Sources, Health and Environmental Effects of Criteria Pollutants.

Pollutant	Sources	Health Effects	Environmental Effects
Ground-level Ozone (O_3)	Secondary pollutant typically formed by chemical reaction of volatile organic compounds (VOCs) and NO_x in the presence of sunlight.	Decreases lung function and causes respiratory symptoms, such as coughing and shortness of breath; aggravates asthma and other lung diseases leading to increased medication use, hospital admissions, emergency department (ED) visits, and premature mortality.	Ozone affects sensitive vegetation and ecosystems, including forests, parks, wildlife refuges and wilderness areas. In particular, ozone harms sensitive vegetation during the growing season.

Particulate Matter (PM)	Emitted or formed through chemical reactions; fuel combustion (e.g., burning coal, wood, diesel); industrial processes; agriculture (plowing, field burning); and unpaved roads.	Short-term exposures can aggravate heart or lung diseases leading to respiratory symptoms, increased medication use, hospital admissions, ED visits, and premature mortality; long-term exposures can lead to the development of heart or lung disease and premature mortality.	Visibility impairment Fine particles ($PM_{2.5}$) are the main cause of reduced visibility (haze) in parts of the United States, including many of our treasured national parks and wilderness areas. Environmental damage Particles can be carried over long distances by wind and then settle on ground or water. Depending on their chemical composition, the effects of this settling may include: · making lakes and streams acidic · changing the nutrient balance in coastal waters and large river basins · depleting the nutrients in soil · damaging sensitive forests and farm crops · affecting the diversity of ecosystems · contributing to acid rain effects. Materials damage PM can stain and damage stone and other materials, including culturally important objects such as statues and monuments. Some of these effects are related to acid rain effects on materials.
Lead	Smelters (metal refineries) and other metal industries; combustion of leaded gasoline in piston engine aircraft; waste incinerators; and battery manufacturing.	Damages the developing nervous system, resulting in IQ loss and impacts on learning, memory, and behavior in children. Cardiovascular and renal effects in adults and early effects related to anemia.	Lead is persistent in the environment and can be added to soils and sediments through deposition from sources of lead air pollution. Other sources of lead to ecosystems include direct discharge of waste streams to water bodies and mining. Elevated lead in the environment can result in decreased growth and reproductive rates in plants and animals, and neurological effects in vertebrates.
Oxides of Nitrogen (NO_x)	Fuel combustion (e.g., electric utilities, industrial boilers, and vehicles) and wood burning.	Aggravate lung diseases leading to respiratory symptoms, hospital admissions, and ED visits; increased susceptibility to respiratory infection.	NO_2 and other NO_x interact with water, oxygen and other chemicals in the atmosphere to form acid rain. Acid rain harms sensitive ecosystems such as lakes and forests. NO_x in the atmosphere contributes to nutrient pollution in coastal waters.

Carbon Monoxide (CO)	Fuel combustion (especially vehicles), industrial processes, fires, waste combustion, and residential wood burning.	Reduces the amount of oxygen reaching the body's organs and tissues; aggravates heart disease, resulting in chest pain and other symptoms leading to hospital admissions and ED visits.	
Sulfur Dioxide (SO_2)	Fuel combustion (especially high-sulfur coal); electric utilities and industrial processes; and natural sources such as volcanoes.	Aggravates asthma and increased respiratory symptoms. Contributes to particle formation with associated health effects.	At high concentrations, gaseous SOx can harm trees and plants by damaging foliage and decreasing growth. SO_2 and other sulfur oxides can contribute to acid rain which can harm sensitive ecosystems.

Source: www.epa.gov

The likelihood of immediate reactions to air pollutants depends on several factors. Age and preexisting medical conditions are two important influences. Some sensitive individuals appear to be at greater risk for air pollution-related health effects, for example, those with pre-existing heart and lung diseases (e.g., heart failure/ischemic heart disease, asthma, emphysema, and chronic bronchitis), diabetics, older adults, and children. In other cases, whether a person reacts to a pollutant depends on individual sensitivity, which varies tremendously from person to person. Some people can become sensitized to biological pollutants after repeated exposures, and it appears that some people can become sensitized to chemical pollutants as well.

Paying the Price

Pollution has a cost. Manufacturing activities that cause air pollution impose health and clean-up costs on the whole of society, whereas the neighbors of an individual who chooses to fire-proof his home may benefit from a reduced risk of a fire spreading to their own homes. A manufacturing activity that causes air pollution is an example of a negative externality in production. A negative externality in production occurs "when a firm's production reduces the well-being of others who are not compensated by the firm." For example, if a laundry firm exists near a polluting steel manufacturing firm, there will be increased costs for the laundry firm because of the dirt and smoke produced by the steel manufacturing firm. If external costs exist, such as those created by pollution, the manufacturer will choose to produce more of the product than would be produced if the manufacturer were required to pay all associated environmental costs. Because responsibility or consequence for self-directed action lies partly outside the self, an element of externalization is involved. If there are external benefits, such as in public safety, less of the good may be produced than would be the case if the producer were to receive payment for the external benefits to others. However, goods and services that involve negative externalities in production, such as those that produce pollution, tend to be over-produced and underpriced since the externality is not being priced into the market.

Pollution can also create costs for the firms producing the pollution. Sometimes firms choose, or are forced by regulation, to reduce the amount of pollution that they are producing. The associated costs of doing this are called abatement costs, or marginal abatement costs if measured by each additional unit. In 2005 pollution abatement capital expenditures and operating costs in the US amounted to nearly $27 billion.

Summary

- The EPA has set National Ambient Air Quality Standards for six principal pollutants, which are called "criteria" air pollutants.
- The six criteria pollutants are carbon monoxide, lead, nitrogen dioxide, ozone, particulate matter, and sulfur dioxide.
- The key air pollutants can cause various environmental and health problems that could affect the respiratory, nervous, and cardiovascular systems.

Contributors and Attributions

- US EPA

- Wikipedia
- Marisa Alviar-Agnew (Sacramento City College)

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14: WATER

14.1: Water - Some Unique Properties
14.2: Water in Nature
14.3: Chemical and Biological Contamination
14.4: Groundwater Contamination to Tainted Tap Water
14.5: Water Who Uses It and How Much?
14.6: Making Water Fit to Drink
14.7: 14.7?- Making Water Fit to Drink
14.8: Wastewater and Sewage Treatment

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14.1: Water - Some Unique Properties

LEARNING OBJECTIVE

Describe the different properties of water as it relates to its polarity and ability to form hydrogen bonds.

Looking Closer: Water, the Most Important Liquid

Earth is the only known body in our solar system that has liquid water existing freely on its surface. That is a good thing because life on Earth would not be possible without the presence of liquid water. Water is a simple molecule consisting of one oxygen atom bonded to two different hydrogen atoms (Figure $14.1.1$). Because of the higher electronegativity of the oxygen atom, the bonds are polar covalent (**polar bonds**). The oxygen atom attracts the shared electrons of the covalent bonds to a significantly greater extent than the hydrogen atoms. As a result, the oxygen atom requires a partial negative charge $(\delta-)$, while the hydrogen atoms each acquire a partial positive charge $(\delta+)$. The molecule adopts a bent structure because of the two lone pairs of electrons on the oxygen atom. The $\mathrm{H-O-H}$ bond angle is about 105°, slightly smaller than the ideal 109.5° of an sp^3 hybridized atomic orbital.The bent shape of the water molecule is critical because the polar $\mathrm{O-H}$ bonds do not cancel one another and the molecule as a whole is polar.

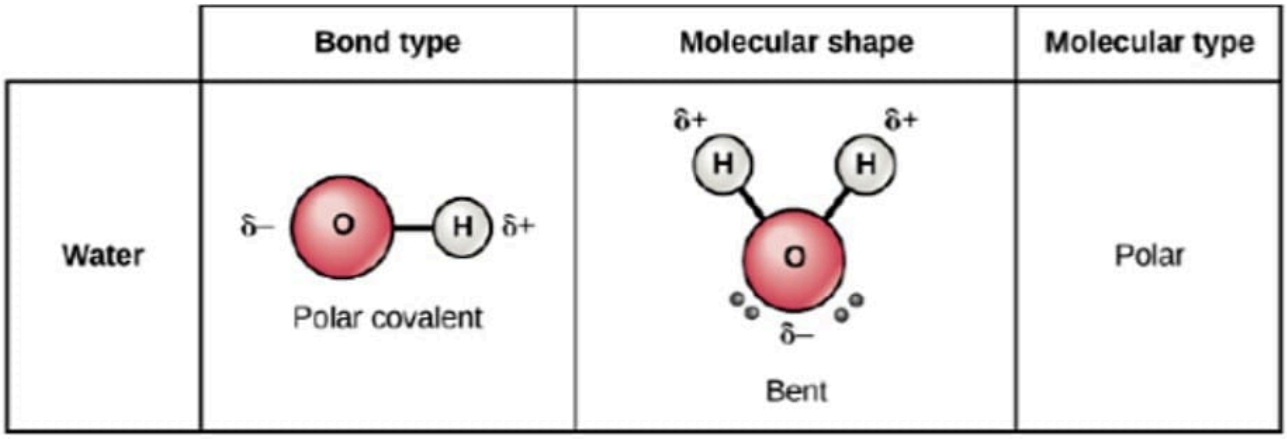


Figure $14.1.1$ *Polarity of the water molecule due to the uneven distribution of electrons in its covalent bond. C (From OpenStax Concepts of Biology text)*

Hydrogen Bonds

Due to water's polarity, each water molecule attracts other water molecules as oppositely charged ends of the molecules attract each other. When this happens, a weak interaction occurs between the *positive* hydrogen end from one molecule and the *negative oxygen* end of another molecule. This interaction is called a **hydrogen bond**. This hydrogen bonding contributes to the following water's unique properties.

1. Water is the universal solvent

2. Exists in nature as a solid, liquid, and gas

3. The density of ice is less than liquid water

4. Water has a high heat capacity

5. Water has a high heat of vaporization

6. Water exists as a liquid at room temperature It is important to note here that even we are only focusing on water in this text book, hydrogen bonding also occurs in other substances that have polar molecules.

Density of Water

Liquid water is a fluid. The hydrogen bonds in liquid water constantly break and reform as the water molecules tumble past one another. As water cools, its molecular motion slows and the molecules move gradually closer to one another. The **density** of any liquid increases as its temperature decreases. For most liquids, this continues as the liquid freezes and the solid state is denser than the liquid state. However, water behaves differently (Table $14.1.1$) . It actually reaches its highest density at about $4^{\circ}\mathrm{C}$.

Table $14.1.1$ *Density of Water and Ice*

Temperature $\left(^{\circ}\mathrm{C}\right)$	Density $\left(\mathrm{g/cm^3}\right)$
100 (liquid)	0.9584
50	0.9881
25	0.9971
10	0.9997
4	1.0000
0 (liquid)	0.9998
0 (solid)	0.9168

Between $4^{\circ}\mathrm{C}$ and $0^{\circ}\mathrm{C}$, the density gradually decreases as the hydrogen bonds begin to form a network characterized by a generally **hexagonal** structure with open spaces in the middle of the hexagons (Figure $14.1.2$).

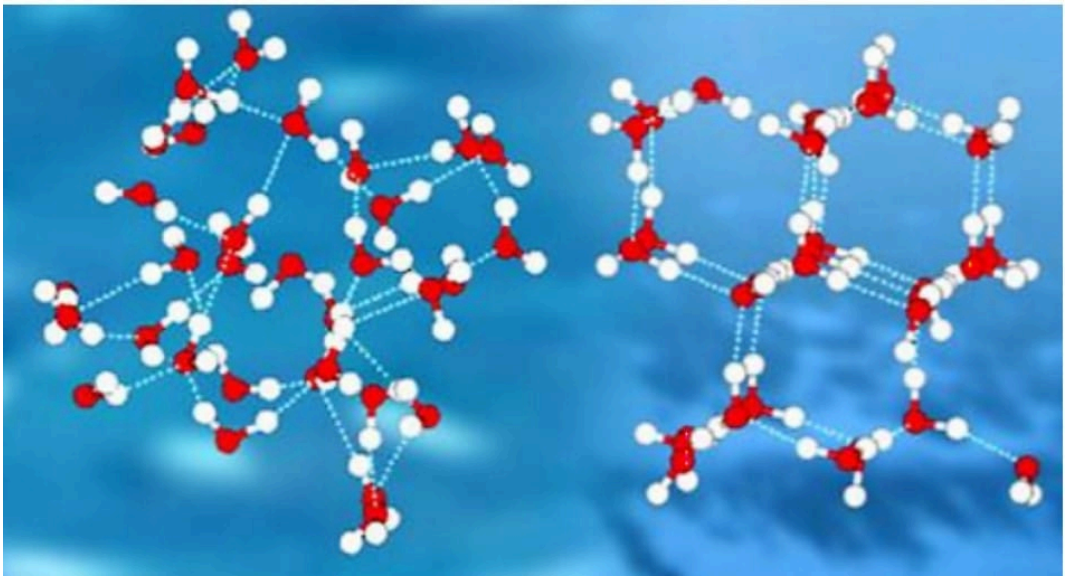


Figure $14.1.2$ *Hydrogen bonding makes ice less dense than liquid water. The lattice structure water is more condensed (left structure) than that of ice (right structure). The lattice structure of ice makes it less dense than freely flowing molecules of liquid water, enabling ice to float on liquid water. (Image credit: Lynn Yarris, http://www2.lbl.gov/Science-Articles...ter-solid.html)*

Ice is less dense than liquid water and so it floats. Ponds or lakes begin to freeze at the surface, closer to the cold air. A layer of ice forms, but does not sink as it would if water did not have this unique structure dictated by its shape, polarity, and hydrogen bonding. If the ice were to sink as it froze, entire lakes would freeze solid. Since the ice does not sink, liquid water remains under the ice all winter long. This is important, as fish and other organisms are capable of surviving through winter. Ice is one of only a very few solids that is less dense than its liquid form.

Solvation Ability of Water

Water typically dissolves many ionic compounds and polar molecules. Nonpolar molecules such as those found in grease or oil do not dissolve in water. We will first examine the process that occurs when an ionic compound such as table salt (sodium chloride) dissolves in water.

Water is attracted to the sodium chloride crystal because water is polar and has both a positive and a negative end. The positively charged sodium ions in the crystal attract the oxygen end of the water molecules because they are partially negative. The negatively charged chloride ions in the crystal attract the hydrogen end of the water molecules because they are partially positive. The action of the polar water molecules takes the crystal lattice apart (see Figure $14.1.3$) .

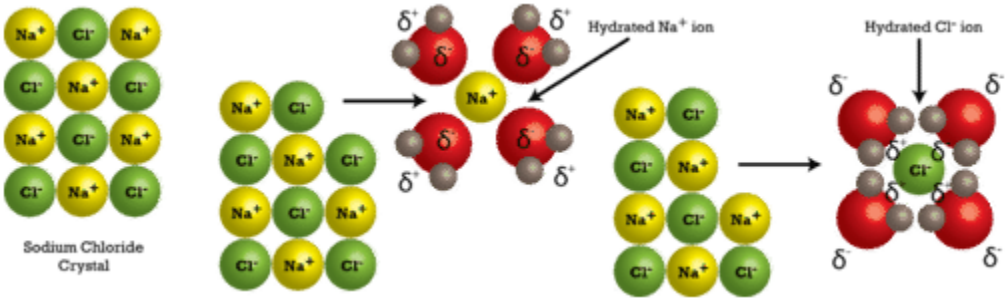


Figure $14.1.3$ *The dissolving of sodium chloride in water.*

After coming apart from the crystal, the individual ions are then surrounded by solvent particles in a process called **solvation**. Note that the individual $\mathrm{Na^+}$ ions are surrounded by water molecules with the oxygen atom oriented near the positive ion. Likewise, the chloride ions are surrounded by water molecules with the opposite orientation. **Hydration** is the process of solute particles being surrounded by water molecules arranged in a specific manner. Hydration helps to stabilize aqueous solutions by preventing the positive and negative ions from coming back together and forming a precipitate.

Table sugar is sucrose $(\mathrm{C_{12}H_{22}O_{11}})$ and is an example of a molecular compound. Solid sugar consists of individual sugar molecules held together by intermolecular attractive forces. When water dissolves sugar, it separates the individual sugar molecules by disrupting the attractive forces, but does not break the covalent bonds between the carbon, hydrogen, and oxygen atoms. Dissolved sugar molecules are also hydrated, but without as distinct an orientation to the water molecules as in the case of the ions. The sugar molecules contain many $-\mathrm{OH}$ groups that can form hydrogen bonds with the water molecules, helping form the sucrose solution.

The Amphoteric Nature of Water

Water is amphoteric: it has the ability to act as either an acid or a base in chemical reactions. According to the Brønsted-Lowry definition, an acid is a proton (H^+) donor and a base is a proton acceptor. When reacting with a stronger acid, water acts as a base; when reacting with a stronger base, it acts as an acid. For instance, water receives an H^+ ion from HCl when hydrochloric acid is formed:

$$\mathrm{HCl(acid) + H_2O(base) \diamond H_3O^+ + Cl^-}$$

In the reaction with ammonia, NH_3, water donates a H^+ ion, and is thus acting as an acid:

$$\mathrm{NH_3(base) + H_2O(acid) \diamond NH^+_4 + OH^-}$$

High Heat Capacity and Specific Heat of Water

Different substances respond to heat in different ways. If a metal chair sits in the bright sun on a hot day, it may become quite hot to the touch. An equal mass of water in the same sun will not become nearly as hot. Table $14.1.2$ list specific heats of various substances compared to water.Water has the highest **specific heat capacity** of any liquid. Water's high heat capacity is a property caused by hydrogen bonding among the water molecules. **Specific heat** is defined as the amount of heat one gram of

a substance must absorb or lose to change its temperature by one degree Celsius. For water, this amount is **1 cal/g°C**. The units for specific heat can either be in the SI units of joules per gram per degree $(\mathrm{J/g^oC})$ or calories per gram per degree $(\mathrm{cal/g^oC})$. This text will use $\mathrm{J/g^oC}$ for specific heat.



Figure 14.1.4 *This power plant in West Virginia, like many others, is located next to a large lake so that the water from the lake can be used as a coolant. Cool water from the lake is pumped into the plant, while warmer water is pumped out of the plant and back into the lake.*

It takes water a long time to heat up and a long time to cool down. In fact, the specific heat capacity of water is about five times more than that of sand. This explains why land cools faster than the sea. Coastal climates are much more moderate than inland climates because of the presence of the ocean. Water in lakes or oceans absorbs heat from the air on hot days and releases it back into the air on cool days. Water is used as a coolant for machinery because it is able to absorb large quantities of heat (Figure 14.1.4). Due to its high heat capacity, warm-blooded animals use water to disperse heat more evenly and maintain temperature in their bodies: it acts in a similar manner to a car's cooling system, transporting heat from warm places to cool places, causing the body to maintain a more even temperature.

Table 14.1.2 *Specific Heats of Some Common Substances*

Substance	Specific Heat $(\mathrm{J/g^oC})$
Water (l)	4.18
Water (s)	2.06
Water (g)	1.87
Ammonia (g)	2.09
Ethanol (l)	2.44
Aluminum (s)	0.897
Carbon, graphite (s)	0.709
Copper (s)	0.385
Gold (s)	0.129
Iron (s)	0.449
Lead (s)	0.129
Mercury (l)	0.140
Silver (s)	0.233

High Heat of Vaporization of Water

Water in its liquid form has an unusually high boiling point temperature, a value close to 100°C. As a result of the network of hydrogen bonding present between water molecules, a high input of energy is required to transform one gram of liquid water into water vapor, an energy requirement called the **heat of vaporization.** Water has a heat of vaporization value of **40.65 kJ/mol**. A considerable amount of heat energy (586 calories) is required to accomplish this change in water. This process occurs on the surface of water. As liquid water heats up, hydrogen bonding makes it difficult to separate the water molecules from each other, which is required for it to enter its gaseous phase (steam). As a result, water acts as a heat sink, or heat reservoir, and requires much more heat to boil than does a liquid such as ethanol (grain alcohol), whose hydrogen bonding with other ethanol molecules is weaker than water's hydrogen bonding.

The fact that hydrogen bonds need to be broken for water to evaporate means that a substantial amount of energy is used in the process. As the water evaporates, energy is taken up by the process, cooling the environment where the evaporation is taking place. In many living organisms, including humans, the evaporation of sweat, which is 90 percent water, allows the organism to cool so that homeostasis of body temperature can be maintained.

Summary

- The polarity of water and its ability to hydrogen bond contributes to its unique properties.
- Ionic solute molecules are hydrated (surrounded by solvent molecules in a specific orientation).
- Ice is less dense than liquid water due to spaces in the intermolecular structure of ice not present in water.
- Heat capacity is the amount of heat required to raise the temperature of an object by $1^{\circ}\mathrm{C}$).
- The specific heat of a substance is the amount of energy required to raise the temperature of 1 gram of the substance by $1^{\circ}\mathrm{C}$.
- The dissociation of liquid water molecules, which changes the substance to a gas, requires a lot of energy.

Contributors and Attributions

-

- Boundless: The Chemical Foundation of Life
- Libretext: Introduction to Environmental Science (Zendher et al.)
- TextMap: Introductory Chemistry (Tro)

- Marisa Alviar-Agnew (Sacramento City College)

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14.2: Water in Nature

Learning Objectives

- Know the distribution of earth's water.
- Describe the water (hydrologic) cycle.
- Know the different natural water contaminants

Water 's influence on the world around us is affected by its unique properties some of which where discussed in the previous section. Without water, life might not be able to exist on Earth, and it certainly would not have the tremendous complexity and diversity that we see.

Distribution of Earth's Water

Earth’s oceans contain 97% of the planet’s water, so just 3% is fresh water, water with low concentrations of salts (Figure 14.2.1). The majority of the Earth's water can be classified as being **saline** (or salt containing). Most freshwater is trapped as ice in the vast glaciers and ice sheets of Greenland. A storage location for water such as an ocean, glacier, pond, or even the atmosphere is known as a **reservoir**.

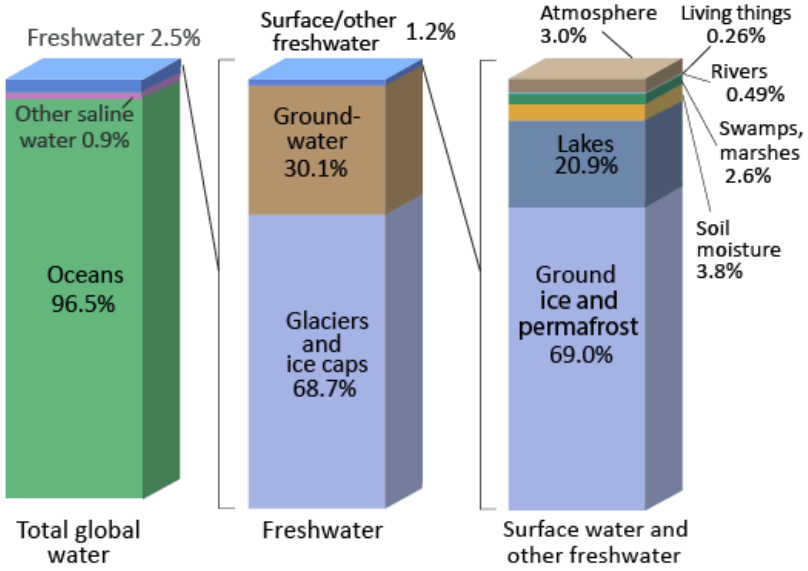


Figure 14.2.1 The distribution of Earth’s water. In the first bar, notice how only 2.5% of Earth's water is freshwater - the amount needed for life to survive. The middle bar shows the breakdown of freshwater. Almost all of it is locked up in ice and in the ground. Only a little more than 1.2% of all freshwater is surface water, which serves most of life's needs.The right bar shows the breakdown of surface freshwater. Source: Igor Shiklomanov's chapter "World Freshwater resources" in Peter H. Gleick (editor), 1993 Water in Crises: A guide to the World's Freshwater Resources. The numbers are rounded.

The Water (Hydrologic) Cycle and Natural Contaminants

Because Earth’s water is present in all three states, it can get into a variety of environments around the planet. The movement of water around Earth’s surface is the **water cycle** (Figure 14.2.2).

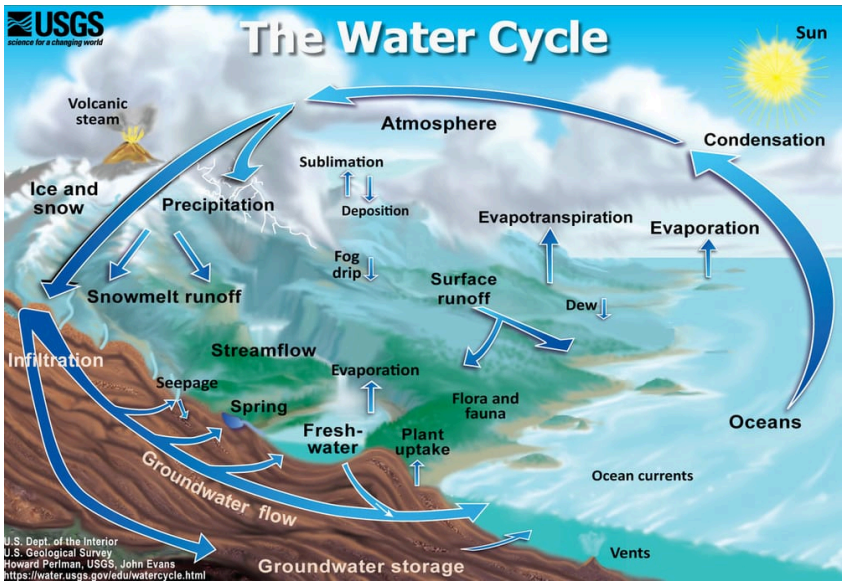


Figure 14.2.2 Because it is a cycle, the water cycle has no beginning and no end. Earth's water is always in movement, and the natural water cycle, also known as the hydrologic cycle, describes the continuous movement of water on, above, and below the surface of the Earth. Water is always changing states between liquid, vapor, and ice, with these processes happening in the blink of an eye and over millions of years.

Water changes from a liquid to a gas by **evaporation** to become water vapor. The Sun's energy can evaporate water from the ocean surface or from lakes, streams, or puddles on land. Only the water molecules evaporate; the salts remain in the ocean or a freshwater reservoir. The water vapor remains in the atmosphere until it undergoes **condensation** and then precipitation. **Precipitation** can be rain, sleet, hail, or snow. At the surface, water or melted water, may eventually evaporate and reenter the atmosphere. A significant amount of water infiltrates into the ground. Water may seep through dirt and rock below the soil through pores infiltrating the ground to go into Earth's groundwater system (Figure Extra close brace or missing open brace). Groundwater enters **aquifers** which are bodies of rock or sediment that store (and yield) large amounts of usable water in their pores. Alternatively, the water may come to the surface through springs or find its way back to the oceans.

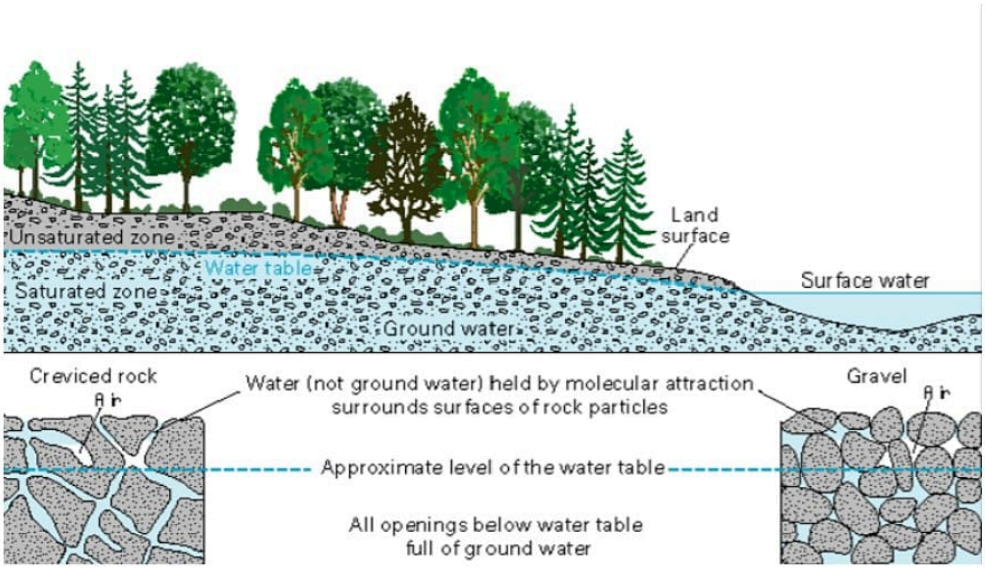


Figure Extra close brace or missing open brace *Model of groundwater system showing the different components of an unconfined groundwater system: http://water.usgs.gov/edu/earthgwaquifer.html*

Substances Present in Natural Waters

The amounts of water present in the atmosphere and on land (as surface runoff, lakes and streams) is great enough to make it a significant agent in transporting substances between the lithosphere (the rigid surface of the earth) and the oceans. Water

interacts with both the atmosphere and the lithosphere (the rigid surface of the earth) acquiring solutes from each, and thus provides the major chemical link between these two realms. The various transformations undergone by water through the different stages of the hydrologic cycle act to transport both dissolved and particulate substances between different geographic locations.

The Safe Drinking Water Act defines the term "**contaminant**" as meaning any physical, chemical, biological, or radiological substance or matter in water. Therefore, the law defines "contaminant" very broadly as being anything other than water molecules.

Gases

The carbon dioxide in natural water creates an interesting phenomenon. Rainwater is saturated with CO_2, and it dissolves limestones. When CO_2 is lost due to temperature changes or escaping from water drops, the reverse reaction takes place. The solid formed, however, may be a less stable phase called aragonite, which has the same chemical formula as, but a different crystal structure than that of calcite.

The rain dissolves calcium carbonate by the two reactions shown above. The water carries the ions with it, sips through the crack of the rocks. When it reached the ceiling of a cave, the drop dangles there for a long time before fallen. During this time, the carbon dioxide escapes and the pH of the water increases. Calcium carbonate crystals begin to appear. Calcite, aragonite, stalactite, and stalagmite are four common solids found in the formation of caves.

Dissolved Minerals

Table 14.2.1 list the major ions present in seawater. The composition does vary, depending on region, depth, latitude, and water temperature. Waters at the river mouths contain less salt. If the ions are utilized by living organism, its contents vary according to the populations of organisms.

Dust particles and ions present in the air are nucleation center of water drops. Thus, waters from rain and snow also contain such ions: Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, NH_4^{+}. These cations are balanced by anions, HCO_3^{-}, SO_4^{-}, NO_2^{-}, Cl^{-}, and NO_3^{-}. The pH of rain is between 5.5 and 5.6. Rain and snow waters eventually become river or lake waters. When the rain or snow waters fall, they interact with vegetation, top soil, bed rock, river bed and lake bed, dissolving whatever is soluble. Bacteria, algae, and water insects also thrive. Solubilities of inorganic salts are governed by the kinetics and equilibria of dissolution. The most common ions in lake and river waters are the same as those present in rainwater, but at higher concentrations. The pH of these waters depends on the river bed and lake bed. Natural waters contain dissolved minerals. Waters containing Ca^{2+} and Mg^{2+} ions are usually called **hard water**.

Table 1 Major Ions in Seawater (These values, expressed in parts per thousand, are for seawater of 35% salinity).

cations	g/kg	anions	g/kg
Na^{+}	10.77	Cl^{-}	19.354
Mg^{2+}	1.29	SO_4^{2-}	2.712
Ca^{2+}	0.412	Br^{-}	0.087
K^{+}	0.399		
Sr^{2+}	0.0079		
Al^{3+}	0.005		

Note

Although most elements are found in seawater only at trace levels, marine organisms may selectively absorb them and make them more detectable. Iodine, for example, was discovered in marine algae (seaweeds) 14 years before it was found in seawater. Other elements that were not detected in seawater until after they were found in marine organisms include barium, cobalt, copper, lead, nickel, silver and zinc. Si-32, presumably deriving from cosmic ray bombardment of Ar, has been discovered in marine sponges.

Hard Water

Minerals usually dissolve in natural water bodies such as lakes, rivers, springs, and underground waterways (ground waters). Calcium carbonate, $CaCO_3$, is one of the most common inorganic compounds in the Earth crust. It is the ingredient for both calcite and aragonite. These two minerals have different crystal structures and appearance. This photograph shows crystals of typical Calcite.

Calcium-carbonate minerals dissolve in water, with a solubility product as shown below.

$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-} \quad K_{sp} = 5 \times 10^{-9}$$

From the solubility product, we can (see example 1) evaluate the molar solubility to be 7.1×10^{-5} M or 7.1 mg/L (7.1 ppm of $CaCO_3$ in water). The solubility increases as the pH decrease (increase acidity). This is compounded when the water is saturated with carbon dioxide, CO_2. Saturated CO_2 solution contains carbonic acid, which help the dissolution due to the reaction:

$$H_2O + CO_2 \rightleftharpoons H_2CO_3$$

$$CaCO_3 + H_2CO_3 \rightleftharpoons Ca^{2+} + 2HCO_3^-$$

Because of these reactions, some natural waters contain more than 300 ppm calcium carbonates or its equivalents.

The composition of the ocean has attracted the attention of some of the more famous names in science, including Robert Boyle, Antoine Lavoisier and Edmund Halley. Their early investigations tended to be difficult to reproduce, owing to the different conditions under which they crystallized the various salts. As many as 54 salts, double salts and hydrated salts can be obtained by evaporating seawater to dryness. At least 73 elements are now known to be present in seawater.

Organic Matter

Most of the organic carbon in seawater is present as dissolved material, with only about 1-2% in particulates. The total organic carbon content ranges between 0.5 mg/L in deep water to 1.5 mg/L near the surface. There is still considerable disagreement about the composition of the dissolved organic matter; much of it appears to be of high molecular weight, and may be polymeric. Substances qualitatively similar to the humic acids found in soils can be isolated. The greenish color that is often associated with coastal waters is due to a mixture of fluorescent, high molecular weight substances of undetermined composition known as *"Gelbstoffe"*. It is likely that the significance of the organic fraction of seawater may be much greater than its low abundance would suggest. For one thing, many of these substances are lipid-like and tend to adsorb onto surfaces. It has been shown that any particle entering the ocean is quickly coated with an organic surface film that may influence the rate and extent of its dissolution or decomposition. Certain inorganic ions may be strongly complexed by humic-like substances. The surface of the ocean is mostly covered with an organic film, only a few molecular layers thick. This is believed to consist of hydrocarbons, lipids, and the like, but glycoproteins and proteoglycans have been reported. If this film is carefully removed from a container of seawater, it will quickly be reconstituted. How significant this film is in its effects on gas exchange with the atmosphere is not known.

Summary

- The water (hydrologic) cycle describes the continuous movement of water on, above and below the surface of the Earth. The water moves from one reservoir to another, such as from river to ocean, or from the ocean to the atmosphere, by the physical processes of evaporation, condensation, precipitation, infiltration, surface runoff, and subsurface flow. In doing so, the water goes through different forms: liquid, solid (ice) and capor.
- Different substances that can be found in natural waters include dissolved minerals, dissolved gases, and organic matter.

Contributors and Attributions

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- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook

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14.3: Chemical and Biological Contamination

Learning Objective

- Describe the impact of human activities on water quality.

The global water crisis also involves water pollution. For water to be useful for drinking and irrigation, it must not be polluted beyond certain thresholds. According to the World Health Organization, in 2008 approximately 880 million people in the world (or 13% of world population) did not have access to safe drinking water. At the same time, about 2.6 billion people (or 40% of world population) lived without improved sanitation, which is defined as having access to a public sewage system, septic tank, or even a simple pit latrine. Each year approximately 1.7 million people die from diarrheal diseases associated with unsafe drinking water, inadequate sanitation, and poor hygiene. Almost all of these deaths are in developing countries, and around 90% of them occur among children under the age of 5 (Figure 1). Compounding the water crisis is the issue of social justice; poor people more commonly lack clean water and sanitation than wealthy people in similar areas. Globally, improving water safety, sanitation, and hygiene could prevent up to 9% of all disease and 6% of all deaths.

In addition to the global waterborne disease crisis, chemical pollution from agriculture, industry, cities, and mining threatens global water quality. In Gallup public polls conducted over the past decade Americans consistently put water pollution and water supply as the top environmental concerns over issues such as air pollution, deforestation, species extinction, and global warming.

Water pollution is the contamination of water by an excess amount of a substance that can cause harm to human beings and/or the ecosystem. The level of water pollution depends on the abundance of the pollutant, the ecological impact of the pollutant, and the use of the water. Pollutants are derived from biological, chemical, or physical processes. Although natural processes such as volcanic eruptions or evaporation sometimes can cause water pollution, most pollution is derived from human, land-based activities. Water pollutants can move through different water reservoirs, as the water carrying them progresses through stages of the water cycle.

Pollutants enter water supplies from **point sources**, which are readily identifiable and relatively small locations, or **nonpoint sources**, which are large and more diffuse areas (Figure $14.3.1$) . Point sources of pollution include animal factory farms that raise a large number and high density of livestock such as cows, pigs, and chickens. Also, pipes included are pipes from a factories or sewage treatment plants. Combined sewer systems that have a single set of underground pipes to collect both sewage and storm water runoff from streets for wastewater treatment can be major point sources of pollutants. During heavy rain, storm water runoff may exceed sewer capacity, causing it to back up and spilling untreated sewage directly into surface waters.

picture6



Figure *Point source and non point source pollution. The Image taken from: https://theskyguys.ca/2017/02/water-...e-great-lakes/ (I took this pic from a site that I don't think is cc). and (CC BY-SA 2.0; N Chadwick).*

This section and the next will focus on how human activities affect water quality.

Too Much Organic Matter Means Too Little Oxygen

Oxygen-demanding waste is an extremely important pollutant to ecosystems. Most surface water in contact with the atmosphere has a small amount of dissolved oxygen, which is needed by aquatic organisms for cellular respiration. Bacteria decompose dead organic matter and remove dissolved oxygen (O_2) according to the following reaction:

$$\text{organic matter} + O_2 \rightarrow CO_2 + H_2O$$

Too much decaying organic matter in water is a pollutant because it removes oxygen from water, which can kill fish, shellfish, and aquatic insects. The amount of oxygen used by **aerobic** (in the presence of oxygen) bacterial decomposition of organic matter is called **biochemical oxygen demand** (BOD). The major source of dead organic matter in many natural waters is sewage; grass and leaves are smaller sources. An unpolluted water body with respect to BOD is a turbulent river that flows through a natural forest. Turbulence continually brings water in contact with the atmosphere where the O_2 content is restored. The dissolved oxygen content in such a river ranges from 10 to 14 ppm O_2, BOD is low, and clean-water fish such as trout. A polluted water body with respect to oxygen is a stagnant deep lake in an urban setting with a combined sewer system. This system favors a high input of dead organic carbon from sewage overflows and limited chance for water circulation and contact with the atmosphere. In such a lake, the dissolved O_2 content is ≤5 ppm O_2, BOD is high, and low O_2-tolerant fish, such as carp and catfish dominate.

Excessive plant nutrients, particularly nitrogen (N) and phosphorous (P), are pollutants closely related to oxygen-demanding waste. Aquatic plants require about 15 nutrients for growth, most of which are plentiful in water. N and P are called **limiting nutrients**, however, because they usually are present in water at low concentrations and therefore restrict the total amount of plant growth. This explains why N and P are major ingredients in most fertilizer. High concentrations of N and P from human sources (mostly agricultural and urban runoff including fertilizer, sewage, and phosphorus-based detergent) can cause cultural **eutrophication**, which leads to the rapid growth of aquatic producers, particularly algae. Thick mats of floating algae or rooted plants lead to a form of water pollution that damages the ecosystem by clogging fish gills and blocking sunlight. A small percentage of algal species produce toxins that can kill animals, including humans. Exponential growths of these algae are called **harmful algal blooms**. When the prolific algal layer dies, it becomes oxygen-demanding waste, which can create very low O_2 concentrations in the water (< 2 ppm O_2), a condition called **hypoxia.** This results in a **dead zone** because it causes death from asphyxiation to organisms that are unable to leave that environment. An estimated 50% of lakes in North America, Europe, and Asia are negatively impacted by cultural eutrophication. In addition, the size and number of marine hypoxic zones have grown dramatically over the past 50 years including a very large dead zone located offshore Louisiana in the Gulf of Mexico. Cultural eutrophication and hypoxia are difficult to combat, because they are caused primarily by nonpoint source pollution, which is difficult to regulate, and N and P, which are difficult to remove from wastewater.

Eutrophication is an increase in the concentration of chemical nutrients in an ecosystem to an extent that increases the primary productivity of the ecosystem. Depending on the degree of eutrophication, subsequent negative environmental effects such as anoxia (oxygen depletion) and severe reductions in water quality may occur, affecting fish and other animal populations.

Chemical Pollution from Waste

Since the 1990s, water contamination by pharmaceuticals has been an environmental issue of concern. In addition, it is important to note that many public health professionals in the United States began writing reports of pharmaceutical contamination in waterways in the 1970s." Most pharmaceuticals are deposited in the environment through human consumption and excretion, and are often filtered ineffectively by municipal sewage treatment plants which are not designed to manage them (Figure $14.3.2$) . Once in the water, they can have diverse, subtle effects on organisms, although research is still limited. Pharmaceuticals may also be deposited in the environment through improper disposal, runoff from sludge fertilizer and reclaimed wastewater irrigation, and leaky sewer pipes. In 2009, an investigative report by Associated Press concluded that U.S. manufacturers had legally released 271 million pounds of compounds used as drugs into the environment, 92% of which was the industrial chemicals phenol and hydrogen peroxide, which are also used as antiseptics. It could not distinguish between drugs released by manufacturers as opposed to the pharmaceutical industry. It also found that an estimated 250 million pounds of pharmaceuticals and contaminated packaging were discarded by hospitals and long-term care facilities.



Figure 14.3.2 Illicit drugs such as ecstasy (above) can be found in waterways. (Public Domain; Willy turner via Wikipedia)

The use of pharmaceuticals and personal care products (PPCPs) is on the rise with an estimated increase from 2 billion to 3.9 billion annual prescriptions between 1999 and 2009 in the United States alone. Figure 14.3.3 illustrates how PPCPs enter into the environment through individual human activity and as residues from manufacturing, agribusiness, veterinary use, and hospital and community use. In Europe, the input of pharmaceutical residues via domestic waste water is estimated to be around 80% whereas 20% is coming from hospitals. Individuals may add PPCPs to the environment through waste excretion and bathing as well as by directly disposing of unused medications to septic tanks, sewers, or trash. Because PPCPs tend to dissolve relatively easily and do not evaporate at normal temperatures, they often end up in soil and water bodies.

Some PPCPs are broken down or processed easily by a human or animal body and/or degrade quickly in the environment . However, others do not break down or degrade easily. The likelihood or ease with which an individual substance will break down depends on its chemical makeup and the metabolic pathway of the compound.

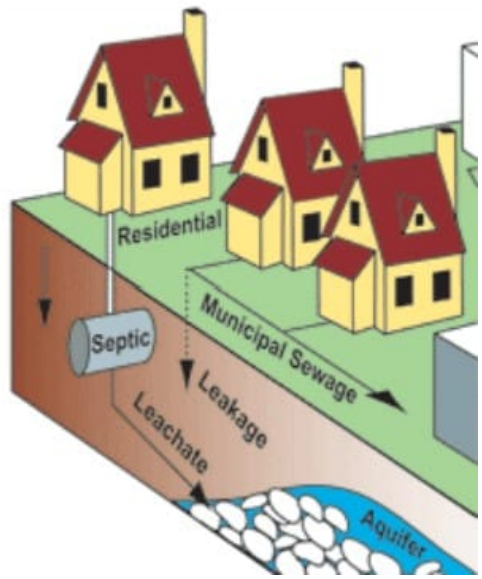


Figure 14.3.3 Methods of PPCP entry into the environment from residential homes via septic and sewage systems.[11]

While the full effects of most PPCPs on the environment are not understood, there is concern about the potential they have for harm because they may act unpredictably when mixed with other chemicals from the environment or concentrate in the food chain. Additionally, some PPCPs are active at very low concentrations, and are often released continuously in large or widespread quantities.

Because of the high solubility of most PPCPs, aquatic organisms are especially vulnerable to their effects. The increased presence of estrogen and other synthetic hormones in waste water due to birth control and hormonal therapies has been linked to increased feminization of exposed fish and other aquatic organisms. The chemicals within these PPCP products could either affect the feminization or masculinization of different fishes, therefore affecting their reproductive rates.

The major route for pharmaceutical residues to reach the aquatic environment is most probably by excretion from patients undergoing pharma treatment. Since many pharmaceutical substances are not metabolized in the body they may be excreted in biologically active form, usually via the urine. Furthermore, many pharmaceutical substances are not fully taken up from the intestine (following oral administration in patients) into their blood stream. The fraction not taken up into the blood stream will remain in the gut and eventually be excreted via the faeces. Hence, both urine and faeces from treated patients contain pharmaceutical residues. Between 30 and 90% of the orally administered dose is generally excreted as active substance in the urine.

An additional source to environmental pollution with pharmaceuticals is improper disposal of unused or expired drug residues. In European countries take-back systems for such residues are usually in place (although not always utilized to full extent) while in e.g. the US only voluntary initiatives on a local basis exist. Though most of the waste goes to incineration and people are asked to throw unused or expired pharmaceuticals into the household waste investigations in Germany showed that up to 24% of liquid pharmaceuticals and 7% of tablets or ointments are disposed always or at least “rarely” via the toilet or sink.

Proper destruction of pharma residues should yield rest products without any pharmaceutical or ecotoxic activity. Furthermore, the residues should not act as components in the environmental formation of new such products. Incineration at a high temperature (>1000 degrees Celsius) is considered to fulfill the requirements, but even following such incineration residual ashes from the incineration should be properly taken care of.

Pharmaceuticals used in veterinary medicine, or as additives to animal food, pose a different problem, since they are excreted into soil or possibly open surface waters. It is well known that such excretions may affect terrestrial organisms directly, leading to extinction of exposed species (e.g. dung-beetles). Lipid-soluble pharma residues from veterinary use may bind strongly to soil particles, with little tendency to leak out to ground water or to local surface waters. More water-soluble residues may be washed out with rain or melting snow and reach both ground water and surface water streams.

Water Borne Diseases

Waterborne diseases are conditions caused by pathogenic micro-organisms that are transmitted in water. These diseases can be spread while bathing, washing, drinking water, or by eating food exposed to contaminated water. While diarrhea and vomiting are the most commonly reported symptoms of waterborne illness, other symptoms can include skin, ear, respiratory, or eye problems. Waterborne diseases are impacted by a country's economy and also impact the economy by being costly to deal with.

Microorganisms causing diseases that characteristically are waterborne prominently include protozoa and bacteria, many of which are intestinal parasites, or invade the tissues or circulatory system through walls of the digestive tract. Various other waterborne diseases are caused by viruses. (In spite of philosophical difficulties associated with defining viruses as "organisms", it is practical and convenient to regard them as microorganisms in this connection.)

Yet other important classes of water-borne diseases are caused by metazoan parasites. Typical examples include certain Nematoda, that is to say "roundworms". As an example of water-borne Nematode infections, one important waterborne nematode disease is Dracunculiasis. It is acquired by swallowing water in which certain copepoda occur that act as vectors for the Nematoda. Anyone swallowing a copepod that happens to be infected with Nematode larvae in the genus Dracunculus, becomes liable to infection. The larvae cause guinea worm disease.

Another class of waterborne metazoan pathogens are certain members of the Schistosomatidae, a family of blood flukes. They usually infect victims that make skin contact with the water. Blood flukes are pathogens that cause Schistosomiasis of various forms, more or less seriously affecting hundreds of millions of people worldwide.

YouTube Video

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

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Video 14.3.1 *The Coalition for Global Community Health is working within existing social structures in Belén, Iquitos, Peru to uphold the human rights of the community members. We speak directly with community members in an open forum to learn about their needs, desires, and ideas for creating an opportunity to change their communities for the better*

The table below shows water-borne diseases that can result from viruses, bacteria, and parasites. In some cases, vaccines are available. When eating, drinking, or swimming, it is important to be aware of how you could be affected by these pathogens. Sanitation of drinking water with chlorine-based compounds reduces the power of these pathogens. In addition, proper handling of foods and beverages could reduce your risk of developing one or more of the following health problems.

Table 14.3.1 *Pathogens That Cause Waterborne Illnesses.*

Pathogen Name	Pathogen Type	Source	Health problem	Prevention/Treatment
Giardia	Parasite	Fecal contamination and uncooked food	Vomiting, diarrhea, and cramps	Medication afterward
Cryptosporidium	Parasite	Fecal contamination	Vomiting, diarrhea, fever, and cramps	Medication afterward
Typhoid	Bacteria	Fecal contamination	High fever, stomach pains, headache, and rash	Vaccination/Antibiotics
E. coli	Bacteria	Fecal contamination	Diarrhea and cramps	Fluids
Legionella	Bacteria	Found naturally in heated water	Causes Legionnaires (a type of pneumonia)	Medications afterward
Cholera	Bacteria	Related to fecal contamination or undercooked or raw shellfish	Diarrhea	Vaccine/Rehydration, antibiotics, and Zinc
Hepatitis A	Virus	Contaminated food and water	Vomiting, dark urine, and yellowing of the eyes.	Vaccination/Fluids
Polio	Virus	Fecal contamination	Flu symptoms, paralysis	Vaccination

(Figure 14.3.4) shows how a person might contract Giardiasis from *giardia,* a parasite. This particular pathogen can live in a body up to six months. Once detected through a stool sample, a patient can be prescribed specific antibiotics like Flagyl to treat the infection. Unfortunately, there is no vaccine for preventing Giardiasis.

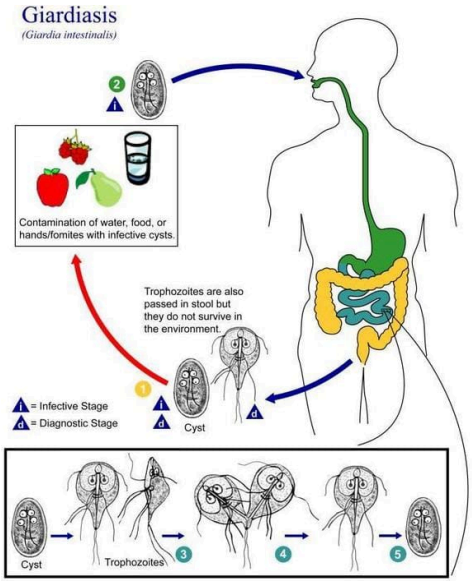


Figure 14.3.4 The life cycle of Giardia.

YouTube Video

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Acidic Waters

Water can become contaminated at any part of the water cycle. Air pollution can affect water vapor and water liquid. Combustion sources like vehicles and power plants generate compounds like NO_xs, SO_xs, CO, CO_2, and other various inorganic and organic volatile organic compounds (VOC) species (Table 14.3.2). Some of these compounds can become soluble in water. This could affect pH (or acidity) level of water surface water. Normally, the pH of water is a neutral value (or pH= 7). When NO_xs, SO_xs, CO, CO_2 enter the water cycle, then the pH level is lowered below 7.0. If these gases are absorbed in rain clouds, then acid rain results. Specific acids involved in acid rain are **sulfuric, nitric,** and **carbonic**. This environmental problem affects living organisms and building materials. Acid solutions can corrode metals and make them soluble as well.

Table 14.3.2: Source of Water Contamination (Due to Acid Rain) in the United States

Combustion products	Sources
CO_2 and CO	Combustion of any material (any fuel or tree)
NO_X (NO_2 and NO^3)	High-temperature combustion of any fuel (gas, diesel, or coal), a product of lightning
SO_x (SO_2 and SO_3)	Combustion of sulfur-based fuels (diesel and coal), volcanic release
VOC (volatile organic compound)	Combustion of any carbon-based fuel (gas, diesel, or coal), fumes from paints or solvents

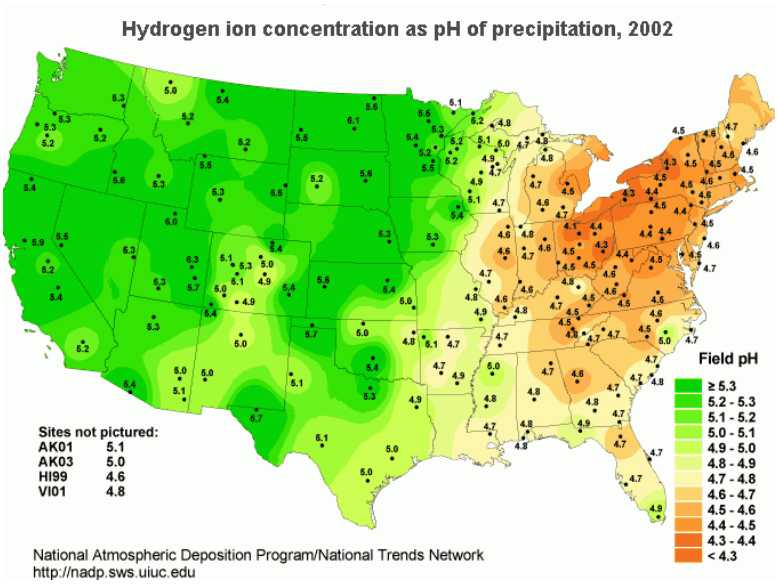


Figure 14.3.5: pH of rainwater over the continental United States.

In the United States, the northeast has the most problems with acid rain. Concentrated populations that use electrical energy and vehicles contribute greatly to the pH reduction of rainwater. Reducing gaseous output requires capping combustion sources (vehicles and power plants). Acidity in rain is measured by collecting samples of rain and measuring its pH. To find the distribution of rain acidity, weather conditions are monitored and rain samples are collected at sites all over the country (Figure 14.3.5). The areas of greatest acidity (lowest pH values) are located in the Northeastern United States. This pattern of high acidity is caused by a large number of cities, the dense population, and the concentration of power and industrial plants in the Northeast. In addition, the prevailing wind direction brings storms and pollution to the Northeast from the Midwest, and dust from the soil and rocks in the Northeastern United States is less likely to neutralize acidity in the rain.

Summary

- Water pollution is the contamination of water by an excess amount of a substance that can cause harm to human beings and/or the ecosystem.
- Pollutants enter water supplies from **point sources**, which are readily identifiable and relatively small locations, or **nonpoint sources**, which are large and more diffuse areas
- Organic matter as well as phosphates and nitrates from human and farm animal waste support the growth of algae and microorganisms, including bacteria.
- Eutrophication is an increase in the concentration of chemical nutrients in an ecosystem to an extent that increases the primary productivity of the ecosystem. Depending on the degree of eutrophication, subsequent negative environmental effects such as anoxia (oxygen depletion) and severe reductions in water quality may occur, affecting fish and other animal populations.
- Acid rain (formed as a consequence of air pollution) could affect building materials and living organisms on land and various bodies of water.

Contributors and Attributions

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- Wikipedia
- US EPA

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14.4: Groundwater Contamination to Tainted Tap Water

Learning Objective

- Define groundwater contamination.
- List other groundwater contaminants and their sources.

Ground water contamination (also called groundwater pollution) occurs when pollutants are released to the ground and make their way down into groundwater. This type of water pollution can also occur naturally due to the presence of a minor and unwanted constituent, contaminant or impurity in the groundwater, in which case it is more likely referred to as contamination rather than pollution.

How Does Groundwater Become Contaminated?

The pollutant often creates a contaminant plume within an aquifer. Movement of water and dispersion within the aquifer spreads the pollutant over a wider area. Its advancing boundary, often called a plume edge, can intersect with groundwater wells or daylight into surface water such as seeps and springs, making the water supplies unsafe for humans and wildlife. The movement of the plume, called a plume front, may be analyzed through a hydrological transport model or groundwater model. Analysis of groundwater pollution may focus on soil characteristics and site geology, hydrogeology, hydrology, and the nature of the contaminants.

Pollution can occur from on-site sanitation systems, landfills, effluent from wastewater treatment plants, leaking sewers, petrol filling stations or from over application of fertilizers in agriculture. Pollution (or contamination) can also occur from naturally occurring contaminants, such as arsenic or fluoride. Using polluted groundwater causes hazards to public health through poisoning or the spread of disease.

Different mechanisms have influence on the transport of pollutants, e.g. diffusion, adsorption, precipitation, decay, in the groundwater. The interaction of groundwater contamination with surface waters is analyzed by use of hydrology transport models.

Pollutant types

Contaminants found in groundwater cover a broad range of physical, inorganic chemical, organic chemical, bacteriological, and radioactive parameters. Principally, many of the same pollutants that play a role in surface water pollution may also be found in polluted groundwater, although their respective importance may differ.

Arsenic and fluoride

Arsenic and fluoride have been recognized by the World Health Organization (WHO) as the most serious inorganic contaminants in drinking-water on a worldwide basis.

Inorganic arsenic is the most common type of arsenic in soil and water. The metalloid arsenic can occur naturally in groundwater, as seen most frequently in Asia, including in China, India and Bangladesh. In the Ganges Plain of northern India and Bangladesh severe contamination of groundwater by naturally occurring arsenic affects 25% of water wells in the shallower of two regional aquifers. Groundwater in these areas is also contaminated by the use of arsenic-based pesticides.

Arsenic in groundwater can also be present where there are mining operations or mine waste dumps that will leach arsenic.

Natural fluoride in groundwater is of growing concern as deeper groundwater is being used, "with more than 200 million people at risk of drinking water with elevated concentrations." Fluoride can especially be released from acidic volcanic rocks and dispersed volcanic ash when water hardness is low. High levels of fluoride in groundwater is a serious problem in the Argentinean Pampas, Chile, Mexico, India, Pakistan, the East African Rift, and some volcanic islands (Tenerife)

In areas that have naturally occurring high levels of fluoride in groundwater which is used for drinking water, both dental and

skeletal fluorosis can be prevalent and severe.

Pathogens

Waterborne diseases can be spread via a groundwater well which is contaminated with fecal pathogens from pit latrines

The lack of proper sanitation measures, as well as improperly placed wells, can lead to drinking water contaminated with pathogens carried in feces and urine. Such fecal-oral transmitted diseases include typhoid, cholera and diarrhea. Of the four pathogen types that are present in feces (bacteria, viruses, protozoa, and helminths or helminth eggs), the first three can be commonly found in polluted groundwater, whereas the relatively large helminth eggs are usually filtered out by the soil matrix.

Deep, confined aquifers are usually considered the safest source of drinking water with respect to pathogens. Pathogens from treated or untreated wastewater can contaminate certain, especially shallow, aquifers.

Nitrate

Nitrate is the most common chemical contaminant in the world's groundwater and aquifers. In some low-income countries, nitrate levels in groundwater are extremely high, causing significant health problems. It is also stable (it does not degrade) under high oxygen conditions.

Nitrate levels above 10 mg/L (10 ppm) in groundwater can cause "blue baby syndrome" (acquired methemoglobinemia). Drinking water quality standards in the European Union stipulate less than 50 mg/L for nitrate in drinking water.

However, the linkages between nitrates in drinking water and blue baby syndrome have been disputed in other studies. The syndrome outbreaks might be due to other factors than elevated nitrate concentrations in drinking water.

Elevated nitrate levels in groundwater can be caused by on-site sanitation, sewage sludge disposal and agricultural activities. It can therefore have an urban or agricultural origin.

Organic compounds

Volatile organic compounds (VOCs) are a dangerous contaminant of groundwater. They are generally introduced to the environment through careless industrial practices. Many of these compounds were not known to be harmful until the late 1960s and it was some time before regular testing of groundwater identified these substances in drinking water sources.

Primary VOC pollutants found in groundwater include aromatic hydrocarbons such as BTEX compounds (benzene, toluene, ethylbenzene and xylenes), and chlorinated solvents including tetrachloroethylene (PCE), trichloroethylene (TCE), and vinyl chloride (VC). BTEX are important components of gasoline. PCE and TCE are industrial solvents historically used in dry cleaning processes and as a metal degreaser, respectively.

Other organic pollutants present in groundwater and derived from industrial operations are the polycyclic aromatic hydrocarbons (PAHs). Due to its molecular weight, Naphthalene is the most soluble and mobile PAH found in groundwater, whereas benzo(a)pyrene is the most toxic one. PAHs are generally produced as byproducts by incomplete combustion of organic matter.

Organic pollutants can also be found in groundwater as insecticides and herbicides. As many other synthetic organic compounds, most pesticides have very complex molecular structures. This complexity determines the water solubility, adsorption capacity, and mobility of pesticides in the groundwater system. Thus, some types of pesticides are more mobile than others so they can more easily reach a drinking-water source.

Metals

Several trace metals occur naturally in certain rock formations and can enter in the environment from natural processes such as weathering. However, industrial activities such as mining, metallurgy, solid waste disposal, paint and enamel works, etc. can lead to elevated concentrations of toxic metals including lead, cadmium and chromium. These contaminants have the potential to make their way into groundwater.

The migration of metals (and metalloids) in groundwater will be affected by several factors, in particular by chemical reactions

which determine the partitioning of contaminants among different phases and species. Thus, the mobility of metals primarily depends on the pH and redox state of groundwater.

Pharmaceuticals

Trace amounts of pharmaceuticals from treated wastewater infiltrating into the aquifer are among emerging ground-water contaminants being studied throughout the United States. Popular pharmaceuticals such as antibiotics, anti-inflammatories, antidepressants, decongestants, tranquilizers, etc. are normally found in treated wastewater. This wastewater is discharged from the treatment facility, and often makes its way into the aquifer or source of surface water used for drinking water.

Trace amounts of pharmaceuticals in both groundwater and surface water are far below what is considered dangerous or of concern in most areas, but it could be an increasing problem as population grows and more reclaimed wastewater is utilized for municipal water supplies.

Others

Other organic pollutants include a range of organohalides and other chemical compounds, petroleum hydrocarbons, various chemical compounds found in personal hygiene and cosmetic products, drug pollution involving pharmaceutical drugs and their metabolites. Inorganic pollutants might include other nutrients such as ammonia and phosphate, and radionuclides such as uranium (U) or radon (Rn) naturally present in some geological formations. Saltwater intrusion is also an example of natural contamination, but is very often intensified by human activities.

Groundwater pollution is a worldwide issue. A study of the groundwater quality of the principal aquifers of the United States conducted between 1991 and 2004, showed that 23% of domestic wells had contaminants at levels greater than human-health benchmarks. Another study suggested that the major groundwater pollution problems in Africa, considering the order of importance are: (1) nitrate pollution, (2) pathogenic agents, (3) organic pollution, (4) salinization, and (5) acid mine drainage.

Potential Health and Other Effects of Groundwater Contaminants

The United States Geological Survey provides an extensive list of groundwater contaminants with their potential health and other effects.

https://www.epa.gov/sites/production/files/2015-08/documents/mgwc-gwc1.pdf

Summary

- Ground water contamination (also called groundwater pollution) occurs when pollutants are released to the ground and make their way down into groundwater.
- Contaminants found in groundwater cover a broad range of physical, inorganic chemical, organic chemical, bacteriological, and radioactive parameters.
- The United States Geological Survey developed an extensive list of groundwater contaminants with their potential health and other effects.

Contributors and Attributions

- Marisa Alviar-Agnew (Sacramento City College)

- Wikipedia
- US Geological Survey (USGS)

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14.5: Water Who Uses It and How Much?

Learning Objective

- List the end uses of water in residential and non residential areas.

Water in Daily Life

Residential water use (also called domestic use, household use, or tap water use) includes all indoor and outdoor uses of drinking quality water at single-family and multifamily dwellings. These uses include a number of defined purposes (or water end uses) such as flushing toilets, washing clothes and dishes, showering and bathing, drinking, food preparation, watering lawns and gardens, and maintaining swimming pools. Some of these end uses are detectable (and measurable) while others are more difficult to gauge.

Indoor water use includes water flows through fixtures and appliances inside the house. Because the distribution of indoor use in the sample of homes measured is positively skewed, a more appropriate measure of central tendency is the median, which is about 125 gphd (gallons per household per day) or 472 lphd, liters per household per day). Toilet flushing is the largest indoor use of water, followed by flows through kitchen and bathroom faucets, showers, clothes washers, leaks, bathtubs, other/miscellaneous uses, and dishwashers. Since the late 1990s, total indoor use has decreased by 22 percent, primarily due to the improved water efficiency of clothes washers and toilets, among other low-flow fixtures.

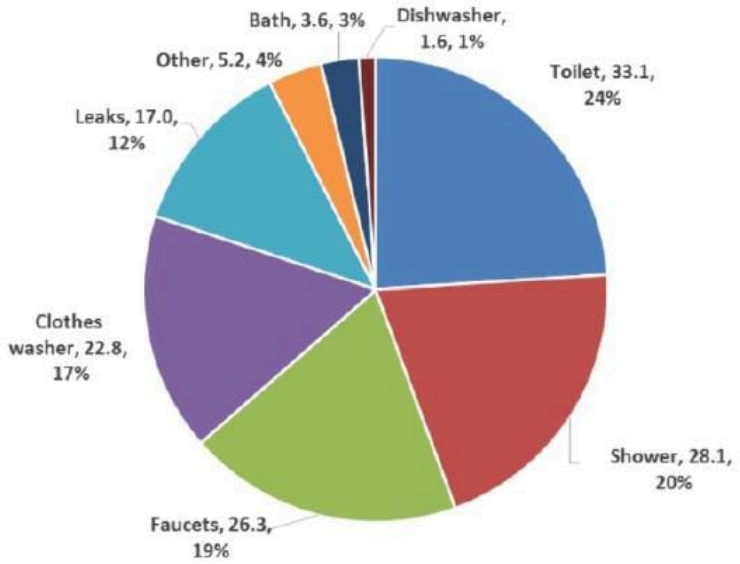


Figure 14.5.1 End uses of water for households in the U.S.in gallons per household per day and percent of indoor use.

The outdoor residential water use includes landscape irrigation, filling and back washing swimming pools, water used through outdoor faucets (hose bibs) for washing pavement and cars, and other outdoor uses. Annual outdoor use in North American cities differs by climatic region and ranged from 13,000 gallons in Waterloo, Canada to 120,400 gallons in Scottsdale, Arizona. The average outdoor use across 9 sampled cities in the Water Research Foundation study was 50,500 gallons per household per year or 138 gallons per day (524 liters per day). Nearly 17 percent of homes irrigate their landscapes in excess of theoretical irrigation requirement. If excess irrigation could be eliminated, the average outdoor use would drop by 8,200 gallons per house, or by 16 percent.

Commercial, Industrial, Agricultural & Electricity Water Use

It's easy to forget that we also use water in ways we don't see every day (Figure 14.5.2). Water is used to grow our food,

manufacture our favorite goods, and keep our businesses running smoothly. We also use a significant amount of water to meet the nation's energy needs.US Freshwater Withdrawals Chart

Figure 14.5.2 *U.S. freshwater withdrawals.*

Water Footprint

A **water footprint** shows the extent of water use in relation to consumption by people. The water footprint of an individual, community or business is defined as the total volume of fresh water used to produce the goods and services consumed by the individual or community or produced by the business. Water use is measured in water volume consumed (evaporated) and/or polluted per unit of time. A water footprint can be calculated for any well-defined group of consumers (e.g., an individual, family, village, city, province, state or nation) or producers (e.g., a public organization, private enterprise or economic sector), for a single process (such as growing rice) or for any product or service.

Traditionally, water use has been approached from the production side, by quantifying the following three columns of water use: water withdrawals in the agricultural, industrial, and domestic sector. While this does provide valuable data, it is a limited way of looking at water use in a globalized world, in which products are not always consumed in their country of origin. International trade of agricultural and industrial products in effect creates a global flow of virtual water, or *embodied water* (akin to the concept of embodied energy).

In 2002, the water footprint concept was introduced in order to have a consumption-based indicator of water use, that could provide useful information in addition to the traditional production-sector-based indicators of water use. It is analogous to the ecological footprint concept introduced in the 1990s. The water footprint is a geographically explicit indicator, not only showing volumes of water use and pollution, but also the locations. Thus, it gives a grasp on how economic choices and processes influence the availability of adequate water resources and other ecological realities across the globe (and vice versa).

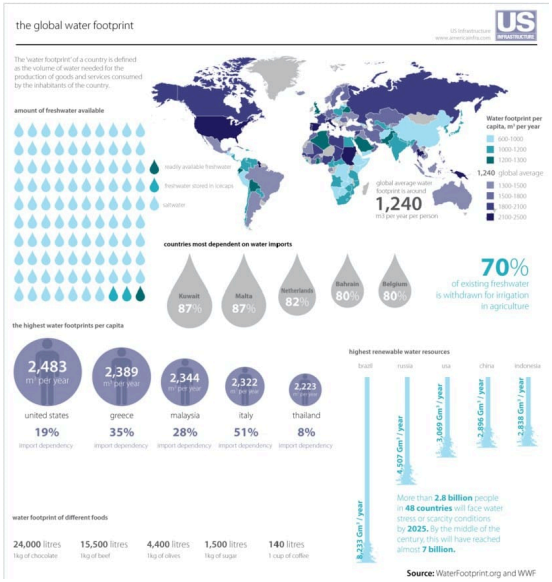


Figure 14.5.3 *The global water footprint.*

The water footprint of a product is the total volume of freshwater used to produce the product, summed over the various steps of the production chain. The water footprints involved in various diets vary greatly, and much of the variation tends to be associated with levels of meat consumption. The following table gives examples of estimated global average water footprints of popular agricultural products.

Table 14.5.3 *Global average water footprints of some agricultural products.*

Product	Global average water footprint, L/kg
almonds, shelled	16,194
beef	15,415

chocolate	17,196
cotton lint	9,114
lettuce	238
milk	1,021
olive oil	14,430
tomatoes, fresh	214
tomatoes, dried	4,275
vanilla beans	126,505
wheat bread	1,608

(For more product water footprints: see the Product Gallery of the Water Footprint Network)

Summary

- The average American family daily indoor water use is approximately 125 gallons per household per day.
- The water footprint is a geographically explicit indicator, not only showing volumes of water use and pollution, but also the locations.

Contributors and Attributions

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- Wikipedia

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14.6: Making Water Fit to Drink

Learning Objectives

- Know the primary standards for various contaminants in drinking water.
- Describe the importance of the different steps in water treatment.

Public Water Systems Fast Facts from US CDC

- Of the approximately 155,693 public water systems in the United States, 52,110 (33.5%) are community systems and 103,583 (66.5%) are noncommunity systems, including 84,744 transient systems and 18,839 nontransient systems [1].
- Over 286 million Americans get their tap water from a community water system [1].
- 8% of U.S. community water systems provide water to 82% of the U.S. population through large municipal water systems [1].
- Although the majority of community water systems (78%) are supplied by ground water, more people (68%) are supplied year-round by community water systems that use surface water .

  Note: EPA. Factoids: drinking water and ground water statistics for 2007. March 2008, April 2008.

Safe Drinking Water Act

Up until 1974, public drinking water supplies in the United States were monitored and regulated by state and local authorities. Lists of contaminants with their various concentrations could vary from state to state. As the chemical industry grew, these same state agencies noted the increased presence of existing and new organic chemicals in public water systems. In order to standardize drinking water across the country, the Environmental Protection Agency (EPA) enacted the Safe Water Drinking Act of 1974.



Figure 14.6.1: AFGE members and environmental activists participated in an event at the Washington, D.C. EPA headquarters to thank EPA workers for their work. (CC BY 2.0; AFGE).

The 1974 act enabled the EPA to monitor and regulate public water systems that serve over 25 people. Implementation and enforcement of drinking water standards would still be performed by each state. Regarding drinking water sources (surface and ground), the EPA and state agencies protect and monitor these as well. Levels of contaminants would be defined using the

concentration terms Maximum Contaminant Level (MCL) and Treatment Technique (TT)

National Primary Standards for Drinking Water

The first set of drinking water standards included only 22 chemicals and/or pathogens. EPA established two major types of contaminants: primary and secondary. The first of these types (primary) contaminants are substances (examples could include Hg, As, and U) that can be toxic in small amounts. On the other hand, secondary contaminants are less toxic species (Fe and Zn) and would include cosmetic issues (color, taste, and odor) of drinking water.

All primary contaminants have enforceable concentration values. For the majority of these pollutants, EPA lists concentration limits by using the term **Maximum Contaminant Level (MCL)**. If a water supplier exceeds a given MCL for a toxin, then fines and penalties could by imposed by the EPA. A few pathogens (Giardia Lamblia and Legionella) use Treatment Technique (TT) notation rather than numerical MCL concentrations. Water that contains any amount of these pathogens must be sanitized immediately with a standardized EPA procedure.

A detailed list of acceptable levels of different contaminants by EPA classification can be found on the the link below.

https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations

The complete table of standards is given below.

https://www.epa.gov/sites/production/files/2016-06/documents/npwdr_complete_table.pdf

Table 14.6.1

Table 14.6.1 *Standards for Various Contaminants in Drinking Water.*

Contaminant	MCLG[1](mg/L)[2]	MCL or TT[1](mg/L)[2]	Potential Health Effects from Long-Term Exposure Above the MCL (unless specified as short-term)	Sources of Contaminant in Drinking Water
Microorganisms- *Cryptosporidium*	zero	TT[3]	Gastrointestinal illness (such as diarrhea, vomiting, and cramps)	Human and animal fecal waste
Microorganisms- *Giardia lamblia*	zero	TT	Gastrointestinal illness (such as diarrhea, vomiting, and cramps)	Human and animal fecal waste
Microorganisms- Total Coliforms (including fecal coliform and *E. Coli*)	zero	5.0%	Not a health threat in itself; it is used to indicate whether other potentially harmful bacteria may be present[5]	Coliforms are naturally present in the environment; as well as feces; fecal coliforms and *E. coli* only come from human and animal fecal waste.
Viruses (enteric)	zero	TT	Gastrointestinal illness (such as diarrhea, vomiting, and cramps)	Human and animal fecal waste
Inorganic Chemicals- Antimony	0.006	0.006	Increase in blood cholesterol; decrease in blood sugar	Discharge from petroleum refineries; fire retardants; ceramics; electronics; solder

Contaminant	MCLG[1](mg/L)[2]	MCL or TT[1](mg/L)[2]	Potential Health Effects from Long-Term Exposure Above the MCL (unless specified as short-term)	Sources of Contaminant in Drinking Water
Inorganic Chemicals- Chromium (total)	0.1	0.1	Allergic dermatitis	Discharge from steel and pulp mills; erosion of natural deposits
Inorganic Chemicals- Nitrate (measured as Nitrogen)	10	10	Infants below the age of six months who drink water containing nitrate in excess of the MCL could become seriously ill and, if untreated, may die. Symptoms include shortness of breath and blue-baby syndrome.	Runoff from fertilizer use; leaking from septic tanks, sewage; erosion of natural deposits
Organic Chemicals- Benzene	zero	0.005	Anemia; decrease in blood platelets; increased risk of cancer	Discharge from factories; leaching from gas storage tanks and landfills
Organic Chemicals- Carbon tetrachloride	zero	0.005	Liver problems; increased risk of cancer	Discharge from chemical plants and other industrial activities
Organic Chemicals- Styrene	0.1	0.1	Liver, kidney, or circulatory system problems	Discharge from rubber and plastic factories; leaching from landfills
Radionuclides ***Alpha particles***	***none ---------- zero***	***15 picocuries per Liter (pCi/L)***	***Increased risk of cancer***	***Erosion of natural deposits of certain minerals that are radioactive and may emit a form of radiation known as alpha radiation***

Notes

[1]Definitions:

- Maximum Contaminant Level Goal (MCLG) - The level of a contaminant in drinking water below which there is no known or expected risk to health. MCLGs allow for a margin of safety and are non-enforceable public health goals.
- Maximum Contaminant Level (MCL) - The highest level of a contaminant that is allowed in drinking water. MCLs are set as close to MCLGs as feasible using the best available treatment technology and taking cost into consideration. MCLs are enforceable standards.
- Maximum Residual Disinfectant Level Goal (MRDLG) - The level of a drinking water disinfectant below which there is no known or expected risk to health. MRDLGs do not reflect the benefits of the use of disinfectants to control microbial contaminants.
- Treatment Technique (TT) - A required process intended to reduce the level of a contaminant in drinking water.
- Maximum Residual Disinfectant Level (MRDL) - The highest level of a disinfectant allowed in drinking water. There is convincing evidence that addition of a disinfectant is necessary for control of microbial contaminants.

[2] Units are in milligrams per liter (mg/L) unless otherwise noted. Milligrams per liter are equivalent to parts per million (PPM).

Calculations of Parts per Million and Parts per Billion

In addition to percentage units, the units for expressing the concentration of extremely dilute solutions are parts per million (ppm) and parts per billion (ppb). Both of these units are mass based and are defined as follows:

$$\text{ppm} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 1,000,000$$

$$\text{ppb} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 1,000,000,000$$

> Similar to parts per million and parts per billion, related units include parts per thousand (ppth) and parts per trillion (ppt).

Concentrations of *trace elements* in the body—elements that are present in extremely low concentrations but are nonetheless necessary for life—are commonly expressed in parts per million or parts per billion. Concentrations of poisons, contaminants, and pollutants are also described in these units. For example, cobalt is present in the body at a concentration of 21 ppb, while the State of Oregon's Department of Agriculture limits the concentration of arsenic in fertilizers to 9 ppm.

ppm and ppb

In aqueous solutions, 1 ppm is essentially equal to 1 mg/L, and 1 ppb is equivalent to 1 µg/L.

$$1 \text{ ppm} = \frac{1 \text{ mg Solute}}{1 \text{ L Solution}}$$

$$1 \text{ ppb} = \frac{1 \ \mu\text{g Solute}}{1 \text{ L Solution}}$$

Amendment SDWA of 1986

This change to the Safe Drinking Water Act established MCLGs and increased the total of regulated contaminants to 83. The EPA would also install more monitoring devices to detect organic contaminants. Research was done to detect pathogens more effectively to reduce disease. Lastly, public notifications from water systems to the consumers would be made announced if severe water issues occurred.

Amendment of SDWA of 1996

This particular legislation provided more protection and assessment of water sources (lakes, river, streams). In addition, water companies were required to provide consumers with a water quality report. States could seek federal money for upgrading their water quality processes. Cost benefit analysis would be done to determine risk and reward of lowering the concentration of a contaminant. For small regulated water companies, more financial and technical assistance would be offered to help them maintain drinking water standards.

Water Treatment (US CDC)

Drinking water supplies in the United States are among the safest in the world. However, even in the U.S., drinking water sources can become contaminated, causing sickness and disease from waterborne germs, such as *Cryptosporidium*, *E. coli*, Hepatitis A, *Giardia intestinalis*, and other pathogens.

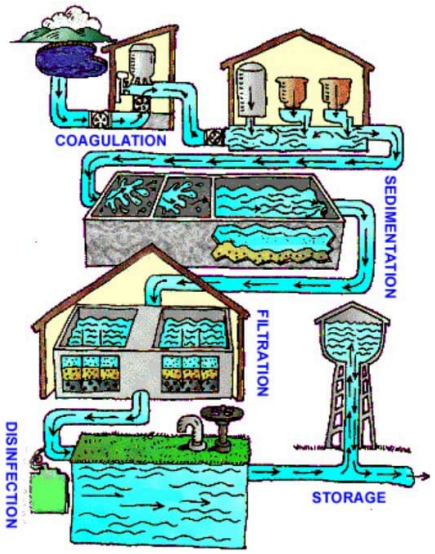


Figure 14.6.1 The common steps in water treatment. Source: US EPA

Drinking water sources are subject to contamination and require appropriate treatment to remove disease-causing agents. Public drinking water systems use various methods of water treatment to provide safe drinking water for their communities. Today, the most common steps in water treatment (Figure 14.6.1) used by community water systems (mainly surface water treatment) include:

Coagulation and Flocculation

Coagulation and flocculation are often the first steps in water treatment. Chemicals with a positive charge are added to the water. The positive charge of these chemicals neutralizes the negative charge of dirt and other dissolved particles in the water. When this occurs, the particles bind with the chemicals and form larger particles, called floc. Historically, dirty water is cleaned by treating with alum, $Al_2(SO_4)_3{\cdot}12\ H_2O$, and lime, $Ca(OH)_2$. These electrolytes cause the pH of the water to change due to the following reactions:

$$Al_2(SO_4)_3.12\ H_2O \rightarrow Al^{3+}(aq) + 3\ SO_4^{2-}(aq) + 12\ H_2O$$
$$SO_4^{2-}(aq) + H_2O \rightarrow HSO_4^{-}(aq) + OH^{-}\ \text{(causing pH change)}$$
$$Ca(OH)_2 \rightarrow Ca^{2+}(aq) + 2\ OH^{-}\ \text{(causing pH change)}$$

The slightly basic water causes $Al(OH)_3$, $Fe(OH)_3$ and $Fe(OH)_2$ to precipitate, bringing the small particulates with them and the water becomes clear. Some records have been found that Egyptians and Romans used these techniques as early as 2000 BC.

Suspension of iron oxide particulates and humic organic matter in water gives water the yellow muddy appearance. Both

iron oxide particulates and organic matter can be removed from coagulation and flocculation. The description given here is oversimplified, and many more techniques have been applied in the treatment of water. Coagulation is a major application of lime in the treatment of wastewater.

Other salts such as iron sulfates $Fe_2(SO_4)_3$ and $FeSO_4$, chromium sulfate $Cr_2(SO_4)_3$, and some special polymers are also useful. Other ions such as sodium, chloride, calcium, magnesium, and potassium also affect the coagulation process. So do temperature, pH, and concentration.

Disposal of coagulation sludge is a concern, however.

Sedimentation

During sedimentation, floc settles to the bottom of the water supply, due to its weight. This settling process is called sedimentation. The floc particles are then removed from the bottom of the basins.

Aeration

Bringing air into intimate contact with water for the purpose of exchanging certain components between the two phases is called **aeration**. Oxygenation is one of the purposes of aeration. Others are removal of volatile organic substances, hydrogen sulfide, ammonia, and volatile organic compounds

Filtration

Once the floc has settled to the bottom of the water supply, the clear water on top will pass through filters of varying compositions (sand, gravel, and charcoal) and pore sizes, in order to remove dissolved particles, such as dust, parasites, bacteria, viruses, and chemicals.

Treatment with Chlorine and/or Chloramine

Most communities use either chlorine or chloramines. Some communities switch back and forth between chlorine and chloramines at different times of the year or for other operational reasons. Less commonly, utilities use other disinfectants, such as chlorine dioxide. Some water systems that use water from a groundwater source (like community wells) do not have to add a disinfectant at all.

Ozone Disinfection

Ozone disinfection, or ozonation, is an unstable molecule which readily gives up one atom of oxygen providing a powerful oxidizing agent which is toxic to most waterborne organisms. It is a very strong, broad spectrum disinfectant that is widely used in Europe and in a few municipalities in the United States and Canada. It is an effective method to inactivate harmful protozoa that form cysts. It also works well against almost all other pathogens. Ozone is made by passing oxygen through ultraviolet light or a "cold" electrical discharge. To use ozone as a disinfectant, it must be created on-site and added to the water by bubble contact. Some of the advantages of ozone include the production of fewer dangerous by-products and the absence of taste and odor problems (in comparison to). No residual ozone is left in the water. In the absence of a residual disinfectant in the water, chlorine or chloramine may be added throughout a distribution system to remove any potential pathogens in the distribution piping.

Ultraviolet Disinfection

Ultraviolet disinfection of water is a purely physical, chemical-free process. Even parasites such as Cryptosporidium or Giardia, which are extremely resistant to chemical disinfectants, are efficiently reduced. UV can also be used to remove chlorine and chloramine species from water; this process is called photolysis, and requires a higher dose than normal disinfection. The dead microorganisms are not removed from the water. UV disinfection does not remove dissolved organics, inorganic compounds or particles in the water. The world's largest water disinfection plant treats drinking water for New York city. The Catskill-Delaware Water Ultraviolet Disinfection Facility, commissioned on 8 October 2013, incorporates a total of 56 energy-efficient UV reactors treating up to 2.2 billion US gallons (8,300,000 m^3) a day.

Ultraviolet can also be combined with ozone or hydrogen peroxide to produce hydroxyl radicals to break down trace contaminants through an advanced oxidation process.

Fluoridation (US CDC)

The mineral fluoride occurs naturally on earth and is released from rocks into the soil, water, and air. All water contains some fluoride. Usually, the fluoride level in water is not enough to prevent tooth decay; however, some groundwater and natural springs can have naturally high levels of fluoride.

Fluoride has been proven to protect teeth from decay. Bacteria in the mouth produce acid when a person eats sugary foods. This acid eats away minerals from the tooth's surface, making the tooth weaker and increasing the chance of developing cavities. Fluoride helps to rebuild and strengthen the tooth's surface, or enamel. Water fluoridation prevents tooth decay by providing frequent and consistent contact with low levels of fluoride. By keeping the tooth strong and solid, fluoride stops cavities from forming and can even rebuild the tooth's surface.

Community water fluoridation is the process of adjusting the amount of fluoride found in water to achieve optimal prevention of tooth decay.

Although other fluoride-containing products, such as toothpaste, mouth rinses, and dietary supplements are available and contribute to the prevention and control of tooth decay, community water fluoridation has been identified as the most cost-effective method of delivering fluoride to all, reducing tooth decay by 25% in children and adults.[1]

Benefits: Strong Teeth (US CDC)

Fluoride benefits children and adults throughout their lives. For children younger than age 8, fluoride helps strengthen the adult (permanent) teeth that are developing under the gums. For adults, drinking water with fluoride supports tooth enamel, keeping teeth strong and healthy. The health benefits of fluoride include having:

- Fewer cavities.
- Less severe cavities.
- Less need for fillings and removing teeth.
- Less pain and suffering because of tooth decay.

Fluoride in the Water Today

In 2012, more than 210 million people, or 75% of the US population, were served by community water systems that contain enough fluoride to protect their teeth.[5] However, approximately 100 million Americans still do not have access to water with fluoride. Because it is so beneficial, the United States has a national goal for 80% of Americans to have water with enough fluoride to prevent tooth decay by 2020.

YouTube Video

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https://www.youtube.com/watch?v=0_ZcCqqpS2o&feature=youtu.be

Summary

- The Safe Drinking Water Act (SDWA) (originally passed by Congress in 1974) protects public health by regulating the nation's

public drinking water supply.
- The different steps in water treatment include floculation, sedimentation, filtration, aeration, and disinfection or combinations thereof. Fluoride is also added to municipal water systems for prevention of tooth decay.

Contributors and Attributions

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- Marisa Alviar-Agnew (Sacramento City College)

- US EPA
- Center for Disease Control (CDC)
- Wikipedia

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14.8: Wastewater and Sewage Treatment

Learning Objectives

- Explain the major steps in wastewater treatment.
- List the different uses of reclaimed water.

Wastewater and sewage is treated in three phases: primary (solid removal), secondary (bacterial decomposition), and tertiary (extra filtration).

Sewage is generated by residential and industrial establishments. It includes household waste liquid from toilets, baths, showers, kitchens, sinks, and so forth that is disposed of via sewers. In many areas, sewage also includes liquid waste from industry and commerce. The separation and draining of household waste into greywater and blackwater is becoming more common in the developed world. Greywater is water generated from domestic activities such as laundry, dishwashing, and bathing, and can be reused more readily. Blackwater comes from toilets and contains human waste.

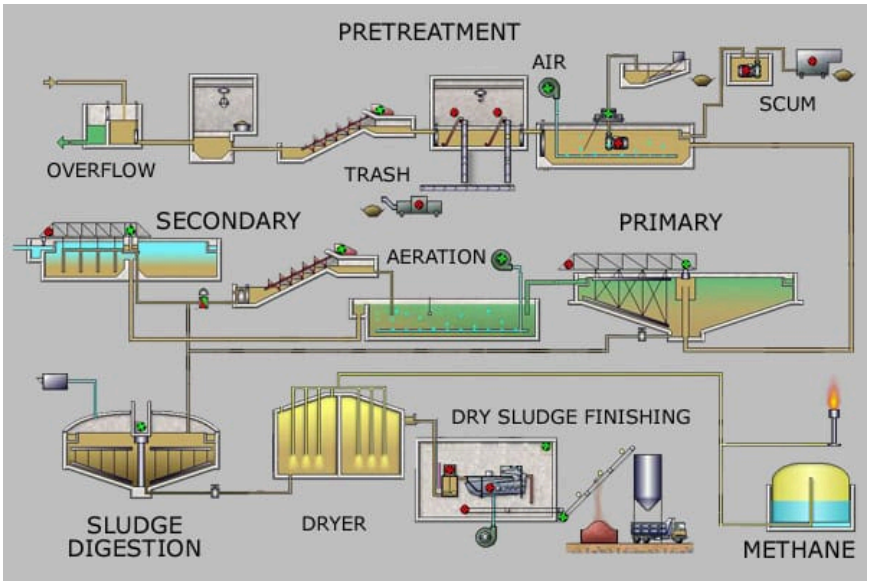


Figure 14.8.1 **Diagram of Sewage Treatment Process**: Sewage passes through primary, secondary, and tertiary treatment.

Primary Treatment

In primary treatment, sewage is stored in a basin where solids (sludge) can settle to the bottom and oil and lighter substances can rise to the top. These layers are then removed and then the remaining liquid can be sent to secondary treatment. Sewage sludge is treated in a separate process called sludge digestion.

Secondary Treatment

Secondary treatment removes dissolved and suspended biological matter, often using microorganisms in a controlled environment. Most secondary treatment systems use aerobic bacteria, which consume the organic components of the sewage (sugar, fat, and so on). Some systems use fixed film systems, where the bacteria grow on filters, and the water passes through them. Suspended growth systems use “activated” sludge, where decomposing bacteria are mixed directly into the sewage. Because oxygen is critical to bacterial growth, the sewage is often mixed with air to facilitate decomposition.

Tertiary Treatment

Tertiary treatment (sometimes called “effluent polishing”) is used to further clean water when it is being discharged into a sensitive ecosystem.

Several methods can be used to further disinfect and purify sewage beyond primary and secondary treatment.

Sand filtration, where water is passed through a sand filter, can be used to remove particulate matter.

Wastewater may still have high levels of nutrients such as nitrogen and phosphorus. These can disrupt the nutrient balance of aquatic ecosystems and cause algae blooms and excessive weed growth. Phosphorus can be removed biologically in a process called **enhanced biological phosphorus removal**. In this process, specific bacteria, called polyphosphate accumulate organisms that store phosphate in their tissue. When the biomass accumulated in these bacteria is separated from the treated water, these biosolids have a high fertilizer value. Nitrogen can also be removed using nitrifying bacteria.

Lagooning is another method for removing nutrients and waste from sewage. Water is stored in a lagoon and native plants, bacteria, algae, and small zooplankton filter nutrients and small particles from the water.

Treatment by activated carbon is mostly due to adsorption or absorption. When a chemical species is adhered to the surface of a solid, it is an **adsorption**. When partial chemical bonds are formed between adsorbed species or when the absorbate got into the channels of the solids, we call it **absorption**. However, these two terms are often used to mean the same, because to distinguish one from type from the other is very difficult.

Application of activated charcoal for the removal of undesirable order and taste in drinking water has been recognized at the dawn of civilization. Using bone char and charred vegetation, gravel, and sand for the filtration of water for domestic application has been practised for thousands of years. Charcoal absorbs many substances, ranging from colored organic particulates to inorganic metal ions. Charcoal has been used to remove the colour of raw sugar from various sources.

Filtration is the process of removing solids from a fluid by passing it through a porous medium. Coarse, medium, and fine porous media have been used depending on the requirement. The filter media are artificial membranes, nets, sand filter, and high technological filter systems. The choice of filters depends on the required filtering speed and the *cleanness* requirement. The flow required for filtration can be achieved using gravity or pressure. In pressure filtration, one side of the filter medium is at higher pressure than that of the other so that the filter plane has a pressure drop. Some portion of this filter type must be enclosed in a container.

When a compartment containing a dilute solution is connected to another compartment containing a concentrated solution by a semipermeable membrane, water molecules move from the dilute solution to concentrated solution. This phenomenon is called **osmosis**. By applying pressure in the higher concentration solution, water molecules migrate from a high concentration solution to a low concentration solution through a semipermeable membrane. This method is called **reverse osmosis water filter system**. In this technique, the membrane must be able to tolerate the high pressure, and prevent solute molecules to pass through. This technology certainly works, and it has been used to convert salt (ocean or sea) water into fresh water. With this technique, the water with higher concentration is discharged. Thus, this technology is costly in regions where the water cost is high.

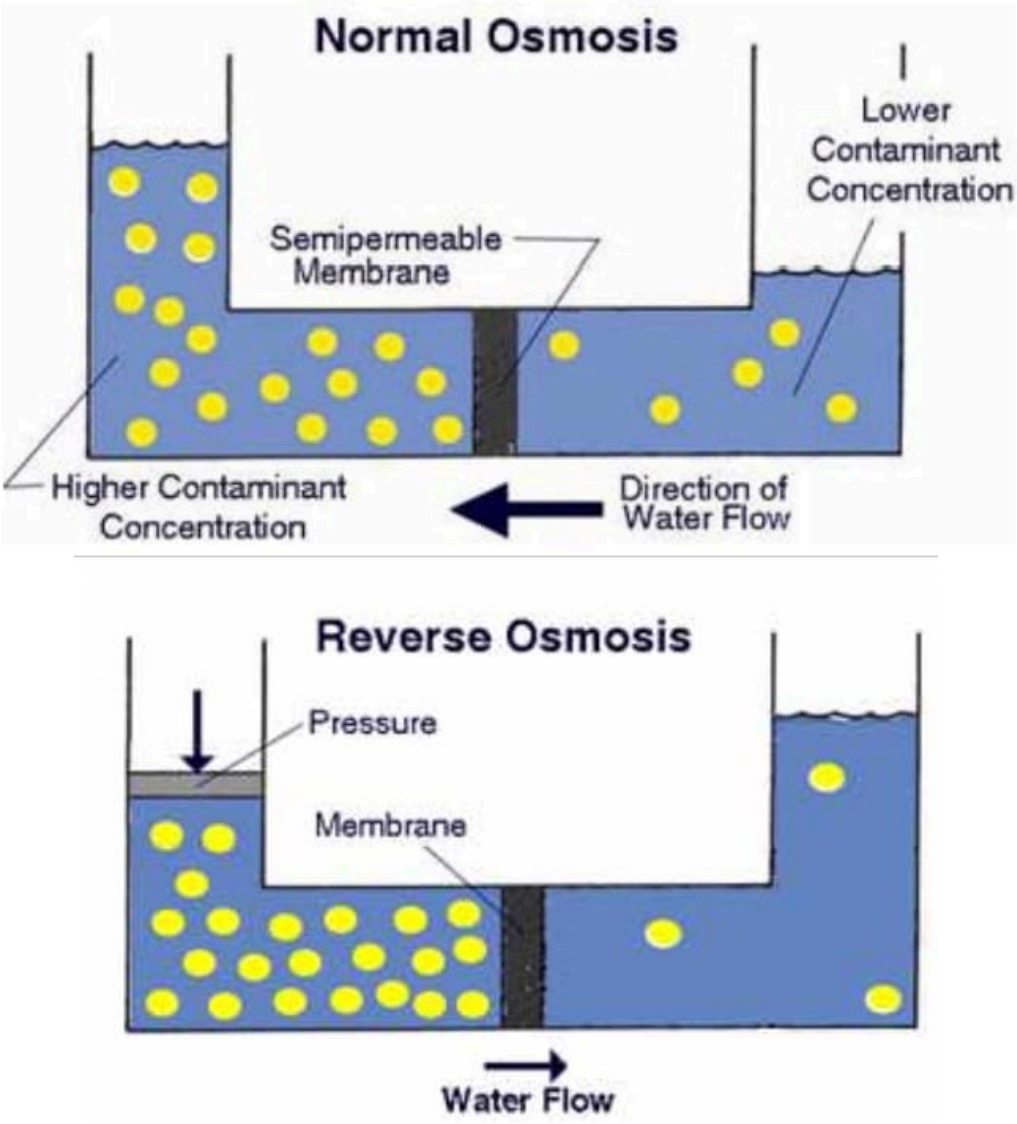


Figure 14.8.2 Comparison of normal osmosis and reverse osmosis. Source: PurePro.

Sludge Digestion

Sewage sludge scraped off the bottom of the settling tank during primary treatment is treated separately from wastewater. Sludge can be disposed of in several ways. First, it can be digested using bacteria; bacterial digestion can sometimes produce methane biogas, which can be used to generate electricity. Sludge can also be incinerated, or condensed, heated to disinfect it, and reused as fertilizer.

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Uses of Reclaimed Wastewater

Water reclamation (also called **wastewater reuse**) is the process of converting wastewater into water that can be reused for other purposes. Reuse may include irrigation of gardens and agricultural fields or replenishing surface water and groundwater (i.e., groundwater recharge). Reused water may also be directed toward fulfilling certain needs in residences (e.g. toilet flushing), businesses, and industry, and could even be treated to reach drinking water standards. This last option is called either "direct potable reuse" or "indirect potable" reuse, depending on the approach used.

Reclaiming water for reuse applications instead of using freshwater supplies can be a water-saving measure. When used water is eventually discharged back into natural water sources, it can still have benefits to ecosystems, improving streamflow, nourishing plant life and recharging aquifers, as part of the natural water cycle.

Wastewater reuse is a long-established practice used for irrigation, especially in arid countries. Reusing wastewater as part of sustainable water management allows water to remain as an alternative water source for human activities. This can reduce scarcity and alleviate pressures on groundwater and other natural water bodies. Another potentially positive aspect is the nutrient content in the wastewater, which might reduce the need of other fertilizers.

Drawbacks or risks often mentioned include the content of potentially harmful substances such as bacteria, heavy metals or organic pollutants (including pharmaceuticals, personal care products and pesticides). Irrigation with wastewater can have both positive and negative effects on soil and plants, depending on the composition of the wastewater and on the soil or plant characteristics.

Figure 14.8.3 *The Sequence of reclamation from left: raw sewage, plant effluent, and finally reclaimed water (after several treatment steps). (Credit: Wikipedia)*

Most of the uses of water reclamation are non potable uses such as washing cars, flushing toilets, cooling water for power plants, concrete mixing, artificial lakes, irrigation for golf courses and public parks, and for hydraulic fracturing. Where applicable, systems run a dual piping system to keep the recycled water separate from the potable water.

The main reclaimed water applications in the world are shown below:

Table 14.8.1 *Uses of Reclaimed Water*

Categories of use	**Uses**
Urban uses	Irrigation of public parks, sporting facilities, private gardens, roadsides; Street cleaning; Fire protection systems; Vehicle washing; Toilet flushing; Air conditioners; Dust control.
Agricultural uses	Food crops not commercially processed; Food crops commercially processed; Pasture for milking animals; Fodder; Fibre; Seed crops; Ornamental flowers; Orchards; Hydroponic culture; Aquaculture; Greenhouses; Viticulture.
Industrial uses	Processing water; Cooling water; Recirculating cooling towers; Washdown water; Washing aggregate; Making concrete; Soil compaction; Dust control.
Recreational uses	Golf course irrigation; Recreational impoundments with/without public access (e.g. fishing, boating, bathing); Aesthetic impoundments without public access; Snowmaking.
Environmental uses	Aquifer recharge; Wetlands; Marshes; Stream augmentation; Wildlife habitat; Silviculture.
Potable uses	Aquifer recharge for drinking water use; Augmentation of surface drinking water supplies; Treatment until drinking water quality.

Astronauts and Reclaimed Urine

If it's good enough for astronauts...

Astronauts about the space station drinking recycled urine.

Astronauts aboard the International Space Station drink reclaimed urine. (Credit: NASA)

In outer space, as on the International Space Station, water is at a premium and not a drop is to be wasted. Astronauts aboard the station must drink recycled water. Water from humidity in the air is condensed and used as drinking water, but American astronauts also drink recycled urine! You can imagine the urine, which is of course almost all water, would go through a rigorous purification process, but this just shows if the need exists, that the same water can serve valuable purposes over and over again.

Summary

- Wastewater treatment is a process used to remove from or and convert it into an that can be returned to the with minimum impact on the environment, or directly reused.
- In a wastewater treatment plant wastewater or sewage undergo primary,secondary, as well as tertiary treatments depending on the end use.
- Most of the uses of water reclamation are non potable uses such as washing cars, flushing toilets, cooling water for power plants, concrete mixing, artificial lakes, irrigation for golf courses and public parks, and for hydraulic fracturing

Contributors and Attributions

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- Wikipedia

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15: ENERGY

15.1: Our Sun, a Giant Nuclear Power Plant

15.2: Energy and Chemical Reactions

15.3: Reaction Rates

15.4: The Laws of Thermodynamics

15.5: Power- People, Horses, and Fossils

15.6: Coal - The Carbon Rock of Ages

15.7: Natural Gas and Petroleum

15.8: Convenient Energy

15.9: Nuclear Energy

15.10: Renewable Energy Sources

It takes energy to launch a spaceship into space. If it takes 1 energy unit to warm 0.25 g of water by 1°C, then it takes over 15,100 energy units to put that 0.25 g of water into earth orbit. The most powerful engines designed to lift rockets into space were part of the Saturn V rocket, that was built by the National Aeronautics and Space Administration (NASA). The rocket had three stages, with the first stage having the capability of launching about 3.5 million kg of mass. About 2.3 million kg was the actual fuel for the first stage; rockets in space have the unpleasant task of having to take their own chemicals with them to provide thrust.



Fig. 7.1.1: Saturn V SA-513 lifts off to boost the Skylab Orbital Workshop into Earth orbit. It takes a lot of energy to launch a rocket into space. The Saturn V rocket used five of the most powerful engines ever built to take its initial step into orbit. (Public Domain; NASA)

Having to carry its own fuel puts a lot of mass burden on an engine in space. This is why NASA is developing other types of engines to minimize fuel mass. An ion thruster uses xenon atoms that have had at least one electron removed from their atoms. The resulting ions can be accelerated by electric fields, causing a thrust. Because xenon atoms are very large for atoms, the thrusting efficiency is high even though the actual thrust is low. Because of this, ion engines are useful only in space.

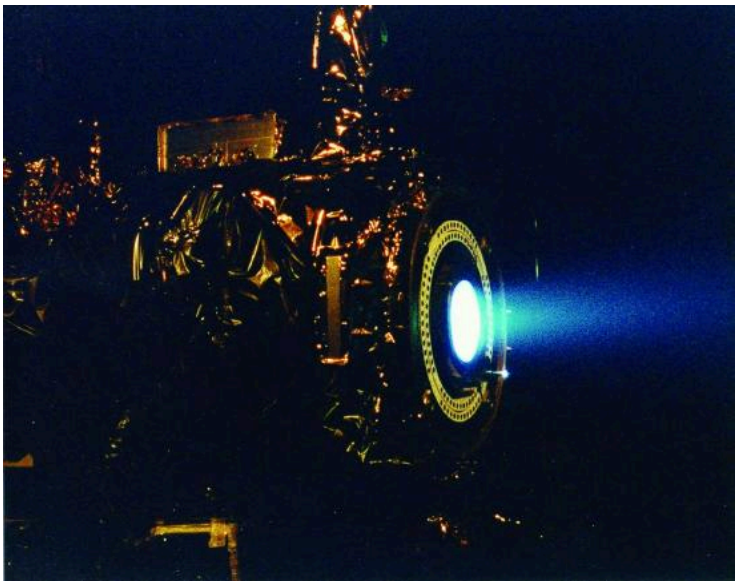


Fig. 7.1.2: An Ion Thruster. Ion drives have low thrust but high efficiency. They have already been used on several space missions, including NASA's *Deep Space 1* spacecraft and Japan's *Hayabusa* asteroid sampling probe. Source: Photo courtesy of NASA, commons.wikimedia.org/wiki/File:Ion_Engine_Test_Firing_-_GPN-2000-000482.jpg.

Energy is a very important quantity in science and the world around us. Although most of our energy ultimately comes from the sun, much of the energy we use on a daily basis is rooted in chemical reactions. The gasoline in your car, the electricity in your house, the food in your diet-all provide substances for chemical reactions to provide energy (gasoline, food) or are produced from chemical reactions (electricity, about 50% of which is generated by burning coal). As such, it is only natural that the study of chemistry involves energy.

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15.1: Our Sun, a Giant Nuclear Power Plant

Learning Objectives

- Define energy and distinguish between kinetic and potential enregy.
- Describe photosynthesis
- Perform calculations involving power and energy.

The Sun currently fuses about 600 million tons of hydrogen into helium every second, converting 4 million tons of matter into energy every second as a result. Sunlight at the top of Earth's atmosphere is composed (by total energy) of about 50% infrared light, 40% visible light, and 10% ultraviolet light.[46] The atmosphere in particular filters out over 70% of solar ultraviolet, especially at the shorter wavelengths.[47] Solar ultraviolet radiation ionizes Earth's dayside upper atmosphere, creating the electrically conducting ionosphere.[48]The energy of sunlight supports almost all life[c] on Earth by photosynthesis,[37] and drives Earth's climate and weather.

Energy can be defined as the capacity to supply heat or do work. One type of work (*w*) is the process of causing matter to move against an opposing force. For example, we do work when we inflate a bicycle tire—we move matter (the air in the pump) against the opposing force of the air surrounding the tire. Energy is measured in SI units, in joules (J). The Joule (= 1 Newton-meter) is a very small unit, however it is equivalent to the amount of work of lifting a small apple (98 grams) vertically up one meter. In terms of heat,

$$1\ \text{cal} = 4.184\ \text{J}$$

The rate of work done or energy transfer is called **power**, and its unit is **watt**.

$$1\ \text{watt} = 1\ \text{J/s}$$

Your calculator may consume some milliwatt, and a computer consumes about 100 watt, as does a 100-W light bulb. The **kilowatt (kW)** is equal to one thousand (10^3) watts. This unit is typically used to express the output power of engines and the power of electric motors, tools, machines, and heaters. It is also a common unit used to express the electromagnetic power output of broadcast radio and television transmitters. Different examples of power are given in Table 15.1.1.

One kilowatt is approximately equal to 1.34 horsepower. A small electric heater with one heating element can use 1.0 kilowatt. The average electric power consumption of a household in the United States is about one kilowatt.

Table 15.1.1 Power in Kilowatts of Various Objects or Phenomenon.

Object or Phenomenon	Power in kilowatts (kW)
Supernova (at peak)	5×10^{34}
Milky Way galaxy	10^{34}
Crab Nebula pulsar	10^{25}
The Sun	4×10^{23}
Volcanic eruption (maximum)	4×10^{12}
Lightning bolt	2×10^{9}
Nuclear power plant (total electric and heat transfer)	3×10^{6}
Aircraft carrier (total useful and heat transfer)	10^{5}
Dragster (total useful and heat transfer)	2×10^{3}
Car (total useful and heat transfer)	8×10^{1}

Object or Phenomenon	Power in kilowatts (kW)
Football player (total useful and heat transfer)	5
Clothes dryer	4
Typical incandescent light bulb (total useful and heat transfer) (60W)	0.06
Electric clock	0.003
Pocket calculator	10^{-6}

Example 15.1.1 Power and Energy Conversion

Calculate the electrical energy, in joules (J) , that is used by a 20W LED bulb that was left "on" for 3.0 hours.

Solution

1. Since 1 W = 1 J/s then 20W = 20 J/s.

2. Convert 3 h to s.

3. Calculate the amount in J for 10,800 s.

Exercise 15.1.1

Calculate the electrical energy, in joules (J) , that is used by a 100W incandescent bulb that was left "on" for 2 hours.

Answer available at the end of this section.

Energy and the Life-Support System

Photosynthesis is essential to all life on earth; both plants and animals depend on it. It is the only biological process that can capture energy that originates in outer space (sunlight) and convert it into chemical compounds (carbohydrates) that every organism uses to power its metabolism. In brief, the energy of sunlight is captured and used to energize electrons, which are then stored in the covalent bonds of sugar molecules. How long lasting and stable are those covalent bonds? The energy extracted today by the burning of coal and petroleum products represents sunlight energy captured and stored by photosynthesis almost 200 million years ago.

Photosynthesis is a multi-step process that requires sunlight, carbon dioxide (which is low in energy), and water as substrates (Figure 15.1.1). After the process is complete, it releases oxygen and produces simple carbohydrate molecules (which are high in energy) that can subsequently be converted into glucose, sucrose, or any of dozens of other sugar molecules. These sugar molecules contain energy and the energized carbon that all living things need to survive.

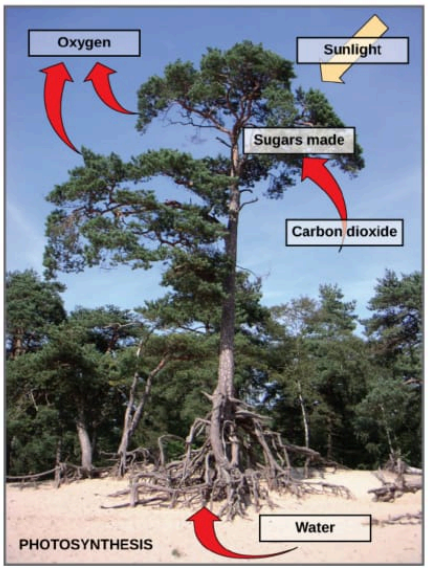


Figure 15.1.1 Photosynthesis uses solar energy , carbon dioxide, and water to produce energy-storing carbohydrates. Oxygen is generated as a waste product of photosynthesis.

The chemical equation for photosynthesis is given in Figure 15.1.2. Although the equation looks simple, the many steps that take place during photosynthesis are actually quite complex. In reality, the process takes place in many steps involving intermediate reactants and products.

Photosynthesis Equation

Carbon dioxide	+	Water	SUNLIGHT →	Sugar	+	Oxygen
$6CO_2$		$6H_2O$		$C_6H_{12}O_6$		$6O_2$

Figure 15.1.2 The basic equation for photosynthesis.

Kinetic and Potential Energy

Like matter, energy comes in different types. One scheme classifies energy into two types: **potential energy**, the energy an object has because of its relative position, composition, or condition, and **kinetic energy**, the energy that an object possesses because of its motion. Water at the top of a waterfall or dam has potential energy because of its position; when it flows downward through generators, it has kinetic energy that can be used to do work and produce electricity in a hydroelectric plant (Figure 15.1.3). A battery has potential energy because the chemicals within it can produce electricity that can do work.

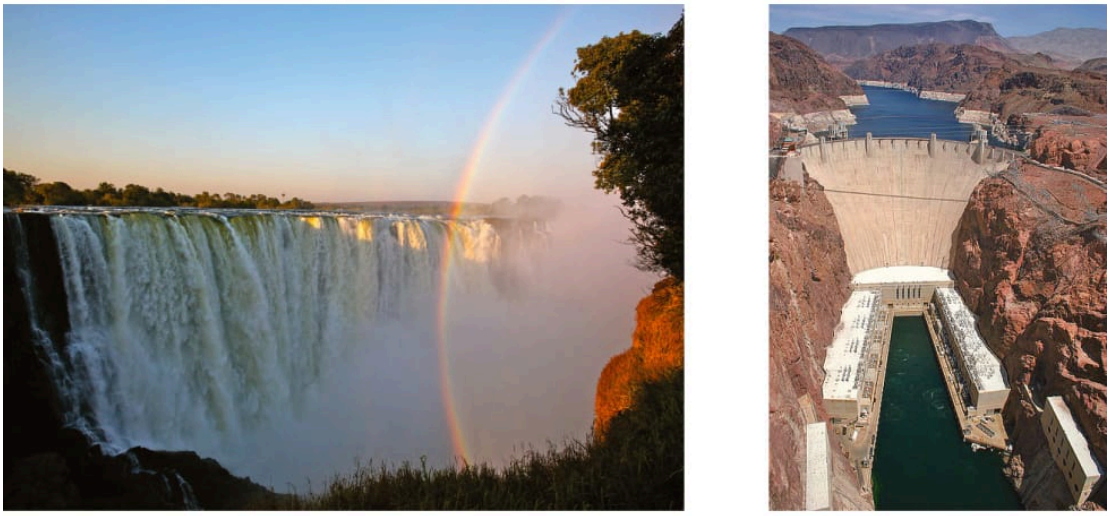


Figure 15.1.3 *The (a) Water that is higher in elevation, for example, at the top of Victoria Falls, has a higher potential energy than water at a lower elevation. As the water falls, some of its potential energy is converted into kinetic energy. (b) If the water flows through generators at the bottom of a dam, such as the Hoover Dam shown here, its kinetic energy is converted into electrical energy. (credit a: modification of work by Steve Jurvetson; credit b: modification of work by "curimedia"/Wikimedia commons).*

Potential energy is not only associated with the location of matter, but also with the structure of matter. Even a spring on the ground has potential energy if it is compressed; so does a rubber band that is pulled taut. On a molecular level, the bonds that hold the atoms of molecules together exist in a particular structure that has potential energy. The fact that energy can be released by the breakdown of certain chemical bonds implies that those bonds have potential energy. In fact, there is potential energy stored within the bonds of all the food molecules we eat, which is harnessed for use. The type of potential energy that exists within chemical bonds, and is released when those bonds are broken, is called **chemical energy**. Chemical energy is responsible for providing living cells with energy from food. The release of energy occurs when the molecular bonds within food molecules are broken.

Summary

- Energy can be defined as the capacity to supply heat or do work and is measured in SI units, in joules (J)
- Photosynthesis is essential to all life on earth and it is the only biological process that can capture energy that originates in outer space (sunlight) and convert it into chemical compounds (carbohydrates) that every organism uses to power its metabolism.
- Energy comes in two fundamentally different forms – kinetic energy and potential energy.
- Kinetic energy is the energy of motion.
- Potential energy is stored energy that depends on the position of an object relative to another object.

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Answers

Exercise 15.1.1

720,000 J

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15.2: Energy and Chemical Reactions

Learning Objectives

- Define endothermic and exothermic reactions.
- Determine whether a reaction is endothermic or exothermic through observations, temperature changes, or an energy diagram.
- Describe the calculation of heat of reaction using bond energies.

When physical or chemical changes occur, they are generally accompanied by a transfer of energy. The **law of conservation of energy** states that in any physical or chemical process, energy is neither created nor destroyed. In other words, the entire energy in the universe is conserved. In order to better understand the energy changes taking place during a reaction, we need to define two parts of the universe, called the system and the surroundings. The **system** is the specific portion of matter in a given space that is being studied during an experiment or an observation. The **surroundings** is everything in the universe that is not part of the system. In practical terms for a laboratory chemist, the system is the particular chemicals being reacted, while the surroundings is the immediate vicinity within the room. During most processes, energy is exchanged between the system and the surroundings.

In the course of an **endothermic** process, the system gains heat from the surroundings and so the **temperature of the surroundings decreases.** A chemical reaction or physical change is **exothermic** if heat is released by the system into the surroundings. Because the surroundings is gaining heat from the system, **the temperature of the surroundings increases** (Figure \(\PageIndex{1}\))**.** Exothermic and endothermic reactions can be thought of as having energy as either a product of the reaction or a reactant. **Exothermic** reactions give off energy, so energy is a product. **Endothermic** reactions require energy, so energy is a reactant.

Phase changes, discussed in the previous section 7.3, are also classified in a similar way. The change from gas to liquid (condensation) and liquid to solid (freezing) are **exothermic**. The change from solid to liquid (melting), and liquid to gas (evaporation and boiling) are **endothermic**. The **exothermic processes release heat** to the surroundings while the **endothermic processes absorb heat** from the surroundings.

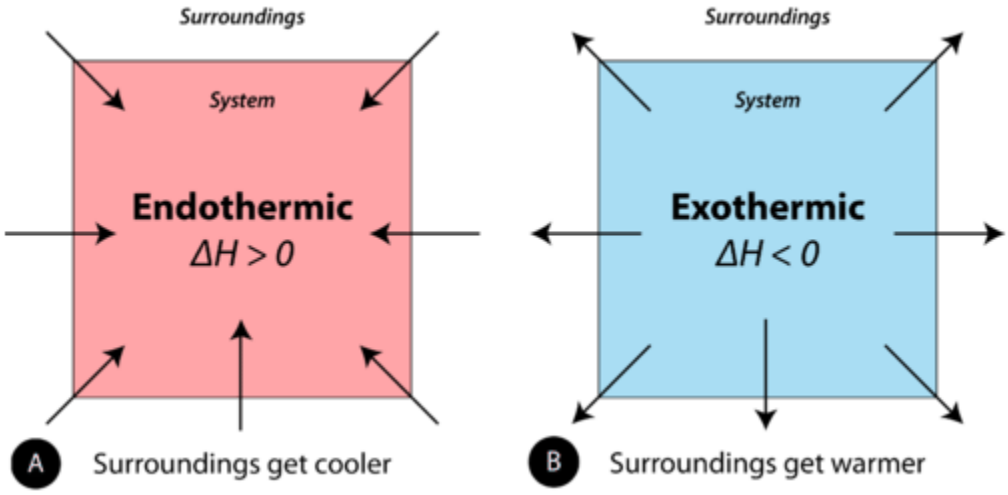


Figure \(\PageIndex{1}\). (A) Endothermic reaction. (B) Exothermic reaction.

When methane gas is combusted, heat is released, making the reaction exothermic. Specifically, the combustion of \(1 \: \text{mol}\) of methane releases 890.4 kilojoules of heat energy. This information can be shown as part of the balanced equation.

\[\ce{CH_4} \left(g \right) + 2 \ce{O_2} \left(g \right) \rightarrow \ce{CO_2} \left(g \right) + 2 \ce{H_2O} \left(l \right) + 890.4 \: \text{kJ} \nonumber \]

The process in the above thermochemical equation can be shown visually in the figure below.

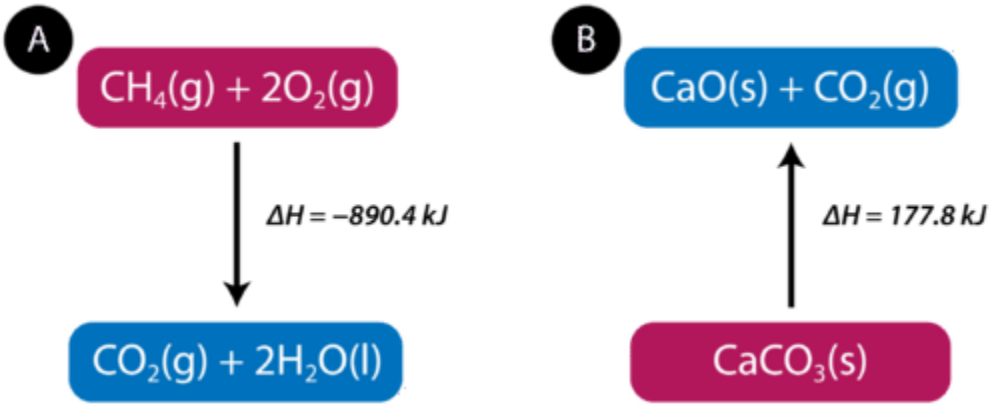


Figure \(\PageIndex{2}\) (A) As reactants are converted to products in an exothermic reaction, enthalpy is released into the surroundings. The enthalpy change of the reaction is negative. (B) As reactants are converted to products in an endothermic reaction, enthalpy is absorbed from the surroundings. The enthalpy change of the reaction is positive. (CC BY-NC; CK-12)

In the combustion of methane example, the enthalpy change is negative because heat is being released by the system. Therefore, the overall enthalpy of the system decreases. The **heat of reaction** is the enthalpy change for a chemical reaction. In the case above, the heat of reaction is \(-890.4 \: \text{kJ}\). The thermochemical reaction can also be written in this way:

\[\ce{CH_4} \left(g \right) + 2 \ce{O_2} \left(g \right) \rightarrow \ce{CO_2} \left(g \right) + 2 \ce{H_2O} \left(l \right) \: \: \: \: \: \Delta H = -890.4 \: \text{kJ} \nonumber \]

Endothermic reactions absorb energy from the surroundings as the reaction occurs. When \(1 \: \text{mol}\) of calcium carbonate decomposes into \(1 \: \text{mol}\) of calcium oxide and \(1 \: \text{mol}\) of carbon dioxide, \(177.8 \: \text{kJ}\) of heat is absorbed. The process is shown visually in the figure above (B). The thermochemical reaction is shown below.

\[\ce{CaCO_3} \left(s \right) + 177.8 \: \text{kJ} \rightarrow \ce{CaO} \left(s \right) + \ce{CO_2} \left(g \right) \nonumber \]

Because the heat is absorbed by the system, the \(177.8 \: \text{kJ}\) is written as a reactant. The heat of reaction is positive for an endothermic reaction.

Example \(\PageIndex{1}\)

Label each of the following processes as endothermic or exothermic.

a. water boiling
b. gasoline burning
c. ice forming on a pond

Solution

a. endothermic - you must put a pan of water on the stove and give it heat in order to get water to boil. Because you are adding heat/energy, the reaction is endothermic.
b. exothermic - when you burn something, it feels hot to you because it is giving off heat into the surroundings.
c. exothermic - think of ice forming in your freezer instead. You put water into the freezer, which takes heat out of the water, to get it to freeze. Because heat is being pulled out of the water, it is exothermic. Heat is leaving.

Exercise \(\PageIndex{1}\)

Label each of the following processes as endothermic or exothermic.

a. water vapor condensing
b. gold melting

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

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

Example \(\PageIndex{2}\)

Is each chemical reaction exothermic or endothermic?

a. $2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell) + 135$ kcal
b. $N_2(g) + O_2(g) + 45$ kcal $\rightarrow 2NO(g)$

Solution

a. Because energy is a product, energy is given off by the reaction. Therefore, this reaction is exothermic.
b. Because energy is a reactant, energy is absorbed by the reaction. Therefore, this reaction is endothermic.

Exercise \(\PageIndex{2}\)

Is each chemical reaction exothermic or endothermic?

a. $H_2(g) + F_2(g) \rightarrow 2HF\ (g) + 130$ kcal
b. $2C(s) + H_2(g) + 5.3$ kcal $\rightarrow C_2H_2(g)$

Answer available at the end of this section.

Bond Energy

Atoms bond together to form compounds because in doing so they attain lower energies than they possess as individual atoms. A quantity of energy, equal to the difference between the energies of the bonded atoms and the energies of the separated atoms, is released, usually as heat. That is, the bonded atoms have a lower energy than the individual atoms do. *When atoms combine to make a compound, energy is always given off, and the compound has a lower overall energy.*

When a chemical reaction occurs, molecular bonds are broken and other bonds are formed to make different molecules. For example, the bonds of two water molecules are broken to form hydrogen and oxygen.

\[2H_2O \rightarrow 2H_2 + O_2 \nonumber \]

Energy is always required to break a bond, which is known as bond energy. While the concept may seem simple, bond energy serves a very important purpose in describing the structure and characteristics of a molecule.

> Energy is always required to break a bond. Energy is released when a bond is made.

Table \(\PageIndex{1}\) Approximate Bond Energies

Bond	Bond Energy (kJ/mol)
C–H	413
C–O	358
C=O*	745
C–N	305

Bond	Bond Energy (kJ/mol)
C–C	347
C=C	614
C≡C	839
N–H	391
O—H	467
H–H	432
H—Cl	427
H—I	295
*C = O(CO_2) = 799	

When a chemical reaction occurs, the atoms in the reactants rearrange their chemical bonds to make products. The new arrangement of bonds does not have the same total energy as the bonds in the reactants. Therefore, when chemical reactions occur, *there will always be an accompanying energy change*. The enthalpy change, for a given reaction can be calculated using the bond energy values from Table \(\PageIndex{1}\).

In this process, one adds energy to the reaction to break bonds, and extracts energy for the bonds that are formed.

$$\text{enthalpy change} = \sum (\text{bonds broken}) - \sum (\text{bonds formed}) \nonumber$$

Example \(\PageIndex{3}\): Generation of Hydrogen Iodide

What is the enthalpy change for this reaction and is it endothermic or exothermic?

$$H_2(g)+I_2(g) \rightarrow 2HI(g) \nonumber$$

Solution

First look at the equation and identify which bonds exist on in the reactants.

- one H-H bond and
- one I-I bond

Now do the same for the products

- two H-I bonds

Then identify the bond energies of these bonds from the table above:

- H-H bonds: 436 kJ/mol
- I-I bonds: 151 kJ/mol

The sum of enthalpies on the reaction side is:

436 kJ/mole + 151 kJ/mole = 587 kJ/mol.

This is how much energy is needed to break the bonds on the reactant side. Then we look at the bond formation which is on the product side:

- 2 mol H-I bonds: 297 kJ/mol

The sum of enthalpies on the product side is:

2 x 297 kJ/mol= 594 kJ/mol

This is how much energy is released when the bonds on the product side are formed. The net change of the reaction is therefore

587 kJ/mol -594 kJ/mol= -7 kJ/mol.

Since this is negative, the reaction is *exothermic*.

Exercise \(\PageIndex{3}\): Decomposition of Water

Using the bond energies given in the chart above, find the enthalpy change for the thermal decomposition of water:

\[2H_2O (g) \rightarrow 2H_2 + O_2 (g) \nonumber \]

Is the reaction written above exothermic or endothermic? Explain.

Solution

The enthalpy change deals with breaking two mole of O-H bonds and the formation of 1 mole of O-O bonds and two moles of H-H bonds (Table \(\PageIndex{1}\)).

- The sum of the energies required to break the bonds on the reactants side is 4 x 460 kJ/mol = 1840 kJ/mol.
- The sum of the energies released to form the bonds on the products side is
  - 2 moles of H-H bonds = 2 x 436.4 kJ/mol = 872.8 kJ/mol
  - 1 moles of O=O bond = 1 x 498.7 kJ/mil = 498.7 kJ/mol

which is an output (released) energy = 872.8 kJ/mol + 498.7 kJ/mol = 1371.5 kJ/mol.

Total energy difference is 1840 kJ/mol – 1371.5 kJ/mol = 469 kJ/mol, which indicates that the reaction is *endothermic* and that 469 kJ of heat is needed to be supplied to carry out this reaction.

This reaction is endothermic since it requires energy in order to create bonds.

Summary

- Chemical processes are labeled as exothermic or endothermic based on whether they give off or absorb energy, respectively.
- Atoms are held together by a certain amount of energy called bond energy.
- Energy is released to generate bonds, which is why the enthalpy change for breaking bonds is positive. Energy is required to break bonds. Atoms are much happier when they are "married" and release energy because it is easier and more stable to be in a relationship (e.g., to generate *octet electronic configurations*). The enthalpy change is negative because the system is releasing energy when forming bond.

Contributors and Attributions

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- Libretext: Introductory Chemistry (Tro)
- Libretext: Fundamentals of General Organic and Biological Chemistry (McMurry et al.)

Answers

Exercise \(\PageIndex{1}\)
exothermic

Exercise \(\PageIndex{1}\)
endothermic

Exercise \(\PageIndex{2}\)

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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15.3: Reaction Rates

Learning Objectives

- Define chemical reaction rate.
- Describe the effects of temperature, concentration, surface area, and catalysis on reaction rates.

The lizard in the photograph is not simply enjoying the sunshine or working on its tan. The heat from the sun's rays is critical to the lizard's survival. A warm lizard can move faster than a cold one because the chemical reactions that allow its muscles to move occur more rapidly at higher temperatures. In the absence of warmth, the lizard is an easy meal for predators.



Figure 15.3.1 An agama lizard basks in the sun. As its body warms, the chemical reactions of its metabolism speed up.

From baking a cake to determining the useful lifespan of a bridge, rates of chemical reactions play important roles in our understanding of processes that involve chemical changes.

A **rate** is a measure of how some property varies with time. Speed is a familiar rate that expresses the distance traveled by an object in a given amount of time. Wage is a rate that represents the amount of money earned by a person working for a given amount of time. Likewise, the rate of a chemical reaction is a measure of how much reactant is consumed, or how much product is produced, by the reaction in a given amount of time.

The rate of reaction is the change in the amount of a reactant or product per unit time. Reaction rates are therefore determined by measuring the time dependence of some property that can be related to reactant or product amounts. Rates of reactions that consume or produce gaseous substances, for example, are conveniently determined by measuring changes in volume or pressure. For reactions involving one or more colored substances, rates may be monitored via measurements of light absorption. For reactions involving aqueous electrolytes, rates may be measured via changes in a solution's conductivity.

For reactants and products in solution, their relative amounts (concentrations) are conveniently used for purposes of expressing reaction rates. If we measure the concentration of hydrogen peroxide, H_2O_2, in an aqueous solution, we find that it changes slowly over time as the H_2O_2 decomposes, according to the equation:

$$2\,H_2O_2(aq) \longrightarrow 2\,H_2O(l) + O_2(g)$$

The rate at which the hydrogen peroxide decomposes can be expressed in terms of the rate of change of its concentration, as shown here:

$$\text{rate of decomposition of } H_2O_2 = -\frac{\text{change in concentration of reactant}}{\text{time interval}}$$

Factors Affecting Reaction Rates

By their nature, some reactions occur very quickly, while others are very slow. However, certain changes in the reacting conditions can have an effect on the rate of a given chemical reaction.

Concentration

The rates of many reactions depend on the concentrations of the reactants. Rates usually increase when the concentration of one or more of the reactants increases. In a polluted atmosphere where the concentration of sulfur dioxide is high, calcium carbonate deteriorates more rapidly than in less polluted air. Similarly, phosphorus burns much more rapidly in an atmosphere of pure oxygen than in air, which is only about 20% oxygen.



Figure 15.3.2 Pollutants like sulfur dioxide can accelerate weathering of statues made from carbonate compounds such as limestone and marble (credit: James P Fisher III).

Phosphorus Burning

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 15.3.1 *Phosphorous burns rapidly in air, but it will burn even more rapidly if the concentration of oxygen in is higher.*

Surface Area

A large log placed in a fire will burn relatively slowly. If the same mass of wood were added to the fire in the form of small twigs, they would burn much more quickly. This is because the twigs provide a greater surface area than the log does. An increase in the surface area of a reactant increases the rate of a reaction. Surface area is larger when a given amount of a solid is present as smaller particles. A powdered reactant has a greater surface area than the same reactant as a solid chunk. In order to increase the surface area of a substance, it may be ground into smaller particles or dissolved into a liquid. In solution, the dissolved particles are separated from each other and will react more quickly with other reactants.

Temperature

Chemical reactions typically occur faster at higher temperatures. Food can spoil quickly when left on the kitchen counter. However, the lower temperature inside of a refrigerator slows that process so that the same food remains fresh for days. We use a burner or a hot plate in the laboratory to increase the speed of reactions that proceed slowly at ordinary temperatures. In many cases, an increase in temperature of only 10 °C will approximately double the rate of a reaction in a homogeneous system.

The Presence of a Catalyst

Hydrogen peroxide solutions foam when poured onto an open wound because substances in the exposed tissues act as catalysts, increasing the rate of hydrogen peroxide's decomposition. However, in the absence of these catalysts (for example, in the bottle in the medicine cabinet) complete decomposition can take months. A catalyst is a substance that increases the rate of a chemical reaction by providing an alternative pathway or mechanism for the reaction to follow.

Summary

- The reaction rate indicates how fast the reaction proceeds.
- Factors affecting reaction rate are:
  - Concentration of reactants
  - Surface area
  - Temperature
  - Presence of catalysts

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15.4: The Laws of Thermodynamics

Learning Objective

- Explain the first and second laws of thermodynamics

Thermodynamics refers to the study of energy and energy transfer involving physical matter. The matter and its environment relevant to a particular case of energy transfer are classified as a system, and everything outside of that system is called the surroundings. For instance, when heating a pot of water on the stove, the system includes the stove, the pot, and the water. Energy is transferred within the system (between the stove, pot, and water). There are two types of systems: open and closed. An open system is one in which energy can be transferred between the system and its surroundings. The stovetop system is open because heat can be lost into the air. A closed system is one that cannot transfer energy to its surroundings.

Biological organisms are open systems. Energy is exchanged between them and their surroundings, as they consume energy-storing molecules and release energy to the environment by doing work. Like all things in the physical world, energy is subject to the laws of physics. The laws of thermodynamics govern the transfer of energy in and among all systems in the universe.

The First Law of Thermodynamics

The first law of thermodynamics deals with the total amount of energy in the universe. It states that this total amount of energy is constant. In other words, there has always been, and always will be, exactly the same amount of energy in the universe. Energy exists in many different forms. According to the first law of thermodynamics, energy may be transferred from place to place or transformed into different forms, but it cannot be created or destroyed. The transfers and transformations of energy take place around us all the time. Light bulbs transform electrical energy into light energy. Gas stoves transform chemical energy from natural gas into heat energy. Plants, during photosynthesis perform one of the most biologically useful energy transformations on earth: that of converting the energy of sunlight into the chemical energy stored within organic molecules. Some examples of energy transformations are shown in Figure 15.4.1.

The challenge for all living organisms is to obtain energy from their surroundings in forms that they can transfer or transform into usable energy to do work. Living cells have evolved to meet this challenge very well. Chemical energy stored within organic molecules such as sugars and fats is transformed through a series of cellular chemical reactions into energy within molecules of ATP (Adenosine triphosphate). Energy in ATP molecules is easily accessible to do work. Examples of the types of work that cells need to do include building complex molecules, transporting materials, powering the beating motion of cilia or flagella, contracting muscle fibers to create movement, and reproduction.

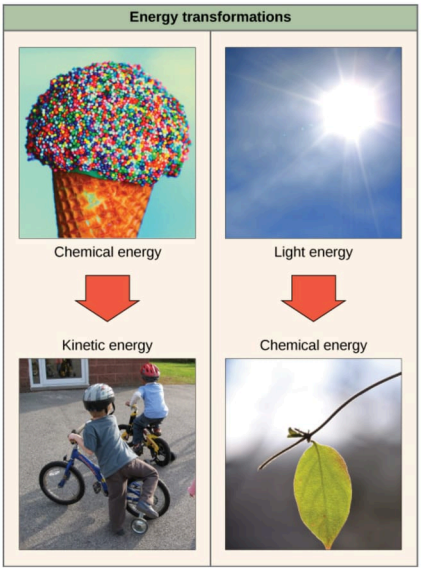


Figure 15.4.1 Two examples of energy being transferred from one system to another and transformed from one form to another. Humans can convert the chemical energy in food, like this ice cream cone, into kinetic energy (the energy of movement to ride a bicycle). Plants can convert electromagnetic radiation (light energy) from the sun into chemical energy. (credit “ice cream”: modification of work by D. Sharon Pruitt; credit “kids on bikes”: modification of work by Michelle Riggen-Ransom; credit “leaf”: modification of work by Cory Zanker)

The Second Law of Thermodynamics

An important concept in physical systems is that of order and disorder (also known as randomness). The more energy that is lost by a system to its surroundings, the less ordered and more random the system is. Scientists refer to the measure of randomness or disorder within a system as entropy. High entropy means high disorder and low energy (Figure 15.4.2). To better understand entropy, think of a student’s bedroom. If no energy or work were put into it, the room would quickly become messy. It would exist in a very disordered state, one of high entropy. Energy must be put into the system, in the form of the student doing work and putting everything away, in order to bring the room back to a state of cleanliness and order. This state is one of low entropy. Similarly, a car or house must be constantly maintained with work in order to keep it in an ordered state. Left alone, the entropy of the house or car gradually increases through rust and degradation. Molecules and chemical reactions have varying amounts of entropy as well. For example, as chemical reactions reach a state of equilibrium, entropy increases, and as molecules at a high concentration in one place diffuse and spread out, entropy also increases.

All physical systems can be thought of in this way: Living things are highly ordered, requiring constant energy input to be maintained in a state of low entropy. As living systems take in energy-storing molecules and transform them through chemical reactions, they lose some amount of usable energy in the process, because no reaction is completely efficient. They also produce waste and by-products that aren’t useful energy sources. This process increases the entropy of the system’s surroundings. Since all energy transfers result in the loss of some usable energy, the second law of thermodynamics states that every energy transfer or transformation increases the entropy of the universe. Even though living things are highly ordered and maintain a state of low entropy, the entropy of the universe in total is constantly increasing due to the loss of usable energy with each energy transfer that occurs. Essentially, living things are in a continuous uphill battle against this constant increase in universal entropy.

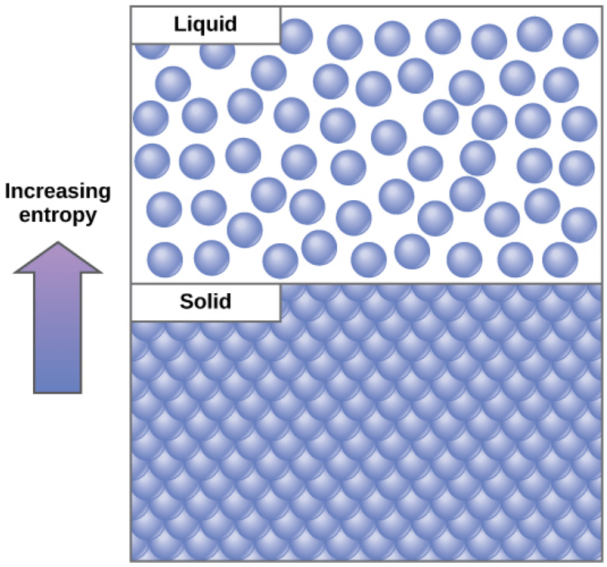


Figure 15.4.2 *Gases have higher entropy than liquids, and liquids have higher entropy than solids.*

Summary

- The first law states that the total amount of energy in the universe is constant. This means that energy can’t be created or destroyed, only transferred or transformed.
- The second law of thermodynamics states that every energy transfer involves some loss of energy in an unusable form, such as heat energy, resulting in a more disordered system. In other words, no energy transfer is completely efficient and tends toward disorder.

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15.5: Power- People, Horses, and Fossils

Learning Objective

- Describe the different fossil fuels.

Fossil fuels is the term given to energy sources with a high **hydrocarbon** content (see Chapter 1 for a review of hydrocarbon molecules) found in the Earth's crust that formed in the geologic past and can be burned to release their energy. They were formed from prehistoric plants and animals that lived hundreds of millions of years ago (100 – 500 million years ago). When these ancient living organisms died they were quickly buried and subjected to immense pressure from overlying earth materials including layers of mud, rock, sand, and sometimes surface water bodies such as oceans and lakes.

During the millions of years that passed, the dead plants and animals slowly decomposed in **anaerobic** (very low to no oxygen) conditions and their chemical energy became concentrated. The organic compounds that once made up tissues of these organisms were chemically changed under high pressures and temperatures. While some fossil fuels may be in the process of formation today, the amount of time required for usable quantities to form is measured in millions of years, so these fuels will never be available for us. Thus for all practical purposes we consider fossil fuels to be finite and **non-renewable**.

Fossil Fuel Types and Formation

There are three main types of fossil fuels – natural gas, oil, and coal – and the specific type formed depends on the combination of organic matter that was present, how long it was buried and what temperature and pressure conditions existed when they were decomposing. **Oil** and **natural gas** were created from organisms that lived in water and were buried under ocean or river sediments. Long after the great prehistoric seas and rivers vanished, heat, pressure, and bacteria combined to compress and transform the organic material under layers of silt or shale rock (Figure 15.5.1). In most areas, a thick liquid called oil formed first, but in deeper, hot regions underground, the transformation process continued until natural gas was formed. Over time, some of this oil and natural gas began working its way upward through the earth's crust until they ran into rock formations called "**caprocks**" that are dense enough to prevent them from seeping to the surface. It is from under these caprocks that most oil and natural gas is retrieved today.

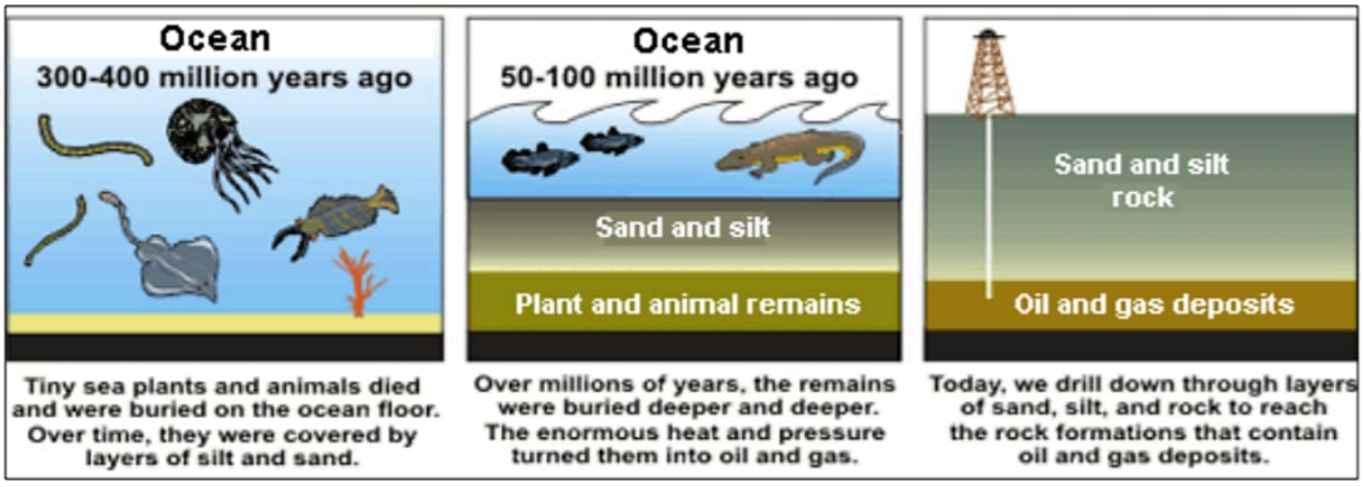


Figure 15.5.1 *Oil and natural gas (petroleum) formation. Source: U.S. Energy Information Administration. http://www.eia.gov/energyexplained/i...tural_gas_home*

Coal is a fossil fuel that formed from the remains of trees, ferns, and other plants that lived 300 to 400 million years ago (Figure 15.5.2). In some areas, such as portions of what is now the eastern United States, coal was formed from swamps covered by sea water. The sea water contained a large amount of sulfur, and as the seas dried up, the sulfur was left behind in the coal. Scientists are working on ways to take the sulfur out of coal because when coal burns, the sulfur is released in to the atmosphere as an air

pollutant (see Chapter 6). Some coal deposits, however, were formed from freshwater swamps which had very little sulfur in them. These coal deposits, located largely in the western part of the United States, have much less sulfur in them.

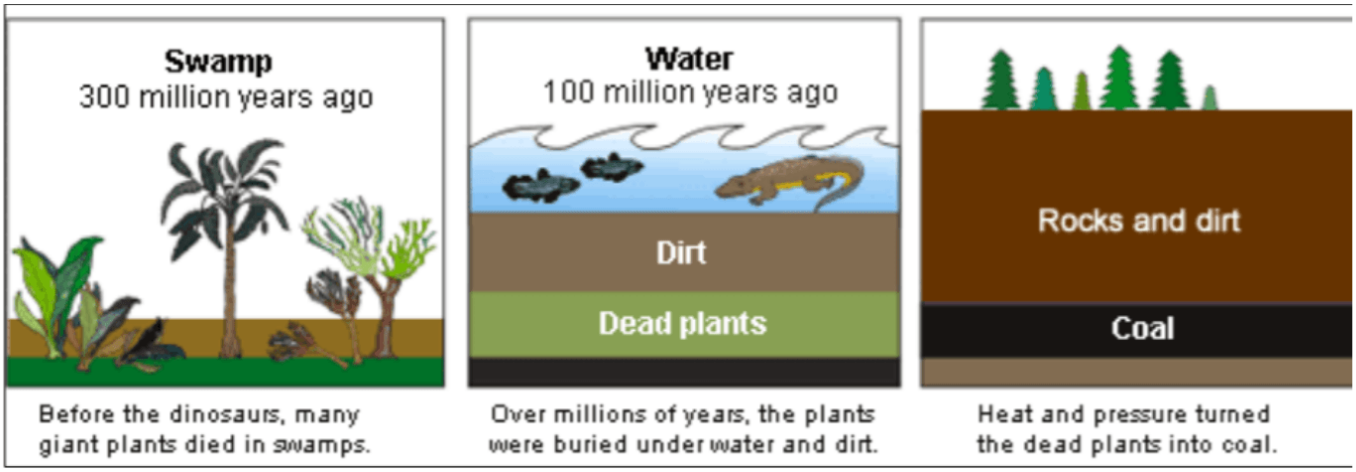


Figure 15.5.2 *The process of coal formation. Source: U.S. Energy Information Administration.*

Consumption and Production

Historically, human prosperity has been directly correlated with energy use. The health and vitality of world societies critically depends on energy, most of which comes from fossil fuels (Figure 15.5.3). Energy resources, however, are unevenly distributed throughout the world, and so are the consumption rates. Developed regions generally consume far more energy than the developing regions. For example, the United States has only about 5% of the world's population but constitutes over 20% of the world's energy consumption. Additionally, developing countries devote a larger proportion of energy consumption to subsistence activities such as growing and preparing food, and heating homes. Industrialized nations rely more on mechanized equipment and technology and, therefore, a greater proportion of their energy consumption goes to transportation and industry.

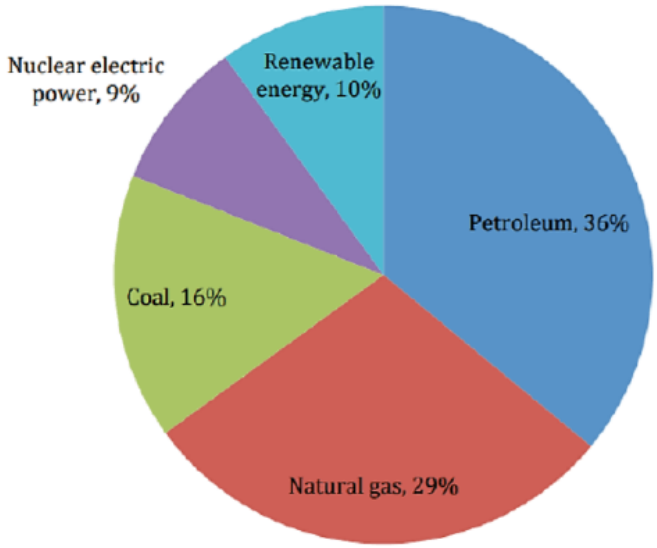


Figure 15.5.3 U.S. primary energy consumption by source (all sectors), 2015, showing that about 80 % of our energy consumption comes from fossil fuels. Data from U.S. Energy Information Administration, April 2016.

Fossil fuels can be utilized without being converted or transformed to another form of energy, this is referred to as **primary energy** consumption. In their primary form, fossil fuels can be used for transportation, heating and cooking, or used to generate electricity. The use of **electricity** is a form of **secondary energy** consumption. Transforming fossil fuel energy into electricity allows for easier transportation over long distances and application to a variety of uses. Additionally, as shown in Figure 15.5.4 , there are four major sectors that consume energy: 1) The industrial sector which includes facilities and equipment used for

manufacturing, agriculture, mining, and construction; 2) The transportation sector includes vehicles that transport people or goods including cars, trucks, buses, motorcycles, trains, aircraft, boats, barges, and ships; 3) The residential sector consists of homes and apartments; 4) The commercial sector includes offices, malls, stores, schools, hospitals, hotels, warehouses, restaurants, places of worship, and more. Each of these sectors also consumes electricity produced by the electric power sector.

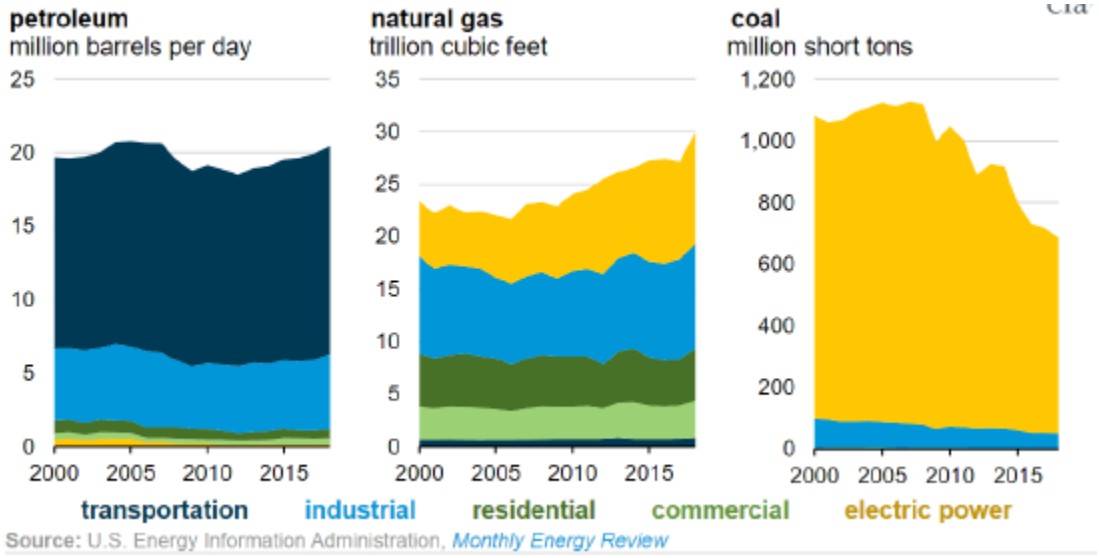


Figure 15.5.4 *U.S. fossil fuel energy consumption by major sector (2000-2018). Source : U.S. Energy Information Administration, April 2019.*

In 2019, U.S. energy production exceeded U.S. energy consumption on an annual basis for the first time since 1957. The United States produced 101.0 quads of energy and consumed 100.2 quads. After record high energy production and consumption in 2018, U.S. energy production grew 5.7% and energy consumption decreased by 0.9% in 2019.

Fossil fuels—petroleum, natural gas, and coal—accounted for about 80% of total U.S. primary energy production in 2019 see Figure 15.5.5.

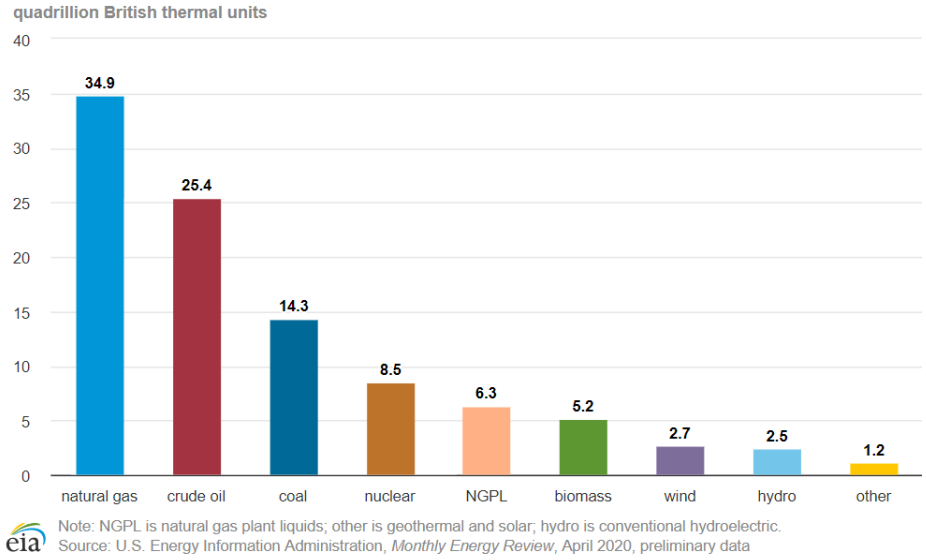


Figure 15.5.5 *U.S. primary energy production by major source, 2019.*

Summary

- Fossil fuels are energy sources from the Earth's crust (that formed in the geologic past) with a high hydrocarbon content and can be burned to release their energy.
- The three main types of fossil fuels that were discussed are natural gas, oil, and coal.

Contributors and Attributions

- U.S. Energy Information Administration
- Libretext: Introduction to Environmental Science (Zendher et al.)

- Marisa Alviar-Agnew (Sacramento City College)

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15.6: Coal - The Carbon Rock of Ages

Learning Objectives

- Describe coal and its processing.
- List the products of coal burning that promotes pollution.

Coal is a complex solid material derived primarily from plants that died and were buried hundreds of millions of years ago and were subsequently subjected to high temperatures and pressures. It is a combustible black or brownish-black sedimentary rock with a high amount of carbon and hydrocarbons. Coal is classified into four main types, or ranks depending on the types and amounts of carbon present and on the amount of heat energy the coal can produce, including anthracite, bituminous, subbituminous, and lignite (highest to lowest ranked, pictured in *Figure* 15.6.1.

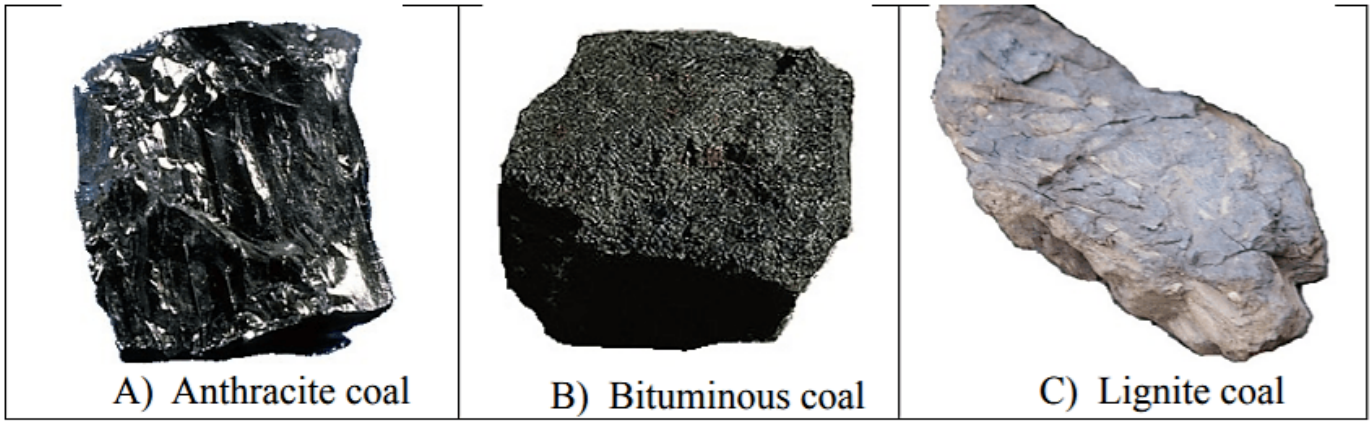


Figure 15.6.1 Different types of coal. Images obtained from Wikimedia Commons.

There are four distinct classes of coal (Table 15.6.1); their hydrogen and oxygen contents depend on the length of time the coal has been buried and the pressures and temperatures to which it has been subjected. The most abundant form in the United States is bituminous coal, which has a high sulfur content becauseof the presence of small particles of pyrite (FeS_2). The combustion of coal releases the sulfur in FeS_2 as SO_2, which is a major contributor to acid rain.

Table 15.6.1 *Properties of Different Types of Coal.*

Type	% Carbon	Hydrogen:Carbon Mole Ratio	% Oxygen	% Sulfur	US Deposits
anthracite	92	0.5	3	1	Pennsylvania, New York
bituminous	80	0.6	8	5	Appalachia, Midwest, Utah
subbituminous	77	0.9	16	1	Rocky Mountains
lignite	71	1.0	23	1	Montana

Peat, a precursor to coal, is the partially decayed remains of plants that grow in swampy areas. It is removed from the ground in the form of soggy bricks of mud that will not burn until they have been dried. If a peat bog were buried under many layers of sediment for a few million years, the peat could eventually be compressed and heated enough to become lignite, the lowest grade of coal; given enough time and heat, lignite would eventually become anthracite, a much better fuel.

For us to use the potential energy stored in coal, it first must be mined from the ground. This process in itself uses a great deal of resources and has its own environmental impacts. Coal then typically undergoes processing to make it suitable for use in **coal-fire power plants**. Finally, the processed coal is burned in these power plants, and the kinetic energy released from its combustion is harnessed for electricity generation or other purposes. Figure 15.6.2 below is a schematic diagram showing a typical layout of a coal-fire power plant. You can also watch a short video of a virtual tour of a coal power plant at the URL provided below.

Power Plant Virtual Tour

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 15.6.1 *Coal-Fueled Power Plant Virtual Tour Video*

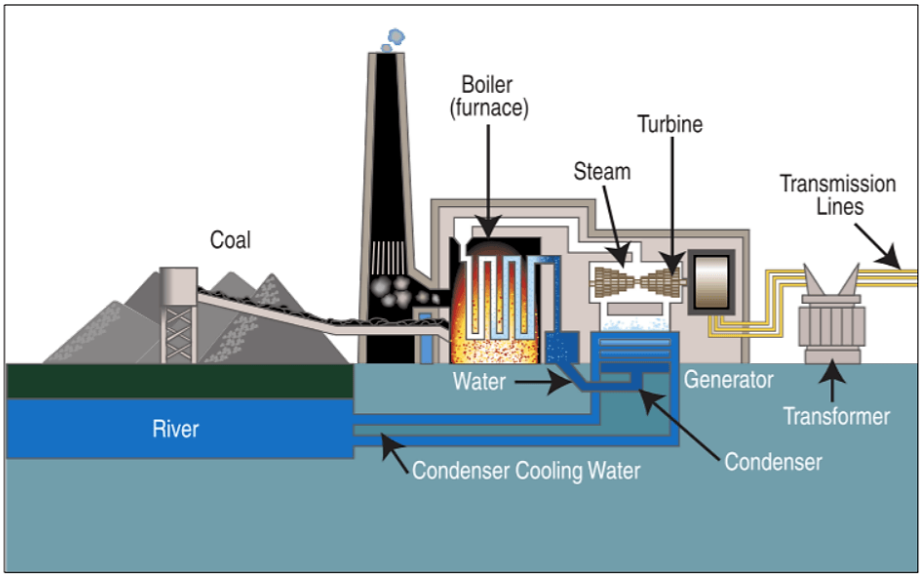


Figure 15.6.2 Diagram of a typical steam-cycle coal power plant (proceeding from left to right). Image by US Tennessee Valley Authority – Public domain. www.tva.com

The Global Carbon Cycle

Figure 15.6.3 illustrates the global carbon cycle, the distribution and flow of carbon on Earth. Normally, the fate of atmospheric CO_2 is to either (1) dissolve in the oceans and eventually precipitate as carbonate rocks or (2) be taken up by plants. The rate of uptake of CO_2 by the ocean is limited by its surface area and the rate at which gases dissolve, which are approximately constant. The rate of uptake of CO_2 by plants, representing about 60 billion metric tons of carbon per year, partly depends on how much of Earth's surface is covered by vegetation. Unfortunately, the rapid deforestation for agriculture is reducing the overall amount of vegetation, and about 60 billion metric tons of carbon are released annually as CO_2 from animal respiration and plant decay. The amount of carbon released as CO_2 every year by fossil fuel combustion is estimated to be about 5.5 billion metric tons. The net result is a system that is slightly out of balance, experiencing a slow but steady increase in atmospheric CO_2 levels. As a result, average CO_2 levels have increased by about 30% since 1850.

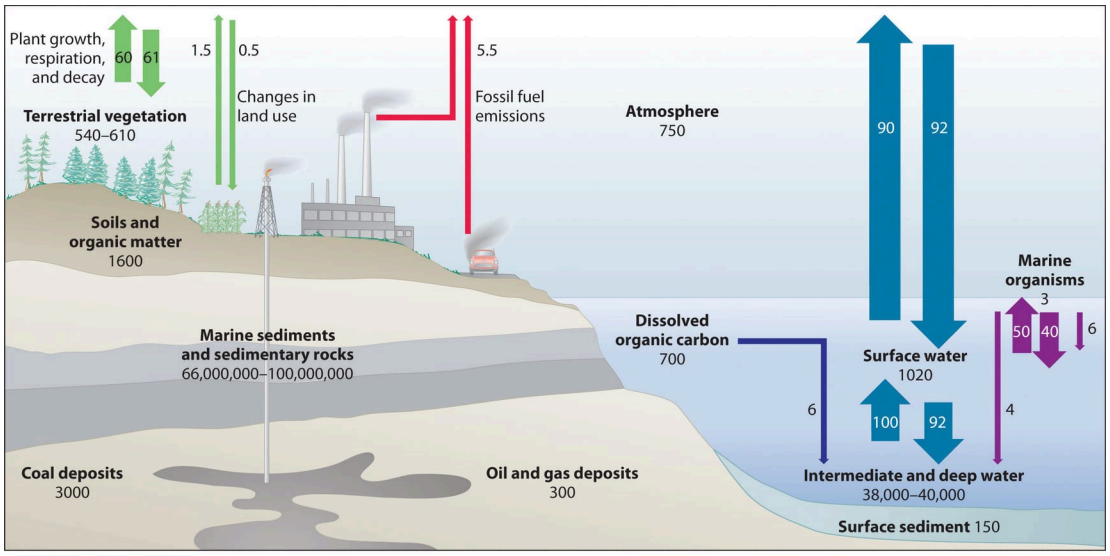


Figure 15.6.3 The global carbon cycle.

Most of Earth's carbon is found in the crust, where it is stored as calcium and magnesium carbonate in sedimentary rocks. The oceans also contain a large reservoir of carbon, primarily as the bicarbonate ion (HCO_3^-). Green plants consume about 60 billion metric tons of carbon per year as CO_2 during photosynthesis, and about the same amount of carbon is released as CO_2 annually from animal and plant respiration and decay. The combustion of fossil fuels releases about 5.5 billion metric tons of carbon per year as CO_2.

Pollution from Coal Burning

In the United States and most of the world, most of the coal consumed is used as a fuel to generate electricity. Burning coal produces emissions such as **sulfur dioxide** (SO_2) and **nitrogen oxides** (NO_x) that are associated with acid rain (more on this in chapter 6). **Carbon dioxide** (CO_2), another emission resulting from burning coal, is a major greenhouse gas that is associated with global warming (see Chapter 13). Burning of coal is classified as incomplete combustion, since the reaction of carbon (in coal) with oxygen produces carbon monoxide and/or carbon (soot) in addition to carbon dioxide.

Burning coal produces emissions that also impact human health. Emissions such as sulfur dioxide (SO_2), nitrogen oxides (NO_x) and particulates contribute to respiratory illnesses. Particulates also contribute to a condition among coal miners and other coal workers known as coal workers' pneumoconiosis (CWP) or black lung disease, which results from long exposure to coal dust. Inhaled coal dust progressively builds up in the lungs and is unable to be removed by the body; this leads to inflammation, fibrosis, and in worse cases, tissue death (necrosis).

Coal is the largest source of **mercury** and also a source of other **heavy metals**, many of which have been linked to both neurological and developmental problems in humans and other animals. Mercury concentrations in the air usually are low and of little direct concern. However, when mercury enters water, either directly or through deposition from the air, biological processes transform it into **methylmercury**, a highly toxic chemical that accumulates in fish and the animals (including humans) that eat fish.

Reducing the Environmental Impacts of Coal Use

Regulations such as the **Clean Air Act** and the **Clean Water Act** require industries to reduce pollutants released into the air and water. Below are some actions that have been taken to reduce the negative impacts of coal on human and environmental health:

- **Clean coal technology**: Industry has found several ways to reduce sulfur, NO_x, and other impurities from coal before burning.
- Coal consumers have shifted toward greater use of low sulfur coal.

• Power plants use **scrubbers**, to clean SO_2, NO_x, particulate matter, and mercury from the smoke before it leaves their smokestacks. In addition, industry and the U.S. government have cooperated to develop technologies that make coal more energy-efficient so less needs to be burned.

• Research is underway to address emissions of carbon dioxide from coal combustion. **Carbon capture & sequestration** separates CO_2 from emissions sources and recovers it in a concentrated stream. The CO_2 can then be sequestered, which puts CO_2 into storage, possibly underground, where it will remain permanently.

• Reuse and recycling can also reduce coal's environmental impact. Land that was previously used for coal mining can be reclaimed and used for airports, landfills, and golf courses. Waste products captured by scrubbers can be used to produce products like cement and synthetic gypsum for wallboard.

Summary

- Coal is a complex solid material derived primarily from plants that died and were buried hundreds of millions of years ago and were subsequently subjected to high temperatures and pressures.
- Coal is classified into four main types, depending on the types and amounts of carbon present and on the amount of heat energy the coal can produce, including anthracite, bituminous, subbituminous, and lignite.
- The processing of coal is described as well as the environmental and health impacts of its use.
- Research is underway and various approaches are implemented (clean coal technology, use of low sulfur coal, use of scrubbers etc.) to reduce the environmental impacts of coal use.

Contributors and Attributions

Libretext: Introduction to Environmental Science (Zendher et al.)

Libretext: General Chemistry (Petrucci et al.)

Anne Marie Helmenstine, Ph.D. "What Is a Combustion Reaction?" *ThoughtCo*, www.thoughtco.com/combustion-reactions-604030.

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15.7: Natural Gas and Petroleum

Learning Objectives

- Describe the nature and processing of natural gas, petroleum, and gasoline.
- List different alternative fuels.

Crude oil is frequently found in reservoirs along with natural gas. In the past, natural gas was either burned or allowed to escape into the atmosphere. Now, technology has been developed to capture the natural gas and either reinject it into the well or compress it into **liquid natural gas** (LNG).

Natural Gas

Natural gas is predominately composed of methane (CH_4). Some of the gases that are produced along with methane, such as butane and propane (by-products), are separated and cleaned at a gas processing plant. The by-products, once removed, are used in a number of ways. For example, propane can be used for cooking on gas grills. Natural gas withdrawn from a well may contain liquid hydrocarbons and non-hydrocarbon gases. This is called "wet" natural gas. The natural gas is separated from these components near the site of the well or at a processing plant. The gas is then considered "dry" and is sent through pipelines to a local distribution company, and, ultimately, to the consumer.

Most of the natural gas consumed in the United States is produced in the United States. Some is imported from Canada and shipped to the United States in pipelines. A small amount of natural gas is shipped to the United States as LNG.

Fracking for Gas

Conventional natural gas is found in permeable reservoirs, typically composed of sandstone or limestone, where extraction is relatively straightforward because the gas generally flows freely. Unconventional gas is found in rocks with extremely low permeability, which makes extracting it much more difficult. Such gas is extracted by employing so-called “unconventional” techniques such as hydraulic fracturing (fracking), which has been in use since the late 1940s. In recent decades, fracking technology has greatly improved, and its use has been expanded. The process of fracking for gas is very similar to that of fracking for oil, and the environmental impacts are similar also.

Petroleum

Petroleum Oil is currently the most widely used fossil fuel and accounts for about one third of global energy consumption. Unlike coal, which is primarily used as a fuel for electricity generation, oil is primarily used as a fuel for **transportation**. Oil is also used to manufacture plastics and other synthetic compounds ubiquitous to our everyday life. **Crude** (unprocessed) oil varies greatly in appearance depending on its composition. It is usually black or dark brown (although it may be yellowish, reddish, or even greenish). In the reservoir it is usually found in association with natural gas, which being lighter forms a gas cap over the oil.

Oil is made up of hydrocarbons which are molecules that contain hydrogen and carbon in various lengths and structures, from straight chains to branching chains to rings. Hydrocarbons contain a lot of energy and many of the things derived from crude oil like gasoline, diesel fuel, paraffin wax and so on take advantage of this energy.

Extraction

Oil is mainly obtained by drilling either on land (**onshore**) or in the ocean (**offshore**). Early offshore drilling was generally limited to areas where the water was less than 300 feet deep. Oil and natural gas drilling rigs now operate in water as deep as two miles. Offshore oil producers are required to take precautions to prevent pollution, spills, and significant changes to the ocean environment. Offshore rigs are designed to withstand hurricanes. Offshore production is much more expensive than land-based production. When offshore oil wells are no longer productive enough to be economical, they are sealed and abandoned according to applicable regulations.

Processing and Refining

When extracted, crude oil consists of many types of hydrocarbons as well as some unwanted substances such as sulfur, nitrogen, oxygen, dissolved metals, and water all mixed together. Unprocessed crude oil is therefore, not generally useful in industrial applications and must first be separated into different useable products at a **refinery** (Figure 15.7.1). All refineries perform three basic steps: separation, conversion, and treatment in the processing and refining of crude oil.



Figure 15.7.1 *Tesoro Corporation Oil Refinery in Anacortes, Washington. Photo by Walter Siegmund.* commons.wikimedia.org/wiki/O...nery_31904.JPG

During **separation**, the various products (hydrocarbons) are separated in to different components (called *fractions*), by taking advantage of the differences in boiling temperature of the components. This process is called *fractional distillation* and involves heating up the crude, letting it vaporize and then condensing the vapor. The lightest components have the lowest boiling temperature and rise to the top while the heaviest which also have the highest boiling temperature remain at the bottom.

Conversion is the chemical processing in which some of the fractions are transformed in to other products, for example, a refinery can turn diesel fuel into gasoline depending on the demand for gasoline. Conversion can involve breaking larger hydrocarbon chains into smaller ones (cracking), combining smaller chains into larger ones (unification) or rearranging the molecules to created desired products (alteration).

Treatment is done to the fractions to remove impurities such as sulfur, nitrogen and water among others. Refineries also combine the various fractions (processed and unprocessed) into mixtures to make desired products. For example, different mixtures of hydrocarbon chains can create gasolines with different octane ratings, with and without additives, lubricating oils of various weights and grades (e.g., WD-40, 10W-40, 5W-30, etc.), heating oil and many others. The products are stored on-site until they can be delivered to various markets such as gas stations, airports and chemical plants.

A 42 U.S. gallon barrel of crude oil yields about 45 gallons of petroleum products because of refinery processing gain. This increase in volume is similar to what happens to popcorn when it is popped. Gasoline makes up the largest fraction of all petroleum products obtained (Figure 15.7.2). Other products include diesel fuel and heating oil, jet fuel, petrochemical feedstocks, waxes, lubricating oils, and asphalt.

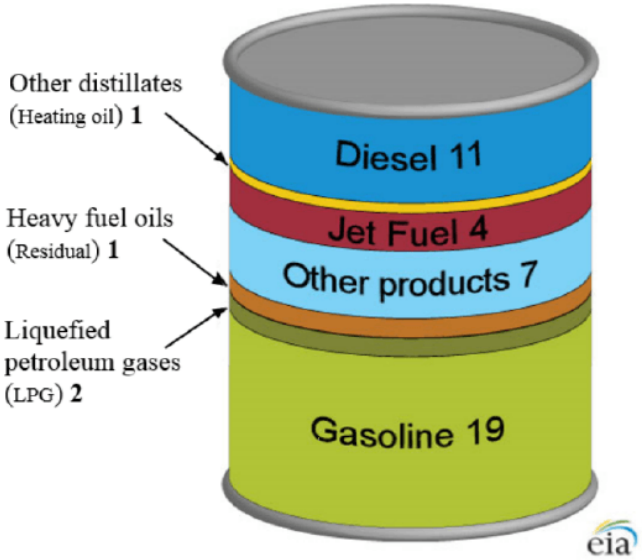


Figure 15.7.2 Main products (measured in gallons) made from a barrel of crude oil, 2013. Source: U.S. Energy information administration http://www.eia.gov/energyexplained/i...?page=oil_home

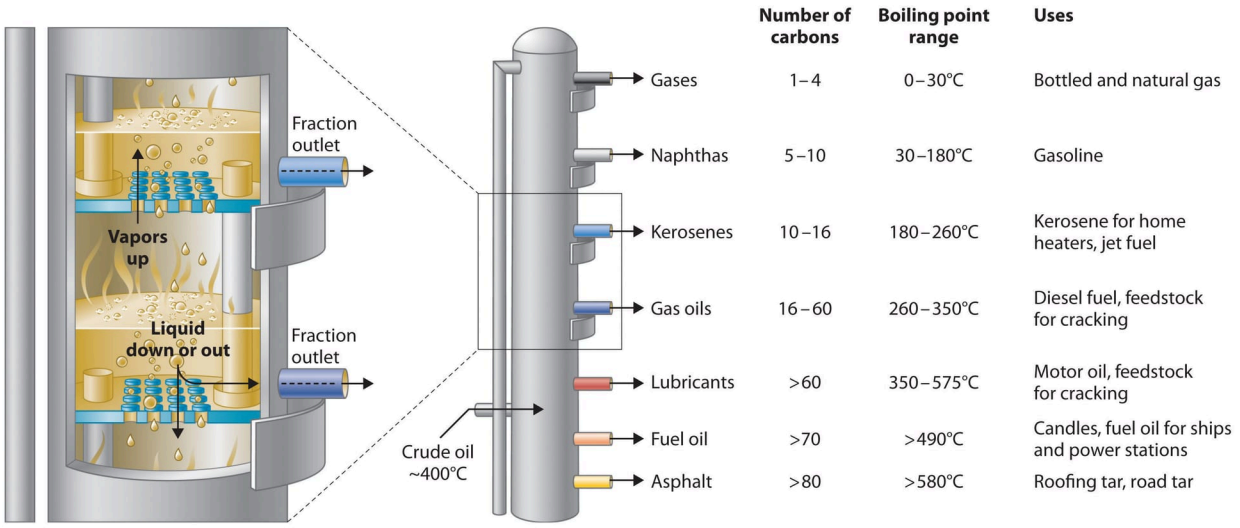
Fracking for oil

Hydraulic fracturing, informally referred to as "fracking," is an oil well development process that typically involves injecting water, sand, and chemicals under high pressure into a bedrock formation via the well. This process is intended to create new fractures in the rock as well as increase the size, extent, and connectivity of existing fractures. Hydraulic fracturing is a well-stimulation technique used commonly in low-permeability rocks like tight sandstone, shale, and some coal beds to increase oil flow to a well from petroleum-bearing rock formations.

There are concerns regarding the potential contamination of fresh groundwater resources from oil and gas extraction wells that use hydraulic fracturing; either from the petroleum resource being produced or from the chemicals introduced in the fracturing process. Fracking fluid flowback – the fluid pumped out of the well and separated from oil and gas – not only contains the chemical additives used in the drilling process but also contains heavy metals, radioactive materials, **volatile organic compounds** (VOCs) and hazardous air pollutants such as benzene, toluene, ethylbenzene and xylene. In some cases, this contaminated water is sent to water treatment plants that are not equipped to deal with some of these classes of contamination.

Gasoline

Petroleum is converted to useful products such as gasoline in three steps: distillation, cracking, and reforming. Part (a) in Figure \({15{.}7{.}\eatSpaces{3} \endSpaces}\ shows a cutaway drawing of a column used in the petroleum industry for separating the components of crude oil. The petroleum is heated to approximately 400°C (750°F), at which temperature it has become a mixture of liquid and vapor. This mixture, called the feedstock, is introduced into the refining tower. The most volatile components (those with the lowest boiling points) condense at the top of the column where it is cooler, while the less volatile components condense nearer the bottom. Some materials are so nonvolatile that they collect at the bottom without evaporating at all. Thus the composition of the liquid condensing at each level is different. These different fractions, each of which usually consists of a mixture of compounds with similar numbers of carbon atoms, are drawn off separately. Part (b) Figure \({15{.}7{.}\eatSpaces{3} \endSpaces}\ shows the typical fractions collected at refineries, the number of carbon atoms they contain, their boiling points, and their ultimate uses. These products range from gases used in natural and bottled gas to liquids used in fuels and lubricants to gummy solids used as tar on roads and roofs.



	Number of carbons	Boiling point range	Uses
Gases	1–4	0–30°C	Bottled and natural gas
Naphthas	5–10	30–180°C	Gasoline
Kerosenes	10–16	180–260°C	Kerosene for home heaters, jet fuel
Gas oils	16–60	260–350°C	Diesel fuel, feedstock for cracking
Lubricants	>60	350–575°C	Motor oil, feedstock for cracking
Fuel oil	>70	>490°C	Candles, fuel oil for ships and power stations
Asphalt	>80	>580°C	Roofing tar, road tar

Figure 15.7.3 *The Distillation of Petroleum. (a) This is a diagram of a distillation column used for separating petroleum fractions. (b) Petroleum fractions condense at different temperatures, depending on the number of carbon atoms in the molecules, and are drawn off from the column. The most volatile components (those with the lowest boiling points) condense at the top of the column, and the least volatile (those with the highest boiling points) condense at the bottom.*

Octane Ratings of Gasolines

The quality of a fuel is indicated by its octane rating, which is a measure of its ability to burn in a combustion engine without knocking or pinging. Knocking and pinging signal premature combustion (Figure 15.7.4) which can be caused either by an engine malfunction or by a fuel that burns too fast. In either case, the gasoline-air mixture detonates at the wrong point in the engine cycle, which reduces the power output and can damage valves, pistons, bearings, and other engine components. The various gasoline formulations are designed to provide the mix of hydrocarbons least likely to cause knocking or pinging in a given type of engine performing at a particular level.

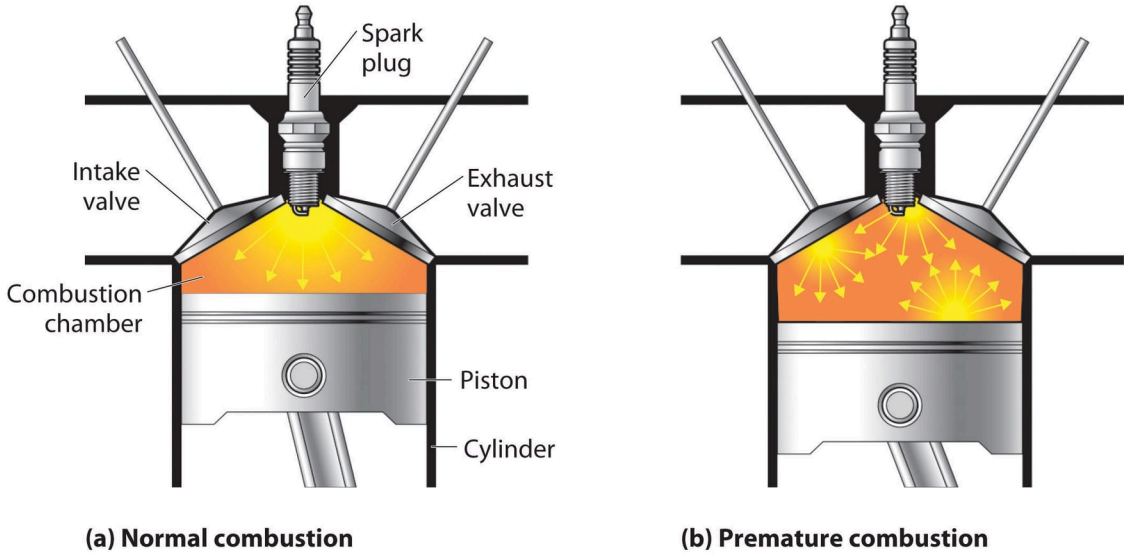


Figure 15.7.4 *The Burning of Gasoline in an Internal Combustion Engine. (a) Normally, fuel is ignited by the spark plug, and combustion spreads uniformly outward. (b) Gasoline with an octane rating that is too low for the engine can ignite prematurely, resulting in uneven burning that causes knocking and pinging.*

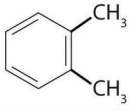
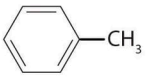
The octane scale was established in 1927 using a standard test engine and two pure compounds: n-heptane and isooctane (2,2,4-trimethylpentane). n-Heptane, which causes a great deal of knocking on combustion, was assigned an octane rating of 0,

whereas isooctane, a very smooth-burning fuel, was assigned an octane rating of 100. Chemists assign octane ratings to different blends of gasoline by burning a sample of each in a test engine and comparing the observed knocking with the amount of knocking caused by specific mixtures of n-heptane and isooctane. For example, the octane rating of a blend of 89% isooctane and 11% n-heptane is simply the average of the octane ratings of the components weighted by the relative amounts of each in the blend. Converting percentages to decimals, we obtain the octane rating of the mixture:

$$0.89(100) + 0.11(0) = 89 \tag{3.8.1}$$

As given in Table \({15{.}7{.}\eatSpaces{1} \endSpaces}\, many compounds that are now available have octane ratings greater than 100, which means they are better fuels than pure isooctane. In addition, antiknock agents, also called octane enhancers, have been developed. One of the most widely used for many years was tetraethyllead [$(C_2H_5)_4Pb$], which at approximately 3 g/gal gives a 10–15-point increase in octane rating. Since 1975, however, lead compounds have been phased out as gasoline additives because they are highly toxic. Other enhancers, such as methyl t-butyl ether (MTBE), have been developed to take their place. They combine a high octane rating with minimal corrosion to engine and fuel system parts. Unfortunately, when gasoline containing MTBE leaks from underground storage tanks, the result has been contamination of the groundwater in some locations, resulting in limitations or outright bans on the use of MTBE in certain areas. As a result, the use of alternative octane enhancers such as ethanol, which can be obtained from renewable resources such as corn, sugar cane, and, eventually, corn stalks and grasses, is increasing.

Table 15.7.1 *The Octane Ratings of Some Hydrocarbons and Common Additives.*

Name	Condensed Structural Formula	Octane Rating	Name	Condensed Structural Formula	Octane Rating
n-heptane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	0	*o*-xylene		107
n-hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$	25	ethanol	CH_3CH_2OH	108
n-pentane	$CH_3CH_2CH_2CH_2CH_3$	62	*t*-butyl alcohol	$(CH_3)_3COH$	113
isooctane	$(CH_3)_3CCH_2CH(CH_3)_2$	100	*p*-xylene		116
benzene		106	methyl *t*-butyl ether	$H_3COC(CH_3)_3$	116
methanol	CH_3OH	107	toluene		118

Alternative Fuels

Alternative means to power vehicles is a hot topic in environmental chemistry. Hybrid vehicles, ethanol, biodiesel (Figure 15.7.5), natural gas, and hydrogen fuel cells are all options for powering vehicles that reduce the environmental impact of greenhouse gases in the environment. The main concern for these alternative fuels is their efficiency vs. cost when compared to fossil fuels. Table 15.7.2 shows the chemical structure for several fuels, as well as the energy content of each.



Figure 15.7.5 *Biofuel station (SECO)*

*Table 15.7.2 Energy Content of Fuels**.

	Gasoline	No. 2 Diesel	Biodiesel	Ethanol	Hydrogen	Liquefied Natural Gas (LNG)	Liquefied Petroleum Gas
Chemical Structure	C4 to C12	C8 to C25	Methyl esters of C12 to C22 fatty acids	CH_3CH_2OH	H_2	CH_4	C^3H_8 (majority) and C4H10 (minority)
Energy Content (Higher Heat Value)	124,340 Btu/gal (g)	137,380 Btu/gal (g)	127,960 Btu/gal for B100 (g)	84,530 Btu/gal for E100 (g)	61,013 Btu/lb (g)	84,820 Btu/gal (g)	91,410 Btu/gal (g
Energy Contained in Various Alternative Fuels as Compared to One Gallon of Gasoline	100%	113%	103%	77%	100%	64%	73%

*Table created at: http://www.afdc.energy.gov/afdc/fuels/properties.html

Ethanol

Ethanol can be used in varying percent grades by vehicles. Gasohol is 10% ethanol, produces less carbon emissions than typical gasoline, but decreases the miles per gallon (MPG) of the vehicle slightly. E85 is up to 85% ethanol, can be less expensive depending upon where you live, but lowers the MPG up to 30% compared to typical gasoline. Let's look at the bond enthalpy change for the burning of fossil fuels vs. the burning of E85 to understand the drop in MPG.

Summary

- The extraction and processing of natural gas (mainly methane) and petroleum oil were discussed.
- Petroleum is converted to useful products such as gasoline by distillation, cracking, and reforming.
- Alternative means to power vehicles and reduce the effect of greenhouse gases in the environment include hybrid vehicles, ethanol, biodiesel , natural gas, and hydrogen fuel cells.

Contributors and Attributions

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15.8: Convenient Energy

Learning Objective

- Describe the gasification and liquefaction of coal and the interest in its conversion.

Oil and natural gas resources are limited. Current estimates suggest that the known reserves of petroleum will be exhausted in about 60 years, and supplies of natural gas are estimated to run out in about 120 years. Coal, on the other hand, is relatively abundant, making up more than 90% of the world's fossil fuel reserves. As a solid, coal is much more difficult to mine and ship than petroleum (a liquid) or natural gas.

Coal Gasification and Liquefaction

A great deal of current research focuses on developing methods to convert coal to gaseous fuels (*coal* gasification) or liquid fuels (coal liquefaction). In the most common approach to coal gasification, coal reacts with steam to produce a mixture of CO and H_2 known as synthesis gas, or syngas:Because coal is 70%–90% carbon by mass, it is approximated as C in Equation 15.8.1.

$$\mathrm{C_{(s)} + H_2O_{(g)} \rightarrow CO_{(g)} + H_{2(g)} \quad \Delta H = 131\ kJ} \tag{15.8.1}$$

Converting coal to syngas removes any sulfur present and produces a clean-burning mixture of gases.

Syngas is also used as a reactant to produce methane and methanol. A promising approach is to convert coal directly to methane through a series of reactions:

$$\begin{array}{l} \mathrm{2C(s) + 2H_2O(g) \rightarrow \cancel{2CO(g)} + \cancel{2H_2(g)} \quad \Delta H_1 = 262\ kJ} \\ \mathrm{\cancel{CO(g)} + \cancel{3H_2(g)} \rightarrow CH_4(g) + \cancel{H_2O(g)} \quad \Delta H_3 = -206\ kJ} \end{array} \quad \begin{array}{l} \mathrm{\cancel{CO(g)} + \cancel{H_2O(g)} \rightarrow CO_2(g) + \cancel{H_2(g)} \quad \Delta H_2 = -41\ kJ} \\ \mathrm{Overall:\ \ 2C(s) + 2H_2O(g) \rightarrow CH_4(g) + CO_2(g) \quad \Delta H_{comb} = 15\ kJ} \end{array}$$

Burning a small amount of coal or methane provides the energy consumed by these reactions. Unfortunately, methane produced by this process is currently significantly more expensive than natural gas. As supplies of natural gas become depleted, however, this coal-based process may well become competitive in cost.

Similarly, the techniques available for converting coal to liquid fuels are not yet economically competitive with the production of liquid fuels from petroleum. Current approaches to coal liquefaction use a catalyst to break the complex network structure of coal into more manageable fragments. The products are then treated with hydrogen (from syngas or other sources) under high pressure to produce a liquid more like petroleum. Subsequent distillation, cracking, and reforming can be used to create products similar to those obtained from petroleum. The total yield of liquid fuels is about 5.5 bbl of crude liquid per ton of coal (1 bbl is 42 gal or 160 L). Although the economics of coal liquefaction are currently even less attractive than for coal gasification, liquid fuels based on coal are likely to become economically competitive as supplies of petroleum are consumed.

Summary

- There is great interest in developing methods to convert coal to gaseous fuels (coal gasification) or liquid fuels (coal liquefaction) as it is more convenient to mine and transport gas and liquid fuels.
- Converting coal to syngas (synthesis gas) removes any sulfur present and produces a clean-burning mixture of gases.

Contributors and Attributions

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15.9: Nuclear Energy

Learning Objective

- List the benefits and problems with nuclear energy.

Nuclear power is the use of nuclear reactions that release nuclear energy to generate heat, which most frequently is then used in steam turbines to produce electricity in a nuclear power plant. Nuclear power can be obtained from nuclear fission, nuclear decay and nuclear fusion reactions. Presently, the vast majority of electricity from nuclear power is produced by nuclear fission of uranium and plutonium. Nuclear decay processes are used in niche applications such as radioisotope thermoelectric generators. Generating electricity from fusion power remains at the focus of international research.

Civilian nuclear power supplied 2,563 terawatt hours (TWh) of electricity in 2018, equivalent to about 10% of global electricity generation, and was the second largest low-carbon power source after hydroelectricity. As of December 2019, there are 443 civilian fission reactors in the world, with a combined electrical capacity of 395 gigawatt (GW). There are also 56 nuclear power reactors under construction and 109 reactors planned, with a combined capacity of 60 GW and 120 GW, respectively. The United States has the largest fleet of nuclear reactors, generating over 800 TWh zero-emissions electricity per year with an average capacity factor of 92%. Most reactors under construction are generation III reactors in Asia.

Nuclear power has one of the lowest levels of fatalities per unit of energy generated compared to other energy sources. Coal, petroleum, natural gas and hydroelectricity each have caused more fatalities per unit of energy due to air pollution and accidents.[10] Since its commercialization in the 1970s, nuclear power has prevented about 1.84 million air pollution-related deaths and the emission of about 64 billion tonnes of carbon dioxide equivalent that would have otherwise resulted from the burning of fossil fuels.

There is a debate about nuclear power. Proponents, such as the World Nuclear Association and Environmentalists for Nuclear Energy, contend that nuclear power is safe and it reduces carbon emissions. Nuclear power opponents, such as Greenpeace and NIRS, contend that nuclear power poses many threats to people and the environment.

There are over thirty countries that use nuclear power to generate electricity (see Table 15.9.1. There were about 450 nuclear power reactors worldwide, producing close to 400,000 MW (MegaWatts) of electrical capacity. Commercial nuclear reactors can be found in North and South America, Europe, Africa, and Asia. The United States has the most reactors of any other countries. There are around ninety-eight reactors in the United States that provide around twenty percent of the electrical energy in the United States. Other countries, like France, employ around sixty nuclear reactors to produce 70% of their electrical power.

Table 15.9.1: Nuclear Share of Electricity Generation and Number of Operated Reactors in 2019. Source: International Atomic Energy Agency (IAEA)

Country	Number of Operated Reactors	Total Net Electrical Capacity [MW]	Nuclear Electricity Supplied [GW.h]	Nuclear Share [%]
UNITED STATES OF AMERICA	98	99648	809358.57	19.7
UNITED KINGDOM	15	8923	51032.09	15.6
UKRAINE	15	13107	78144.26	53.9
SWITZERLAND	5	3333	25369.65	23.9
SWEDEN	8	8592	64428.86	34.0
SPAIN	7	7121	55856.07	21.4
SOUTH AFRICA	2	1860	13602.57	6.7
SLOVENIA	1	688	5532.98	37.0
Total	449	392779	2586163.02	N

Country	Number of Operated Reactors	Total Net Electrical Capacity [MW]	Nuclear Electricity Supplied [GW.h]	Nuclear Share [%]
SLOVAKIA	4	1814	14282.25	53.9
RUSSIA	39	28448	195535.15	19.7
ROMANIA	2	1300	10368.21	18.5
PAKISTAN	5	1318	9065.80	6.6
NETHERLANDS	1	482	3700.71	3.2
MEXICO	2	1552	10880.73	4.5
KOREA, REPUBLIC OF	25	23833	138809.35	26.2
JAPAN	38	36476	65681.92	7.5
IRAN, ISLAMIC REPUBLIC OF	1	915	5865.73	1.8
INDIA	22	6255	40740.49	3.2
HUNGARY	4	1902	15414.83	49.2
FRANCE	58	63130	382402.75	70.6
FINLAND	4	2794	22914.88	34.7
CZECH REPUBLIC	6	3932	28581.12	35.2
CHINA	48	45518	330122.19	4.9
CANADA	19	13554	94853.85	14.9
BULGARIA	2	2006	15868.88	37.5
BRAZIL	2	1884	15224.11	2.7
BELGIUM	7	5930	41421.66	47.6
ARMENIA	1	375	2028.96	27.8
ARGENTINA	3	1641	7926.96	5.9
Total	449	392779	2586163.02	N

Nuclear Power Plants

After fabrication, fuel assemblies are transported to nuclear power plants where they are used as a source of energy for generating electricity. They are stored onsite until they are needed by the reactor operators. At this stage, the uranium is only mildly radioactive, and essentially all radiation is contained within the metal tubes. When needed, the fuel is loaded into a reactor core (Figure 15.9.2). Typically, about one third of the reactor core (40 to 90 fuel assemblies) is changed out every 12 to 24 months.

The most common type of reactors are the **pressurized water reactors** (PWR) (Figure 15.9.2) in which water is pumped through the reactor core and heated by the fission process. The water is kept under high pressure inside the reactor so it does not boil. The heated water from the reactor passes through tubes inside the steam generator where the heat is transferred to water flowing around the tubes in the steam generator. The water in the steam generator boils and turns to steam. The steam is piped to the turbines. The force of the expanding steam drives the turbines, which spin a magnet in coil of wire – the generator– to produce electricity.

After passing through the turbines, the steam is converted back to water by circulating it around tubes carrying cooling water in the condenser. The condensed steam – now water – is returned to the steam generators to repeat the cycle.

The three water systems (condenser, steam generator, and reactor) are separate from each other and are not permitted to mix. Water in the reactor is radioactive and is contained within the containment structure whereas water in the steam generator and

condenser is nonradioactive.

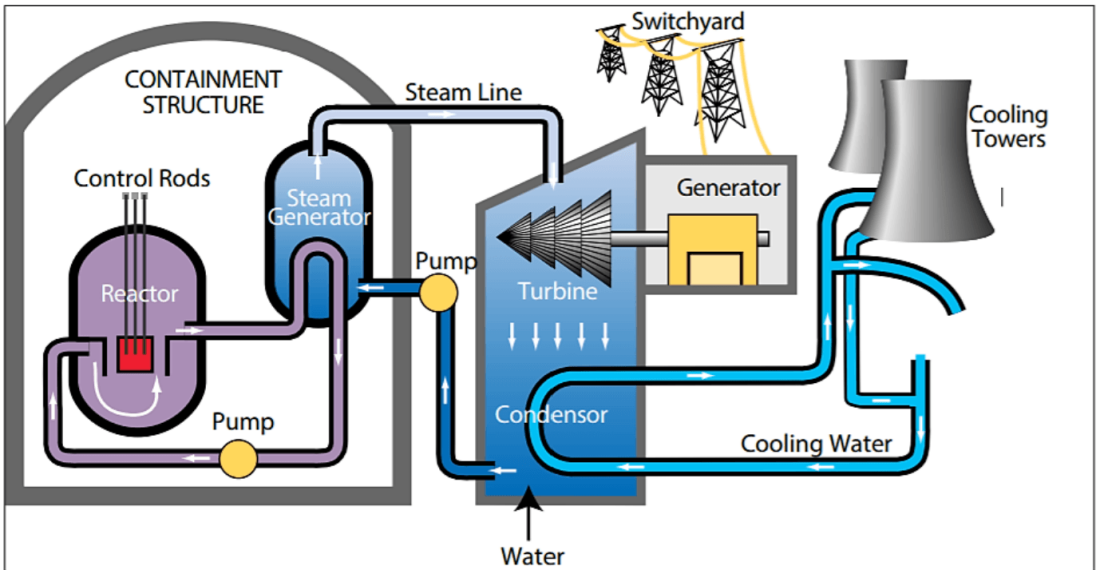


Figure 15.9.1: A schematic diagram of a pressurized water reactor (PWR), the most common type of nuclear reactor. (Public Domain; Tennessee Valley Authority)

The Nuclear Advantage: Minimal Air Pollution

By using fission, nuclear power plants generate electricity without emitting air pollutants like those emitted by fossil fuel-fired power plants. This means that financial costs related to chronic health problems caused by air pollutants such as particulate material, carbon monoxide, nitrogen oxides and ozone among others are significantly reduced. In addition nuclear reactors do not produce carbon dioxide while operating which means that nuclear energy does not contribute to the global warming problem.

Another benefit of nuclear energy over fossil fuels especially coal is that uranium generates far more power per unit weight or volume. This means that less of it needs to be mined and consequently the damage to the landscapes is less especially when compared to the damage that results from coal mining such as mountaintop removal.

Problems with Nuclear Power

The main environmental concern related to nuclear power is the creation of radioactive wastes such as uranium mill tailings, spent (used) reactor fuel, and other radioactive wastes. These materials can remain radioactive and dangerous to human health for thousands of years. Radioactive wastes are classified as low-level and high-level. By volume, most of the waste related to the nuclear power industry has a relatively low-level of radioactivity. Uranium mill tailings contain the radioactive element radium, which decays to produce **radon**, a radioactive gas. Most uranium mill tailings are placed near the processing facility or mill where they come from. Uranium mill tailings are covered with a barrier of material such as clay to prevent radon from escaping into the atmosphere, and they are then covered by a layer of soil, rocks, or other materials to prevent erosion of the sealing barrier.

The other types of low-level radioactive waste are the tools, protective clothing, wiping cloths, and other disposable items that get contaminated with small amounts of radioactive dust or particles at nuclear fuel processing facilities and power plants. These materials are subject to special regulations that govern their handling, storage, and disposal so they will not come in contact with the outside environment.

High-level radioactive waste consists of spent nuclear reactor fuel (i.e., fuel that is no longer useful for producing electricity). The spent reactor fuel is in a solid form consisting of small fuel pellets in long metal tubes called rods. Spent reactor fuel assemblies are initially stored in specially designed pools of water, where the water cools the fuel and acts as a radiation shield. Spent reactor fuel assemblies can also be stored in specially designed dry storage containers. An increasing number of reactor operators now store their older spent fuel in dry storage facilities using special outdoor concrete or steel containers with air cooling. There is currently no permanent disposal facility in the United States for high-level nuclear waste.

When a nuclear reactor stops operating, it must be **decommissioned**. This involves safely removing the reactor and all equipment that has become radioactive from service and reducing radioactivity to a level that permits other uses of the property. The U.S. Nuclear Regulatory Commission has strict rules governing nuclear power plant decommissioning that involve cleanup of radioactively contaminated plant systems and structures, and removal of the radioactive fuel.

The processes for mining and refining uranium ore and making reactor fuel require large amounts of energy. Nuclear power plants have large amounts of metal and concrete, which also require large amounts of energy to manufacture. If fossil fuels are used for mining and refining uranium ore or in constructing the nuclear plant, then the emissions from burning those fuels could be associated with the electricity that nuclear power plants generate.

Nuclear Accidents

A **nuclear meltdown**, or uncontrolled nuclear reaction in a nuclear reactor, can potentially result in widespread contamination of air and water. Some serious nuclear and radiation accidents have occurred worldwide. The most severe accident was the Chernobyl accident of 1986 in the then Soviet Union (now Ukraine) which killed 31 people directly and sickened or caused cancer in thousands more. The Fukushima Daiichi nuclear disaster (2011) in Japan was caused by a 9.0 magnitude earthquake that shut down power supply and a tsunami that flooded the plant's emergency power supply. This resulted in the release of radioactivity although it did not directly result in any deaths at the time of the disaster. Another nuclear accident was the Three Mile Island accident (1979) in Pennsylvania, USA. This accident resulted in a near disastrous core meltdown that was due to a combination of human error and mechanical failure but did not result in any deaths and no cancers or otherwise have been found in follow up studies of this accident. While there are potentially devastating consequences to a nuclear meltdown, the likelihood of one occurring is extremely small. After every meltdown, including the 2011 Fukushima Daiichi disaster, new international regulations were put in place to prevent such an event from occurring again.

Breeder Reactors: Making More Fuel Than They Burn

Because $^{235}_{92}\mathrm{U}$ is only 0.7 percent of naturally occurring uranium, its supply is fairly limited and could well only last for about 50 years of full-scale use. The other 99 percent of the uranium can also be utilized if it is first converted into plutonium by neutron bombardment:

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{239}_{94}\mathrm{Pu} + 2\,{}^{0}_{-1}\mathrm{e}$$

$^{239}_{94}\mathrm{Pu}$ is also fissionable, and so it could be used in a nuclear reactor as well as $^{235}_{92}\mathrm{U}$.

The production of plutonium can be carried out in a breeder reactor which not only produces energy like other reactors but is designed to allow some of the fast neutrons to bombard the $^{235}_{92}\mathrm{U}$, producing plutonium at the same time. More fuel is then produced than is consumed.

Breeder reactors present additional safety hazards to those already outlined. They operate at higher temperatures and use very reactive liquid metals such as sodium in their cooling systems, and so the possibility of a serious accident is higher. In addition the large quantities of plutonium which would be produced in a breeder economy would have to be carefully safeguarded. Plutonium is an α emitter and is very dangerous if taken internally. Its half-life is 24,000 years, and so it will remain in the environment for a long time if dispersed. Moreover, $^{239}_{94}\mathrm{Pu}$ can be separated chemically (not by the much more expensive gaseous diffusion used to concentrate $^{235}_{92}\mathrm{U}$ from fission products and used to make bombs. Such a material will obviously be attractive to terrorist groups, as well as to countries which are not currently capable of producing their own atomic weapons.

Today many nations are considering an expanded role for nuclear power in their energy portfolios. This expansion is driven by concerns about global warming, growth in energy demand, and relative costs of alternative energy sources. In 2008, 435 nuclear reactors in 30 countries provided 16% of the world's electricity. In January 2009, 43 reactors were under construction in 11 countries, with several hundred more projected to come on line globally by 2030.

Nuclear Fusion

The most important fusion process in nature is the one that powers stars. The fusion of hydrogen and helium, which is the primary energy producer in the sun has been discussed in Chapter 11. This section briefly discusses harnessing energy from nuclear fusion to generate electricity.

The fusion reaction of great interest is known as deuterium–tritium fusion (D–T fusion) wherein a deuterium atom and a tritium atom fuse to produce helium-4 (Figure 15.9.3).

$$^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{0}\mathrm{n} \tag{21.6.13}$$

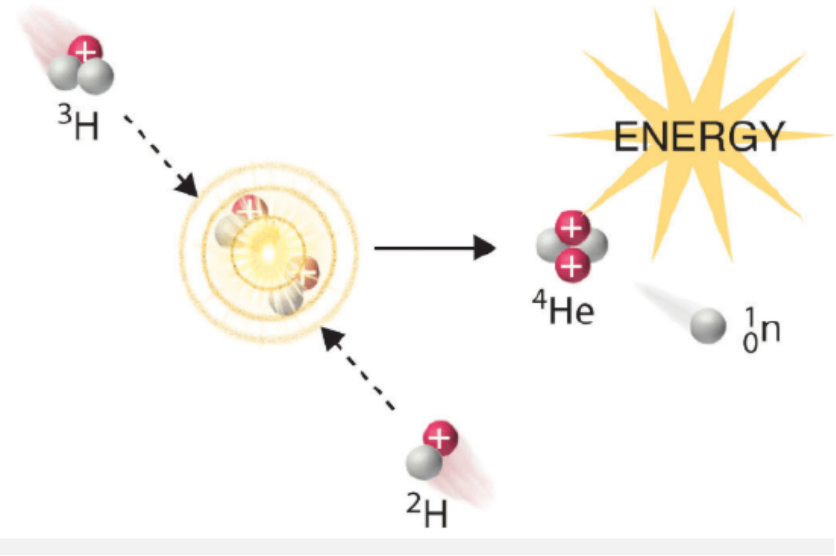


Figure 15.9.2: Nuclear fusion. The fusion of $^{3}\mathrm{H}$ and $^{2}\mathrm{H}$ produces $^{4}\mathrm{He}$ and a neutron and releases an enormous amount of energy.

Fusion power has the potential to provide sufficient energy to satisfy mounting demand, and to do so sustainably, with a relatively small impact on the environment. Nuclear fusion has many potential attractions. Firstly, its hydrogen isotope fuels are relatively abundant – one of the necessary isotopes, deuterium, can be extracted from seawater, while the other fuel, tritium, would be bred from a lithium blanket using neutrons produced in the fusion reaction itself. Furthermore, a fusion reactor would produce virtually no CO_2 or atmospheric pollutants, and its radioactive waste products would mostly be very short-lived compared to those produced by conventional nuclear reactors (fission reactors).

Useful fusion reactions require very high temperatures for their initiation—about 15,000,000 K or more. At these temperatures, all molecules dissociate into atoms, and the atoms ionize, forming plasma. These conditions occur in an extremely large number of locations throughout the universe—stars are powered by fusion. Humans have already figured out how to create temperatures high enough to achieve fusion on a large scale in thermonuclear weapons. A thermonuclear weapon such as a hydrogen bomb contains a nuclear fission bomb that, when exploded, gives off enough energy to produce the extremely high temperatures necessary for fusion to occur.

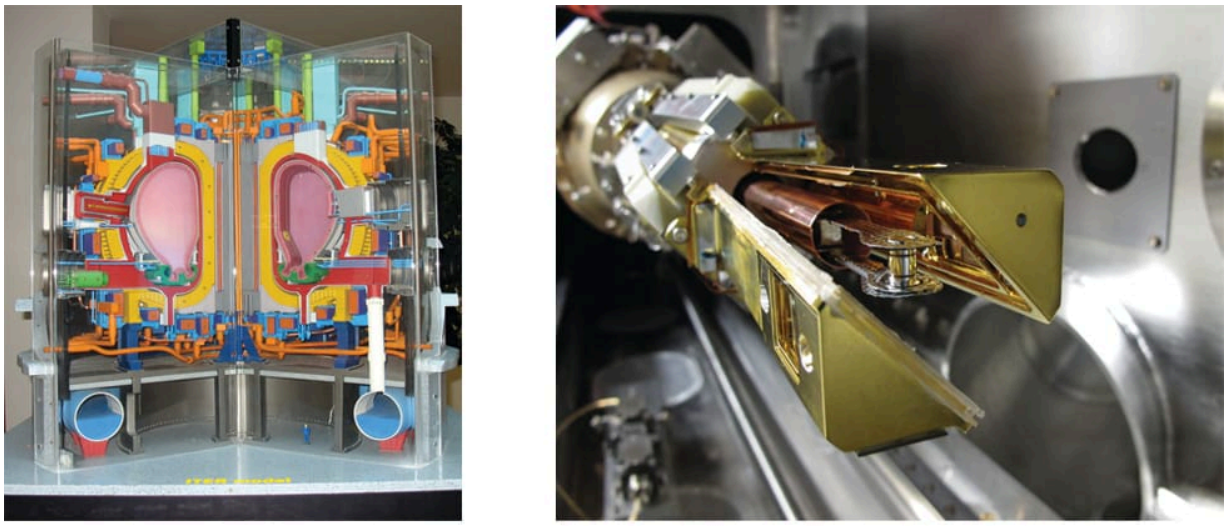


Figure 15.9.3: (a) This model is of the International Thermonuclear Experimental Reactor (ITER) reactor. Currently under construction in the south of France with an expected completion date of 2027, the ITER will be the world's largest experimental Tokamak nuclear fusion reactor with a goal of achieving large-scale sustained energy production. (b) In 2012, the National Ignition Facility at Lawrence Livermore National Laboratory briefly produced over 500,000,000,000 watts (500 terawatts, or 500 TW) of peak power and delivered 1,850,000 joules (1.85 MJ) of energy, the largest laser energy ever produced and 1000 times the power usage of the entire United States in any given moment. Although lasting only a few billionths of a second, the 192 lasers attained the conditions needed for nuclear fusion ignition. This image shows the target prior to the laser shot. (credit a: modification of work by Stephan Mosel)

Another much more beneficial way to create fusion reactions is in a fusion reactor, a nuclear reactor in which fusion reactions of light nuclei are controlled. Because no solid materials are stable at such high temperatures, mechanical devices cannot contain the plasma in which fusion reactions occur. Two techniques to contain plasma at the density and temperature necessary for a fusion reaction are currently the focus of intensive research efforts: containment by a magnetic field and by the use of focused laser beams (Figure 15.9.3). A number of large projects are working to attain one of the biggest goals in science: getting hydrogen fuel to ignite and produce more energy than the amount supplied to achieve the extremely high temperatures and pressures that are required for fusion. The US Department of Energy is funding several sites conducting fusion research as given on the link https://www.usiter.org/fusion/us-fusion-research-sites. One of the research sites is features in the video below Video 15.9.1.

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 15.9.1: The D-III National Fusion Facility, San Diego California.

Summary

- There is still ongoing debate about nuclear power.
- Proponents, such as the World Nuclear Association and Environmentalists for Nuclear Energy, contend that nuclear power is a safe, energy source that reduces carbon emissions.
- Nuclear power opponents, such as Greenpeace and NIRS, contend that nuclear power poses many threats to people and the environment.
- There are over thirty countries that use nuclear power to generate electricity.

Contributor

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15.10: Renewable Energy Sources

Learning Objectives

- Describe the different renewable energy sources.
- List any impacts it may have on the environment.

Energy sources that are more or less continuously made available in a time frame useful to people are called **renewable energy.** Renewable energy sources are often considered alternative sources because, in general, most industrialized countries do not rely on them as their main energy source. Instead, they tend to rely on the conventional energy sources such as fossil fuels or nuclear power that are non-renewable. Because of the energy crisis in the United States during the 1970s, dwindling supplies of fossil fuels and hazards associated with nuclear power, use of renewable energy sources such as solar energy, hydroelectric, wind, biomass, and geothermal has grown. Renewable energy comes from the sun (considered an "unlimited" supply) or other sources that can theoretically be renewed at least as quickly as they are consumed. If used at a sustainable rate, these sources will be available for consumption for thousands of years or longer. Renewable alternatives derive from wind, water, solar or biomass (Figure 15.10.1). Note that wind, water and biomass energy sources are indirect sources of solar energy. One limitation currently associated with most forms of renewable energy is that the energy is not concentrated and not easily portable.



Figure 15.10.1 A variety of voltage sources (clockwise from top left): the Brazos Wind Farm in Fluvanna, Texas (credit: Leaflet, Wikimedia Commons); the Krasnoyarsk Dam in Russia (credit: Alex Polezhaev); a solar farm (credit: U.S. Department of Energy); and a group of nickel metal hydride batteries (credit: Tiaa Monto). The voltage output of each depends on its construction and load, and equals emf only if there is no load.

Energy is an important ingredient in all phases of society. We live in a very interdependent world, and access to adequate and reliable energy resources is crucial for economic growth and for maintaining the quality of our lives. The principal energy resources used in the world are shown in Figure 15.10.2. With the rapid growth of electricity generation, renewables—including solar, wind, and hydroelectric power—are the fastest-growing energy source between 2018 and 2050, surpassing petroleum and other liquids to become the most used energy source in the Reference case. Worldwide renewable energy consumption increases by 3.1% per year between 2018 and 2050, compared with 0.6% annual growth in petroleum and other liquids, 0.4% growth in coal, and 1.1% annual growth in natural gas consumption.

Global natural gas consumption increases more than 40% between 2018 and 2050, and total consumption reaches nearly 200 quadrillion Btu by 2050. In addition to the natural gas used in electricity generation, natural gas consumption increases in the industrial sector. Chemical and primary metals manufacturing, as well as oil and natural gas extraction, account for most of the growing industrial demand.

Global liquid fuels consumption increases more than 20% between 2018 and 2050, and total consumption reaches more than 240 quadrillion Btu in 2050. Demand in OECD (Organisation for Economic Cooperation and Development) countries remains relatively stable during the projection period, but non-OECD demand increases by about 45%.

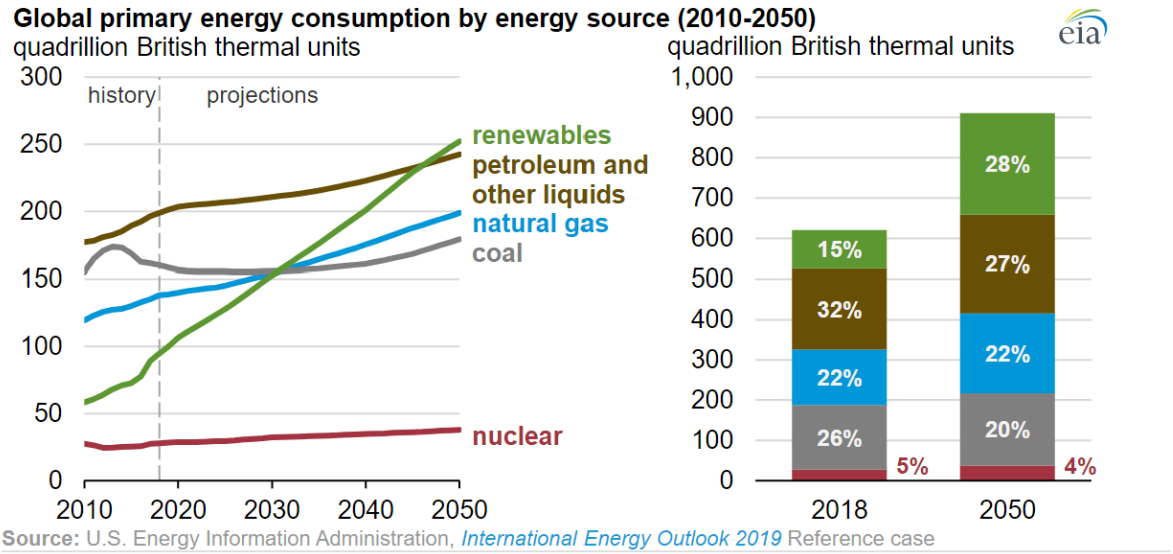


Figure 15.10.2: Global primary energy consumption by energy source (2010-2050)

Why Use Renewable Energy Sources?

Majority of renewable energy sources including solar, wind, water, and biomass can be directly or indirectly attributed to the sun. The fact that the sun will continue burning for another 4-5 billion years makes it inexhaustible as an energy source for human civilization. With appropriate technology, renewable energy sources allow for local, decentralized control over power. Homes, businesses, and isolated communities can use sources such as solar to produce electricity without being near a power plant or being connected to a grid. This eliminates problems such as spills associated with extraction and transportation of fossil fuels that is needed in order to supply these fossil fuels to those areas that are lacking. Most renewable energy sources do not pollute the air with greenhouse gas emissions and other air pollutants associated with fossil fuels. This is especially important in combating climate change.

Solar Energy

Solar energy is the ultimate energy source driving life on earth and many human activities. Though only one billionth of the energy that leaves the sun (Figure 15.10.3) actually reaches the earth's surface, this is more than enough to meet the world's energy requirement. In fact, all other sources of energy, renewable and non-renewable, are actually stored forms of solar energy. The process of directly converting solar energy to heat or electricity is considered a renewable energy source. Solar energy represents an essentially unlimited supply of energy as the sun will long outlast human civilization on earth. The difficulties lie in harnessing the energy. Solar energy has been used for centuries to heat homes and water, and modern technology (photovoltaic cells) has provided a way to produce electricity from sunlight. There are two basic forms of solar energy collectors are passive and active.

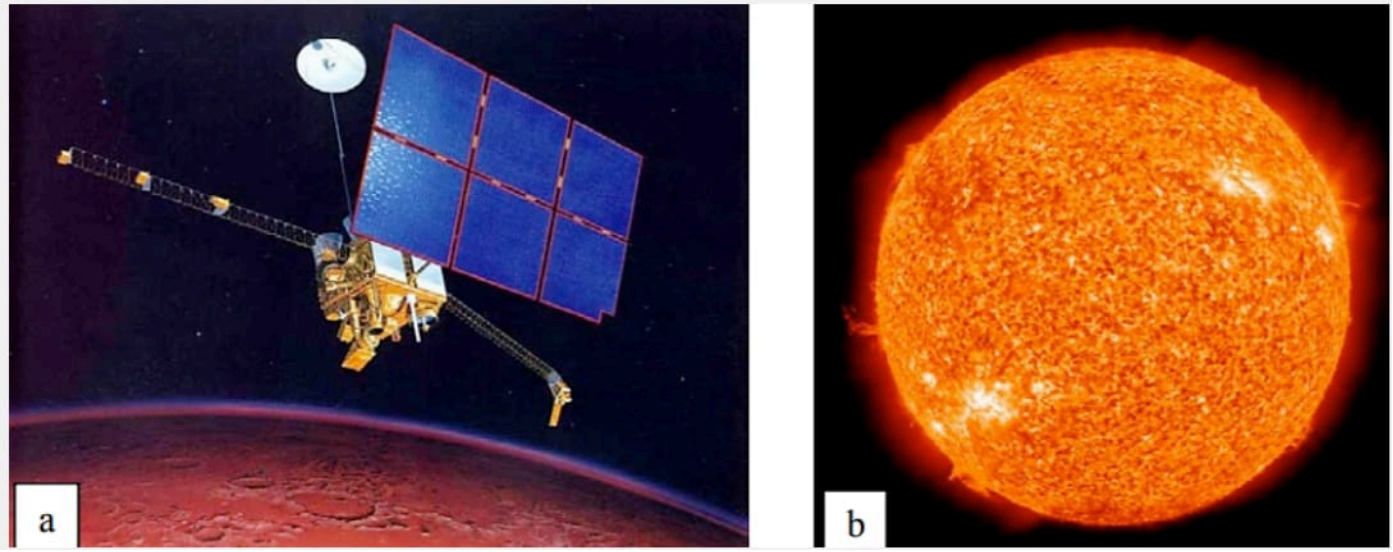


Figure 15.10.3: a) Mars Observer in Mars Orbit showing the solar panel. (Picture: Wikimedia Commons www.jpl.nasa.gov/images/space...t1-browse.jpg,). b) The Sun photographed at 304 angstroms by the Atmospheric Imaging Assembly (AIA 304) of NASA's Solar Dynamics Observatory (SDO). This is a false-color image of the Sun observed in the extreme ultraviolet region of the spectrum. sdo.gsfc.nasa.gov/assets/img/..._4096_0304.jpg, NASA/SDO (AIA)

Solar photovoltaic (PV) devices, or solar cells, change sunlight directly into electricity. PV uses semiconducting materials such as silicon to produce electricity from sunlight: when light hits the cells, the material produces free electrons that migrate across the cell, creating an electric current. Small PV cells can power calculators, watches, and other small electronic devices. Arrangements of many solar cells in PV panels and arrangements of multiple PV panels in PV arrays can produce electricity for an entire house or building (Figure 15.10.4a). Some PV power plants have large arrays that cover many acres to produce electricity for thousands of homes.

Hundreds of thousands of houses and buildings around the world have PV systems on their roofs. Many multi-megawatt PV power plants have also been built. Covering 4% of the world's desert areas with photovoltaics could supply the equivalent of all of the world's electricity. The Gobi Desert alone could supply almost all of the world's total electricity demand.

Solar thermal power plants, like the one in Figure 15.10.4b use concentrating solar collector systems to collect and concentrate sunlight to produce the high temperature heat needed to generate electricity.

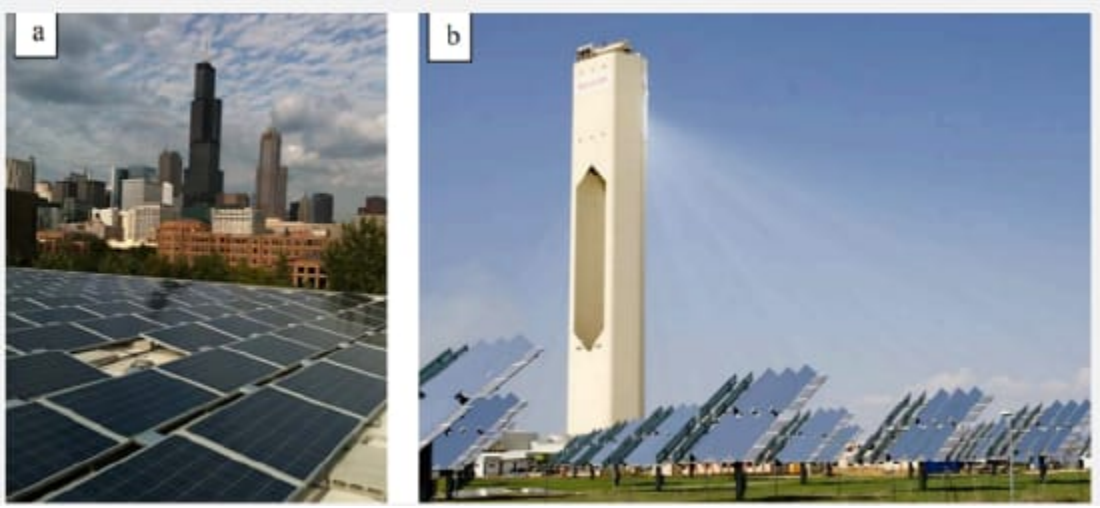


Figure 15.10.4 a) Rooftop Solar Installations on Douglas Hall at the University of Illinois at Chicago has no effect on land resources, while producing electricity with zero emissions. Source: Office of Sustainability. b) Solucar PS10 solar power tower in Andalusia, Spain, is a solar thermal power plant that generates electricity commercially. (Photo by Afloresm Solucar PS10 CC BY 2.0)

Solar power has minimal impact on the environment, depending on where it is placed. The manufacturing of photovoltaic (PV)

cells generates some hazardous waste from the chemicals and solvents used in processing. Often solar arrays are placed on roofs of buildings or over parking lots or integrated into construction in other ways. However, large systems may be placed on land and particularly in deserts where those fragile ecosystems could be damaged if care is not taken. Some solar thermal systems use potentially hazardous fluids (to transfer heat) that require proper handling and disposal. Concentrated solar systems may need to be cleaned regularly with water, which is also needed for cooling the turbine-generator. Using water from underground wells may affect the ecosystem in some arid locations.

Biomass Energy

Biomass energy is from the energy stored in materials of biological origin such as plants and animals. Biomass energy is the oldest energy source used by humans. Until the Industrial Revolution prompted a shift to fossil fuels in the mid-18th century, biomass energy was the world's dominant fuel source. Currently, about 12 percent of the world's energy comes from biomass. Biomass is most frequently used as a fuel source in many developing nations, but with the decline of fossil fuel availability and the increase in fossil fuel prices, biomass is increasingly being used as a fuel source even in developed nations.

Direct combustion of solid biomass. The most common source for direct combustion is wood, but energy can also be generated by burning animal manure (dung), herbaceous plant material (non-wood), peat (partially decomposed plant and animal tissues), or converted biomass such as charcoal (wood that has been partially burned to produce a coal-like substance). Using wood and charcoal made from wood, for heating and cooking can replace fossil fuels and may result in lower CO_2 emissions. If wood is harvested from forests or woodlots that have to be thinned or from urban trees that fall down or needed be cut down anyway, then using it for biomass does not impact those ecosystems.

Biomass is also being used on a larger scale, where small power plants are powered by biomass such as woodchips (Figure 15.10.5). For instance, Central State Hospital, Milledgeville, GA has a woodchip burning plant that was the most advanced system available for its time and operating today. Colgate University in Hamilton, New York, has had a wood-burning boiler since the mid-1980's that processes about 20,000 tons of locally and sustainably harvested wood chips, the equivalent of 1.17 million gallons (4.43 million liters) of fuel oil, avoiding 13,757 tons of emissions, and saving the university over $1.8 million in heating costs. The University's steam-generating wood-burning facility now satisfies more than 75 percent of the campus's heat and domestic hot water needs. For more information about this, click here Colgate University.



Figure 15.10.5 A biomass (woodchip) power plant in Germany. Image from Wikimedia Public Domain.

Gaseous Biomass. Organic material can be converted to methane, the main component of natural gas, by anaerobic decomposition or fermentation, a process that utilizes anaerobic bacteria. Methane is a relatively clean fuel that burns efficiently. It can be generated from any kind of organic waste such as municipal sewage and garbage, livestock manure, kitchen, and garden scraps. In fact, municipal landfills are active sites of methane production contributing annually to methane in the atmosphere and to global warming. This gas can and is currently being captured by numerous landfills around the United States that burn it to generate electricity at power plants or supply it to homes for heating.

Liquid Biofuels. Biofuels are transportation fuels produced from plant sources and used to power vehicles. The most common ones are ethanol and biodiesel.

- **Ethanol**, also known as ethyl alcohol or grain alcohol, is produced by fermenting crops such as corn, sugarcane, and other crops and then mixed with conventional gasoline. As an additive, ethanol lowers reliance on conventional oil and increases the combustion efficiency of gasoline, reducing pollutant emissions.
- **Biodiesel** which is essentially vegetable oil, can also be derived from a wide range of plant sources, including rapeseed, sunflowers, and soybeans, and can be used in most conventional diesel engines. Biodiesel can also be made from used vegetable oil and has been produced on a very local basis. Because it burns more cleanly than its petroleum-based counterpart, biodiesel can reduce pollution from heavy-duty vehicles such as trucks and buses. Compared to petroleum diesel, biodiesel combustion produces less sulfur oxides, particulate matter, carbon monoxide, and unburned and other hydrocarbons, but more nitrogen oxide.

Environmental Impacts of Biomass Energy

A major challenge of biomass is determining if it is really a more sustainable option. The energy content of some biomass energy sources may not be as high as fossil fuels so more must be burned to generate the same energy. It often takes energy to make energy and biomass is one example where the processing to make it may not be offset by the energy it produces. If traditional monoculture crops like corn or soybeans are used, they require major quantities of fossil fuel to manufacture fertilizer, run farm machines, and ship the fuel to markets, so these biofuels do not always offer significant net energy savings over gasoline and diesel fuel. In such instances, biofuels may not be carbon-neutral because the process of producing the biofuels results in more CO_2 added to the atmosphere than that removed by the growing crops.

Burning biomass directly (wood, manure, etc.) produces high particulate material pollution (see chapter 13 on Air Pollution), produces CO_2 and deprives the soil of nutrients it normally would have received from the decomposition of the organic matter. Each type of biomass energy source, therefore, must be evaluated for its full life-cycle impact in order to determine if it is really advancing sustainability and reducing environmental impacts.

Hydrogen: Light and Powerful

Hydrogen gas may be an important clean fuel of the future. Hydrogen is considered an energy carrier, like electricity and batteries, it carries energy that can be converted for use later. Hydrogen gas does not tend to exist freely but rather hydrogen atoms bind to other atoms and molecules becoming incorporated in everything from water to organic compounds. Therefore, to obtain hydrogen gas for fuel, energy is needed to force these substances to release their hydrogen atoms. One such procedure is known as **electrolysis** in which an electric current is passed through water to decompose the water molecule into oxygen and hydrogen (Figure $15.10.6$). Hydrogen can also be produced from hydrocarbons such as natural gas and coal, fermentation of plant waste material, and using algae.

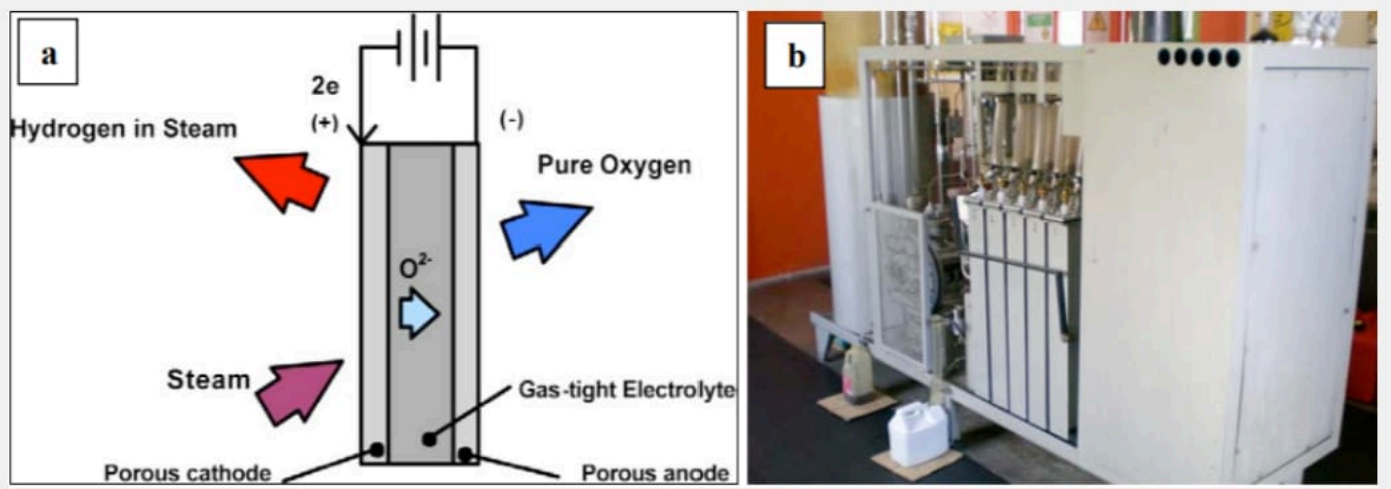


Figure 15.10.6 *a) An electric current passed through water resulting in the separation of hydrogen atoms from oxygen to produce the hydrogen fuel. b) An electrolyser used in the production of hydrogen by CambridgeBayWeather. After production the hydrogen is used to inflate weather balloons to which a radiosonde is attached. The oxygen produced is vented to the outside.*

Fuel cells are highly efficient power plants that produce electricity using hydrogen fuel in a chemical reaction that is a reverse of the electrolysis process that produced the hydrogen fuel (Figure 15.10.7). Energy is released by an exothermic electrochemical reaction that combines hydrogen and oxygen ions through an electrolyte material to generate electricity and heat. Experimental fuel cells that can power automobiles have been developed (Figure 15.10.2).



Figure 15.10.7 The electrochemical processes showing how hydrogen fuel is combined with oxygen generating heat energy along with water as a waste product. Some vehicles that use the fuel cell include buses (photo is a hydrogen fuel bus on Tower Bridge London, photo by Sludge G.), cars (The Toyota Fine N car based on fuel cell technology, photo by Chris 73, CC BY-SA 3.0) and motorcycles (Suzuki Burgman Fuel Cell cutaway model shown here, Photo by Mario CC BY-SA 3.0).

Challenges of Hydrogen

Currently, the infrastructure for using hydrogen fuel is lacking and converting a nation such as the United States to hydrogen would require massive and costly development of facilities to produce, store, transport, and provide the fuel. The environmental impact of hydrogen production itself depends on the source of material used to supply the hydrogen. For example, biomass and fossil fuel sources result in carbon-based emissions. Some research suggests that leakage of hydrogen from its production, transport, and use could potentially deplete stratospheric ozone. Research into this is still ongoing.

Other Renewable Sources

Wind Power

Wind is a renewable energy source that uses the power of moving air to generate electricity. Wind turbines use blades to collect the wind's kinetic energy. Wind flows over the blades creating lift (similar to the effect on airplane wings), which causes the blades to turn. The blades are connected to a drive shaft that turns an electric generator, which produces electricity (Figure 15.10.8). Wind turbines are becoming a more prominent sight across the United States, even in regions that are considered to have less wind potential. Wind turbines (often called windmills) do not release emissions that pollute the air or water (with rare exceptions), and they do not require water for cooling. The U.S. wind industry had 40,181 MW of wind power capacity installed at the end of 2010, with 5,116 MW installed in 2010 alone, providing more than 20 % of installed wind power around the globe. According to the American Wind Energy Association, over 35 % of all new electrical generating capacity in the United States since 2006 was due to wind, surpassed only by natural gas.

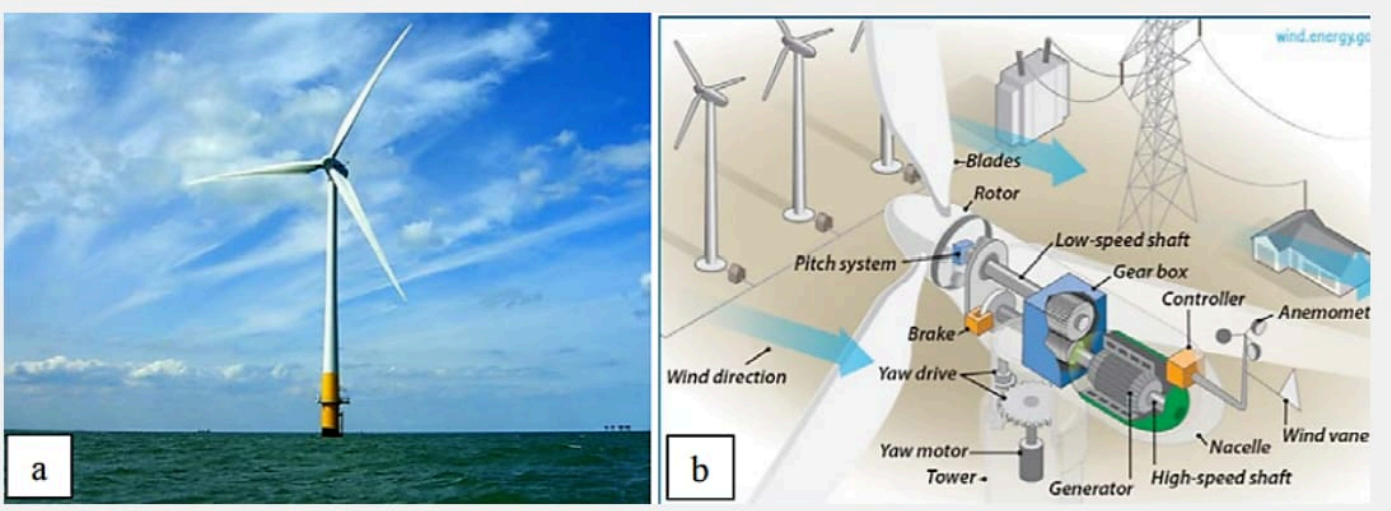


Figure 15.10.8 a) This wind turbine in the Thames Estuary in the UK is an example of induction at work, (credit: Phault, Flickr). Wind pushes the blades of the turbine, spinning a shaft attached to magnets, see image b for parts. The magnets spin around a conductive coil, inducing an electric current in the coil, and eventually feeding the electrical grid.

Most windmills generate about 1kW of electricity, which is only practical for decentralized power generation. California has about 17,000 windmills with a capacity of about 1,400 MW. This is about 80% of all windmills in the U.S. In West Europe windmill generators are quite common. Since a wind turbine has a small physical footprint relative to the amount of electricity it produces, many wind farms are located on crop, pasture, forest land, or coastal areas. They contribute to economic sustainability by providing extra income to farmers and ranchers, allowing them to stay in business and keep their property from being developed for other uses. For example, energy can be produced by installing wind turbines in the Appalachian Mountains of the United States instead of engaging in mountain top removal for coal mining.

Offshore wind turbines on lakes or the ocean may have smaller environmental impacts than turbines on land. Wind turbines do have a few environmental challenges. There are aesthetic concerns to some people when they see them on the landscape. A few wind turbines have caught on fire, and some have leaked lubricating fluids, though this is relatively rare. Some people do not like the sound that wind turbine blades make. Turbines have been found to cause bird and bat deaths particularly if they are located along their migratory path. This is of particular concern if these are threatened or endangered species. There are ways to mitigate that impact and it is currently being researched. There are some small impacts from the construction of wind projects or farms, such as the construction of service roads, the production of the turbines themselves, and the concrete for the foundations. However, overall life cycle analysis has found that turbines make much more energy than the amount used to make and install them.

Geothermal Energy

Geothermal energy uses heat from the Earth's internal geologic processes in order to produce electricity or provide heating. The subsurface temperature of the Earth provides an endless energy resource. One source of geothermal energy is steam.

Groundwater percolates down through cracks in the subsurface rocks until it reaches rocks heated by underlying magma, and the heat converts the water to steam. Sometimes this steam makes its way back to the surface in the form of a geyser or hot spring. Wells can be dug to tap the steam reservoir and bring it to the surface, to drive generating turbines and produce electricity (Figure 15.10.9a). Hot water can be circulated to heat buildings. Regions near tectonic plate boundaries have the best potential for geothermal activity.

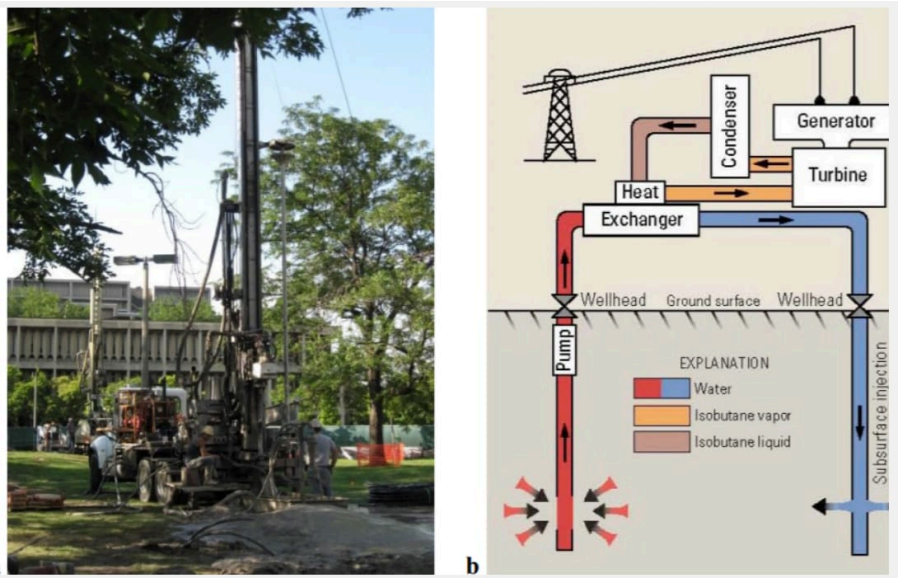


Figure 15.10.9 a) Installing a Geothermal Pipe System Drilling to install geothermal ground source pipe system. Source: Office of Sustainability. b) Electricity generation at a moderate-temperature hydrothermal system. The geothermal water is used to boil a second fluid (isobutane in this example) whose vapor then drives a turbine generator. The wastewater is injected back into the subsurface. Source: USGS.

The environmental impact of geothermal energy depends on how it is being used. Direct use and heating applications have almost no negative impact on the environment. Geothermally heated water can release dissolved gases, including carbon dioxide, methane, ammonia and hydrogen sulfide, although these are usually in very small quantities when compared to those released from fossil fuel plants. In addition, geothermal plants use scrubber systems to clean the air of hydrogen sulfide that is naturally found in the steam and hot water. They emit 97 % less acid rain-causing sulfur compounds than are emitted by fossil fuel plants.

Hydroelectric Power (Hydropower)

This is the second largest source of renewable energy used, next to biomass energy. The majority of hydropower currently comes from dams built across a river to block the flow of river water. The water stored behind the dam contains potential energy and when released, the potential energy is converted to kinetic energy as the water rushes down. This energy is used to turn blades of turbines and causing a generator to generate electricity. Electricity generated in the powerhouse of a dam is transmitted to the electric grid by transmission lines while the water flows into the riverbed below the dam and continues down river. An alternative approach considered less disruptive involves diverting a portion of the river's water through a pipe or channel and passed through a powerhouse to generate electricity and returned to the river. Another approach involves pumping water from a lower reservoir to a higher reservoir and then allowed to flow downhill through a turbine, generating electricity. This approach, however, requires energy input to pump the water. Figure 15.10.10 show a hydroelectric facility (a) and also illustrates the generation of electricity (b).

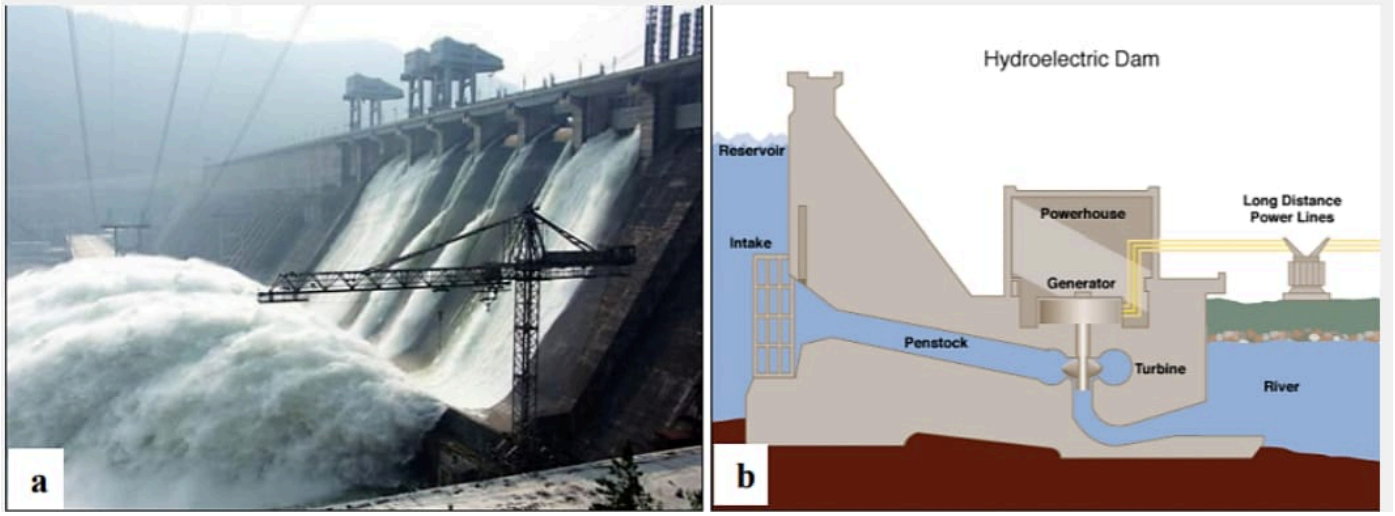


Figure 15.10.10 a) Hydroelectric facility (credit: Denis Belevich, Wikimedia Commons); b) An illustration showing how water is funneled through a portion of the dam to rotate turbines and generate electricity. (Image from Wikimedia, public domain).

Hydropower (hydro-electric) is considered a clean and renewable source of energy since it does not directly produce emissions of air pollutants and the source of power is regenerated. However, hydropower dams, reservoirs, and the operation of generators can have serious environmental impacts. A dam that is used to create a reservoir or to divert water to a run-ofriver hydropower plant can obstruct migration of fish to their upstream spawning areas in areas where salmon must travel upstream to spawn, such as along the Columbia River in Washington and Oregon. Hydro turbines kill and injure some of the fish that pass through the turbine although there are ways to reduce that effect. This problem can be partially alleviated by using 'fish ladders' that help the salmon get up the dams.

A reservoir and operation of the dam can affect the natural water habitat due to changes in water temperatures, chemistry, flow characteristics, and silt loads, all of which can lead to significant changes in the ecology and physical characteristics of the river upstream and downstream.

Potential of Tidal Power

Tidal power involves placing turbines in zones of the ocean with significant tides and currents, and using the power of flowing water to turn the blades of a turbine to generate electricity. Ocean power systems are still being researched and currently still experimental. For example, the Bay of Fundy, which has a 15 m tide, a dam constructed across the estuary would let water enter on the incoming tide, then release the water through turbines at low tide. The energy potential is great http://www.ialtenergy.com/tidal-power-news.html , and so is the environmental cost. Tapping tidal energy resources involves building major dams on inlets and estuaries that are prized for other purposes, so few tidal energy facilities have been developed. Harnessing waves and currents on a significant scale will involve designing turbine structures that are large, inexpensive, and can operate for long periods under the physical stresses and corrosive forces of ocean environments. Though proposed, a tidal power plant has not been constructed at Fundy. There is a 240,000 kW tidal plant at La Rance, France.

Summary

- Renewable sources of energy are derived from wind, water, solar or biomass.
- One limitation currently associated with most forms of renewable energy is that the energy is not concentrated and not easily portable.
- There is a projected increase from 15% (2018) to 28% of global renewable energy consumption.

Contributor

US Energy Information Administration

Libretext: Introduction to Environmental Science (Zendher et al.)

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16: BIOCHEMISTRY

16.1: Energy and the Living Cell
16.2: Carbohydrates- A Storehouse of Energy
16.3: Fats and Other Lipids
16.4: Proteins- Polymers of Amino Acids
16.5: Structure and Function of Proteins
16.6: Nucleic Acids- Parts, Structure, and Function
16.7: The Human Genome
16.8: RNA Protein Synthesis and the Genetic Code

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16.1: Energy and the Living Cell

Learning Objective

- Know the similarities and differences between plant and animal cells.
- Know the functions of the major parts of plant and animal cells.

Biochemistry, sometimes called **biological chemistry**, is the study of chemical processes within and relating to living organisms. Biochemical processes give rise to the complexity of life. Biochemistry focuses on understanding how biological molecules give rise to the processes that occur within living cells and between cells, which in turn relates greatly to the study and understanding of tissues, organs, and organism structure and function. Much of biochemistry deals with the structures, functions and interactions of biological macromolecules, such as proteins, nucleic acids, carbohydrates and lipids, which provide the structure of cells and perform many of the functions associated with life. The mechanisms by which cells harness energy from their environment via chemical reactions are known as metabolism. The findings of biochemistry are applied primarily in medicine, nutrition, and agriculture. In medicine, biochemists investigate the causes and cures of diseases. In nutrition, they study how to maintain health wellness and study the effects of nutritional deficiencies. In agriculture, biochemists investigate soil and fertilizers, and try to discover ways to improve crop cultivation, crop storage and pest control.

The major parts of plant and animal cells (Figure 16.1.1) include the plasma membrane, nucleus, ribosomes, and mitochondria.

The plasma membrane is made up of a phospholipid bilayer with embedded proteins that separates the internal contents of the cell from its surrounding environment. A phospholipid is a lipid molecule composed of two fatty acid chains, a glycerol backbone, and a phosphate group. The plasma membrane regulates the passage of some substances, such as organic molecules, ions, and water, preventing the passage of some to maintain internal conditions, while actively bringing in or removing others. Other compounds move passively across the membrane.

Nucleus

Typically, the **nucleus** is the most prominent organelle in a cell . The nucleus (plural = nuclei) houses the cell's DNA in the form of chromatin and directs the synthesis of ribosomes and proteins.

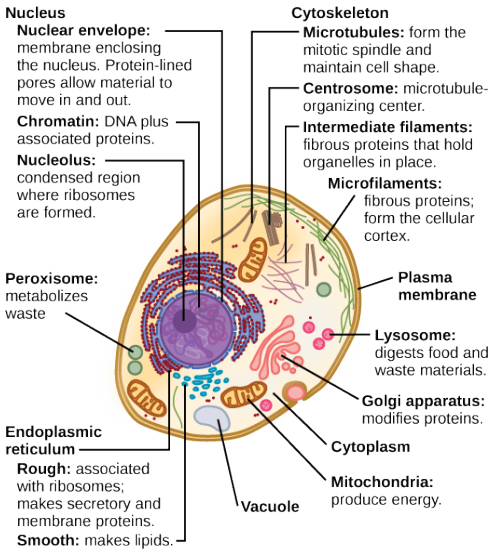
Ribosomes

Ribosomes are the cellular structures responsible for protein synthesis. When viewed through an electron microscope, free ribosomes appear as either clusters or single tiny dots floating freely in the cytoplasm. Ribosomes may be attached to either the cytoplasmic side of the plasma membrane or the cytoplasmic side of the endoplasmic reticulum. Electron microscopy has shown that ribosomes consist of large and small subunits. Ribosomes are enzyme complexes that are responsible for protein synthesis.

Because protein synthesis is essential for all cells, ribosomes are found in practically every cell, although they are smaller in prokaryotic cells. They are particularly abundant in immature red blood cells for the synthesis of hemoglobin, which functions in the transport of oxygen throughout the body.

Mitochondria

Mitochondria (singular = mitochondrion) are often called the "powerhouses" or "energy factories" of a cell because they are responsible for making adenosine triphosphate (ATP), the cell's main energy-carrying molecule. The formation of ATP from the breakdown of glucose is known as cellular respiration. In keeping with our theme of form following function, it is important to point out that muscle cells have a very high concentration of mitochondria because muscle cells need a lot of energy to contract.



(a)

Figure_03_03_01b_new.png?revision=1&size=bestfit&width=519&height=476" style="width: 490.994px; height: 450px;" />

Figure 16.1.1***:*** *This figure shows (a) a typical animal cell and (b) a typical plant cell.*

Animal Cells versus Plant Cells

Despite their fundamental similarities, there are some striking differences between animal and plant cells. Animal cells have centrioles, centrosomes (discussed under the cytoskeleton), and lysosomes, whereas plant cells do not. Plant cells have a cell wall (made of cellulose), chloroplasts, plasmodesmata, and plastids used for storage, and a large central vacuole, whereas animal cells do not.

Energy in Biological Systems

Green plants are capable of synthesizing glucose ($C_6H_{12}O_6$) from carbon dioxide (CO_2) and water (H_2O) by using solar energy in the process known as photosynthesis:

$$6\,CO_2 + 6\,H_2O + 686\ \text{kcal} \rightarrow C_6H_{12}O_6 + 6\,O_2 \tag{16.1.1}$$

(The 686 kcal come from solar energy.) Chloroplasts function in photosynthesis and can be found in cells of plants and algae. The chloroplasts contain a green pigment called chlorophyll, which captures the energy of sunlight for photosynthesis. Plants can use the glucose for energy or convert it to larger carbohydrates, such as starch or cellulose. Starch provides energy for later use, perhaps as nourishment for a plant's seeds, while cellulose is the structural material of plants. We can gather and eat the parts of a plant that store energy—seeds, roots, tubers, and fruits—and use some of that energy ourselves. Carbohydrates are also needed for the synthesis of nucleic acids and many proteins and lipids. This is the major difference between plants and animals: Plants are able to make their own food, like glucose, whereas animals must rely on other organisms for their organic compounds or food source.

Summary

The major parts of plant and animal cells (Figure 16.1.1) include the plasma membrane, nucleus, ribosomes, and mitochondria.

Animal cells have centrioles, centrosomes (discussed under the cytoskeleton), and lysosomes, whereas plant cells do not.

Plant cells have a cell wall (made of cellulose), chloroplasts, plasmodesmata, and plastids used for storage, and a large central vacuole, whereas animal cells do not.

Green plants are capable of synthesizing glucose ($C_6H_{12}O_6$) from carbon dioxide (CO_2) and water (H_2O) by using solar energy in

the process known as photosynthesis.

Contributors and Attributions

- Template:ContribOpenStaxConcepts
- Libretext: The Basics of GOB Chemistry (Ball et al.)
- Wikipedia

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16.2: Carbohydrates- A Storehouse of Energy

Learning Objective

- Know the difference between starch, cellulose and glycogen.
- List the key steps in carbohydrate digestion.

All carbohydrates consist of carbon, hydrogen, and oxygen atoms and are polyhydroxy aldehydes or ketones or are compounds that can be broken down to form such compounds. Examples of carbohydrates include starch, fiber, the sweet-tasting compounds called sugars, and structural materials such as cellulose. Different carbohydrates that will be discussed below include the simple sugars, oligosaccharides and polysaccharides (Figure 16.2.1.

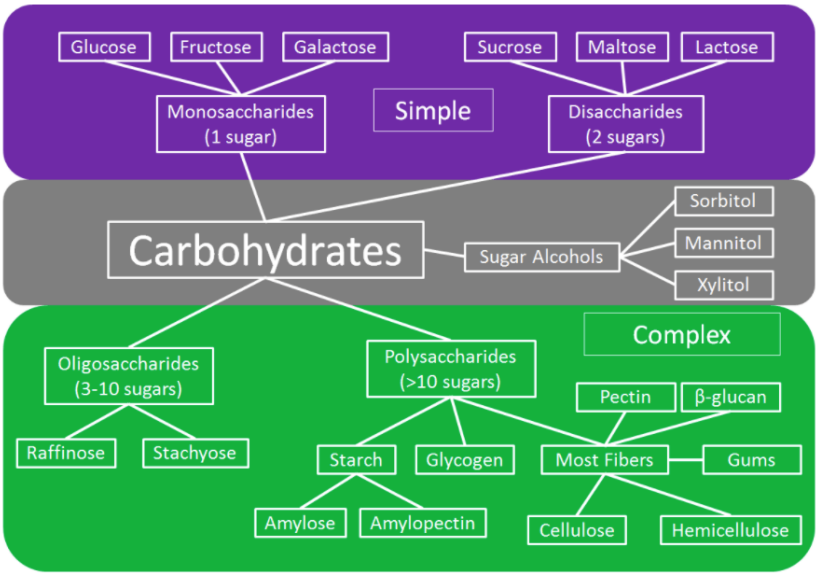
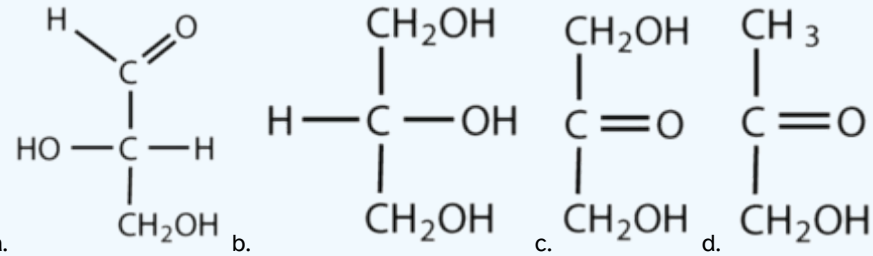


Figure 16.2.1 *Overview of carbohydrates*

Example 16.2.1

Which compounds would be classified as carbohydrates?



a. b. c. d.

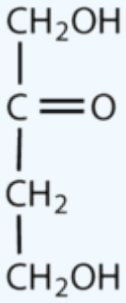
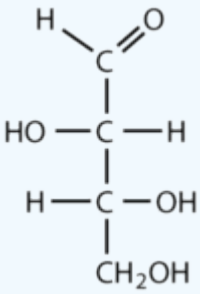
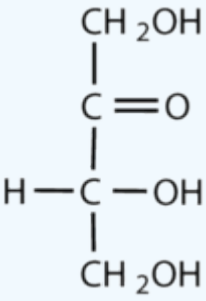
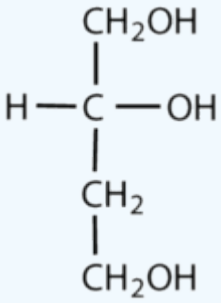
Solution

a. This is a carbohydrate because the molecule contains an aldehyde functional group with OH groups on the other two carbon atoms.
b. This is not a carbohydrate because the molecule does not contain an aldehyde or a ketone functional group.
c. This is a carbohydrate because the molecule contains a ketone functional group with OH groups on the other two carbon atoms.

d. This is not a carbohydrate; although it has a ketone functional group, one of the other carbons atoms does not have an OH group attached.

Exercise 16.2.1

Which compounds would be classified as carbohydrates?

1. 
2. 
3. 
4. 

Some Simple Sugars

The naturally occurring **monosaccharides** contain three to seven carbon atoms per molecule (one sugar unit) . Monosaccharides (or simple sugars) of specific sizes may be indicated by names composed of a stem denoting the number of carbon atoms and the suffix *-ose*. For example, the terms *triose*, *tetrose*, *pentose*, and *hexose* signify monosaccharides with, respectively, three, four, five, and six carbon atoms. Monosaccharides are also classified as aldoses or ketoses. Those monosaccharides that contain an aldehyde functional group are called aldoses; those containing a ketone functional group on the second carbon atom are ketoses. Combining these classification systems gives general names that indicate both the type of carbonyl group *and* the number of carbon atoms in a molecule. Thus, monosaccharides are described as aldotetroses, aldopentoses, ketopentoses, ketoheptoses, and so forth.

Although a variety of monosaccharides are found in living organisms, three hexoses are particularly abundant: D-glucose, D-galactose, and D-fructose (Figure 16.2.2). Glucose and galactose are both aldohexoses, while fructose is a ketohexose.

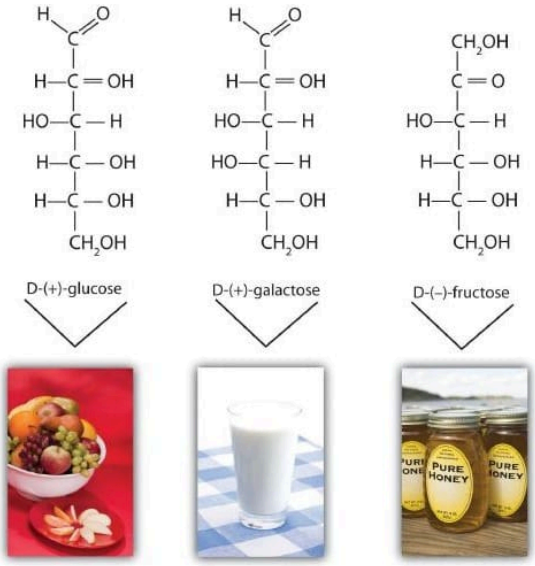


Figure 16.2.2: Structures of Three Important Hexoses. Each hexose is pictured with a food source in which it is commonly found. Source: Photos © Thinkstock.

In aqueous solution, the predominant forms are not the straight-chain structure shown above. Rather, they adopt a cyclic structure. The representative ring structures of glucose, fructose, and galactose are shown in Figure 16.2.3. Notice that all are 6-carbon

sugars (hexoses). However, fructose has a five member ring, while glucose and galactose have 6 member rings. Also notice that the only structural difference between glucose and galactose is the position of the alcohol (OH) group that is shown in red.

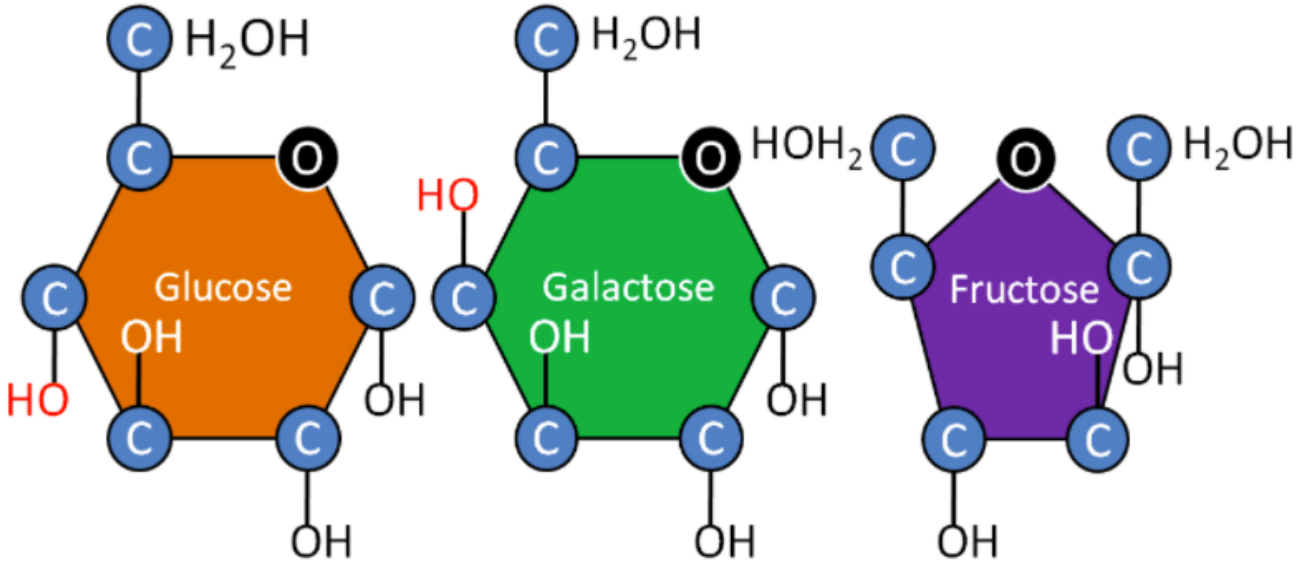


Figure 16.2.3 *The ring structures of glucose, galactose, and fructose.*

A **disaccharide** contains two monosaccharides joined together. Examples include and . They are composed of two monosaccharide units bound together by a bond known as a formed via a , resulting in the loss of a atom from one monosaccharide and a from the other. The of unmodified disaccharides is $C_{12}H_{22}O_{11}$. Although there are numerous kinds of disaccharides, a handful of disaccharides are particularly notable.

Sucrose, which may be obtained by condensing a molecule of α-glucose with one of the cyclic forms of fructose called β-fructose. The structure of sucrose is shown in Figure 16.2.4.

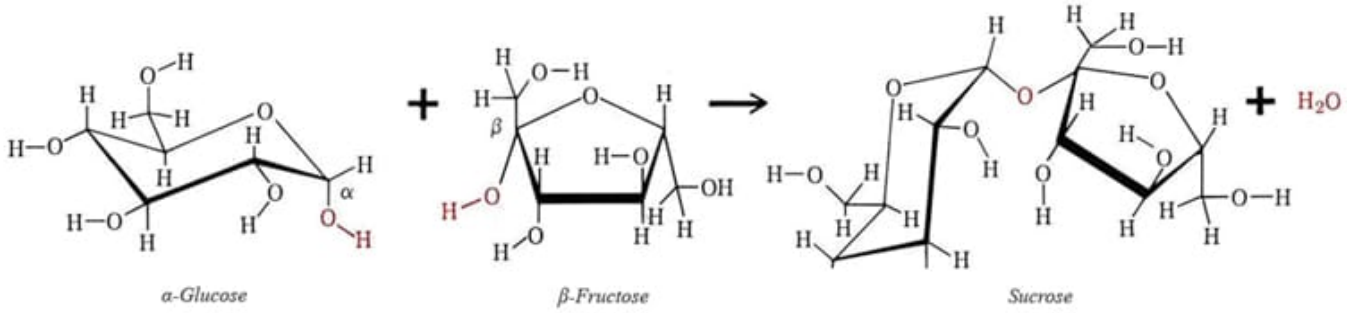


Figure 16.2.4 *The formation of sucrose from glucose and fructose.*

Other, less familiar, examples of disaccharides are lactose, which occurs in milk, and maltose, which are shown in Figure 16.2.5. In order to digest a disaccharide like sucrose or lactose, the human body must have an enzyme which can catalyze hydrolysis of the linkage between the two monosaccharide units. Many Asians, Africans, and American Indians are incapable of synthesizing lactase, the enzyme that speeds hydrolysis of lactose. If such persons drink milk, the undigested lactose makes them sick.

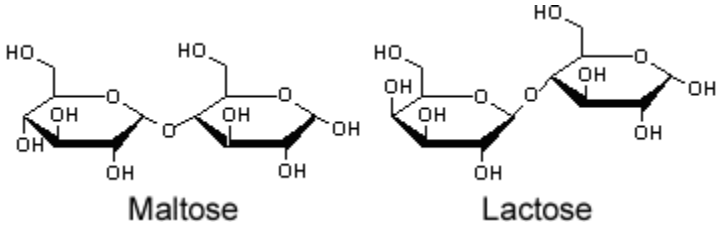


Figure 16.2.5 Two other common disaccharides, maltose and lactose.

The polysaccharides are the most abundant carbohydrates in nature and serve a variety of functions, such as energy storage or as components of plant cell walls. Polysaccharides are very large polymers composed of tens to thousands of monosaccharides joined together by glycosidic linkages. The three most abundant polysaccharides are starch, glycogen, and cellulose. These three are referred to as *homopolymers* because each yields only one type of monosaccharide (glucose) after complete hydrolysis. *Heteropolymers* may contain sugar acids, amino sugars, or noncarbohydrate substances in addition to monosaccharides. Heteropolymers are common in nature (gums, pectins, and other substances) but will not be discussed further in this textbook. The polysaccharides are nonreducing carbohydrates, are not sweet tasting, and do not undergo mutarotation.

Starch

Starch is the most important source of carbohydrates in the human diet and accounts for more than 50% of our carbohydrate intake. It occurs in plants in the form of granules, and these are particularly abundant in seeds (especially the cereal grains) and tubers, where they serve as a storage form of carbohydrates. The breakdown of starch to glucose nourishes the plant during periods of reduced photosynthetic activity. We often think of potatoes as a “starchy” food, yet other plants contain a much greater percentage of starch (potatoes 15%, wheat 55%, corn 65%, and rice 75%). Commercial starch is a white powder.

Starch is a mixture of two polymers: amylose and amylopectin. Natural starches consist of about 10%–30% amylose and 70%–90% amylopectin. Amylose is a linear polysaccharide composed entirely of D-glucose units joined by the α-1,4-glycosidic linkages we saw in maltose (part (a) of Figure 16.2.6). Experimental evidence indicates that amylose is not a straight chain of glucose units but instead is coiled like a spring, with six glucose monomers per turn (part (b) of Figure 16.2.6). When coiled in this fashion, amylose has just enough room in its core to accommodate an iodine molecule. The characteristic blue-violet color that appears when starch is treated with iodine is due to the formation of the amylose-iodine complex. This color test is sensitive enough to detect even minute amounts of starch in solution.

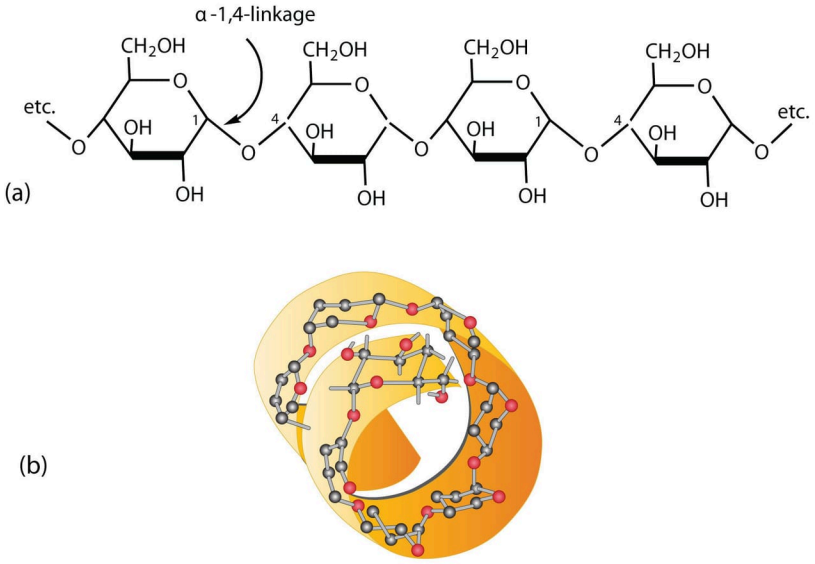


Figure 16.2.6 Amylose. (a) Amylose is a linear chain of α-D-glucose units joined together by α-1,4-glycosidic bonds. (b) Because of hydrogen bonding, amylose acquires a spiral structure that contains six glucose units per turn.

Amylopectin is a branched-chain polysaccharide composed of glucose units linked primarily by α-1,4-glycosidic bonds but with occasional α-1,6-glycosidic bonds, which are responsible for the branching. A molecule of amylopectin may contain many thousands of glucose units with branch points occurring about every 25–30 units (Figure 16.2.7). The helical structure of amylopectin is disrupted by the branching of the chain, so instead of the deep blue-violet color amylose gives with iodine, amylopectin produces a less intense reddish brown.

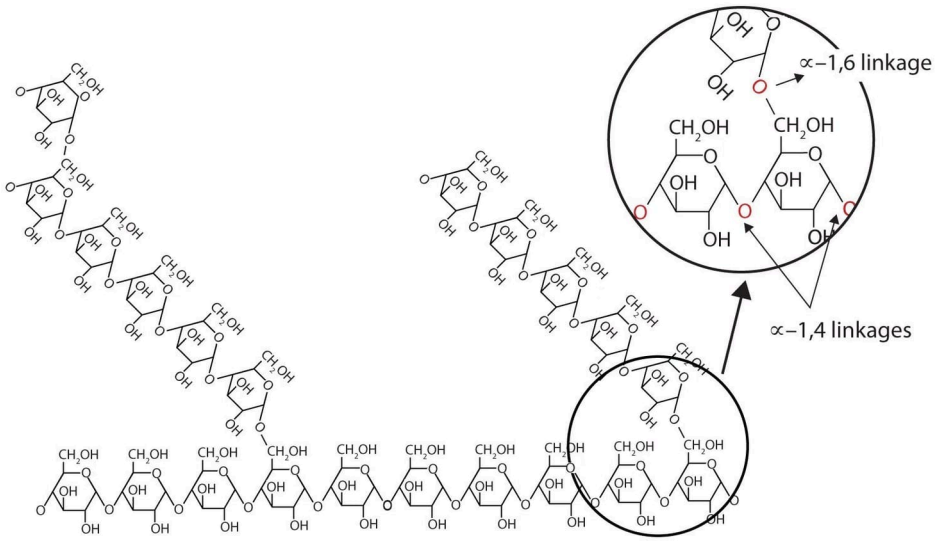


Figure 16.2.7 Representation of the Branching in Amylopectin and Glycogen. Both amylopectin and glycogen contain branch points that are linked through α-1,6-linkages. These branch points occur more often in glycogen.

Dextrins are glucose polysaccharides of intermediate size. The shine and stiffness imparted to clothing by starch are due to the presence of dextrins formed when clothing is ironed. Because of their characteristic stickiness with wetting, dextrins are used as adhesives on stamps, envelopes, and labels; as binders to hold pills and tablets together; and as pastes. Dextrins are more easily digested than starch and are therefore used extensively in the commercial preparation of infant foods.

The complete hydrolysis of starch yields, in successive stages, glucose:

$$\text{starch} \rightarrow \text{dextrins} \rightarrow \text{maltose} \rightarrow \text{glucose}$$

In the human body, several enzymes known collectively as amylases degrade starch sequentially into usable glucose units.

Glycogen

Glycogen is the energy reserve carbohydrate of animals. Practically all mammalian cells contain some stored carbohydrates in the form of glycogen, but it is especially abundant in the liver (4%–8% by weight of tissue) and in skeletal muscle cells (0.5%–1.0%). Like starch in plants, glycogen is found as granules in liver and muscle cells. When fasting, animals draw on these glycogen reserves during the first day without food to obtain the glucose needed to maintain metabolic balance.

Glycogen is structurally quite similar to amylopectin, although glycogen is more highly branched (8–12 glucose units between branches) and the branches are shorter. When treated with iodine, glycogen gives a reddish brown color. Glycogen can be broken down into its D-glucose subunits by acid hydrolysis or by the same enzymes that catalyze the breakdown of starch. In animals, the enzyme phosphorylase catalyzes the breakdown of glycogen to phosphate esters of glucose.

> About 70% of the total glycogen in the body is stored in muscle cells. Although the percentage of glycogen (by weight) is higher in the liver, the much greater mass of skeletal muscle stores a greater total amount of glycogen.

Cellulose

Cellulose, a fibrous carbohydrate found in all plants, is the structural component of plant cell walls. Because the earth is covered with vegetation, cellulose is the most abundant of all carbohydrates, accounting for over 50% of all the carbon found in the vegetable kingdom. Cotton fibrils and filter paper are almost entirely cellulose (about 95%), wood is about 50% cellulose, and the dry weight of leaves is about 10%–20% cellulose. The largest use of cellulose is in the manufacture of paper and paper products. Although the use of noncellulose synthetic fibers is increasing, rayon (made from cellulose) and cotton still account for over 70% of textile production.

Like amylose, cellulose is a linear polymer of glucose. It differs, however, in that the glucose units are joined by β-1,4-glycosidic linkages, producing a more extended structure than amylose (part (a) of Figure 16.2.8). This extreme linearity allows a great deal of hydrogen bonding between OH groups on adjacent chains, causing them to pack closely into fibers (part (b) of Figure 16.2.8). As a result, cellulose exhibits little interaction with water or any other solvent. Cotton and wood, for example, are completely insoluble in water and have considerable mechanical strength. Because cellulose does not have a helical structure, it does not bind to iodine to form a colored product.

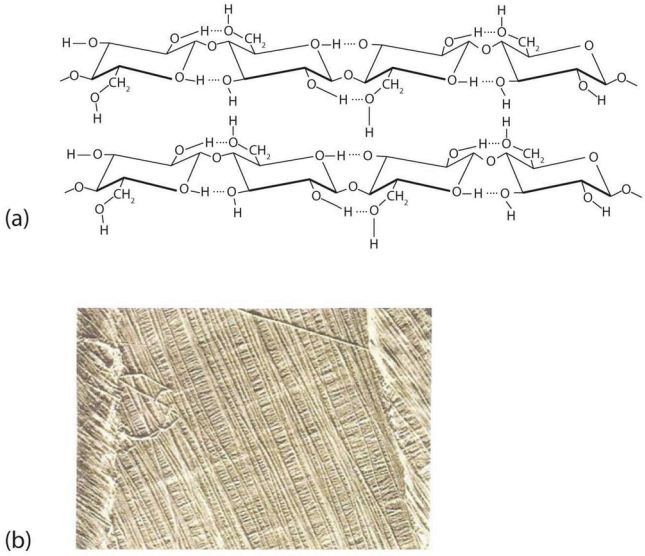


Figure 16.2.8 Cellulose. (a) There is extensive hydrogen bonding in the structure of cellulose. (b) In this electron micrograph of the cell wall of an alga, the wall consists of successive layers of cellulose fibers in parallel arrangement.

Cellulose yields D-glucose after complete acid hydrolysis, yet humans are unable to metabolize cellulose as a source of glucose. Our digestive juices lack enzymes that can hydrolyze the β-glycosidic linkages found in cellulose, so although we can eat potatoes, we cannot eat grass. However, certain microorganisms can digest cellulose because they make the enzyme cellulase, which catalyzes the hydrolysis of cellulose. The presence of these microorganisms in the digestive tracts of herbivorous animals (such as cows, horses, and sheep) allows these animals to degrade the cellulose from plant material into glucose for energy. Termites also contain cellulase-secreting microorganisms and thus can subsist on a wood diet. This example once again demonstrates the extreme stereospecificity of biochemical processes.

Summary

- Starch is a storage form of energy in plants. It contains two polymers composed of glucose units: amylose (linear) and amylopectin (branched).
- Glycogen is a storage form of energy in animals. It is a branched polymer composed of glucose units. It is more highly branched than amylopectin.
- Cellulose is a structural polymer of glucose units found in plants. It is a linear polymer with the glucose units linked through β-1,4-glycosidic bonds.

Sources

Wikipedia

Contributors and Attributions

- Template:ContribLindshield
- Libretext: The Basics of GOB Chemistry (Ball et al.)

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16.3: Fats and Other Lipids

Learning Objectives

- Recognize the structures of common fatty acids.
- Describe the structure of fats and oils and classify them as saturated, monounsaturated, or polyunsaturated.

Fats and oils, found in many of the foods we eat, belong to a class of biomolecules known as lipids. Gram for gram, they pack more than twice the caloric content of carbohydrates: the oxidation of fats and oils supplies about 9 kcal of energy for every gram oxidized, whereas the oxidation of carbohydrates supplies only 4 kcal/g. Although the high caloric content of fats may be bad news for the dieter, it says something about the efficiency of nature's designs. Our bodies use carbohydrates, primarily in the form of glucose, for our *immediate* energy needs. Our capacity for storing carbohydrates for later use is limited to tucking away a bit of glycogen in the liver or in muscle tissue. We store our *reserve* energy in lipid form, which requires far less space than the same amount of energy stored in carbohydrate form. Lipids have other biological functions besides energy storage. They are a major component of the membranes of the 10 trillion cells in our bodies. They serve as protective padding and insulation for vital organs. Furthermore, without lipids in our diets, we would be deficient in the fat-soluble vitamins A, D, E, and K.

Lipids are not defined by the presence of specific functional groups, as carbohydrates are, but by a physical property—solubility. Compounds isolated from body tissues are classified as lipids if they are more soluble in organic solvents, such as dichloromethane, than in water. By this criterion, the lipid category includes not only fats and oils, which are esters of the trihydroxy alcohol glycerol and fatty acids, but also compounds that incorporate functional groups derived from phosphoric acid, carbohydrates, or amino alcohols, as well as steroid compounds such as cholesterol (Figure 16.3.1 presents one scheme for classifying the various kinds of lipids). We will discuss the various kinds of lipids by considering one subclass at a time and pointing out structural similarities and differences as we go.

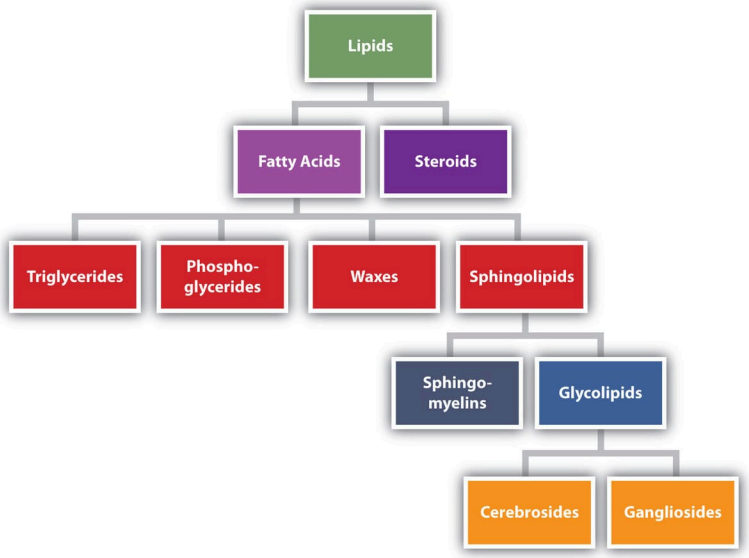
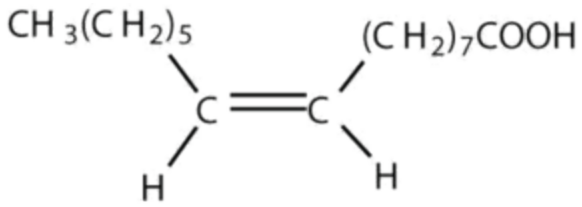


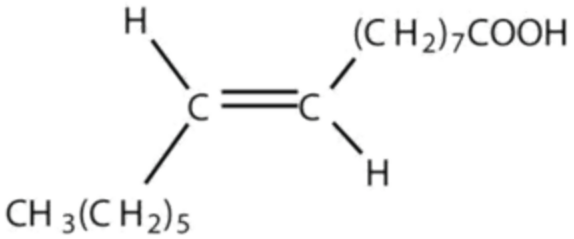
Figure 16.3.1 *Lipid organization based on structural relationships*

Fatty Acids

Fatty acids are carboxylic acids that are structural components of fats, oils, and all other categories of lipids, except steroids. More than 70 have been identified in nature. They usually contain an even number of carbon atoms (typically 12–20), are generally unbranched, and can be classified by the presence and number of carbon-to-carbon double bonds. Thus, saturated fatty acids contain no carbon-to-carbon double bonds, monounsaturated fatty acids contain one carbon-to-carbon double bond, and polyunsaturated fatty acids contain two or more carbon-to-carbon double bonds.



cis fatty acid



trans fatty acid

Table 16.3.1 *lists some common fatty acids and one important source for each. The atoms or groups around the double bonds in unsaturated fatty acids can be arranged in either the cis or trans isomeric form. Naturally occurring fatty acids are generally in the cis configuration.*

Table 16.3.1 *Some Common Fatty Acids Found in Natural Fats.*

Name	Abbreviated Structural Formula	Condensed Structural Formula	Melting Point (°C)	Source
lauric acid	$C_{11}H_{23}COOH$	$CH_3(CH_2)_{10}COOH$	44	palm kernel oil
myristic acid	$C_{13}H_{27}COOH$	$CH_3(CH_2)_{12}COOH$	58	oil of nutmeg
palmitic acid	$C_{15}H_{31}COOH$	$CH_3(CH_2)_{14}COOH$	63	palm oil
palmitoleic acid	$C_{15}H_{29}COOH$	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$	0.5	macadamia oil
stearic acid	$C_{17}H_{35}COOH$	$CH_3(CH_2)_{16}COOH$	70	cocoa butter
oleic acid	$C_{17}H_{33}COOH$	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	16	olive oil
linoleic acid	$C_{17}H_{31}COOH$	$CH_3(CH_2)_3(CH_2CH{=}CH)_2(CH_2)_7COOH$	−5	canola oil
α-linolenic acid	$C_{17}H_{29}COOH$	$CH_3(CH_2CH{=}CH)_3(CH_2)_7COOH$	−11	flaxseed
arachidonic acid	$C_{19}H_{31}COOH$	$CH_3(CH_2)_4(CH_2CH{=}CH)_4(CH_2)_2COOH$	−50	liver

Two polyunsaturated fatty acids—linoleic and α-linolenic acids—are termed essential fatty acids because humans must obtain them from their diets. Both substances are required for normal growth and development, but the human body does not synthesize them. The body uses linoleic acid to synthesize many of the other unsaturated fatty acids, such as arachidonic acid, a precursor for the synthesis of prostaglandins. In addition, the essential fatty acids are necessary for the efficient transport and metabolism of cholesterol. The average daily diet should contain about 4–6 g of the essential fatty acids.

Fats and oils are the most abundant lipids in nature. They provide energy for living organisms, insulate body organs, and transport fat-soluble vitamins through the blood. Although we often draw the carbon atoms in a straight line, they actually have more of a zigzag configuration (Figure 16.3.2*a*). Viewed as a whole, however, the saturated fatty acid molecule is relatively straight (Figure 16.3.2*b*). Such molecules pack closely together into a crystal lattice, maximizing the strength of dispersion forces and causing fatty acids and the fats derived from them to have relatively high melting points. In contrast, each *cis* carbon-to-carbon double bond in an unsaturated fatty acid produces a pronounced bend in the molecule, so that these molecules do not stack neatly. As a result, the intermolecular attractions of unsaturated fatty acids (and unsaturated fats) are weaker, causing these substances to have lower melting points. Most are liquids at room temperature.

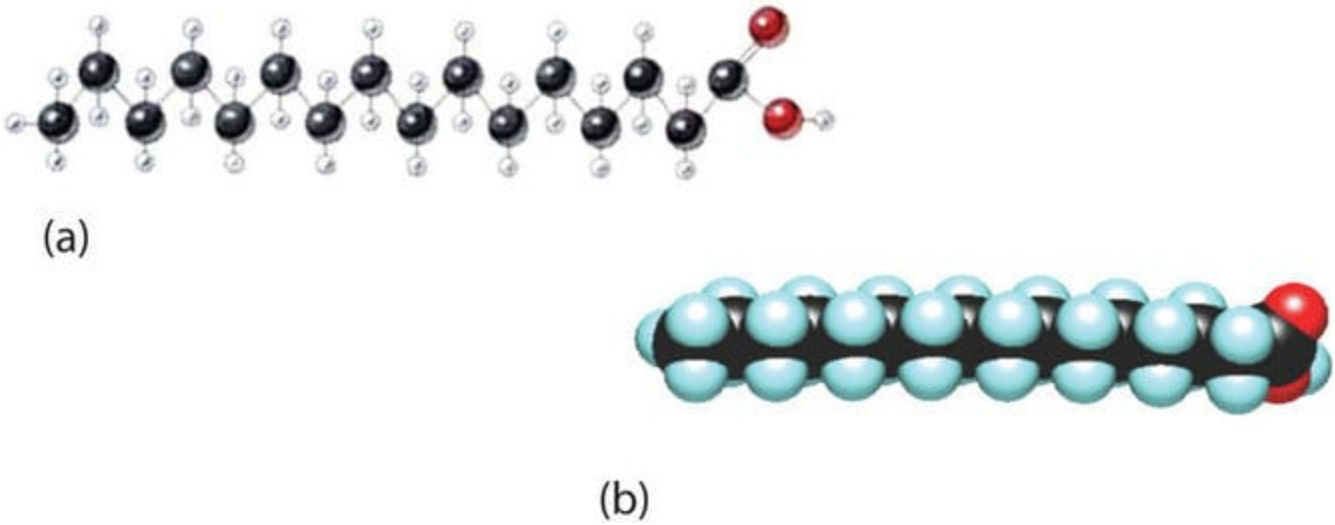
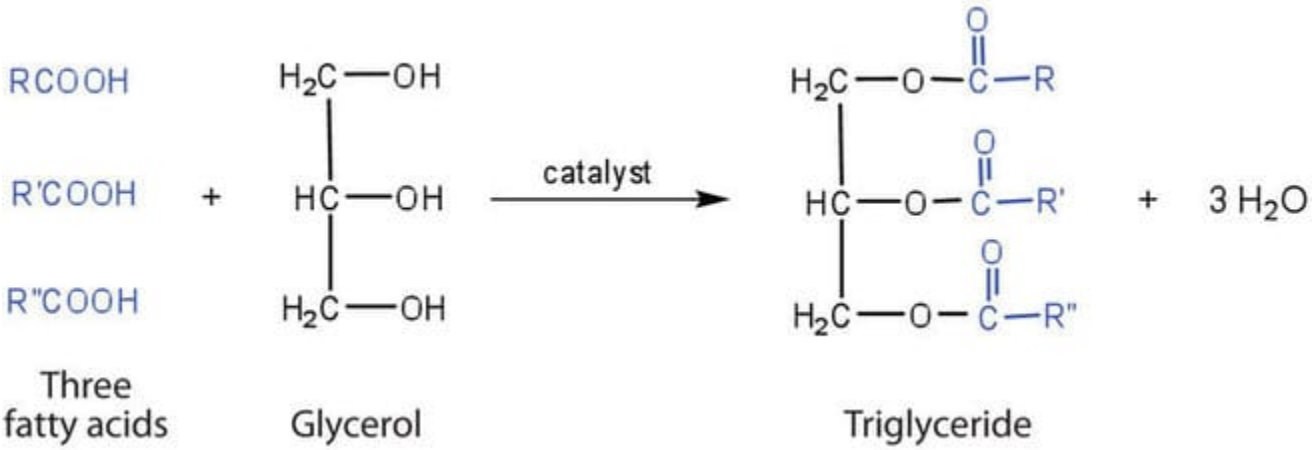


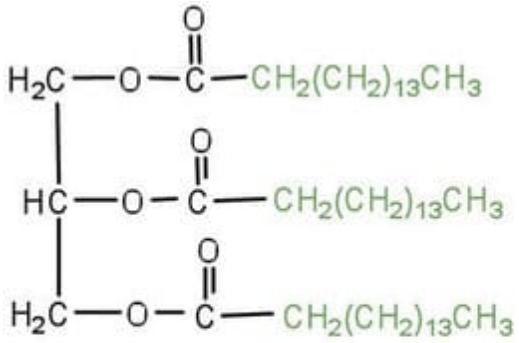
Figure 16.3.2 The Structure of Saturated Fatty Acids. (a) There is a zigzag pattern formed by the carbon-to-carbon single bonds in the ball-and-stick model of a palmitic acid molecule. (b) A space-filling model of palmitic acid shows the overall straightness of a saturated fatty acid molecule.

Structures of Fats and Oils

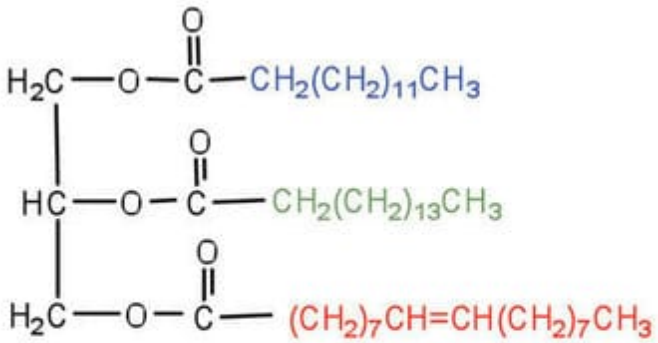
Fats and oils are called triglycerides (or *triacylcylgerols*) because they are esters composed of three fatty acid units joined to *glycerol*, a trihydroxy alcohol:



If all three OH groups on the glycerol molecule are esterified with the same fatty acid, the resulting ester is called a *simple triglyceride*. Although simple triglycerides have been synthesized in the laboratory, they rarely occur in nature. Instead, a typical triglyceride obtained from naturally occurring fats and oils contains two or three different fatty acid components and is thus termed a *mixed triglyceride*.



Tristearin
a simple triglyceride



a mixed triglyceride

A triglyceride is called a fat if it is a solid at 25°C; it is called an oil if it is a liquid at that temperature. These differences in melting points reflect differences in the degree of unsaturation and number of carbon atoms in the constituent fatty acids. Triglycerides obtained from animal sources are usually solids, while those of plant origin are generally oils. Therefore, we commonly speak of animal fats and vegetable oils.

No single formula can be written to represent the naturally occurring fats and oils because they are highly complex mixtures of triglycerides in which many different fatty acids are represented. Table 16.3.2 shows the fatty acid compositions of some common fats and oils. The composition of any given fat or oil can vary depending on the plant or animal species it comes from as well as on dietetic and climatic factors. To cite just one example, lard from corn-fed hogs is more highly saturated than lard from peanut-fed hogs. Palmitic acid is the most abundant of the saturated fatty acids, while oleic acid is the most abundant unsaturated fatty acid.

Table 16.3.2 Average Fatty Acid Composition of Some Common Fats and Oils (%).*

	Lauric	Myristic	Palmitic	Stearic	Oleic	Linoleic	Linolenic
Fats							
butter (cow)	3	11	27	12	29	2	1
tallow		3	24	19	43	3	1
lard		2	26	14	44	10	
Oils							
canola oil			4	2	62	22	10
coconut oil†	47	18	9	3	6	2	
corn oil			11	2	28	58	1
olive oil			13	3	71	10	1
peanut oil			11	2	48	32	
soybean oil			11	4	24	54	7

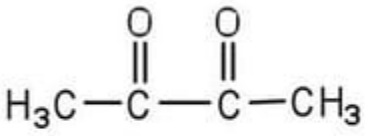
***Totals less than 100% indicate the presence of fatty acids with fewer than 12 carbon atoms or more than 18 carbon atoms.**

†Coconut oil is highly saturated. It contains an unusually high percentage of the low-melting C_8, C_{10}, and C_{12} saturated fatty acids.

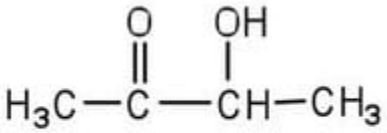
Terms such as ***saturated fat*** or *unsaturated oil* are often used to describe the fats or oils obtained from foods. **Saturated fats** contain a high proportion of saturated fatty acids, while **unsaturated oils** contain a high proportion of unsaturated fatty acids. The high consumption of saturated fats is a factor, along with the high consumption of cholesterol, in increased risks of heart disease.

Physical Properties of Fats and Oils

Contrary to what you might expect, *pure* fats and oils are colorless, odorless, and tasteless. The characteristic colors, odors, and flavors that we associate with some of them are imparted by foreign substances that are lipid soluble and have been absorbed by these lipids. For example, the yellow color of butter is due to the presence of the pigment carotene; the taste of butter comes from two compounds—diacetyl and 3-hydroxy-2-butanone—produced by bacteria in the ripening cream from which the butter is made.



Diacetyl

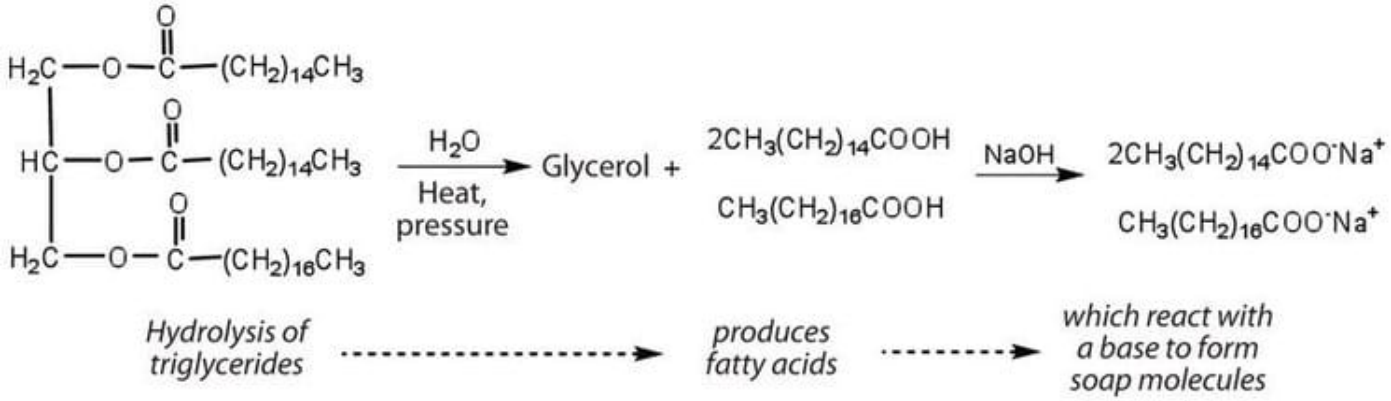


3-hydroxy-2-butanone

Fats and oils are lighter than water, having densities of about 0.8 g/cm^3. They are poor conductors of heat and electricity and therefore serve as excellent insulators for the body, slowing the loss of heat through the skin.

Chemical Reactions of Fats and Oils

Fats and oils can participate in a variety of chemical reactions—for example, because triglycerides are esters, they can be hydrolyzed in the presence of an acid, a base, or specific enzymes known as lipases. The hydrolysis of fats and oils in the presence of a base is used to make soap and is called saponification. Today most soaps are prepared through the hydrolysis of triglycerides (often from tallow, coconut oil, or both) using water under high pressure and temperature [700 lb/in^2 (~50 atm or 5,000 kPa) and 200°C]. Sodium carbonate or sodium hydroxide is then used to convert the fatty acids to their sodium salts (soap molecules):



Iodine Value

The **iodine value** (or **iodine adsorption value** or **iodine number** or **iodine index**, commonly abbreviated as **IV**) in chemistry is the mass of iodine in grams that is consumed by 100 grams of a chemical substance. Iodine numbers are often used to determine the amount of unsaturation in fats, oils and waxes. In fatty acids, unsaturation occurs mainly as double bonds which are very reactive towards halogens, the iodine in this case. Thus, the higher the iodine value, the more unsaturations are present in the fat. It can be seen from the table that coconut oil is very saturated, which means it is good for making soap. On the other hand, linseed oil is highly unsaturated, which makes it a drying oil, well suited for making oil paints.

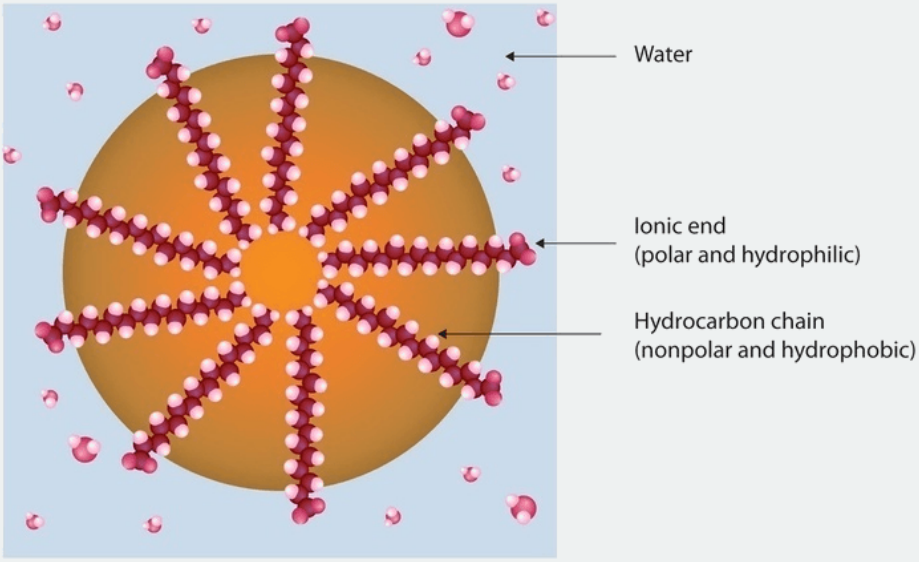
Table 16.3.1 *Iodine Numbers of Common Fats and Oils. Source Wikipedia*

Fat	Iodine Value (g/100g)
Beef tallow	42-48

Butter	25-42
Canola Oil	110-126
Coconut Oil	6-11
Fish oil	190-205
Linseed Oil	170-204
Olive Oil	75-94
Safflower Oil	135-150
Walnut Oil	132-162

Looking Closer: Soaps

Ordinary soap is a mixture of the sodium salts of various fatty acids, produced in one of the oldest organic syntheses practiced by humans (second only to the fermentation of sugars to produce ethyl alcohol). Both the Phoenicians (600 BCE) and the Romans made soap from animal fat and wood ash. Even so, the widespread production of soap



did not begin until the 1700s. Soap was traditionally made by treating molten lard or tallow with a slight excess of alkali in large open vats. The mixture was heated, and steam was bubbled through it. After saponification was completed, the soap was precipitated from the mixture by the addition of sodium chloride (NaCl), removed by filtration, and washed several times with water. It was then dissolved in water and reprecipitated by the addition of more NaCl. The glycerol produced in the reaction was also recovered from the aqueous wash solutions.

Pumice or sand is added to produce scouring soap, while ingredients such as perfumes or dyes are added to produce fragrant, colored soaps. Blowing air through molten soap produces a floating soap. Soft soaps, made with potassium salts, are more expensive but produce a finer lather and are more soluble. They are used in liquid soaps, shampoos, and shaving creams.

Dirt and grime usually adhere to skin, clothing, and other surfaces by combining with body oils, cooking fats, lubricating greases, and similar substances that act like glues. Because these substances are not miscible in water, washing with water alone does little to remove them. Soap removes them, however, because soap molecules have a dual nature. One end, called the *head*, carries an ionic charge (a carboxylate anion) and therefore dissolves in water; the other end, the *tail*, has a hydrocarbon structure and dissolves in oils. The hydrocarbon tails dissolve in the soil; the ionic heads remain in the aqueous phase, and the soap breaks the oil into tiny soap-enclosed droplets called *micelles*, which disperse throughout the solution. The droplets repel each other because of their charged surfaces and do not coalesce. With the oil no longer “gluing” the dirt to the soiled surface (skin, cloth, dish), the soap-enclosed dirt can easily be rinsed away.

Summary

- Fatty acids are carboxylic acids that are the structural components of many lipids.
- Saturated fatty acids contain no carbon-to-carbon double bonds, monounsaturated fatty acids contain one carbon-to-carbon double bond, and polyunsaturated fatty acids contain two or more carbon-to-carbon double bonds.
- Fats and oils are composed of molecules known as triglycerides, which are esters composed of three fatty acid units linked to glycerol.
- Fats and oils can participate in a variety of chemical reactions—for example, because triglycerides are esters, they can be hydrolyzed in the presence of an acid, a base, or specific enzymes known as lipases.
- The hydrolysis of fats and oils in the presence of a base is used to make soap and is called saponification.
- Animal fats and oils which are made up mostly of saturated fatty acids have low iodine values (numbers), while those oils with high degree of unsaturation (with more C=C bonds) have high iodine values.

Contributors and Attributions

- Libretext: The Basics od GOB Chemistry (Ball et al.)
- Wikipedia

- Marisa Alviar-Agnew (Sacramento City College)

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16.4: Proteins- Polymers of Amino Acids

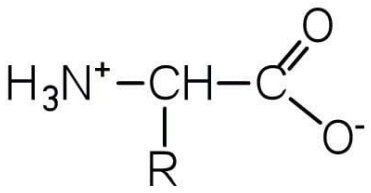
Learning Objectives

- Identify different amino acids.
- Describe how short chain proteins (polypeptides) are formed from amino acids.

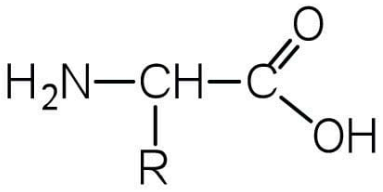
Proteins may be defined as compounds of high molar mass consisting largely or entirely of chains of amino acids. Their masses range from several thousand to several million daltons (Da). In addition to carbon, hydrogen, and oxygen atoms, all proteins contain nitrogen and sulfur atoms, and many also contain phosphorus atoms and traces of other elements. Proteins serve a variety of roles in living organisms and are often classified by these biological roles. Muscle tissue is largely protein, as are skin and hair. Proteins are present in the blood, in the brain, and even in tooth enamel. Each type of cell in our bodies makes its own specialized proteins, as well as proteins common to all or most cells. We begin our study of proteins by looking at the properties and reactions of amino acids, which is followed by a discussion of how amino acids link covalently to form peptides and proteins. We end the chapter with a discussion of enzymes—the proteins that act as catalysts in the body.

The proteins in all living species, from bacteria to humans, are constructed from the same set of 20 amino acids, so called because each contains an amino group attached to a carboxylic acid. The amino acids in proteins are α-amino acids, which means the amino group is attached to the α-carbon of the carboxylic acid. Humans can synthesize only about half of the needed amino acids; the remainder must be obtained from the diet and are known as essential amino acids. However, two additional amino acids have been found in limited quantities in proteins: Selenocysteine was discovered in 1986, while pyrrolysine was discovered in 2002.

The amino acids are colorless, nonvolatile, crystalline solids, melting and decomposing at temperatures above 200°C. These melting temperatures are more like those of inorganic salts than those of amines or organic acids and indicate that the structures of the amino acids in the solid state and in neutral solution are best represented as having both a negatively charged group and a positively charged group. Such a species is known as a zwitterion.



α-Amino acid drawn as a zwitterion



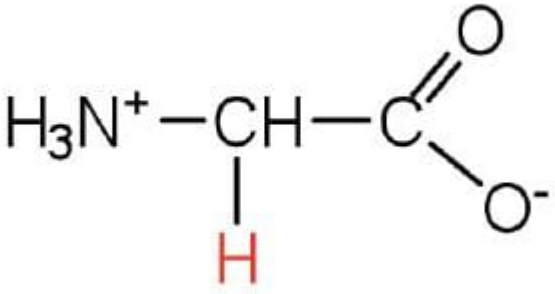
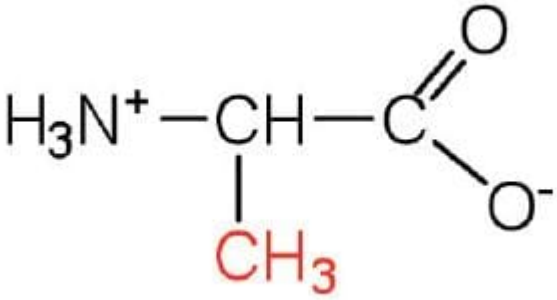
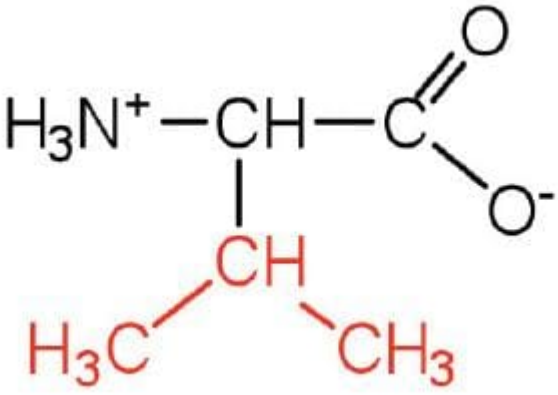
α-Amino acid drawn as an uncharged molecule; not an accurate respresentation of amino acid structure

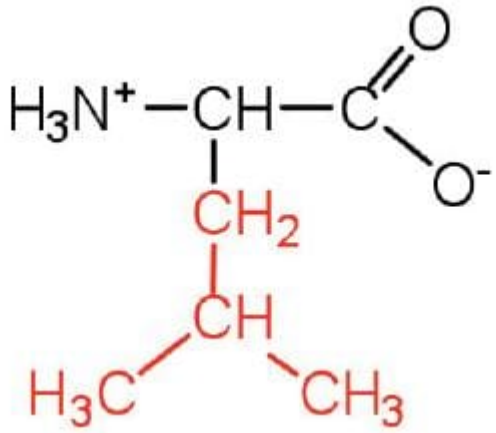
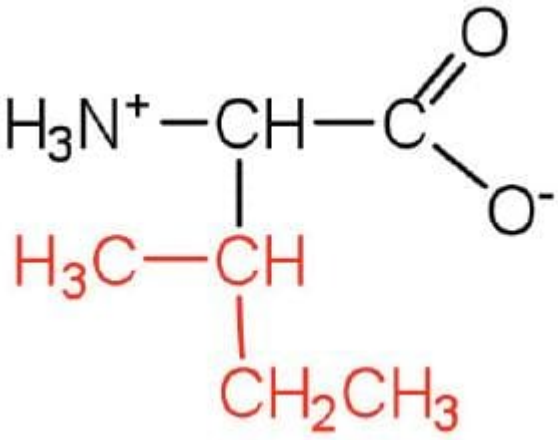
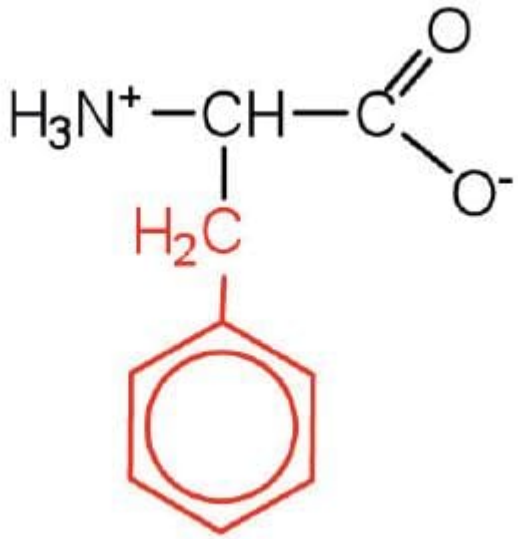
Classification

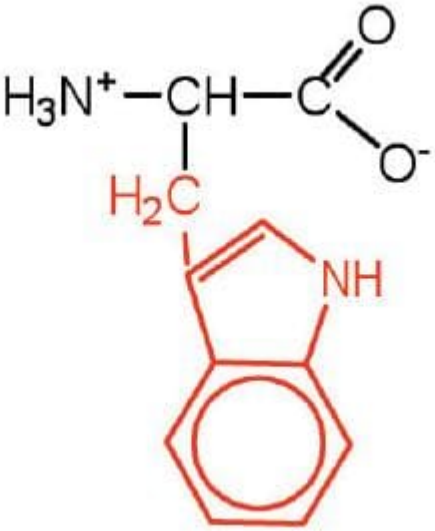
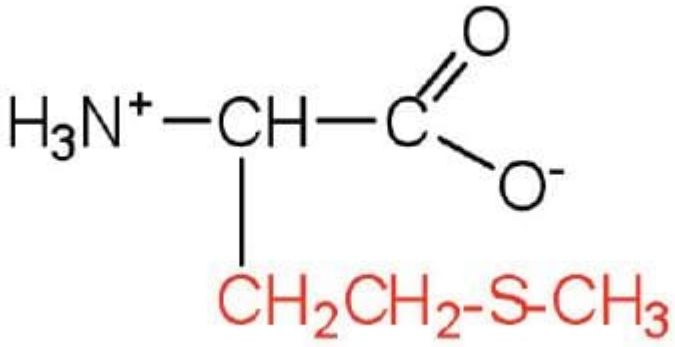
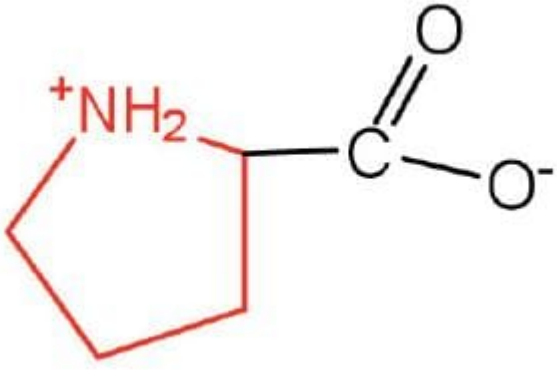
In addition to the amino and carboxyl groups, amino acids have a side chain or R group attached to the α-carbon. Each amino acid has unique characteristics arising from the size, shape, solubility, and ionization properties of its R group. As a result, the side chains of amino acids exert a profound effect on the structure and biological activity of proteins. Although amino acids can be classified in various ways, one common approach is to classify them according to whether the functional group on the side chain at neutral pH is nonpolar, polar but uncharged, negatively charged, or positively charged. The structures and names of the

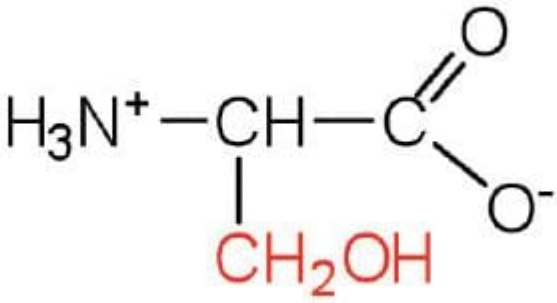
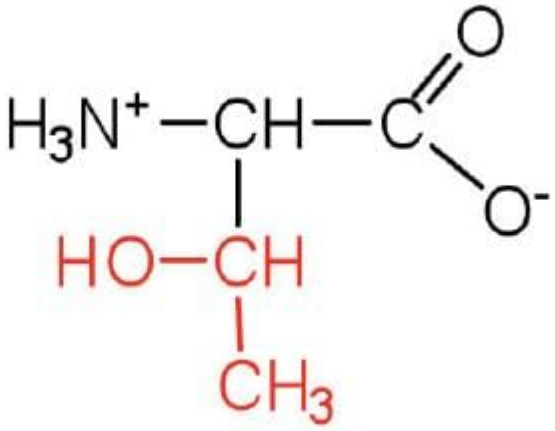
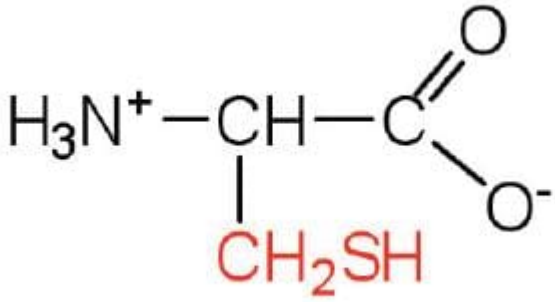
20 amino acids, their one- and three-letter abbreviations, and some of their distinctive features are given in Table 16.4.1.

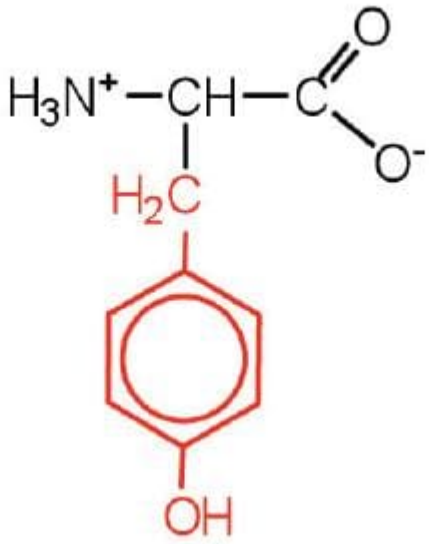
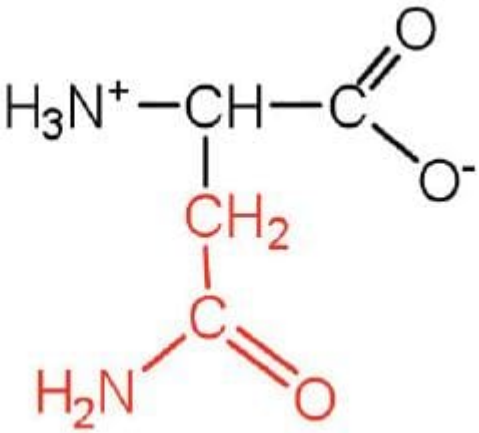
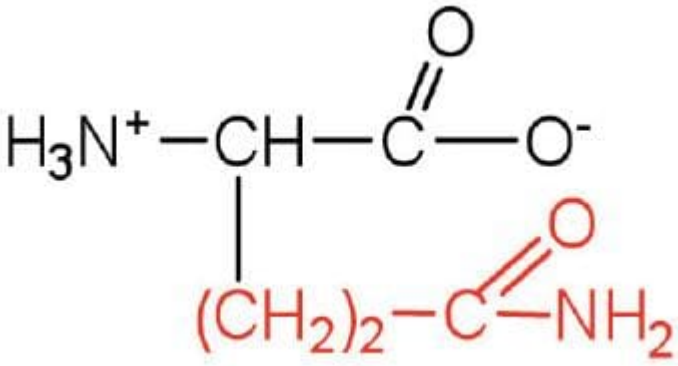
Table 16.4.1: Common Amino Acids Found in Proteins

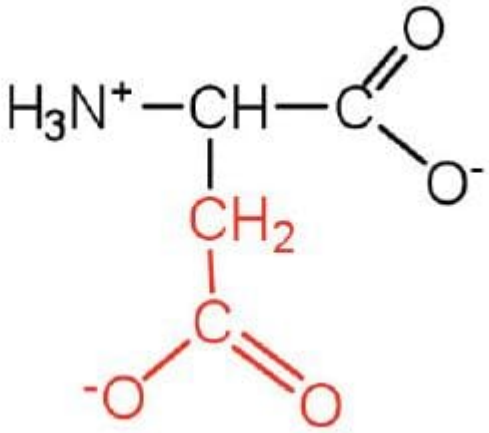
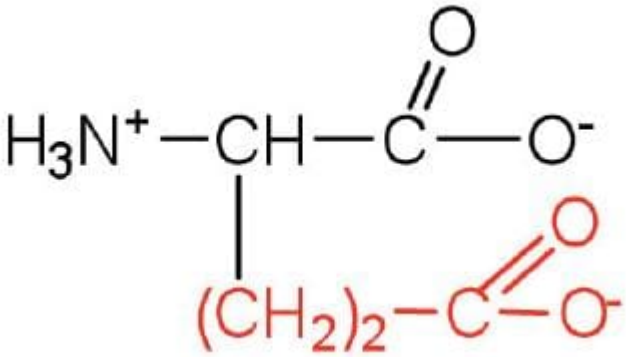
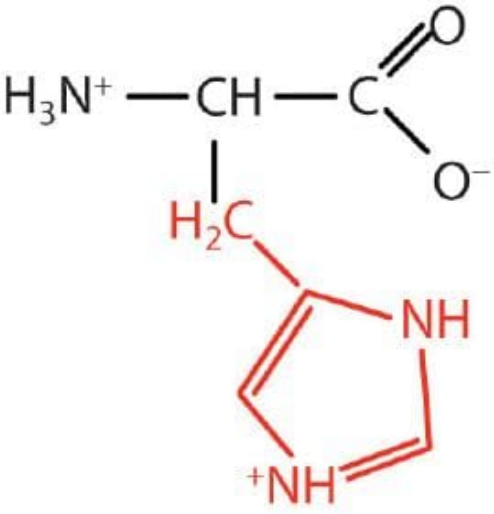
Common Name	Abbreviation	Structural Formula (at pH 6)
		Amino acids with a nonpolar R group
glycine	gly (G)	
alanine	ala (A)	
valine	val (V)	

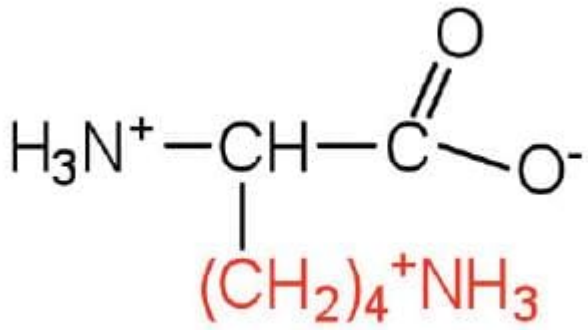
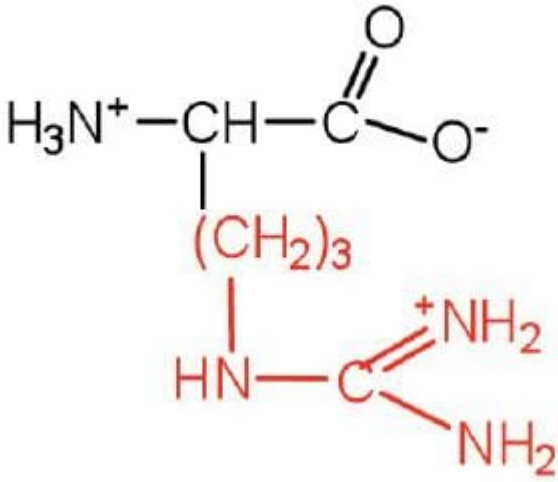
Common Name	Abbreviation	Structural Formula (at pH 6)
leucine	leu (L)	
isoleucine	ile (I)	
phenylalanine	phe (F)	

Common Name	Abbreviation	Structural Formula (at pH 6)
tryptophan	trp (W)	
methionine	met (M)	
proline	pro (P)	
		Amino acids with a polar but neutral R group

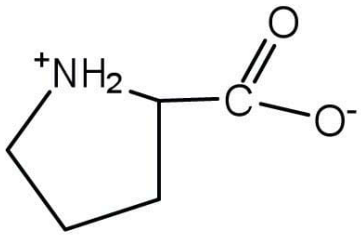
Common Name	Abbreviation	Structural Formula (at pH 6)
serine	ser (S)	
threonine	thr (T)	
cysteine	cys (C)	

Common Name	Abbreviation	Structural Formula (at pH 6)
tyrosine	tyr (Y)	
asparagine	asn (N)	
glutamine	gln (Q)	
		Amino acids with a negatively charged R group

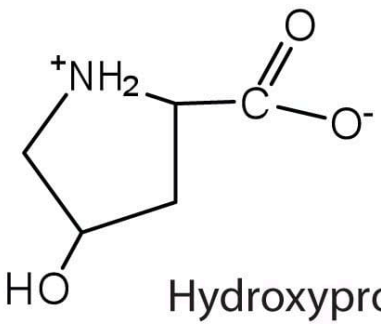
Common Name	Abbreviation	Structural Formula (at pH 6)
aspartic acid	asp (D)	
glutamic acid	glu (E)	
		Amino acids with a positively charged R group
histidine	his (H)	

Common Name	Abbreviation	Structural Formula (at pH 6)
lysine	lys (K)	
arginine	arg (R)	

The first amino acid to be isolated was asparagine in 1806. It was obtained from protein found in asparagus juice (hence the name). Glycine, the major amino acid found in gelatin, was named for its sweet taste (Greek *glykys*, meaning "sweet"). In some cases an amino acid found in a protein is actually a derivative of one of the common 20 amino acids (one such derivative is hydroxyproline). The modification occurs *after* the amino acid has been assembled into a protein.



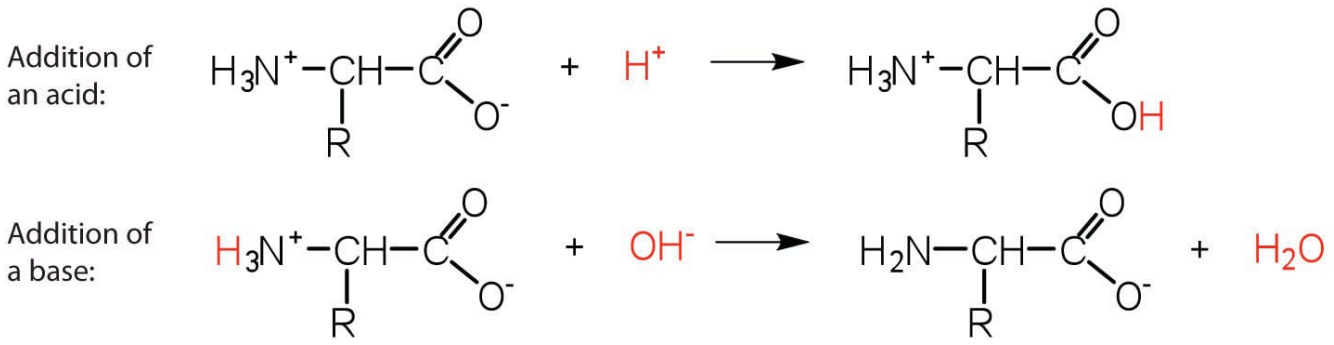
Proline



Hydroxyproline

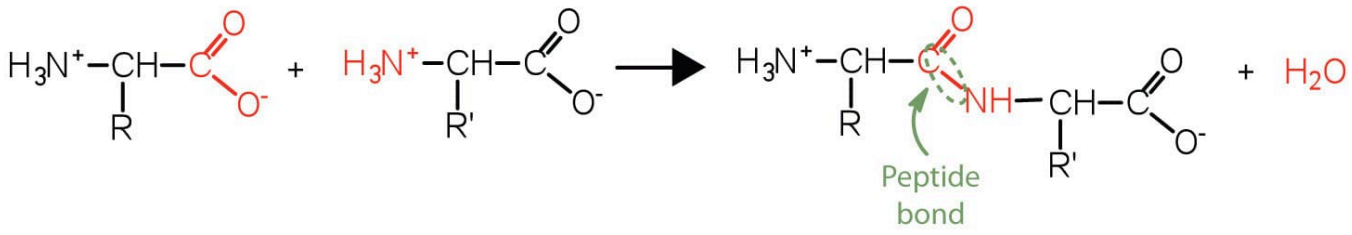
Zwitterions

The structure of an amino acid allows it to act as both an acid and a base. An amino acid has this ability because at a certain pH value (different for each amino acid) nearly all the amino acid molecules exist as zwitterions. If acid is added to a solution containing the zwitterion, the carboxylate group captures a hydrogen (H^+) ion, and the amino acid becomes positively charged. If base is added, ion removal of the H^+ ion from the amino group of the zwitterion produces a negatively charged amino acid. In both circumstances, the amino acid acts to maintain the pH of the system—that is, to remove the added acid (H^+) or base (OH^-) from solution.



The Peptide Bond: Peptides and Proteins

Two or more amino acids can join together into chains called peptides. Previously, we discussed the reaction between ammonia and a carboxylic acid to form an amide. In a similar reaction, the amino group on one amino acid molecule reacts with the carboxyl group on another, releasing a molecule of water and forming an amide linkage as shown in Figure 16.4.1



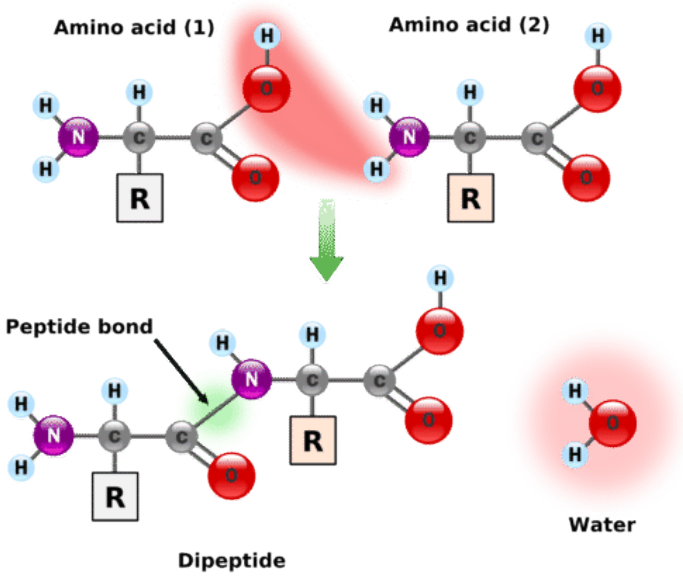
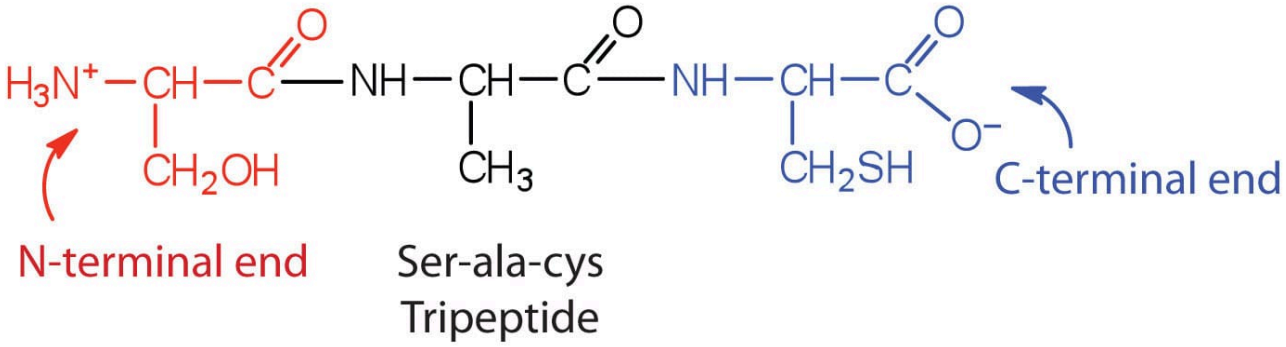


Figure 16.4.1 *Amino acids undergo condensation to form a molecule called a dipeptide. The* C—N *bond is called a peptide bond.*

An amide bond joining two amino acid units is called a peptide bond. Note that the product molecule still has a reactive amino group on the left and a reactive carboxyl group on the right. These can react with additional amino acids to lengthen the peptide. The process can continue until thousands of units have joined, resulting in large proteins.

A chain consisting of only two amino acid units is called a *dipeptide*; a chain consisting of three is a *tripeptide*. By convention, peptide and protein structures are depicted with the amino acid whose amino group is free (the N-terminal end) on the left and the amino acid with a free carboxyl group (the C-terminal end) to the right.



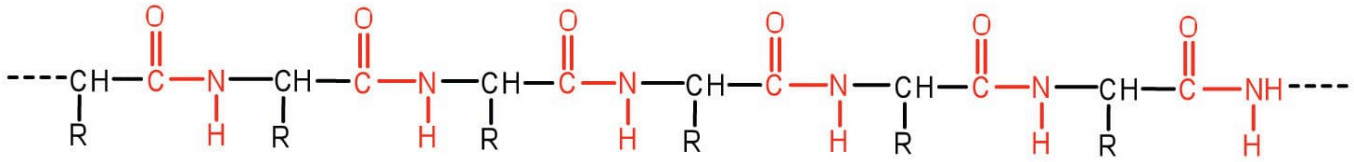
The general term *peptide* refers to an amino acid chain of unspecified length. However, chains of about 50 amino acids or more are usually called proteins or polypeptides. In its physiologically active form, a protein may be composed of one or more polypeptide chains.

Peptide cells in our bodies have an intricate mechanism for the manufacture of proteins. Humans have to use other techniques in order to synthesize the same proteins in a lab. The chemistry of peptide synthesis is complicated. Both active groups on an amino acid can react and the amino acid sequence must be a specific one in order for the protein to function. Robert Merrifield developed the first synthetic approach for making proteins in the lab, a manual approach which was lengthy and tedious (and, he won the Nobel Prize in Chemistry in 1984 for his work). Today, however, automated systems can crank out a peptide in a very short period of time.

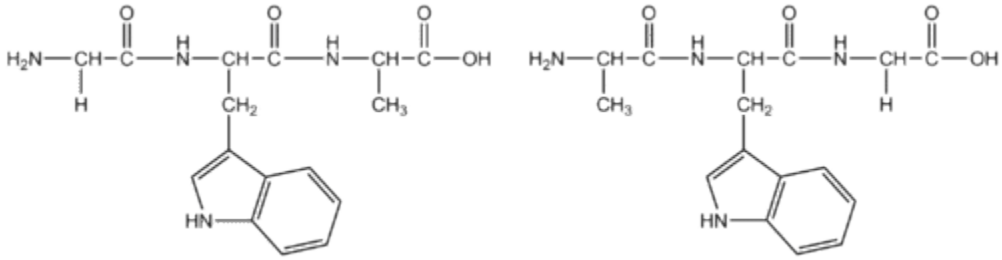
The Sequence of Amino Acids

The particular sequence of amino acids in a longer chain is called an amino acid sequence. By convention, the amino acid sequence is listed in the order such that the free amine group is on the left end of the molecule and the free carboxyl group is on

the right end of the molecule.



For example, suppose that a sequence of the amino acids glycine, tryptophan, and alanine is formed with the free amine group as part of the glycine and the free carboxyl group as part of the alanine. The amino acid sequence can be easily written using the abbreviations as Gly-Trp-Ala. This is a different sequence from Ala-Trp-Gly because the free amine and carboxyl groups would be on different amino acids in that case.



Gly-Trp-Ala

Ala-Trp-Gly

Bradykinin

For peptides and proteins to be physiologically active, it is not enough that they incorporate certain amounts of specific amino acids. The order, or *sequence*, in which the amino acids are connected is also of critical importance. Bradykinin is a nine-amino acid peptide (Figure 16.4.2) produced in the blood that has the following amino acid sequence:

arg-pro-pro-gly-phe-ser-pro-phe-arg

This peptide lowers blood pressure, stimulates smooth muscle tissue, increases capillary permeability, and causes pain. When the order of amino acids in bradykinin is reversed,

arg-phe-pro-ser-phe-gly-pro-pro-arg

the peptide resulting from this synthesis shows none of the activity of bradykinin.

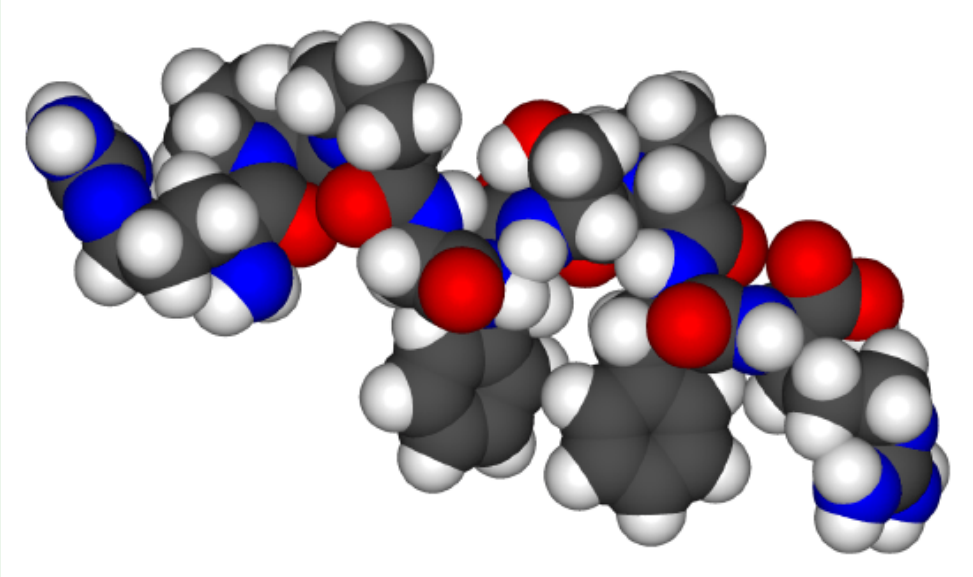


Figure 16.4.2 Space-filling model of bradykinin. (Public Domain; Fvasconcellos)

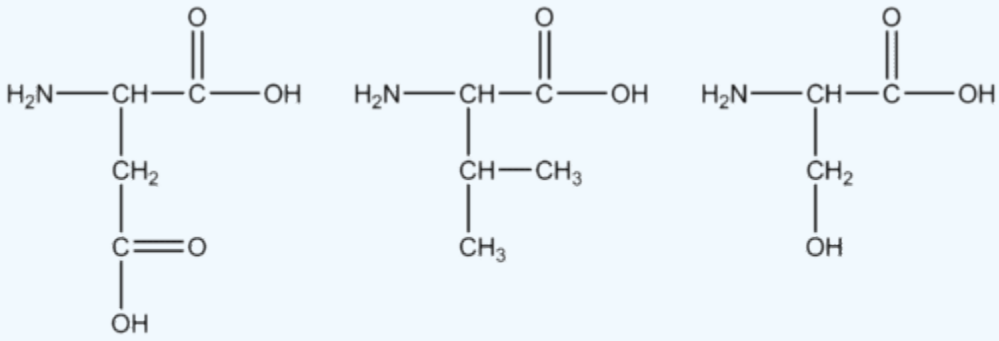
Just as millions of different words are spelled with our 26-letter English alphabet, millions of different proteins are made with the 20 common amino acids. However, just as the English alphabet can be used to write gibberish, amino acids can be put together in the *wrong sequence* to produce nonfunctional proteins. Although the correct sequence is ordinarily of utmost importance, it is not always absolutely required. Just as you can sometimes make sense of incorrectly spelled English words, a protein with a small percentage of "incorrect" amino acids may continue to function. However, it rarely functions as well as a protein having the correct sequence. There are also instances in which seemingly minor errors of sequence have disastrous effects. For example, in some people, every molecule of hemoglobin (a protein in the blood that transports oxygen) has a single incorrect amino acid unit out of about 300 (a single valine replaces a glutamic acid). That "minor" error is responsible for sickle cell anemia, an inherited condition that usually is fatal.

Example 16.4.1

Draw the polypeptide Asp-Val-Ser.

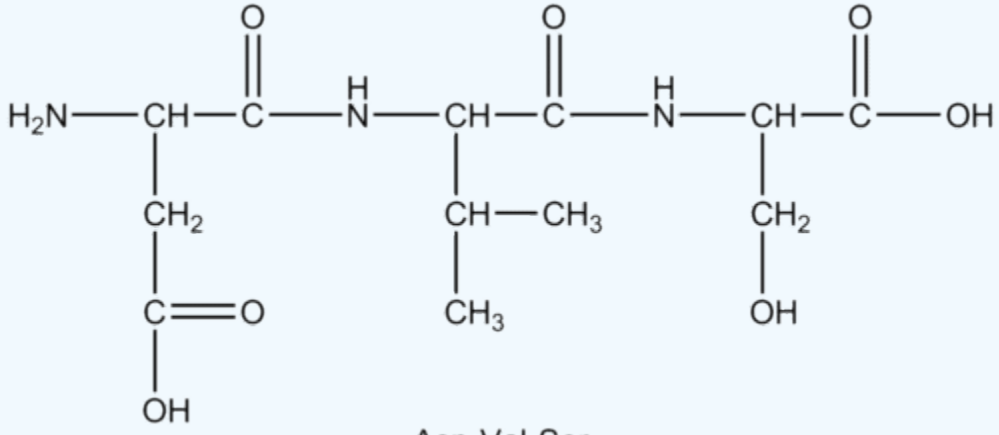
Solution

1. Identify the structures of each of the three given amino acids and draw them in the same order as given in the name.



Asp Val Ser

2. Leaving the order the same, connect the amino acids to one another by forming peptide bonds. Note that the order given in the name is the same way the amino acids are connected in the molecule. The first one listed is always the N-terminus of the polypeptide.



Asp-Val-Ser

Example 16.4.2

List all of the possible polypeptides that can be formed from cysteine (Cys), leucine (Leu), and arginine (Arg).

Solution

Although there are only three amino acids, the order in which they are bonded changes the identity, properties, and function of the resulting polypeptide. There are six possible polypeptides formed from these three amino acids.

Cys-Leu-Arg

Cys-Arg-Leu

Leu-Cys-Arg

Leu-Arg-Cys

Arg-Cys-Leu

Arg-Leu-Cys

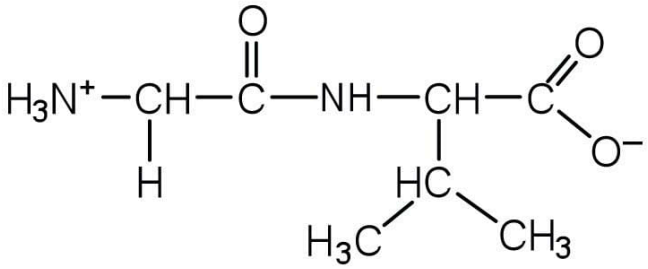
Exercise 16.4.1

Draw the structure for each peptide.

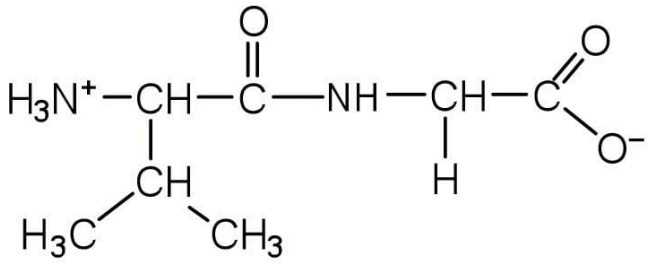
a. gly-val
b. val-gly

Answers

a.



b.



Summary

- The amino group of one amino acid can react with the carboxyl group on another amino acid to form a peptide bond that links the two amino acids together.
- Additional amino acids can be added on through the formation of addition peptide (amide) bonds.
- A chain consisting of only two amino acid units is called a *dipeptide*; a chain consisting of three is a *tripeptide*.
- Chains of about 50 amino acids or more are usually called proteins or polypeptides.
- A sequence of amino acids in a peptide or protein is written with the N-terminal amino acid first and the C-terminal amino acid at the end (writing left to right).
- The order, or *sequence*, in which the amino acids are connected is also of critical importance in order for a peptide or protein to be physiologically active.

Contributors and Attributions

- Libretext: The Basics of GOB Chemistry (Ball et al.)
-

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16.5: Structure and Function of Proteins

Learning Objectives

- Describe the four levels of protein structure.
- Identify the types of attractive interactions that hold proteins in their most stable three-dimensional structure
- Explain the role of an enzyme in the body.

Each of the thousands of naturally occurring proteins has its own characteristic amino acid composition and sequence that result in a unique three-dimensional shape. Since the 1950s, scientists have determined the amino acid sequences and three-dimensional conformation of numerous proteins and thus obtained important clues on how each protein performs its specific function in the body.

Proteins are compounds of high molar mass consisting largely or entirely of chains of amino acids. Because of their great complexity, protein molecules cannot be classified on the basis of specific structural similarities, as carbohydrates and lipids are categorized. The two major structural classifications of proteins are based on far more general qualities: whether the protein is (1) fiberlike and insoluble or (2) globular and soluble. Some proteins, such as those that compose hair, skin, muscles, and connective tissue, are fiberlike. These fibrous proteins are insoluble in water and usually serve structural, connective, and protective functions. Examples of fibrous proteins are keratins, collagens, myosins, and elastins. Hair and the outer layer of skin are composed of keratin. Connective tissues contain collagen. Myosins are muscle proteins and are capable of contraction and extension. Elastins are found in ligaments and the elastic tissue of artery walls.

Globular proteins, the other major class, are soluble in aqueous media. In these proteins, the chains are folded so that the molecule as a whole is roughly spherical. Familiar examples include egg albumin from egg whites and serum albumin in blood. Serum albumin plays a major role in transporting fatty acids and maintaining a proper balance of osmotic pressures in the body. Hemoglobin and myoglobin, which are important for binding oxygen, are also globular proteins.

Levels of Protein Structure

The structure of proteins is generally described as having four organizational levels. The first of these is the **primary structure**, which is the number and sequence of amino acids in a protein's polypeptide chain or chains, beginning with the free amino group and maintained by the peptide bonds connecting each amino acid to the next. The primary structure of insulin, composed of 51 amino acids, is shown in Figure 16.5.1.

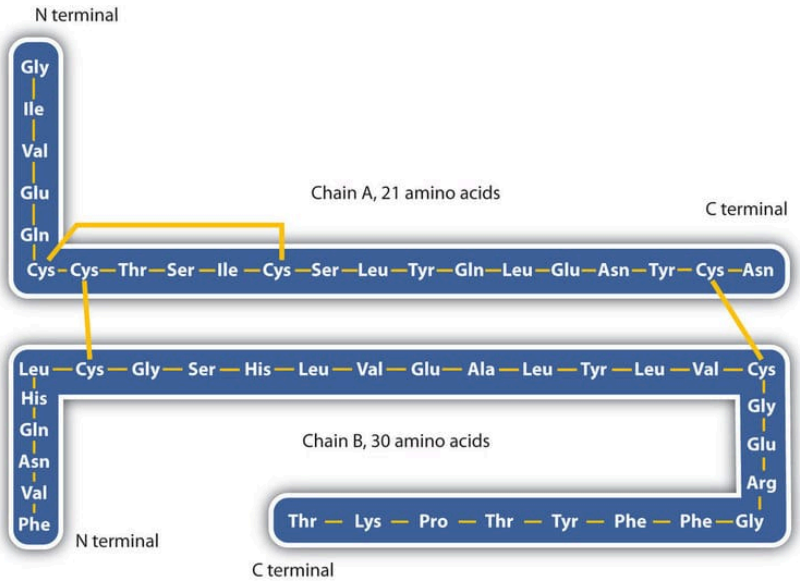


Figure 16.5.1 Primary Structure of Human Insulin. Human insulin, whose amino acid sequence is shown here, is a hormone that is required for the proper metabolism of glucose.

A protein molecule is not a random tangle of polypeptide chains. Instead, the chains are arranged in unique but specific conformations. The term **secondary structure** refers to the fixed arrangement of the polypeptide backbone. On the basis of X ray studies, Linus Pauling and Robert Corey postulated that certain proteins or portions of proteins twist into a spiral or a helix. This helix is stabilized by *intrachain* hydrogen bonding between the carbonyl oxygen atom of one amino acid and the amide hydrogen atom four amino acids up the chain (located on the next turn of the helix) and is known as a right-handed α-helix. X ray data indicate that this helix makes one turn for every 3.6 amino acids, and the side chains of these amino acids project outward from the coiled backbone (Figure 16.5.2). The α-keratins, found in hair and wool, are exclusively α-helical in conformation. Some proteins, such as gamma globulin, chymotrypsin, and cytochrome c, have little or no helical structure. Others, such as hemoglobin and myoglobin, are helical in certain regions but not in others.

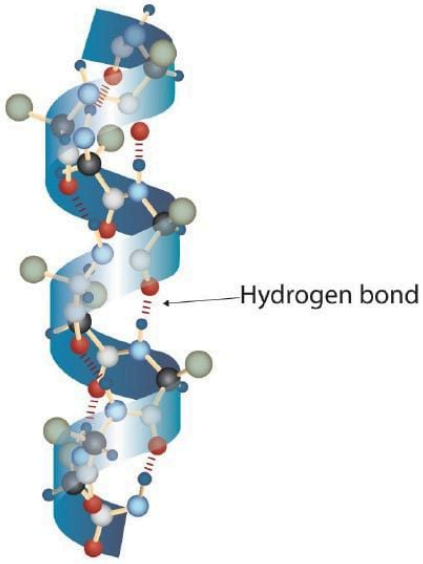


Figure 16.5.2 A Ball-and-Stick Model of an α-Helix. This ball-and-stick model shows the intrachain hydrogen bonding between carbonyl oxygen atoms and amide hydrogen atoms. Each turn of the helix spans 3.6 amino acids. Note that the side chains (represented as green spheres) point out from the helix.

Another common type of secondary structure, called the *β-pleated sheet conformation*, is a sheetlike arrangement in which two or more extended polypeptide chains (or separate regions on the same chain) are aligned side by side. The aligned segments can run either parallel or antiparallel—that is, the N-terminals can face in the same direction on adjacent chains or in different directions—and are connected by *interchain* hydrogen bonding (Figure 16.5.3). The β-pleated sheet is particularly important in

structural proteins, such as silk fibroin. It is also seen in portions of many enzymes, such as carboxypeptidase A and lysozyme.

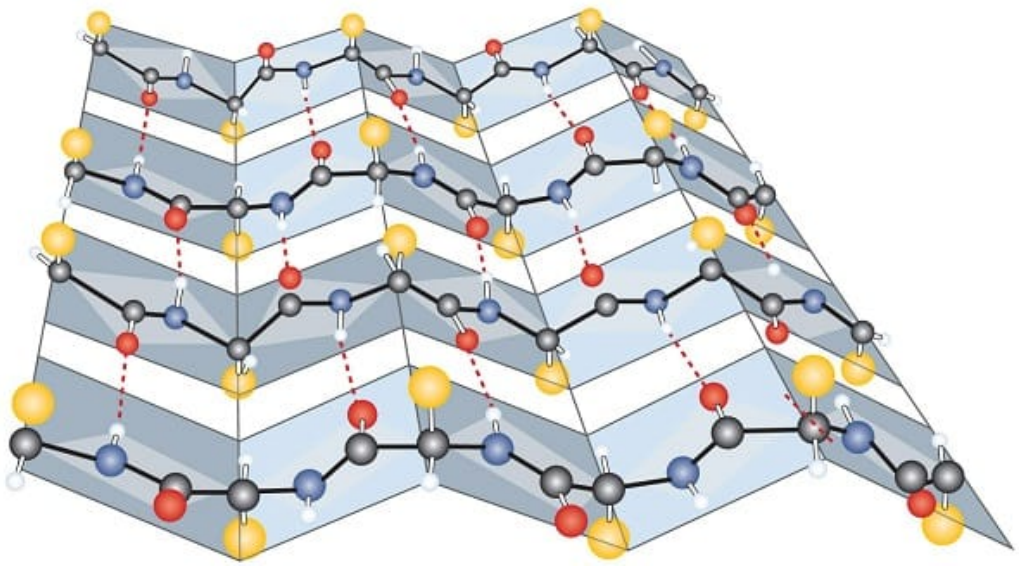


Figure 16.5.3 A Ball-and-Stick Model of the β-Pleated Sheet Structure in Proteins. The side chains extend above or below the sheet and alternate along the chain. The protein chains are held together by interchain hydrogen bonding.

Tertiary structure refers to the unique three-dimensional shape of the protein as a whole, which results from the folding and bending of the protein backbone. The tertiary structure is intimately tied to the proper biochemical functioning of the protein. Figure 16.5.4 shows a depiction of the three-dimensional structure of insulin.

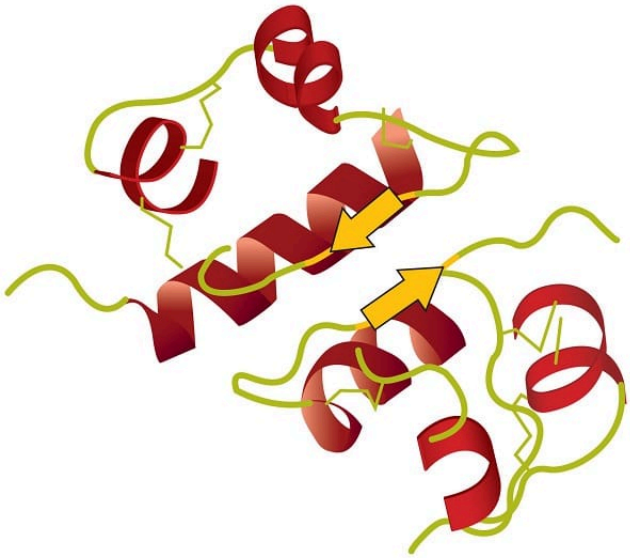


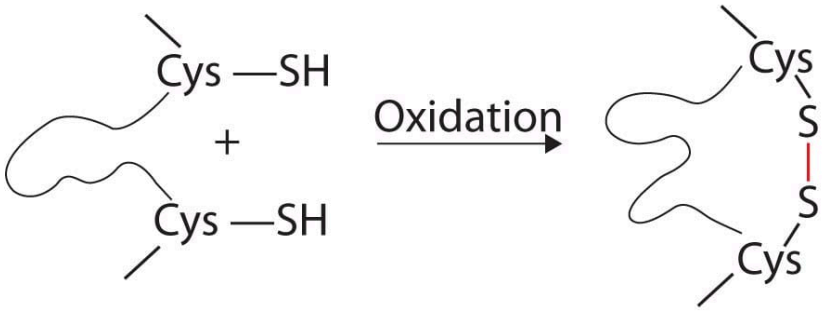
Figure 16.5.4 A Ribbon Model of the Three-Dimensional Structure of Insulin. The spiral regions represent sections of the polypeptide chain that have an α-helical structure, while the broad arrows represent β-pleated sheet structures.

Four major types of attractive interactions determine the shape and stability of the tertiary structure of proteins.

You studied several of them previously.

1. Ionic bonding. Ionic bonds result from electrostatic attractions between positively and negatively charged side chains of amino acids. For example, the mutual attraction between an aspartic acid carboxylate ion and a lysine ammonium ion helps to maintain a particular folded area of a protein (part (a) of Figure 16.5.5).

2. Hydrogen bonding. Hydrogen bonding forms between a highly electronegative oxygen atom or a nitrogen atom and a hydrogen atom attached to another oxygen atom or a nitrogen atom, such as those found in polar amino acid side chains. Hydrogen bonding (as well as ionic attractions) is extremely important in both the intra- and intermolecular interactions of proteins (part (b) of Figure 16.5.5).
3. Disulfide linkages. Two cysteine amino acid units may be brought close together as the protein molecule folds. Subsequent oxidation and linkage of the sulfur atoms in the highly reactive sulfhydryl (SH) groups leads to the formation of cystine (part (c) of Figure 16.5.5). Intrachain disulfide linkages are found in many proteins, including insulin (yellow bars in Figure 16.5.1) and have a strong stabilizing effect on the tertiary structure.



4. Dispersion forces. Dispersion forces arise when a normally nonpolar atom becomes momentarily polar due to an uneven distribution of electrons, leading to an instantaneous dipole that induces a shift of electrons in a neighboring nonpolar atom. Dispersion forces are weak but can be important when other types of interactions are either missing or minimal (part (d) of Figure 16.5.5). This is the case with fibroin, the major protein in silk, in which a high proportion of amino acids in the protein have nonpolar side chains. The term *hydrophobic interaction* is often misused as a synonym for dispersion forces. Hydrophobic interactions arise because water molecules engage in hydrogen bonding with other water molecules (or groups in proteins capable of hydrogen bonding). Because nonpolar groups cannot engage in hydrogen bonding, the protein folds in such a way that these groups are buried in the interior part of the protein structure, minimizing their contact with water.

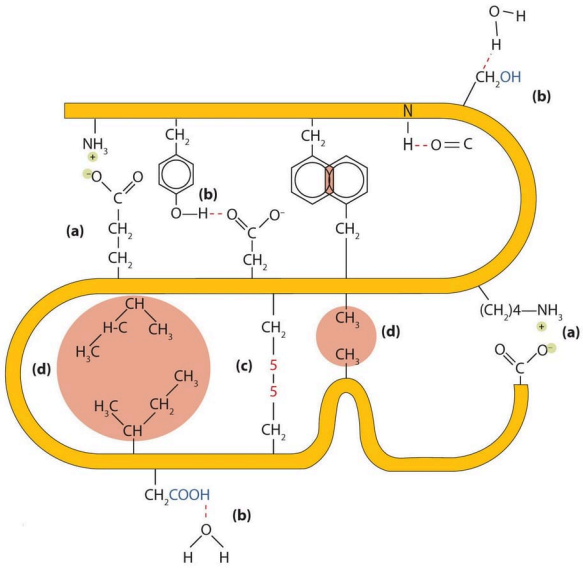


Figure 16.5.5 Tertiary Protein Structure Interactions. Four interactions stabilize the tertiary structure of a protein: (a) ionic bonding, (b) hydrogen bonding, (c) disulfide linkages, and (d) dispersion forces.

When a protein contains more than one polypeptide chain, each chain is called a *subunit*. The arrangement of multiple subunits represents a fourth level of structure, the quaternary structure of a protein. Hemoglobin, with four polypeptide chains or subunits, is the most frequently cited example of a protein having quaternary structure (Figure 16.5.6). The quaternary structure of a protein is produced and stabilized by the same kinds of interactions that produce and maintain the tertiary structure. A schematic representation of the four levels of protein structure is in Figure 16.5.7.



Figure 16.5.6 The Quaternary Structure of Hemoglobin. Hemoglobin is a protein that transports oxygen throughout the body.

Source: Image from the RCSB PDB (www.pdb.org) of PDB ID 1I3D (R.D. Kidd, H.M. Baker, A.J. Mathews, T. Brittain, E.N. Baker (2001) Oligomerization and ligand binding in a homotetrameric hemoglobin: two high-resolution crystal structures of hemoglobin Bart's (gamma(4)), a marker for alpha-thalassemia. Protein Sci. 1739–1749).

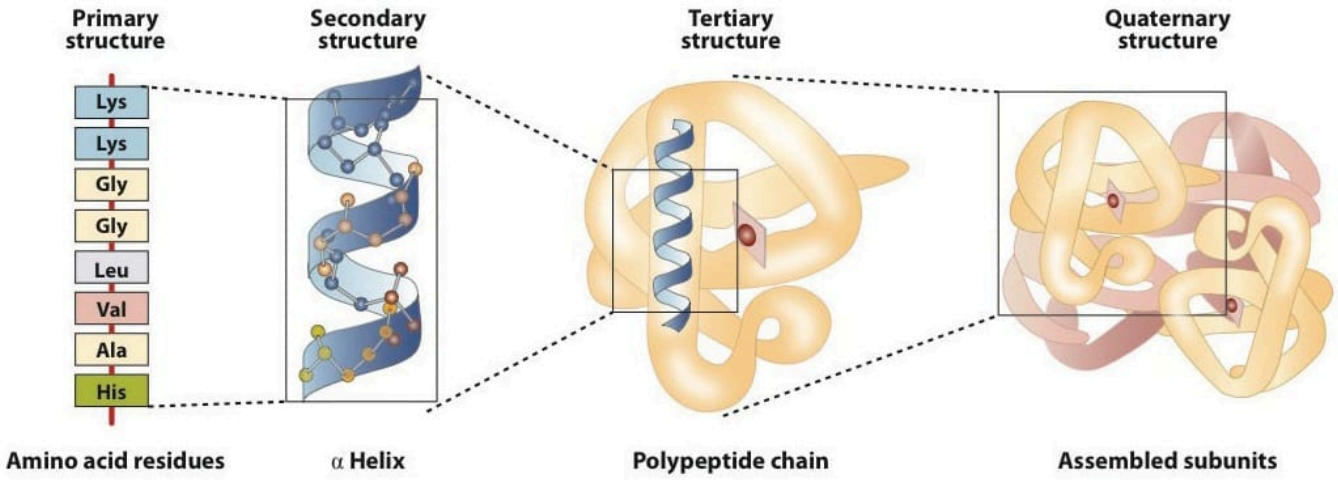


Figure 16.5.7 Levels of Structure in Proteins.

The *primary structure* consists of the specific amino acid sequence. The resulting peptide chain can twist into an α-helix, which is one type of *secondary structure*. This helical segment is incorporated into the *tertiary structure* of the folded polypeptide chain. The single polypeptide chain is a subunit that constitutes the *quaternary structure* of a protein, such as hemoglobin that has four polypeptide chains.

Globular and Fibrous Proteins

Once proteins form and have developed all levels of their structure, they can be classified as either fibrous or globular. These classifications give the basic shape of the entire protein molecule. While many proteins are **globular proteins** (see figure below), keratin proteins are **fibrous** (see figure below) and make up the hair, nails, and the outer layer of skin.

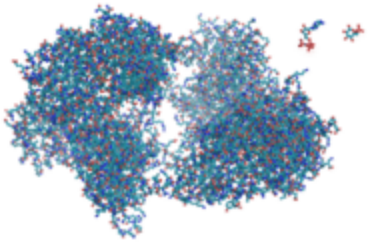


Figure 16.5.8 Globular protein.

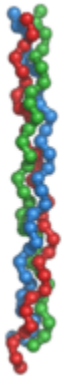


Figure 16.5.9 Fibrous protein.

Enzymes: Exquisite Precision Machines

The first enzyme to be isolated was discovered in 1926 by American chemist James Sumner, who crystallized the protein. The enzyme was urease, which catalyzes the hydrolytic decomposition of urea, a component of urine, into ammonia and carbon dioxide.

$$\mathrm{H_2NCON_2}\,(aq) + \mathrm{H_2O}\,(l) \overset{\text{urease}}{\rightarrow} 2\mathrm{NH_3}\,(g) + \mathrm{CO_2}\,(g)$$

His discovery was ridiculed at first because nobody believed that enzymes would behave the same way that other chemicals did. Sumner was eventually proven right and won the Nobel Prize in Chemistry in 1946.

Enzymes and Biochemical Reactions

Most chemical reactions within organisms would be impossible under the conditions in cells. For example, the body temperature of most organisms is too low for reactions to occur quickly enough to carry out life processes. Reactants may also be present in such low concentrations that it is unlikely they will meet and collide. Therefore, the rate of most biochemical reactions must be increased by a catalyst. A **catalyst** is a chemical that speeds up chemical reactions. In organisms, catalysts are called **enzymes**. Essentially, enzymes are biological catalysts.

Like other catalysts, enzymes are not reactants in the reactions they control. They help the reactants interact but are not used up in the reactions. Instead, they may be used over and over again. Unlike other catalysts, enzymes are usually highly specific for particular chemical reactions. They generally catalyze only one or a few types of reactions.

Enzymes are extremely efficient in speeding up reactions. They can catalyze up to several million reactions per second. As a result, the difference in rates of biochemical reactions with and without enzymes may be enormous. A typical biochemical reaction might take hours or even days to occur under normal cellular conditions without an enzyme, but less than a second with an enzyme.

Figure 16.5.10 diagrams a typical enzymatic reaction. A **substrate** is the molecule or molecules on which the enzyme acts. In the urease catalyzed reaction, urea is the substrate.

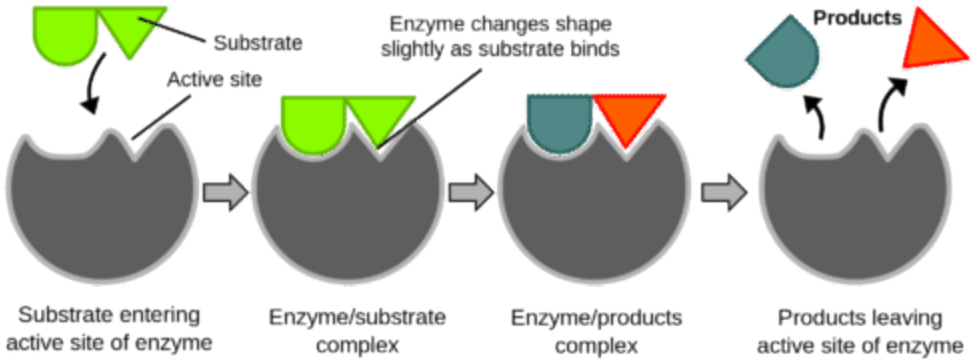


Figure 16.5.10 The sequence of steps for a substrate binding to an enzyme in its active site, reacting, then being released as products.

The first step in the reaction is that the substrate binds to a specific part of the enzyme molecule, known as the active site. The binding of the substrate is dictated by the shape of each molecule. Side chains on the enzyme interact with the substrate in a specific way, resulting in the making and breaking of bonds. The **active site** is the place on an enzyme where the substrate binds. An enzyme folds in such a way that it typically has one active site, usually a pocket or crevice formed by the folding pattern of the protein. Because the active site of an enzyme has such a unique shape, only one particular substrate is capable of binding to that enzyme. In other words, each enzyme catalyzes only one chemical reaction with only one substrate. Once the enzyme/substrate complex is formed, the reaction occurs and the substrate is transformed into products. Finally, the product molecule or molecules are released from the active site. Note that the enzyme is left unaffected by the reaction and is now capable of catalyzing the reaction of another substrate molecule.

For many enzymes, the active site follows a **lock and key** (Figure $16.5.11A$) model where the substrate fits exactly into the active site. The enzyme and substrate must be a perfect match so the enzyme only functions as a catalyst for one reaction. Other enzymes have an **induced fit** (Figure $16.5.11B$) model. In an induced fit model, the active site can make minor adjustments to accommodate the substrate. This results in an enzyme that is capable of interacting with a small group of similar substrates. Look at the shape of the active site compared to the shape of the substrate in B of the figure below. The active site adjusts to accommodate the substrate.

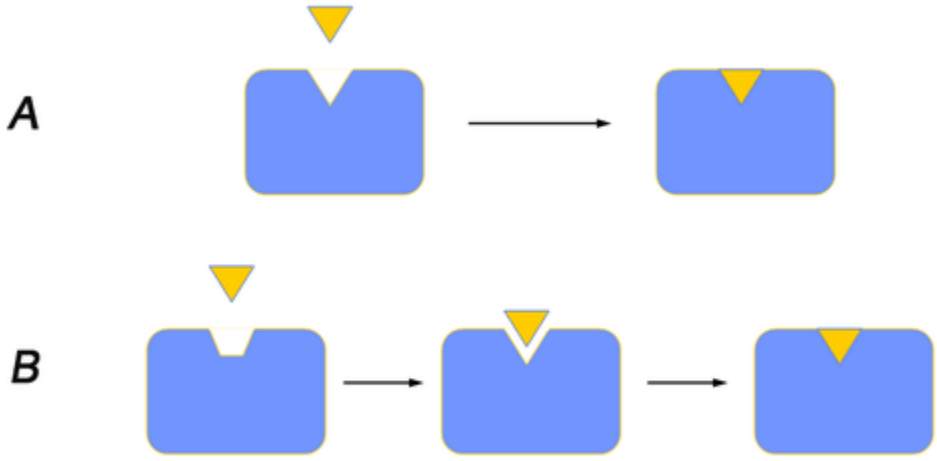


Figure 16.5.11 (A) Lock and key enzyme model and (B) induced fit enzyme model.

Inhibitors

An **inhibitor** is a molecule which interferes with the function of an enzyme, either by slowing or stopping the chemical reaction. Inhibitors can work in a variety of ways, but one of the most common is illustrated in the figure below.

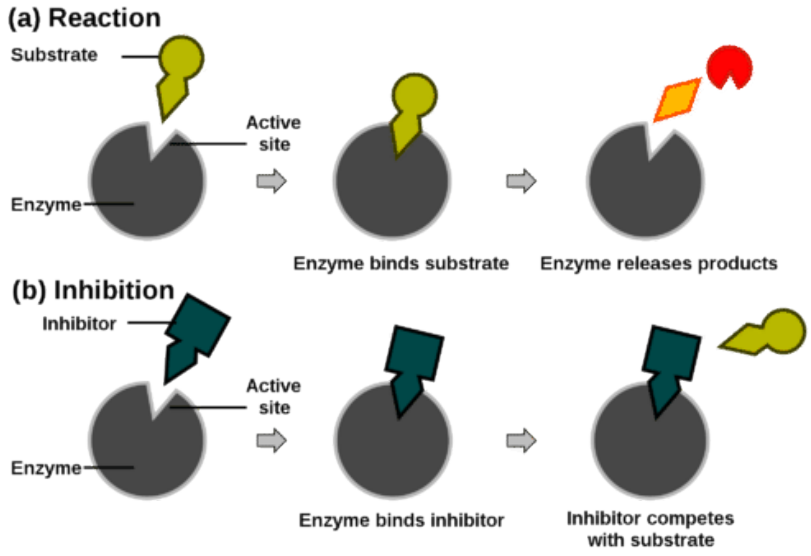


Figure 16.5.12 A competitive inhibitor is a molecule that binds to the active site of an enzyme without reacting, thus preventing the substrate from binding.

A **competitive inhibitor** binds competitively at the active site and blocks the substrate from binding. Since no reaction occurs with the inhibitor, the enzyme is prevented from catalyzing the reaction.

A **non-competitive inhibitor** does not bind at the active site. It attaches at an **allosteric site**, which is some other site on the enzyme, and changes the shape of the protein. The allosteric site is any site on the enzyme that is not the active site. The attachment of the non-competitive inhibitor to the allosteric site results in a shift in three-dimensional structure that alters the shape of the active site so that the substrate will no longer fit in the active site properly (see figure below).

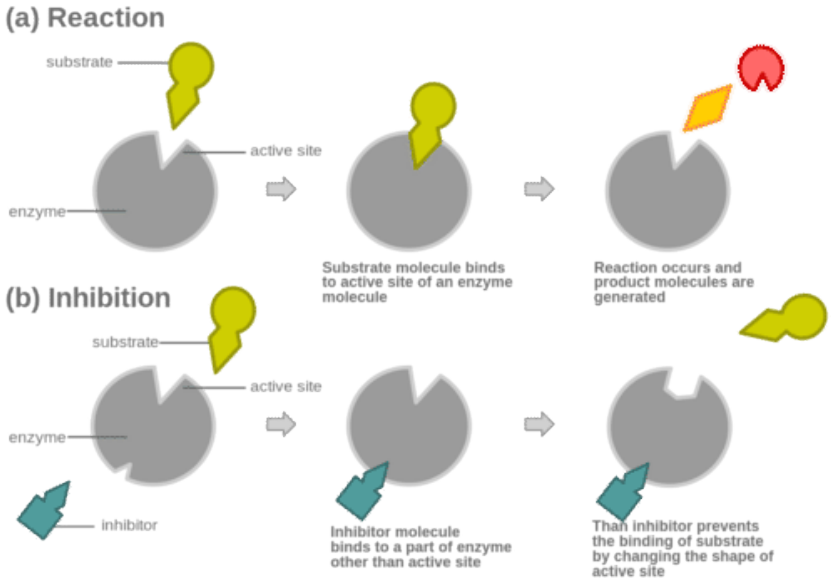


Figure 16.5.13 Non-competitive inhibition.

Cofactors and Coenzymes

Some enzymes require the presence of another substrate as a "helper" molecule in order to function properly. **Cofactors** and **coenzymes** serve in this role. Cofactors are inorganic species and coenzymes are small organic molecules. Many vitamins, such as B vitamins, are coenzymes. Some metal ions which function as cofactors for various enzymes include zinc, magnesium, potassium, and iron.

Catalytic Activity of Enzymes

Enzymes generally lower activation energy by reducing the energy needed for reactants to come together and react. One way that enzymes act is to bring reactants (substrates) together so they don't have to expend energy moving about until they collide at random. Enzymes bind both reactant molecules (substrates), tightly and specifically, at a site on the enzyme's active site. Enzymes can also bring molecules to the active site to break them apart. For example, sucrase is the enzyme for the breakdown of sucrose which enters the active site of the enzyme and helps weaken the interactions between the fructose and glucose that make up sucrose. Sucrase is specific to the breakdown of sucrose as are most enzymes. The active site is specific for the reactants of the biochemical reaction the enzyme catalyzes. Similar to puzzle pieces fitting together, the active site can only bind certain substrates. The activities of enzymes also depend on the temperature, concentration, and the pH of the surroudings.

Concentration

As with most reactions, the concentration of the reactant(s) affects the reaction rate. This is also true in enzyme concentration. When either substrate or enzyme concentration is low, the rate of the reaction will be slower than where there are higher concentrations. The two species must interact for a reaction to occur and higher concentrations of one or both will result in more effective interactions between the two.

However, continuing to increase the substrate's concentration will not always increase the reaction rate. This is because at some point, all of the enzymes will be occupied and unavailable to bind with another substrate molecule until the substrate forms a product molecule and is released from the enzyme.

pH

Some enzymes work best at acidic pHs, while others work best in neutral environments. For example, digestive enzymes secreted in the acidic environment (low pH) of the stomach help break down proteins into smaller molecules. The main digestive enzyme in the stomach is **pepsin**, which works best at a pH of about 1.5. These enzymes would not work optimally at other pHs. Trypsin is another enzyme in the digestive system, which breaks protein chains in food into smaller particles. **Trypsin** works in the small intestine, which is not an acidic environment. Trypsin's optimum pH is about 8.

Different reactions and different enzymes will achieve their maximum rate at certain pH values. As shown in the figure below, the enzyme achieves a maximum reaction rate at a pH of 4. Notice that the reaction will continue at lower and higher pH values because the enzyme will still function at other pH values but will not be as effective. At very high or very low pH values, denaturation will occur because an enzyme is just a protein with a specific function.

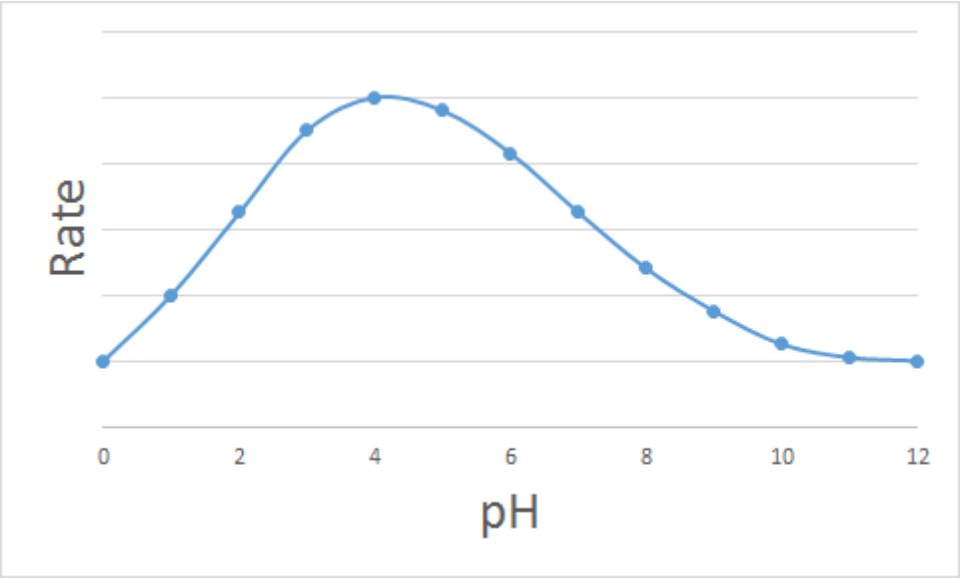


Figure 16.5.14 Relationship between rate and pH.

Temperature

As with pH, reactions also have an ideal temperature where the enzyme functions most effectively. It will still function at higher and lower temperatures, but the rate will be less. For many biological reactions, the ideal temperature is at physiological conditions which is around $37^{\circ}C$ which is normal body temperature. Many enzymes lose function at lower and higher temperatures. At higher temperatures, an enzyme's shape deteriorates. Only when the temperature comes back to normal does the enzyme regain its shape and normal activity unless the temperature was so high that it caused irreversible damage.

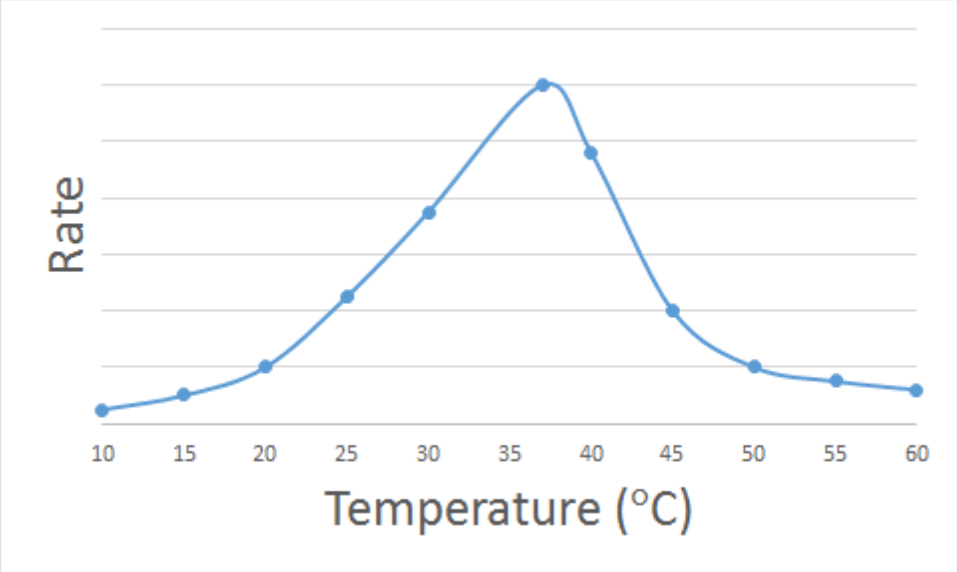


Figure 16.5.15 *Relationship between temperature and rate.*

Applications of Enzymes

Enzymes are used in the and other industrial applications when extremely specific catalysts are required (Table 16.5.1). Enzymes in general are limited in the number of reactions they have evolved to catalyze and also by their lack of stability in and at high temperatures. As a consequence, is an active area of research and involves attempts to create new enzymes with novel properties, either through rational design or *in vitro* evolution. These efforts have begun to be successful, and a few enzymes have now been designed "from scratch" to catalyze reactions that do not occur in nature.

Table 16.5.1 Uses of Enzymes in Various Industries. Source: Wikipedia

Application	**Enzymes used**	**Uses**
Biofuel industry	Cellulases	Break down cellulose into sugars that can be fermented to produce cellulosic ethanol.
	Ligninases	Pretreatment of biomass for biofuel production.
Biological detergent	Proteases, amylases, lipases	Remove protein, starch, and fat or oil stains from laundry and dish ware.
	Mannanases	Remove food stains from the common food additive guar gum.
Brewing industry	Amylase, glucanases, proteases	Split polysaccharides and proteins in the malt.
	Betaglucanases	Improve the wort and beer filtration characteristics.
	Amyloglucosisdase and pullulanases	Make low-calorie beer and adjust fermentability.
	Acetolacatate deacrboxylase (ALDC)	Increase fermentation efficiency by reducing diacetyl formation.
Culinary uses	Papain	Tenderize meat for cooking.
Dairy industry	Renin	Hydrolyze protein in the manufacture of cheese.

	Lipases	Produce Camembert cheese and blue cheese such as Roquefort.
Food processing	Amylases	Produce sugars from starch, such as in making high-fructose corn syrup.
	Proteases	Lower the protein level of flour, as in biscuit-making.
	Trypsin	Manufacture hypoallergenic baby foods.
	Cellulases, pectinases	Clarify fruit juices.
Molecular biology	Nucleases, DNA ligase, and polymerases	Use restriction digestion and the polymerase chain reaction to create recombinant DNA.
Paper industry	Xylanases, hemicellulases, and lignin peroxidases	Remove lignin from Kraft pulp.
Personal care	Proteases	Remove proteins on cotact lenses to prevent infections.
Starch industry	Amylases	Convert starch into glucose and various syrups.

YouTube Video

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Summary

- Proteins can be divided into two categories: fibrous, which tend to be insoluble in water, and globular, which are more soluble in water. A protein may have up to four levels of structure.
- The primary structure consists of the specific amino acid sequence.
- The resulting peptide chain can form an α-helix or β-pleated sheet (or local structures not as easily categorized), which is known as secondary structure. These segments of secondary structure are incorporated into the tertiary structure of the folded polypeptide chain.
- The quaternary structure describes the arrangements of subunits in a protein that contains more than one subunit. Four major types of attractive interactions determine the shape and stability of the folded protein: ionic bonding, hydrogen bonding, disulfide linkages, and dispersion forces.
- An enzyme is an organic catalyst produced by a living cell. Enzymes are such powerful catalysts that the reactions they promote occur rapidly at body temperature.
- The molecule or molecules on which an enzyme acts are called its substrates.
- An enzyme has an active site where its substrate or substrates bind to form an enzyme-substrate complex.
- The original lock and key model of enzyme and substrate binding pictured a rigid enzyme of unchanging configuration binding to the appropriate substrate. The newer induced fit model describes the enzyme active site as changing its conformation after binding to the substrate.
- Enzymes have numerous applications in the food and dairy industry, biofuel industry, paper industry etc.

Contributors and Attributions

- Libretext: The Basics of GOB Chemistry (Ball et al.)
-

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16.6: Nucleic Acids- Parts, Structure, and Function

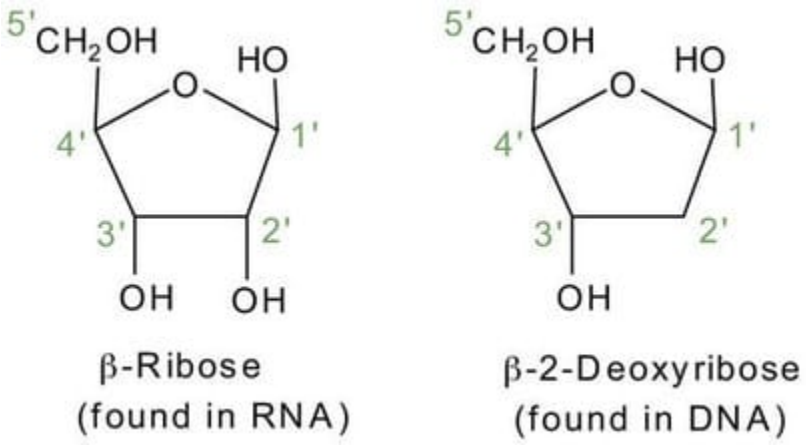
Learning Objectives

- Describe the two types of nucleic acids and the function of each type.
- Describe the secondary structure of DNA and the importance of complementary base pairing.
- Describe how a new copy of DNA is synthesized.

The repeating, or monomer, units that are linked together to form nucleic acids are known as nucleotides. The deoxyribonucleic acid (DNA) of a typical mammalian cell contains about 3×10^9 nucleotides. Nucleotides can be further broken down to phosphoric acid (H_3PO_4), a pentose sugar (a sugar with five carbon atoms), and a nitrogenous base (a base containing nitrogen atoms).

$$\text{nucleic acids} \xrightarrow[\text{down into}]{\text{can be broken}} \text{nucleotides} \xrightarrow[\text{down into}]{\text{can be broken}} H_3PO_4 + \text{nitrogen base} + \text{pentose sugar}$$

If the pentose sugar is ribose, the nucleotide is more specifically referred to as a *ribonucleotide*, and the resulting nucleic acid is ribonucleic acid (RNA). If the sugar is 2-deoxyribose, the nucleotide is a *deoxyribonucleotide*, and the nucleic acid is DNA.



The nitrogenous bases found in nucleotides are classified as pyrimidines or purines. Pyrimidines are heterocyclic amines with two nitrogen atoms in a six-member ring and include uracil, thymine, and cytosine. Purines are heterocyclic amines consisting of a pyrimidine ring fused to a five-member ring with two nitrogen atoms. Adenine and guanine are the major purines found in nucleic acids (Figure 16.6.1).

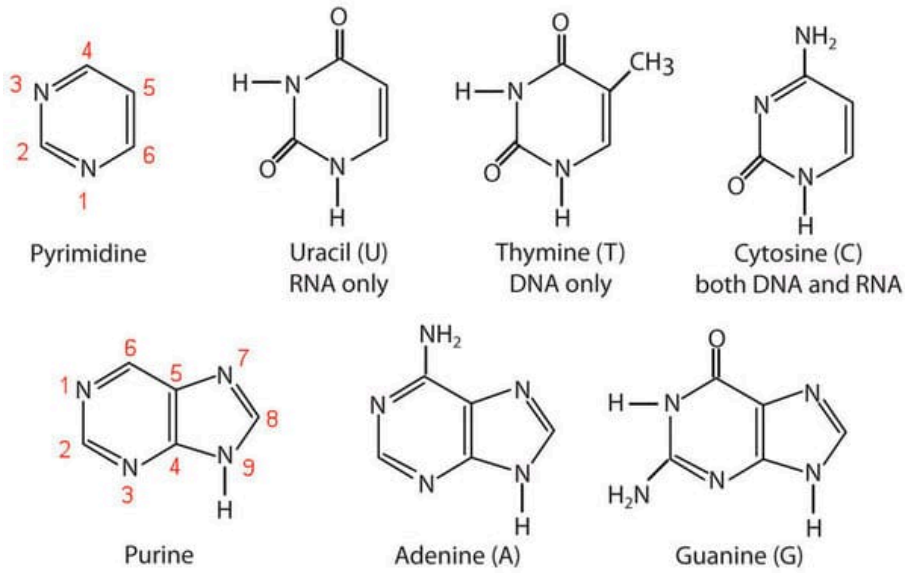


Figure 16.6.1 The Nntrogenous bases found in DNA and RNA.

The formation of a bond between C1′ of the pentose sugar and N1 of the pyrimidine base or N9 of the purine base joins the pentose sugar to the nitrogenous base. In the formation of this bond, a molecule of water is removed. Table 16.6.1 summarizes the similarities and differences in the composition of nucleotides in DNA and RNA.

> The numbering convention is that primed numbers designate the atoms of the pentose ring, and unprimed numbers designate the atoms of the purine or pyrimidine ring.

Table 16.6.1 Composition of Nucleotides in DNA and RNA.

Composition	DNA	RNA
purine bases	adenine and guanine	adenine and guanine
pyrimidine bases	cytosine and thymine	cytosine and uracil
pentose sugar	2-deoxyribose	ribose
inorganic acid	phosphoric acid (H_3PO_4)	H_3PO_4

The names and structures of the major ribonucleotides and one of the deoxyribonucleotides are given in Figure 16.6.2.

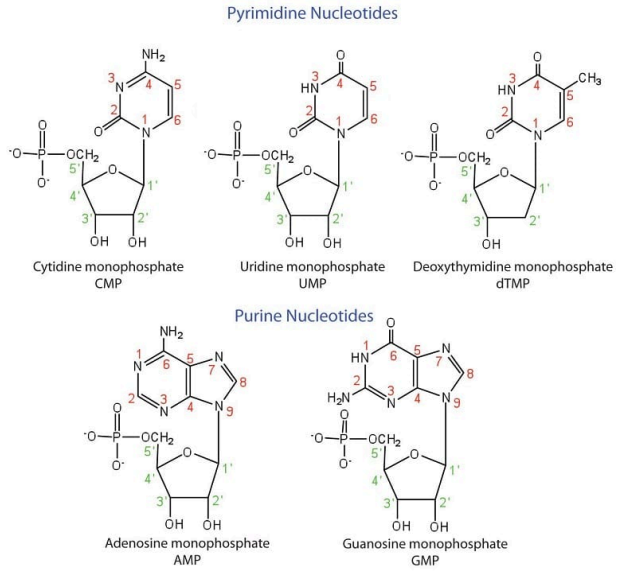


Figure 16.6.2 The pyrimidine and purine nucleotides

Apart from being the monomer units of DNA and RNA, the nucleotides and some of their derivatives have other functions as well. Adenosine diphosphate (ADP) and adenosine triphosphate (ATP), shown in Figure 16.6.3, have a role in cell metabolism. Moreover, a number of coenzymes, including flavin adenine dinucleotide (FAD), nicotinamide adenine dinucleotide (NAD^+), and coenzyme A, contain adenine nucleotides as structural components.

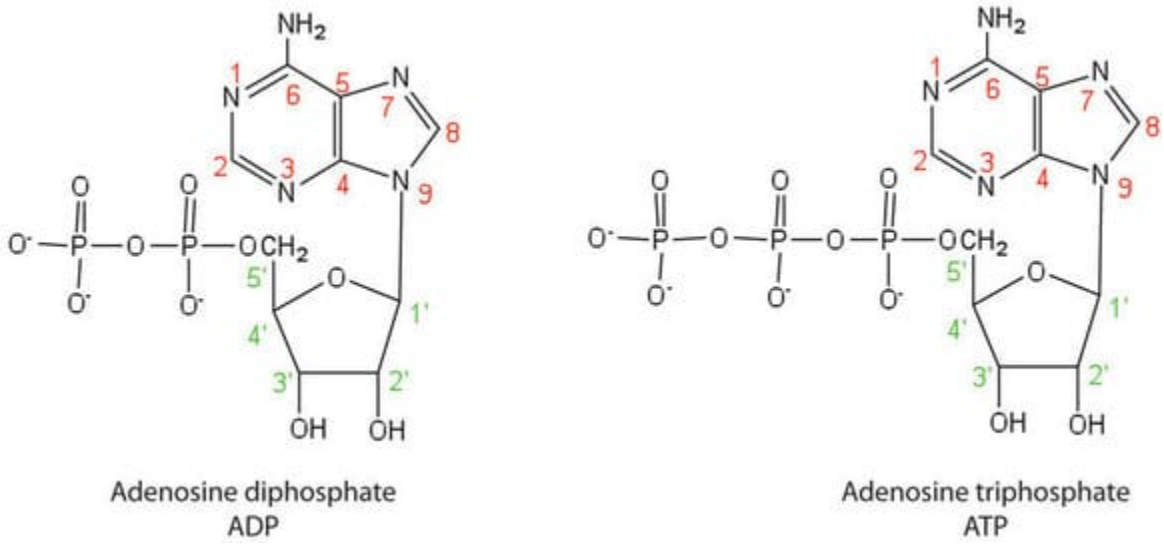


Figure 16.6.3 *Structures of two important adenine-containing nucleotides.*

Nucleic acids are large polymers formed by linking nucleotides together and are found in every cell. Deoxyribonucleic acid (DNA) is the nucleic acid that stores genetic information. If all the DNA in a typical mammalian cell were stretched out end to end, it would extend more than 2 m. Ribonucleic acid (RNA) is the nucleic acid responsible for using the genetic information encoded in DNA to produce the thousands of proteins found in living organisms.

Primary Structure of Nucleic Acids

Nucleotides are joined together through the phosphate group of one nucleotide connecting in an ester linkage to the OH group on the third carbon atom of the sugar unit of a second nucleotide. This unit joins to a third nucleotide, and the process is repeated to produce a long nucleic acid chain (Figure 16.6.4). The backbone of the chain consists of alternating phosphate and sugar units (2-deoxyribose in DNA and ribose in RNA). The purine and pyrimidine bases branch off this backbone.

Each phosphate group has one acidic hydrogen atom that is ionized at physiological pH. This is why these compounds are known as nucleic acids.

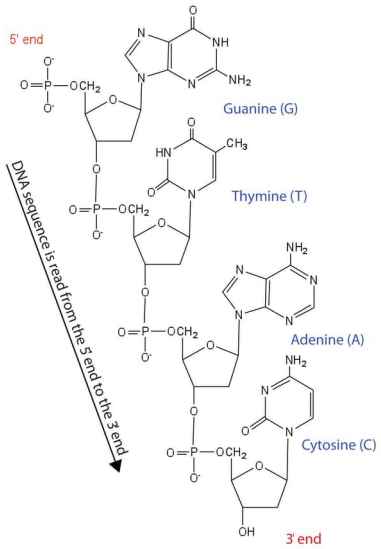


Figure 16.6.4 Structure of a segment of DNA. A similar segment of RNA would have OH groups on each C2′, and uracil would replace thymine.

Like proteins, nucleic acids have a primary structure that is defined as the sequence of their nucleotides. Unlike proteins, which have 20 different kinds of amino acids, there are only 4 different kinds of nucleotides in nucleic acids. For amino acid sequences in proteins, the convention is to write the amino acids in order starting with the N-terminal amino acid. In writing nucleotide sequences for nucleic acids, the convention is to write the nucleotides (usually using the one-letter abbreviations for the bases, shown in Figure 16.6.4) starting with the nucleotide having a free phosphate group, which is known as the 5′ end, and indicate the nucleotides in order. For DNA, a lowercase *d* is often written in front of the sequence to indicate that the monomers are deoxyribonucleotides. The final nucleotide has a free OH group on the 3′ carbon atom and is called the *3′ end*. The sequence of nucleotides in the DNA segment shown in Figure 16.6.4 would be written 5′-dG-dT-dA-dC-3′, which is often further abbreviated to dGTAC or just GTAC.

Secondary Structure of DNA

The three-dimensional structure of DNA was the subject of an intensive research effort in the late 1940s to early 1950s. Initial work revealed that the polymer had a regular repeating structure. In 1950, Erwin Chargaff of Columbia University showed that the molar amount of adenine (A) in DNA was always equal to that of thymine (T). Similarly, he showed that the molar amount of guanine (G) was the same as that of cytosine (C). Chargaff drew no conclusions from his work, but others soon did.

At Cambridge University in 1953, James D. Watson and Francis Crick announced that they had a model for the secondary structure of DNA. Using the information from Chargaff's experiments (as well as other experiments) and data from the X ray studies of Rosalind Franklin (which involved sophisticated chemistry, physics, and mathematics), Watson and Crick worked with models that were not unlike a child's construction set and finally concluded that DNA is composed of two nucleic acid chains running antiparallel to one another—that is, side-by-side with the 5′ end of one chain next to the 3′ end of the other. Moreover, as their model showed, the two chains are twisted to form a double helix—a structure that can be compared to a spiral staircase, with the phosphate and sugar groups (the backbone of the nucleic acid polymer) representing the outside edges of the staircase. The purine and pyrimidine bases face the inside of the helix, with guanine always opposite cytosine and adenine always opposite thymine. These specific base pairs, referred to as complementary bases, are the steps, or treads, in our staircase analogy (Figure 16.6.5).

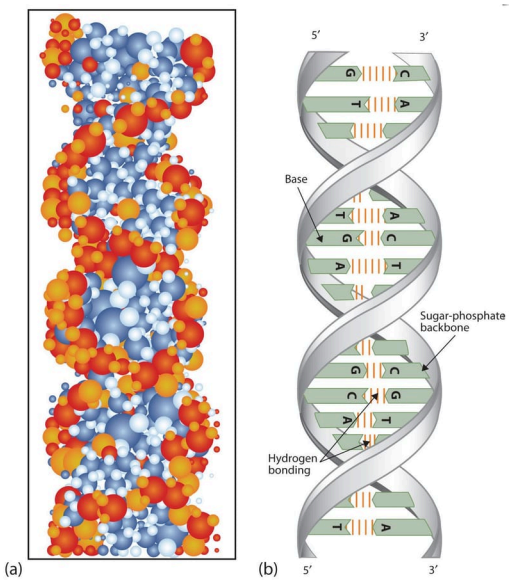


Figure 16.6.5 DNA Double Helix. (a) This represents a computer-generated model of the DNA double helix. (b) This represents a schematic representation of the double helix, showing the complementary bases.

The structure proposed by Watson and Crick provided clues to the mechanisms by which cells are able to divide into two identical, functioning daughter cells; how genetic data are passed to new generations; and even how proteins are built to required specifications. All these abilities depend on the pairing of complementary bases. Figure 16.6.6 shows the two sets of base pairs and illustrates two things. First, a pyrimidine is paired with a purine in each case, so that the long dimensions of both pairs are identical (1.08 nm).

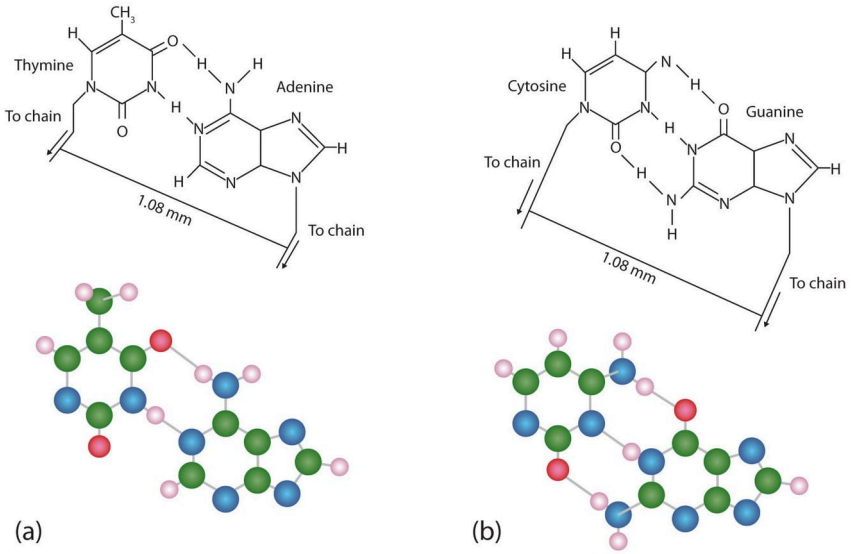


Figure 16.6.6 Complementary Base Pairing. Complementary bases engage in hydrogen bonding with one another: (a) thymine and adenine; (b) cytosine and guanine.

If two pyrimidines were paired or two purines were paired, the two pyrimidines would take up less space than a purine and a pyrimidine, and the two purines would take up more space, as illustrated in Figure 16.6.7. If these pairings were ever to occur, the structure of DNA would be like a staircase made with stairs of different widths. For the two strands of the double helix to fit neatly, a pyrimidine must always be paired with a purine. The second thing you should notice in Figure 16.6.6 is that the correct pairing enables formation of three instances of hydrogen bonding between guanine and cytosine and two between adenine and thymine. The additive contribution of this hydrogen bonding imparts great stability to the DNA double helix.

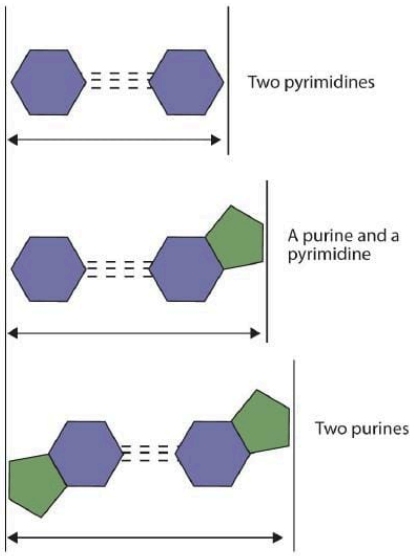


Figure 16.6.7 Difference in Widths of Possible Base Pairs

We previously stated that deoxyribonucleic acid (DNA) stores genetic information, while ribonucleic acid (RNA) is responsible for transmitting or expressing genetic information by directing the synthesis of thousands of proteins found in living organisms. But how do the nucleic acids perform these functions? Three processes are required: (1) *replication*, in which new copies of DNA are made; (2) *transcription*, in which a segment of DNA is used to produce RNA; and (3) *translation*, in which the information in RNA is translated into a protein sequence.

DNA: Self-Replication

New cells are continuously forming in the body through the process of cell division. For this to happen, the DNA in a dividing cell must be copied in a process known as replication. The complementary base pairing of the double helix provides a ready model for how genetic replication occurs. If the two chains of the double helix are pulled apart, disrupting the hydrogen bonding between base pairs, each chain can act as a *template*, or pattern, for the synthesis of a new complementary DNA chain.

The nucleus contains all the necessary enzymes, proteins, and nucleotides required for this synthesis. A short segment of DNA is “unzipped,” so that the two strands in the segment are separated to serve as templates for new DNA. DNA polymerase, an enzyme, recognizes each base in a template strand and matches it to the complementary base in a free nucleotide. The enzyme then catalyzes the formation of an ester bond between the 5′ phosphate group of the nucleotide and the 3′ OH end of the new, growing DNA chain. In this way, each strand of the original DNA molecule is used to produce a duplicate of its former partner (Figure 16.6.8). Whatever information was encoded in the original DNA double helix is now contained in each replicate helix. When the cell divides, each daughter cell gets one of these replicates and thus all of the information that was originally possessed by the parent cell.

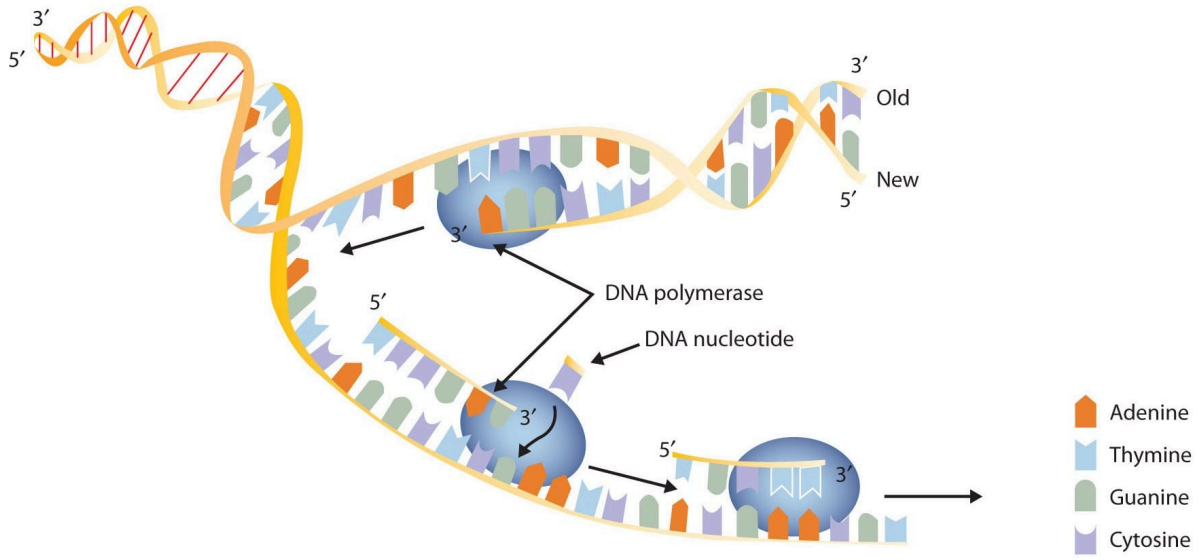


Figure 16.6.8 A Schematic Diagram of DNA Replication. DNA replication occurs by the sequential unzipping of segments of the double helix. Each new nucleotide is brought into position by DNA polymerase and is added to the growing strand by the formation of a phosphate ester bond. Thus, two double helixes form from one, and each consists of one old strand and one new strand, an outcome called s*emiconservative replications*. (This representation is simplified; many more proteins are involved in replication.)

Example 16.6.1

A segment of one strand from a DNA molecule has the sequence 5′-TCCATGAGTTGA-3′. What is the sequence of nucleotides in the opposite, or complementary, DNA chain?

Solution

Knowing that the two strands are antiparallel and that T base pairs with A, while C base pairs with G, the sequence of the complementary strand will be 3′-AGGTACTCAACT-5′.

Exercise 16.6.1

A segment of one strand from a DNA molecule has the sequence 5′-CCAGTGAATTGCCTAT-3′. What is the sequence of nucleotides in the opposite, or complementary, DNA chain?

Answer

3′-GGTCACTTAACGGATA-5′.

Summary

- Nucleotides are composed of phosphoric acid, a pentose sugar (ribose or deoxyribose), and a nitrogen-containing base (adenine, cytosine, guanine, thymine, or uracil). Ribonucleotides contain ribose, while deoxyribonucleotides contain deoxyribose.
- DNA is the nucleic acid that stores genetic information. RNA is the nucleic acid responsible for using the genetic information in DNA to produce proteins.
- Nucleic acid sequences are written starting with the nucleotide having a free phosphate group (the 5′ end).
- Two DNA strands link together in an antiparallel direction and are twisted to form a double helix. The nitrogenous bases face the inside of the helix. Guanine is always opposite cytosine, and adenine is always opposite thymine.

- In DNA replication, each strand of the original DNA serves as a template for the synthesis of a complementary strand.
- DNA polymerase is the primary enzyme needed for replication.

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16.7: The Human Genome

Learning Objectives

- Describe the human genome project.
- Describe the advances made possible by recombinant DNA technology.

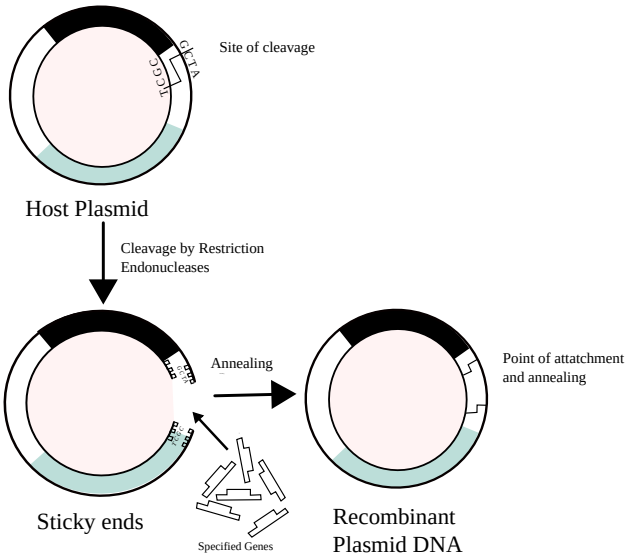
The Human Genome

This collective body of genes is called the **human genome** and the project to map it is called the Human Genome Project. The original impetus for this project in the U. S. arose because of interest in the damage to human DNA by radiation, such as that from nuclear weapons. But, from the beginning, it was recognized that the project had enormous commercial potential, especially in the pharmaceutical industry, and could be very valuable in human health.

The announcement in 2001 that mapping of the human genome was complete promised great progress in biology, especially in medicine. Genes function by directing the synthesis of specific proteins and the action of most pharmaceuticals is to alter the activities of proteins, the drug's target. In some cases proteins are made more active and in others their activity is diminished. Knowledge of the human genome enables a better understanding of protein activity and should facilitate the development of more specific drugs, something that has developed only slowly. For example, the gene responsible for cystic fibrosis was discovered in 1989 by examination of family histories of the disease and only in 2010 were two drugs designed to combat that disease in clinical trials.

Recombinant DNA Technology

Recombinant DNA technology: the process of taking a gene from one organism and inserting it into the DNA of another. Recombinant DNA technology is the latest biochemical analysis that came about to satisfy the need for specific DNA segments. In this process, surrounding DNA from an existing cell is clipped in the desired amount of segments so that it can be copied millions of times.



(Figure 16.7.1) **Construction of recombinant DNA**: A foreign DNA fragment is inserted into a plasmid vector. In this example, the gene indicated by the white color is inactivated upon insertion of the foreign DNA fragment.

Recombinant DNA technology engineers microbial cells for producing foreign proteins, and its success solely depends on the precise reading of equivalent genes made with the help of bacterial cell machinery. This process has been responsible for

fueling many advances related to modern molecular biology. The last two decades of cloned-DNA sequence studies have revealed detailed knowledge about gene structure as well as its organization. It has provided hints to regulatory pathways with the aid of which gene expression in myriad cell types is controlled by the cells, especially in those organisms having body plan with basic vertebrae structure.

Recombinant DNA technology, apart from being an important tool of scientific research, has also played a vital role in the diagnosis and treatment of various diseases, especially those belonging to genetic disorders.

Some of the recent advances made possible by recombinant DNA technology are:

1. Isolating proteins in large quantities: many recombinant products are now available, including follicle stimulating hormone (FSH), Follistim AQ vial, growth hormone, insulin and some other proteins.

2. Making possible mutation identification: due to this technology, people can be easily tested for mutated protein presence that can lead to breast cancer, neurofibromatosis, and retinoblastoma.

3. Hereditary diseases carrier diagnosis: tests now available to determine if a person is carrying the gene for cystic fibrosis, the Tay-Sachs diseases, Huntington's disease or Duchenne muscular dystrophy.

4. Gene transfer from one organism to other: the advanced gene therapy can benefit people with cystic fibrosis, vascular disease, rheumatoid arthritis and specific types of cancers.

Summary

- This collective body of genes is called the **human genome** and the project to map it is called the Human Genome Project. Recombinant DNA (rDNA) is widely used in biotechnology, medicine and research. Proteins and other products that result from the use of rDNA technology are found in essentially every western pharmacy, doctor's or veterinarian's office, medical testing laboratory, and biological research laboratory.
- Organisms that have been manipulated using recombinant DNA technology, and products derived from those organisms have found their way into many farms, supermarkets, home medicine cabinets, and even pet shops.
- Biochemical products of recombinant DNA technology in medicine and research include: human recombinant insulin, growth hormone, blood clotting factors, hepatitis B vaccine, and diagnosis of HIV infection.
- Biochemical products of recombinant DNA technology in agriculture include: golden rice, herbicide-resistant crops, and insect-resistant crops.

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16.8: RNA Protein Synthesis and the Genetic Code

Learning Objectives

- Describe the characteristics of the genetic code.
- Describe how a protein is synthesized from mRNA.

One of the definitions of a gene is as follows: a segment of deoxyribonucleic acid (DNA) carrying the code for a specific polypeptide. Each molecule of messenger RNA (mRNA) is a transcribed copy of a gene that is used by a cell for synthesizing a polypeptide chain. If a protein contains two or more different polypeptide chains, each chain is coded by a different gene. We turn now to the question of how the sequence of nucleotides in a molecule of ribonucleic acid (RNA) is translated into an amino acid sequence.

How can a molecule containing just 4 different nucleotides specify the sequence of the 20 amino acids that occur in proteins? If each nucleotide coded for 1 amino acid, then obviously the nucleic acids could code for only 4 amino acids. What if amino acids were coded for by groups of 2 nucleotides? There are 4^2, or 16, different combinations of 2 nucleotides (AA, AU, AC, AG, UU, and so on). Such a code is more extensive but still not adequate to code for 20 amino acids. However, if the nucleotides are arranged in groups of 3, the number of different possible combinations is 4^3, or 64. Here we have a code that is extensive enough to direct the synthesis of the primary structure of a protein molecule.

YouTube Video

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***Video**: NDSU Virtual Cell Animations project animation "Translation". For more information, see http://vcell.ndsu.nodak.edu/animations*

The genetic code can therefore be described as the identification of each group of three nucleotides and its particular amino acid. The sequence of these triplet groups in the mRNA dictates the sequence of the amino acids in the protein. Each individual three-nucleotide coding unit, as we have seen, is called a *codon*.

Protein synthesis is accomplished by orderly interactions between mRNA and the other ribonucleic acids (transfer RNA [tRNA] and ribosomal RNA [rRNA]), the ribosome, and more than 100 enzymes. The mRNA formed in the nucleus during transcription is transported across the nuclear membrane into the cytoplasm to the ribosomes—carrying with it the genetic instructions. The process in which the information encoded in the mRNA is used to direct the sequencing of amino acids and thus ultimately to synthesize a protein is referred to as translation.

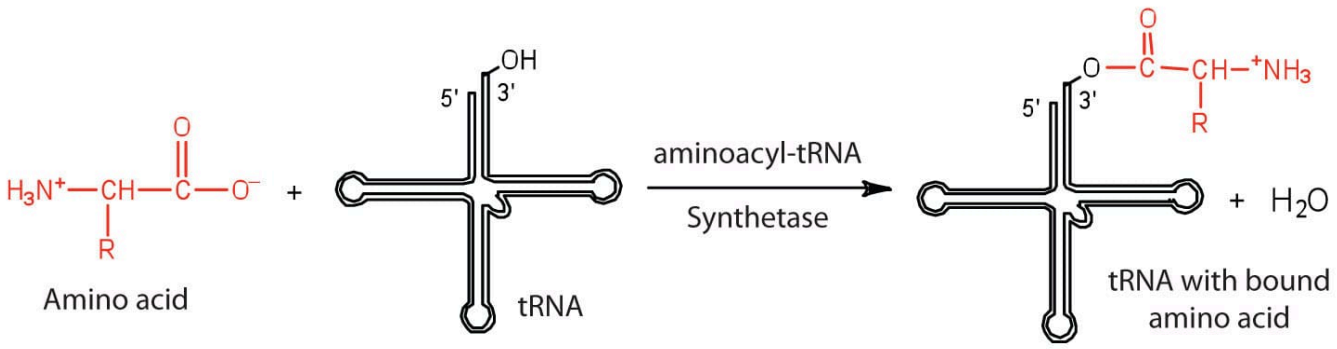


Figure 16.8.1: Binding of an Amino Acid to Its tRNA

Before an amino acid can be incorporated into a polypeptide chain, it must be attached to its unique tRNA. This crucial process requires an enzyme known as aminoacyl-tRNA synthetase (Figure 16.8.1). There is a specific aminoacyl-tRNA synthetase for each amino acid. This high degree of specificity is vital to the incorporation of the correct amino acid into a protein. After the amino acid molecule has been bound to its tRNA carrier, protein synthesis can take place. Figure 16.8.2 depicts a schematic stepwise representation of this all-important process.

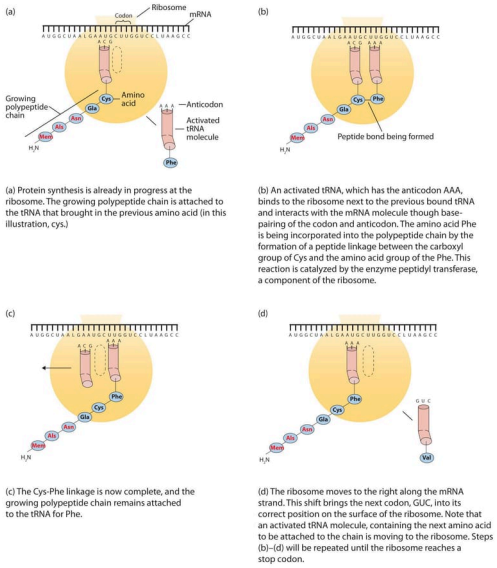


Figure 16.8.2: The Elongation Steps in Protein Synthesis

Early experimenters were faced with the task of determining which of the 64 possible codons stood for each of the 20 amino acids. The cracking of the genetic code was the joint accomplishment of several well-known geneticists—notably Har Khorana, Marshall Nirenberg, Philip Leder, and Severo Ochoa—from 1961 to 1964. The genetic dictionary they compiled, summarized in Figure 16.8.3, shows that 61 codons code for amino acids, and 3 codons serve as signals for the termination of polypeptide synthesis (much like the period at the end of a sentence). Notice that only methionine (AUG) and tryptophan (UGG) have single codons. All other amino acids have two or more codons.

First base	Second base: U	Second base: C	Second base: A	Second base: G	Third base
U	Phe	Ser	Tyr	Cys	U
	Phe	Ser	Tyr	Cys	C
	Leu	Ser	Stop	Stop	A
	Leu	Ser	Stop	Trp	G
C	Leu	Pro	His	Arg	U
	Leu	Pro	His	Arg	C
	Leu	Pro	Gln	Arg	A
	Leu	Pro	Gln	Arg	G
A	Ile	Thr	Asn	Ser	U
	Ile	Thr	Asn	Ser	C
	Ile	Thr	Lys	Arg	A
	Met	Thr	Lys	Arg	G
G	Val	Ala	Asp	Gly	U
	Val	Ala	Asp	Gly	C
	Val	Ala	Glu	Gly	A
	Val	Ala	Glu	Gly	G

Figure 16.8.3: The Genetic Code

Example 16.8.1: Using the Genetic Code

A portion of an mRNA molecule has the sequence 5′-AUGCCACGAGUUGAC-3′. What amino acid sequence does this code for?

Solution

Use Figure 16.8.3 to determine what amino acid each set of three nucleotides (codon) codes for. Remember that the sequence is read starting from the 5′ end and that a protein is synthesized starting with the N-terminal amino acid. The sequence 5′-AUGCCACGAGUUGAC-3′ codes for met-pro-arg-val-asp.

Exercise 16.8.1

A portion of an mRNA molecule has the sequence 5′-AUGCUGAAUUGCGUAGGA-3′. What amino acid sequence does this code for?

met-leu-asn-cys-val-gly

The Nature of the Genetic Code

Further experimentation threw much light on the nature of the genetic code, as follows:

1. The code is virtually universal; animal, plant, and bacterial cells use the same codons to specify each amino acid (with a few exceptions).
2. The code is “degenerate”; in all but two cases (methionine and tryptophan), more than one triplet codes for a given amino acid.
3. The first two bases of each codon are most significant; the third base often varies. This suggests that a change in the third base by a mutation may still permit the correct incorporation of a given amino acid into a protein. The third base is sometimes called the “wobble” base.
4. The code is continuous and nonoverlapping; there are *no* nucleotides between codons, and adjacent codons do not overlap.

5. The three termination codons are read by special proteins called release factors, which signal the end of the translation process.
6. The codon AUG codes for methionine and is also the initiation codon. Thus methionine is the first amino acid in each newly synthesized polypeptide. This first amino acid is usually removed enzymatically before the polypeptide chain is completed; the vast majority of polypeptides do not begin with methionine.

Summary

- In transcription, a segment of DNA serves as a template for the synthesis of an RNA sequence.
- RNA polymerase is the primary enzyme needed for transcription.
- In translation, the information in mRNA directs the order of amino acids in protein synthesis. A set of three nucleotides (codon) codes for a specific amino acid.

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17: FOOD

17.1: Carbohydrates in the Diet
17.2: Fats and Cholesterol
17.3: Proteins- Muscle and Much More
17.4: Minerals, Vitamins, and Other Essentials
17.5: Starvation, Fasting, and Malnutrition
17.6: Flavorings- Spicy and Sweet
17.7: Other Food Additives- Beneficial or Dangerous
17.8: Problems with our Food

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17.1: Carbohydrates in the Diet

Learning Objectives

- Describe the metabolism of carbohydrates.
- Know the source and function of common carbohydrates in the diet.

Carbohydrates are sugars and sugar derivatives whose formulas can be written in the general form: $C_x(H_2O)_y$. (The subscripts *x* and *y* are whole numbers.) Some typical carbohydrates are sucrose (ordinary cane sugar), $C_{12}H_{22}O_{11}$; glucose (dextrose), $C_6H_{12}O_6$; fructose (fruit sugar), $C_6H_{12}O_6$; and ribose, $C_5H_{10}O_5$. Since the atom ratio H/O is 2/1 in each formula, these compounds were originally thought to be hydrates of carbon, hence their general name.

In scientific literature, the term "carbohydrate" has many synonyms, like "sugar" (in the broad sense), "saccharide", "ose", "glucide", "hydrate of carbon" or "polyhydroxy compounds with aldehyde or ketone". Some of these terms, specially "carbohydrate" and "sugar", are also used with other meanings.

In food science and in many informal contexts, the term "carbohydrate" often means any food that is particularly rich in the complex carbohydrate starch (such as cereals, bread and pasta) or simple carbohydrates, such as sugar (found in candy, jams, and desserts).

Carbohydrates may be classified according to their degree of polymerization, and may be divided initially into three principal groups, namely sugars, oligosaccharides and polysaccharidesas shown in Table 17.1.1.

Table 17.1.1 *The Major Dietary Carbohydrates. Source: Wikipedia*

Class (DP*)	Subgroup	
Sugars (1–2)	Monosaccharides	Glucose,
	Disaccharides	Sucrose,
	Polyols	Sorbitol,
Oligosaccharides (3–9)	Malto-oligosaccharides	Maltodex
	Other oligosaccharides	Raffinos
Polysaccharides (>9)	Starch	Amylose
	Non-starch polysaccharides	Glycoger

DP * = Degree of polymerization

Digestion of Carbohydrates

The human body breaks down complex carbohydrates into **glucose**. Glucose in the blood (often referred to as “blood sugar”) is the **primary energy source** for the body. Sugars provide calories, or “energy,” for the body. Each gram of sugar provides **4 calories**. Glucose can be used immediately or stored in the liver and muscles for later use.

Carbohydrate digestion begins in the mouth (Figure 17.1.1) 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.

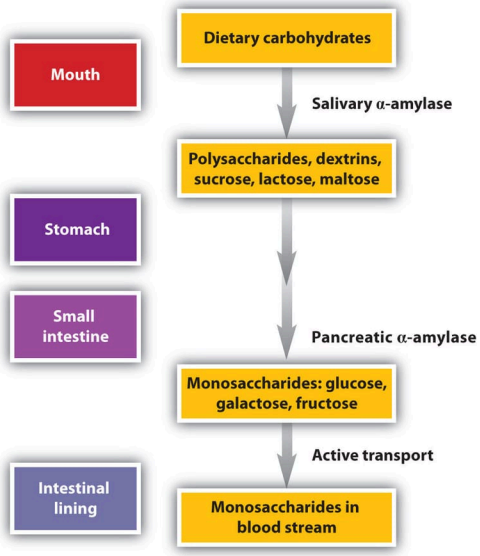


Figure 17.1.1 The Principal events and sites of carbohydrate digestion.

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.

Fuel for the Brain

The brain is a marvelous organ. And it's a hungry one, too. The major fuel for the brain is the carbohydrate glucose. The average adult brain represents about 2% of our body's weight, but uses 25% of the glucose in the body. Moreover, specific areas of the brain use glucose at different rates. If you are concentrating hard (taking a test, for example), certain parts of the brain need a lot of extra glucose while other parts of the brain only use their normal amount. Something to think about.

Some foods that are high in carbohydrates include bread, pasta, and potatoes (Figure 17.1.2) . Because carbohydrates are easily digested, athletes often rely on carbohydrate rich foods to enable a high level of performance.



Figure 17.1.2 *Foods that serve as carbohydrate sources.*

Common Monosaccharides and Disaccharides

Monosaccharides and disaccharides commonly found in our diets are listed in Table 17.1.3. Although a variety of monosaccharides are found in living organisms, three hexoses are particularly abundant: D-glucose, D-galactose, and D-fructose (Figure 17.1.3). Glucose and galactose are both aldohexoses, while fructose is a ketohexose.

Table 17.1.2 . *Monosaccharides and disaccharides. Source: US FDA*

Simple sugars (monosaccharides) are small enough to be absorbed directly into the bloodstream. They include:	**Sugars that contain two molecules of sugar linked together (disaccharides) are broken down in your body into single sugars. They include:**
Fructose	**Sucrose** (table sugar) = glucose + fructose
Galactose	**Lactose** (milk sugar) = glucose + galactose
Glucose	**Maltose** (malt sugar) = glucose + glucose

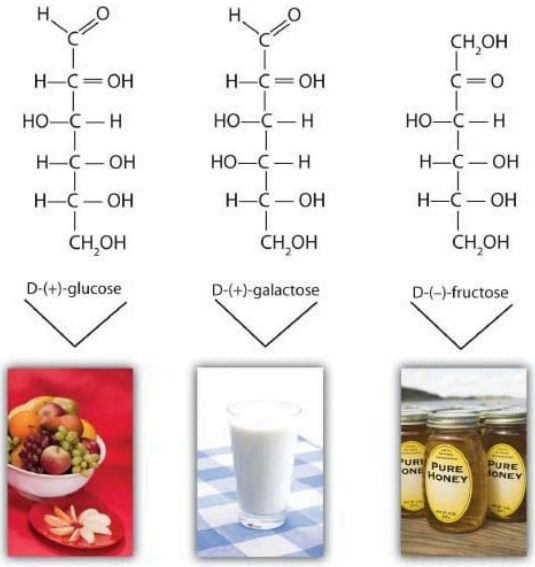


Figure 17.1.3 *Structures of three important hexoses. Each hexose is pictured with a food source in which it is commonly found. Source: Photos © Thinkstock.*

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.

Galactose

D-Galactose does not occur in nature in the uncombined state. It is released when lactose, a disaccharide found in milk, is hydrolyzed. The galactose needed by the human body for the synthesis of lactose is obtained by the metabolic conversion of D-glucose to D-galactose. Galactose is also an important constituent of the glycolipids that occur in the brain and the myelin sheath of nerve cells. For this reason it is also known as *brain sugar*. The structure of D-galactose is shown in Figure 17.1.3. Notice that the configuration differs from that of glucose only at the fourth carbon atom.

Fructose

D-Fructose, also shown in Figure 17.1.3, is the most abundant ketohexose. Note that from the third through the sixth carbon atoms, its structure is the same as that of glucose. It occurs, along with glucose and sucrose, in honey (which is 40% fructose) and sweet fruits. Fructose (from the Latin *fructus*, meaning "fruit") is also referred to as *levulose* because it has a specific rotation that is strongly levorotatory (−92.4°). It is the sweetest sugar, being 1.7 times sweeter than sucrose, although many nonsugars are several hundred or several thousand times as sweet (Table 17.1.1).

Sucrose

Sucrose, probably the largest-selling pure organic compound in the world, is known as *beet sugar*, *cane sugar*, *table sugar*, or simply *sugar*. Most of the sucrose sold commercially is obtained from sugar cane and sugar beets (whose juices are 14%–20% sucrose) by evaporation of the water and recrystallization. The dark brown liquid that remains after the recrystallization of sugar is sold as molasses.

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*.

Lactose

Lactose is known as *milk sugar* because it occurs in the milk of humans, cows, and other mammals. In fact, the natural synthesis of lactose occurs only in mammary tissue, whereas most other carbohydrates are plant products. Human milk contains about 7.5% lactose, and cow's milk contains about 4.5%. This sugar is one of the lowest ranking in terms of sweetness, being about one-sixth as sweet as sucrose. Lactose is produced commercially from whey, a by-product in the manufacture of cheese. It is important as an infant food and in the production of penicillin.

Many adults and some children suffer from a deficiency of lactase. These individuals are said to be lactose intolerant because they cannot digest the lactose found in milk. A more serious problem is the genetic disease galactosemia, which results from the absence of an enzyme needed to convert galactose to glucose. Certain bacteria can metabolize lactose, forming lactic acid as one of the products. This reaction is responsible for the "souring" of milk.

The different disaccharides and the monosaccharides components are illustrated in Figure 17.1.4 below.

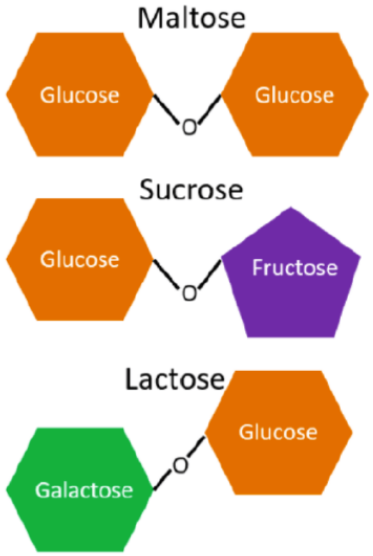


Figure 17.1.4 The three disaccharides.

Each of these disaccharides contains glucose and all the reactions are dehydration reactions. Also notice the difference in the bond structures. Maltose and sucrose have alpha-bonds, which are depicted as v-shaped above. You might hear the term glycosidic used in some places to describe bonds between sugars. A **glycoside** is a sugar, so **glycosidic** is referring to a sugar bond. Lactose, on the other hand, contains a beta-bond. We need a special enzyme, **lactase**, to break this bond, and the absence of lactase activity leads to lactose intolerance.

Naturally Occurring and Added Sugars

Sugars are found *naturally* in many nutritious foods and beverages and are also added to foods and beverages for taste, texture, and preservation.

Naturally occurring sugars are found in a variety of foods, including:	**Added sugars** are often found in foods low in other nutrients, including:
• Dairy products • Fruit (fresh, frozen, dried, and canned in 100% fruit juice) • 100% fruit and vegetable juice • Vegetables	• Dairy desserts (such as ice cream, other frozen desserts, and puddings) • Grain-based desserts (such as brownies, cakes, cookies, doughnuts, pastries, pies, and sweet rolls) • Sugar-sweetened beverages (such as energy drinks, flavored waters, fruit drinks, soft drinks, sports drinks, and sweetened coffee and tea) • Sweets (such as candies, jams, sweet toppings, and syrups)

The relative sweetness of the different sugars previously discussed are given in Table 17.1.3.

Table 17.1.3: The Relative Sweetness of Some Sugars (Sucrose = 100)

Compound	Relative Sweetness
lactose	16
maltose	32
glucose	74
sucrose	100
fructose	173

High-Fructose Corn Syrup

Figure 17.1.5U.S. per capita sugar and sweetener consumption

Opponents claim that high-fructose corn syrup is contributing to the rise in obesity rates. As a result, some manufactures have started releasing products made with natural sugar. You can read about this trend in the following New York Times article in the link below. Also, manufacturers tried to rebrand high-fructose corn syrup as corn sugar to get around the negative perception of the name. But the FDA rejected the Corn Refiners Association request to change the name officially to corn sugar as described in the second link. The last link is a video made by the American Chemical Society that gives some background on how HFCS is produced and how it compares to sucrose.

Links and Video

Links

Sugar is back on labels, this time as a selling point - http://www.nytimes.com/2009/03/21/dining/21sugar.html?_r=1&ref=nutrition

No new name for high-fructose corn syrup - http://well.blogs.nytimes.com/2012/05/31/no-new-name-for-high-fructose-corn-syrup/?_r=0

Video

Sugar vs. High Fructose Corn Syrup - What's the Difference? - https://www.youtube.com/watch?v=fXMvregmU1g

Complex Carbohydrates: Oligosaccharides and Polysaccharides

An **oligosaccharide,** from the Greek *olígos*, "a few", and *sácchar*, "sugar") is a saccharide polymer containing a small number (typically three to ten) of monosaccharides (simple sugars). Oligosaccharides are a component of fiber from plant tissue. Fructoologosaccharides (FOS) and inulin (Figure 17.1.6) are present in Jerusalem artichoke, burdock, chicory, leeks, onions, and asparagus. Inulin is a significant part of the daily diet of most of the world's population. FOS can also be synthesized by enzymes of the fungus *Aspergillus niger* acting on sucrose. Galatoologosaccharide (GOS) is naturally found in soybeans and can be synthesized from lactose. FOS, GOS, and inulin are also sold as nutritional supplements.[*citation needed*]

Figure 17.1.6 The structure of inulin. Source: Wikipedia

As the name suggests, **polysaccharides** are substances built up by the condensation of a very large number of monosaccharide units. Cellulose, for example, is a polymer of β-glucose, containing upwards of 3000 glucose units in a chain. Starch is largely a polymer of α-glucose.

These two substances are a classic example of how a minor difference in the monomer can lead to major differences in the macroscopic properties of the polymer. Good-quality cotton and paper are almost pure cellulose, and they give us a good idea of its properties. Cellulose forms strong but flexible fibers and does not dissolve in water. By contrast, starch has no mechanical strength at all, and some forms are water soluble. Part of the molecular structure of cellulose and starch are shown in Fig. 17.1.6.

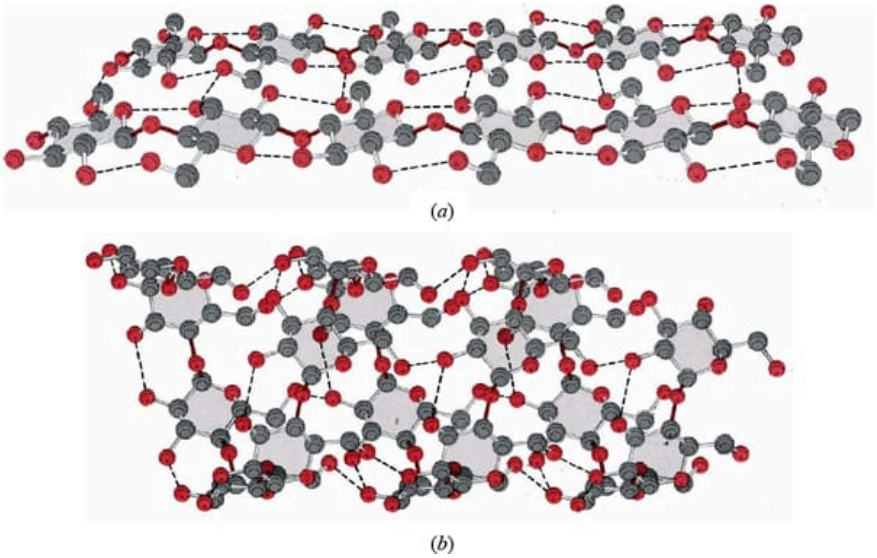


Figure 17.1.6 Structures of (a) cellulose and (b) amylose (starch). The C—O bonds linking glucose units are shown in color and hydrogen bonds are shown as single black lines. Hydrogen atoms have been omitted to simplify the structure. Note how the β-glucose units in cellulose form a linear chain because the C—O hands on either side of the glucose unit are parallel. In amylose, where α-glucose is the monomer, the chain is forced to curve. Note also the numerous hydrogen bonds between the two cellulose chains shown and the hydrogen bonds connecting successive turns of the spiral chain of amylose. When iodine contacts starch, I_2 molecules can fit lengthwise within the spiral of each amylose molecule. The starch-iodine complex which results is responsible for the dark blue color observed when iodine contacts starch.

Cellulose and starch are different not only in overall structure and macroscopic properties. From a biochemical point of view they behave so differently that it is difficult to believe that they are both polymers of the same monosaccharide. Enzymes which are capable of hydrolyzing starch will not touch cellulose, and vice versa. From a plant's point of view this is just as well since cellulose makes up structural material while starch serves as a storehouse for energy. If there were not a sharp biochemical distinction between the two, the need for a bit more energy by the plant might result in destruction of cell walls or other necessary structural components.

Starches in Food

Starch is the most common carbohydrate in the human diet and is contained in many staple foods. The major sources of starch intake worldwide are the cereals (rice, wheat, and maize) and the root vegetables (potatoes and cassava). Many other starchy foods are grown, some only in specific climates, including acorns, arrowroot, arracacha, bananas, barley, breadfruit, buckwheat, canna, colocasia, katakuri, kudzu, malanga, millet, oats, oca, polynesian arrowroot, sago, sorghum, sweet potatoes, rye, taro, chestnuts, water chestnuts and yams, and many kinds of beans, such as favas, lentils, mung beans, peas, and chickpeas.

Widely used prepared foods containing starch are bread, pancakes, cereals, noodles, pasta, porridge and tortilla.

Digestive enzymes have problems digesting crystalline structures. Raw starch is digested poorly in the duodenum and small intestine, while bacterial degradation takes place mainly in the colon. When starch is cooked, the digestibility is increased. Starch gelatinization during cake baking can be impaired by sugar competing for water, preventing gelatinization and improving texture.

Before the advent of processed foods, people consumed large amounts of uncooked and unprocessed starch-containing plants, which contained high amounts of resistant starch. Microbes within the large intestine fermented the starch, produced short-chain fatty acids, which are used as energy, and support the maintenance and growth of the microbes. More highly processed foods are more easily digested and release more glucose in the small intestine—less starch reaches the large intestine and more energy is absorbed by the body. It is thought that this shift in energy delivery (as a result of eating more processed foods) may be one of the contributing factors to the development of metabolic disorders of modern life, including obesity and diabetes.

Fibers in Food

Dietary fiber (British spelling **fibre**) or **roughage** is the portion of plant-derived food that cannot be completely broken down by human digestive enzymes. Dietary fiber consists of non-starch polysaccharides and other plant components such as cellulose,

resistant starch, resistant dextrins, inulin, lignins, chitins, pectins, beta-glucans, and oligosaccharides.

Polysaccharide fiber differs from other polysaccharides in that it contains beta-glycosidic bonds (as opposed to alpha-glycosidic bonds). To illustrate these differences, consider the structural differences between amylose and cellulose (type of fiber) in the figure below. Both are linear chains of glucose, the only difference is that amylose has alpha-glycosidic bonds, while cellulose has beta-glycosidic bonds as shown below. The beta-bonds in fiber cannot be broken down by the digestive enzymes in the small intestine so they continue into the large intestine.

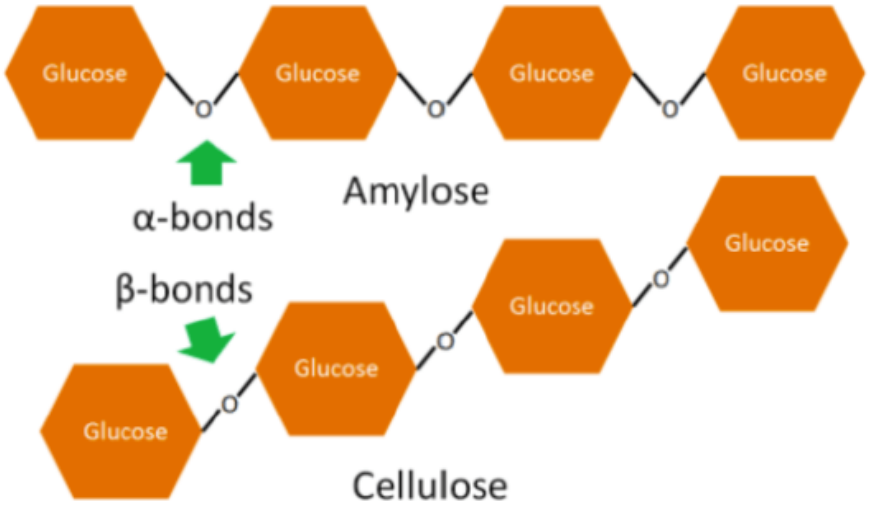


Figure 17.1.7 Structures of amylose and cellulose

Fiber can be classified by its physical properties. In the past, fibers were commonly referred to as soluble and insoluble. This classification distinguished whether the fiber was soluble in water. However, this classification is being phased out in the nutrition community. Instead, most fibers that would have been classified as insoluble fiber are now referred to as **nonfermentable and/or nonviscous** and **soluble fiber as fermentable**, **and/or viscous** because these better describe the fiber's characteristics. **Viscous** refers to the capacity of certain fibers to form a thick gel-like consistency.

Fermentable (soluble fiber) dissolves in water and is readily fermented in the colon into gases and physiologically active by-products, such as short-chain fatty acids produced in the colon by gut bacteria;it is viscous, may be called prebiotic fiber, and delays gastric emptying which, in humans, can result in an extended feeling of fullness.

Non-fermentable (insoluble fiber) does not dissolve in water and is inert to digestive enzymes in the upper gastrointestinal tract and provides bulking. Some forms of insoluble fiber, such as resistant starches, can be fermented in the colon. Bulking fibers absorb water as they move through the digestive system, easing defecation.

Table lists some of the common types of fiber and provides a brief description about each. Specific sources of the different types of soluble and insoluble fiber as well as the amount of fiber found in common foods are discussed in section 17.4.

Table 17.1.4 *Common Types of Fermentable (Soluble) Fiber and Non-Fermentable (Insoluble) Fiber.*

Fermentable (Soluble) Fiber	Description	Non (In
Hemicellulose (soluble type)	Surround cellulose in plant cell walls	Cellulose

Fermentable (Soluble) Fiber	Description	Non (In
Pectin	Found in cell walls and intracellular tissues of fruits and berries	Hemicellulose (insoluble type)
Beta-glucans	Found in cereal brans	Lignin
Gums	Viscous, usually isolated from seeds	

Summary

- Carbohydrate digestion begins in the mouth (in the presence of salivary α-amylase) and continues in the small intestine. 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.
- Simple sugars like glucose, fructose and the disaccharide sucrose function as natural sweeteners.
- More complex carbohydrates (oligosaccharides and polysaccharides) are now significant parts of the daily diet promoting gut health that leads to other health benefits.

Contributors and Attributions

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- Libretext: Basics of GOB Chemistry (Ball, et al.)
- Template:ContribLindshield
-
- Wikipedia
- US FDA

- Marisa Alviar-Agnew (Sacramento City College)

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17.2: Fats and Cholesterol

Learning Objectives

- Describe the digestion of lipids.
- Know the properties and functions of the different types of lipoproteins.
- Know the sources and function of common dietary lipids.

How Does Fat Differ From Lipids? The answer you receive from this question will depend on who you ask, so it is important to have an understanding of lipids and fats from a chemical and nutritional perspective.

To a chemist, lipids consist of triglycerides, fatty acids, phospholipids, waxes, and sterols. These compounds are grouped together because of their structural and physical property similarities. For instance, all lipids have hydrophobic (water-fearing) properties. Chemists further separate lipids into fats and oils based on their physical properties at room temperature:

- **Fats** are solid at room temperature
- **Oils** are liquid at room temperature

From a nutritional perspective, the definition of lipids is the same. The definition of a fat differs, however, because nutrition-oriented people define fats based on their caloric contribution rather than whether they are solid at room temperature. Thus, from a nutrition perspective, **Fats** are triglycerides, fatty acids, and phospholipids that provide 9 kcal/g. The other difference is that from a caloric perspective, an oil is a fat. For example, let's consider olive oil. Clearly, it is an oil according to a chemist definition, but from a caloric standpoint it is a fat because it provides 9 kcal/g.

Digestion of Lipids

Lipid digestion begins in the upper portion of the small intestine (Figure 17.2.1). 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.

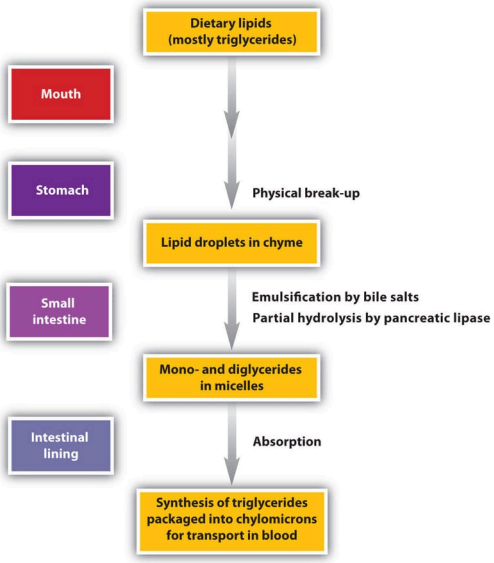
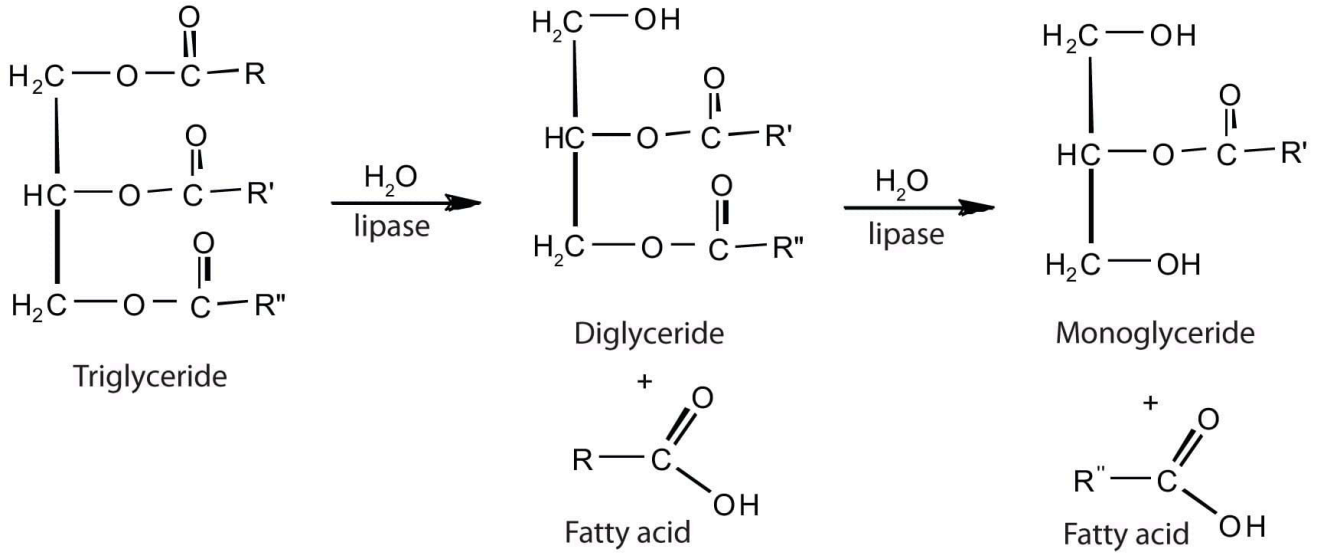


Figure 17.2.1 The principal events and sites of lipid (primarily triglyceride) digestion.

The lipases in pancreatic juice catalyze the digestion of triglycerides first to diglycerides and then to 2-monoglycerides and fatty acids:



The monoglycerides and fatty acids cross the intestinal lining into the bloodstream, where they are resynthesized into triglycerides and transported as lipoprotein complexes known as chylomicrons. Phospholipids and cholesteryl esters undergo similar hydrolysis in the small intestine, and their component molecules are also absorbed through the intestinal lining.

Fats, Cholesterol, and Human Health

The primary sterol that we consume is **cholesterol**. The structure of cholesterol is shown below.

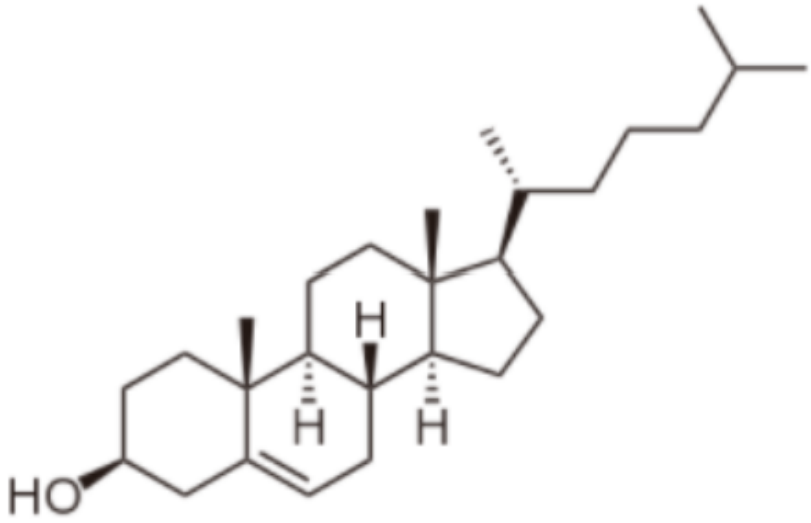


Figure 17.2.2 *The carbon ring structure of cholesterol*[1]

Cholesterol is frequently found in foods as a cholesterol ester, meaning that there is a fatty acid attached to it. The structure of a cholesterol ester is shown below. All sterols have a similar structure to cholesterol. Cholesterol is only found in foods of animal origin. If consumers were more knowledgeable, intentionally misleading practices, such as labeling a banana “cholesterol free”, would not be as widespread as they currently are today.

Function

Although cholesterol has acquired the status of a nutrition "villain", it is a vital component of cell membranes and is used to produce vitamin D, hormones, and bile acids. You can see the similarity between the structures of vitamin D and estradiol, one of the forms of estrogen shown below.



Figure 17.2.3 *Structures of vitamin D_3 and estradiol (a form of estrogen)*[2,3]

We do not need to consume any cholesterol from our diets (not essential) because our bodies have the ability to synthesize the required amounts. The figure below gives you an idea of the cholesterol content of a variety of foods.

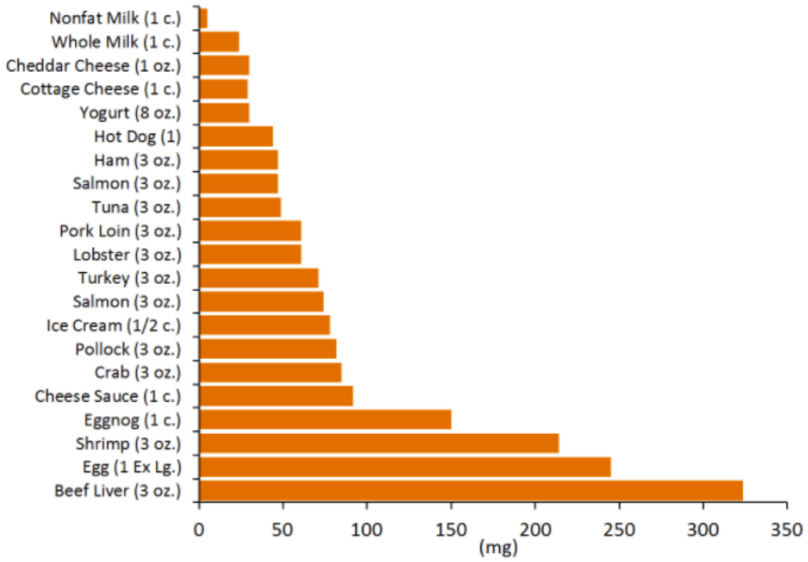


Figure 17.2.4 *The cholesterol content (mg) of foods*[4]

There is neither bad nor good cholesterol, despite these descriptions being commonly used for LDL and HDL, respectively. Cholesterol is cholesterol. HDL and LDL contain cholesterol but are actually lipoproteins that will be described below.

Too much cholesterol in the blood can combine with other substances to form plaque. Plaque sticks to the walls of the arteries. This buildup of plaque is known as atherosclerosis. It can lead to coronary artery disease, wherein the coronary arteries become narrow or even blocked.

The most common cause of high cholesterol is an unhealthy lifestyle. This can include:

- **Unhealthy eating habits,** such as eating lots of bad fats. One type, saturated fat, is found in some meats, dairy products, chocolate, baked goods, and deep-fried and processed foods. Another type, trans fat, is in some fried and processed foods. Eating these fats can raise your LDL (bad) cholesterol.

- **Lack of physical activity,** with lots of sitting and little exercise. This lowers your HDL (good) cholesterol.
- **Smoking,** which lowers HDL cholesterol, especially in women. It also raises your LDL cholesterol.

Genetics may also cause people to have high cholesterol. For example, familial hypercholesterolemia (FH) is an inherited form of high cholesterol. Other medical conditions and certain medicines may also cause high cholesterol.

HDL, LDL, and VLDL

Lipoproteins, as the name suggests, are complexes of lipids and protein. The proteins within a lipoprotein are called apolipoproteins (aka apoproteins). T

There are a number of lipoproteins in the body. They differ by the **apolipoproteins** they contain, size (diameter), density, and composition. The table below shows the difference in density and diameter of different lipoproteins. Notice that as diameter decreases, density increases.

Table Extra close brace or missing open brace *Properties of different lipoproteins.*

Lipoprotein	Density (g/dL)	Diameter (nm)	Purpos
HDL (high-density lipoproteins)	1.063-1.21	5-12	It is son parts of body.
LDL (low-density lipoproteins)	1.019-1.063	18-25	It is son of plaqu
VLDL (very low-density lipoproteins)	0.95-1.006	30-80	Some p buildup carries

This inverse relationship is a result of the larger lipoproteins being composed of a higher percentage of triglyceride and a lower percentage of protein as shown below.

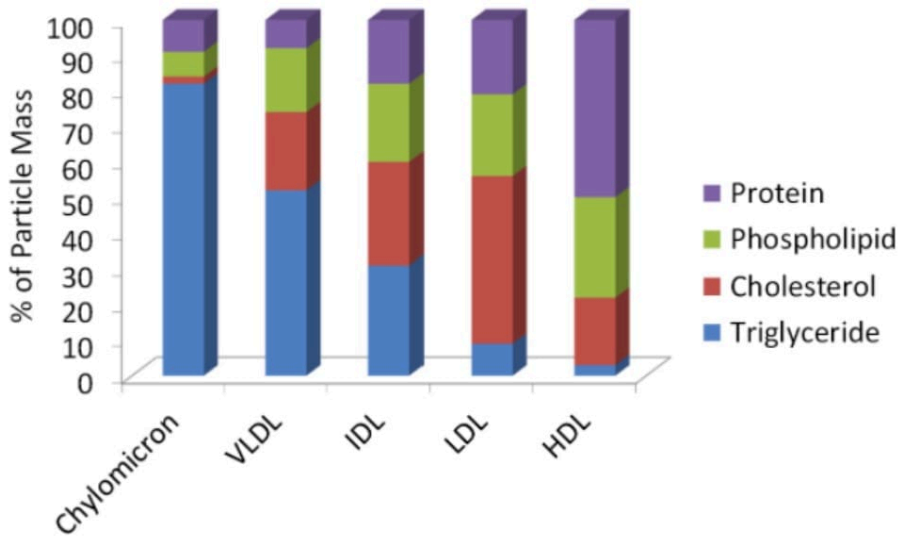


Figure 17.2.5 *Composition of lipoproteins*

Protein is more dense than triglyceride (why muscle weighs more than fat), thus the higher protein/lower triglyceride composition, the higher the density of the lipoprotein. Many of the lipoproteins are named based on their densities (i.e. very low-density lipoproteins).

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."

What's so bad about LDL? LDL enters the endothelium where it is oxidized. This oxidized LDL is engulfed by white blood cells (macrophages), leading to the formation of what are known as foam cells. The foam cells eventually accumulate so much LDL that they die and accumulate, forming a fatty streak. From there the fatty streak, which is the beginning stages of a lesion, can continue to grow until it blocks the artery. This can result in a myocardial infarction (heart attack) or a stroke. HDL is good in that it scavenges cholesterol from other lipoproteins or cells and returns it to the liver. The figure below shows the formation of the fatty streak and how this can progress to a point where it greatly alters blood flow.

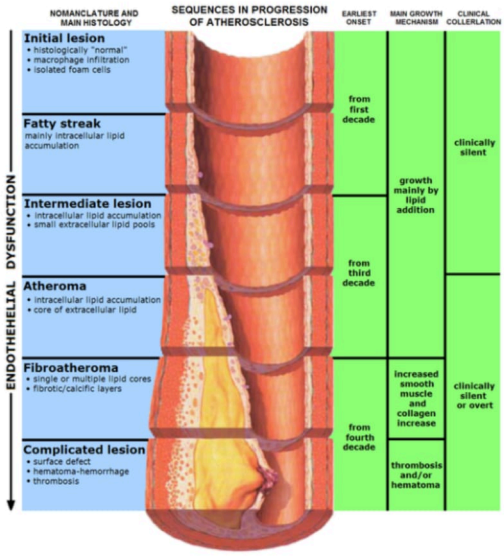


Figure 17.2.6 *The formation of a lesion in an artery*[5]

Web links

The video below does an excellent job of illustrating this process. However, there are two caveats to point out. First, it incorrectly refers to cholesterol (LDL-C etc.), and second, it is clearly made by a drug company, so keep these factors in mind. The link below is the American Heart Association's simple animation of how atherosclerosis develops.

Video: Atherosclerosis (5:36)

Cholesterol and CAD

Despite what you learned above about HDL, a recent study questions its importance in preventing cardiovascular disease. It found that people who have genetic variations that lead to higher HDL levels were not at decreased risk of developing cardiovascular disease. You can read more about this interesting finding in the first link below. In addition, another recent study is questioning whether saturated fat is associated with an increased risk of cardiovascular disease.

Doubt Cast on the 'Good' in 'Good Cholesterol'

Study Questions Fat and Heart Disease Link

The following video gives a general overview of macronutrient digestion, uptake, and absorption.

Video: Small Intestine (1:29)

Saturated Fats, Unsaturated Fats, Essential Fatty Acids, and Trans Fats

Chain Length of Fatty Acids

Fatty acids have different chain lengths, typically between four and 24 carbons, and most contain an even number of carbon atoms. When the carbon chain length is shorter, the melting point of the fatty acid becomes lower (such as fats found in dairy products) and the fatty acid becomes more liquid. Longer chain lengths tend to result in more solid fats, although melting point is also influenced by the degree of saturation.

Degrees of Saturation of Fatty Acids

Fatty acid chains are composed primarily of carbon and hydrogen atoms that are bonded to each other. The term “saturation” refers to whether the carbon atom in a fatty acid chain is filled (or “saturated”) to capacity with hydrogen atoms. In a ***saturated fatty acid,*** each carbon is bonded to two hydrogen atoms, with single bonds between the carbons.

Alternatively, fatty acids can have points where hydrogen atoms are missing, because there is a double bond between carbons (C=C). This is referred to as a point of unsaturation, because the carbon is only bonded to one hydrogen atom instead of two. ***Unsaturated fatty acids*** have one or more points of unsaturation, or double bonds between the carbons. A ***monounsaturated fatty acid*** is a fatty acid with one double bond, and a ***polyunsaturated fatty acid*** is a fatty acid with two or more double bonds.

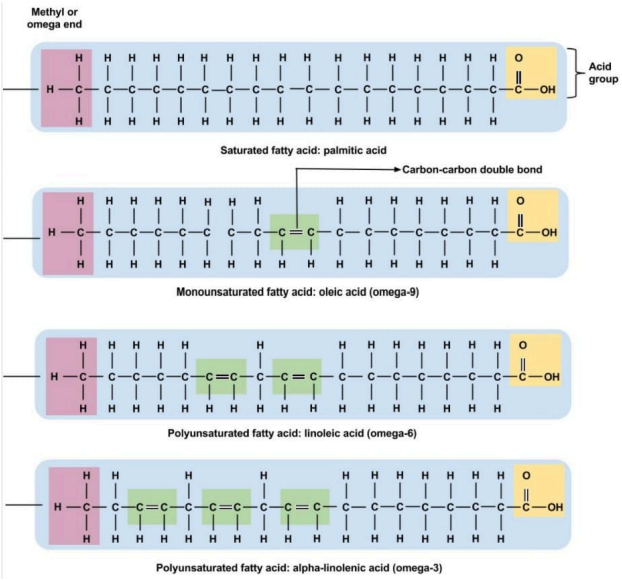


Figure 17.2.1: The structures of a saturated, monounsaturated, and polyunsaturated fat. Note the differences in points of unsaturation (C=C double bonds) on some of the fatty acids.

Triglycerides in food contain a mixture of saturated, monounsaturated, and polyunsaturated fatty acids, but some foods are better sources of these types of fatty acids than others (Figure 5.13). For example, coconut oil is very high in saturated fat, but it still contains some monounsaturated and polyunsaturated fatty acids. Peanut oil is often thought of as a good source of monounsaturated fat, because that is the predominant fatty acid in the oil, but peanut oil also contains a fair amount of polyunsaturated fatty acids and even some saturated fatty acids.

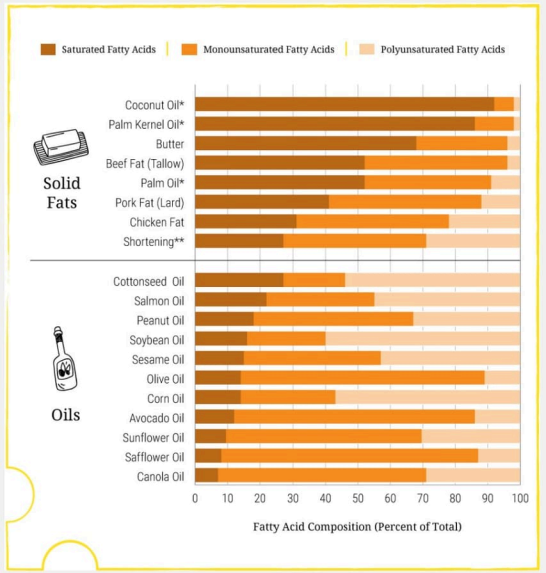


Figure 17.2.2: Dietary fats contain a mixture of saturated, monounsaturated, and polyunsaturated fatty acids. Foods are often categorized by the predominant type of fatty acids they contain, even though foods contain all three types. (Copyright; author via source)

Saturated Fatty Acids

Fat sources with a high percentage of **saturated fatty acids tend to be solid at room temperature**. This is because the lack of double bonds in the carbon chains of saturated fatty acids makes them very straight, so they pack together well (like a box of toothpicks). Fats that have mostly saturated fatty acids, like butter and coconut oil, are solid at room temperature, as are the visible fat layers in a strip of bacon or a cut of beef. Consuming a diet high in saturated fats is associated with an increased risk of heart disease, because such a diet increases blood cholesterol, specifically the LDL ("bad") cholesterol level. (More on this later.) **Food sources of predominately saturated fatty acids** include most animal fats (with the exception of poultry and eggs, which contain more unsaturated fatty acids), dairy products, tropical oils (like coconut and palm oil), cocoa butter, and partially or fully hydrogenated oils.



Figure 17.2.3: Examples of foods high in saturated fat, such as meat and dairy products.

Unsaturated Fatty Acids

Fat sources rich in **unsaturated fatty acids tend to be liquid at room temperature**, because the C=C double bonds create bends in the carbon chain, making it harder for fatty acids to pack together tightly. Consuming a diet rich in mono- and polyunsaturated fats is associated with a lower LDL cholesterol level and a lower risk of heart disease.

Food sources of predominately monounsaturated fats include nuts and seeds like almonds, pecans, cashews, and peanuts; plant oils like canola, olive, and peanut oils; and avocados. The fat in poultry and eggs is predominantly unsaturated and contains more monounsaturated than polyunsaturated fatty acids.



Figure 17.2.4: Examples of foods high in monounsaturated fat, such as olive oil, avocado, nut butters, and seeds. (Copyright; author via source).

Food sources of predominately polyunsaturated fats include plant oils (soybean, corn); fish; flaxseed; and some nuts like walnuts and pecans.

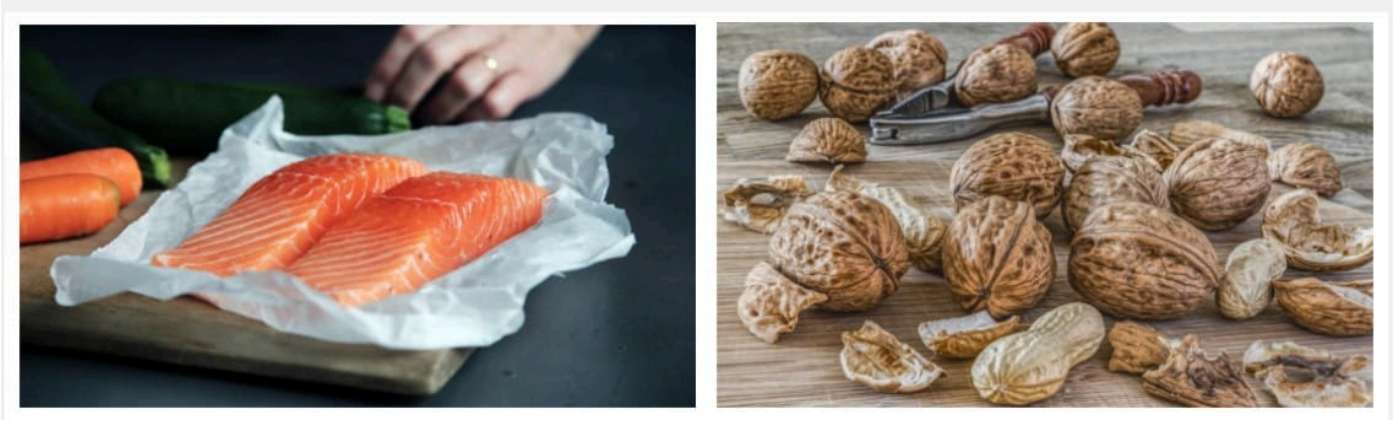


Figure 17.2.5: Examples of foods high in polyunsaturated fats, like fish and nuts.

Omega-3, Omega-6, and Essential Fatty Acids

In addition to the length of the carbon chain and the number of double bonds, **unsaturated fatty acids are also classified by the position of the first double bond relative to the methyl (-CH_3) or "omega" end of the carbon chain** (the end furthest from the glycerol backbone in a triglyceride). Fatty acids with the first double bond at the third carbon from the omega end are called ***omega-3 fatty acids***. Those with the first double bond at the sixth carbon from the omega end are called ***omega-6 fatty acids***. (There are also omega-9 fatty acids.)

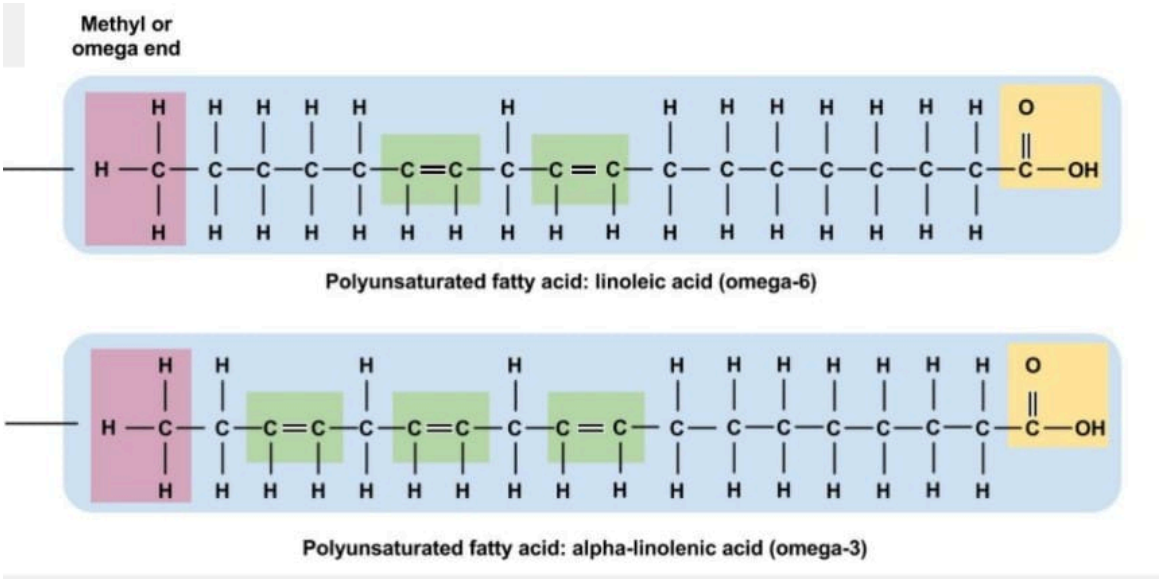
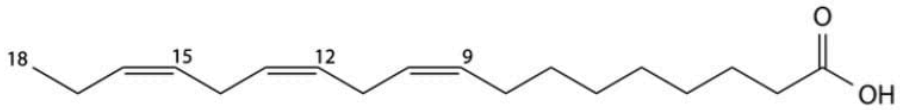
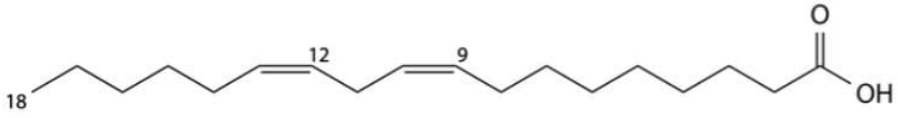


Figure 17.2.6: The position of the first C=C double bond determines whether an unsaturated fatty acid is classified as omega-3 or omega-6. The two essential fatty acids, linoleic acid (an omega-6) and alpha-linolenic acid (an omega-3) are shown here.

Fatty acids are vital for the normal operation of all body systems, but the body is capable of synthesizing most of the fatty acids it needs. However, there are two fatty acids that the body cannot synthesize: ***linoleic acid*** (an omega-6) and ***alpha-linolenic acid*** (ALA, an omega-3). These are called ***essential fatty acids*** because they must be consumed in the diet. Other fatty acids are called nonessential fatty acids, but that doesn't mean they're unimportant; the classification is based solely on the ability of the body to synthesize the fatty acid. Excellent **food sources of linoleic fatty acid** include plant oils such as corn oil and soybean oil, often found in salad dressings and margarine. **Rich food sources of alpha-linolenic acid (ALA)** include nuts, flaxseed, whole grains, legumes, and dark green leafy vegetables.



Alpha-linolenic acid (ALA). Note the first double bond occurs at the third carbon from the omega end of the fatty acid, thus making it an omega-3 fatty acid.



Linoleic acid. Note the first double bond occurs at the sixth carbon from the omega end of the fatty acid, thus making it an omega-6 fatty acid.

Figure 17.2.7: The chemical structure of the essential fatty acids shown in shorthand, without individual carbon and hydrogen atoms marked.

Most Americans easily consume enough linoleic acid and other omega-6 fatty acids, because corn and soybean oil are common ingredients in our food supply. However, sources of ALA and other omega-3 fatty acids are less common in the American diet, and many people could benefit from incorporating more sources of these into their diet. As an added benefit, whole foods rich in ALA come packaged with other healthful nutrients, like fiber, protein, vitamins, minerals, and phytochemicals.

A true **essential fatty acid deficiency** is rare in the developed world, but it can occur, usually in people who eat very low-fat diets or have impaired fat absorption. Symptoms include dry and scaly skin, poor wound healing, increased vulnerability to infections, and impaired growth in infants and children.[1]

Omega-3 and omega-6 fatty acids are precursors to a large family of important signaling molecules called ***eicosanoids*** (prostaglandins are one type of eicosanoid). Among the many functions of eicosanoids in the body, one of the most important is to regulate inflammation. Without these hormone-like molecules, the body would not be able to heal wounds or fight off infections each time a foreign germ presented itself. In addition to their role in the body's immune and inflammatory processes, eicosanoids also help to regulate circulation, respiration, and muscle movement.

Eicosanoids derived from omega-6 fatty acids tend to increase blood pressure, blood clotting, immune response, and inflammation. These are necessary functions, but they can be associated with disease when chronically elevated. In contrast, eicosanoids derived from omega-3 fatty acids tend to lower blood pressure, inflammation, and blood clotting, functions that can benefit heart health. Omega-3 and omega-6 fatty acids compete for the same enzymatic pathways in the formation of different eicosanoids, so increasing omega-3 fatty acids in the diet may have anti-inflammatory effects.

Two additional omega-3 fatty acids with important health benefits are ***eicosapentaenoic acid (EPA)*** and ***docosahexaenoic acid (DHA)***. These long-chain polyunsaturated fatty acids have been shown to help lower blood triglycerides and blood pressure, reduce inflammation, and prevent blood clot formation. They also promote normal growth and development in infants, especially in the development of the brain and eyes. Both of these important omega-3 fatty acids can be synthesized in the body from ALA, so **they are not considered essential fatty acids**. However, the rate of conversion of ALA to these omega-3s is limited, so it is beneficial to consume them regularly in the diet. **Fish, shellfish, fish oils, seaweed, and algae are all good sources of EPA and DHA**. DHA is also found in human breast milk in quantities dependent on the mother's own intake of DHA sources.

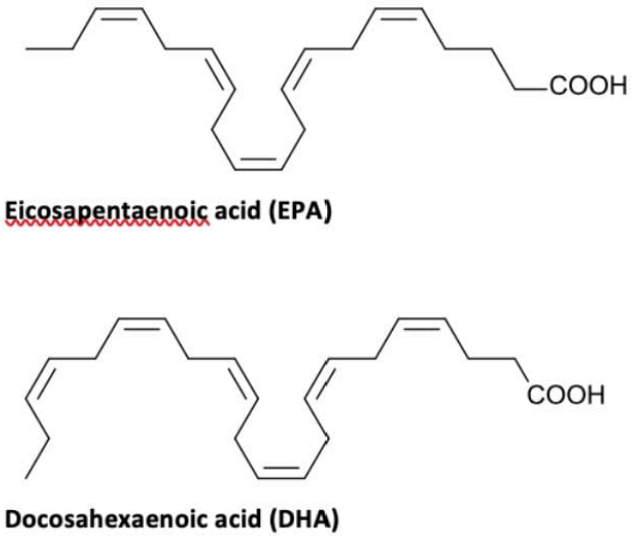


Figure 17.2.8: EPA and DHA are important but non-essential omega-3 fatty acids that can be made in the body from ALA.

Fish oil and omega-3 supplements are among the most commonly used dietary supplements in the United States. Researchers have hypothesized that these supplements might decrease risk of cardiovascular disease, be helpful for those with rheumatoid arthritis, and improve infant brain development when taken in pregnancy or in infancy. Some studies have found such benefits of the supplements, but others haven't. One reason for these inconsistent results may be that studies often don't measure participants' baseline omega-3 levels and intake from foods, and those already consuming adequate omega-3s are less likely to benefit from a supplement. The Dietary Guidelines for Americans recommends consuming 8 ounces of a variety of seafood each week, and in general, people who meet this recommendation likely consume enough omega-3 fatty acids already (along with the other healthful nutrients found in fish) and are unlikely to see an added benefit of taking a fish oil supplement. Some doctors may recommend that people at risk of cardiovascular disease take a fish oil or omega-3 supplement, especially if they don't eat fish regularly.[2]

A Word About *Trans* Fats

The carbon-carbon double bond in an unsaturated fatty acid chain can result in different shapes depending on whether the fatty acid is in a *cis* or *trans* configuration. When the hydrogen atoms are bonded to the same side of the carbon chain, it is called a *cis* fatty acid. Because the hydrogen atoms are on the same side (and repelling one another), the carbon chain has a bent structure. Naturally-occurring fatty acids usually have a *cis* configuration.

In a ***transfatty acid***, the hydrogen atoms are bonded on opposite sides of the carbon chain, resulting in a more linear structure. Unlike *cis* fatty acids, most *trans* fatty acids are not found naturally in foods, but instead are a result of an industrial process called hydrogenation. ***Hydrogenation*** is the process of adding hydrogen to the carbon-carbon double bonds, thus making the fatty acid saturated (or less unsaturated, in the case of partial hydrogenation).

Hydrogenation creates both saturated and trans fatty acids. Trans fatty acids are actually unsaturated fatty acids, but they have the linear shape of saturated fatty acids. (The carbon chains are not bent like naturally-occurring unsaturated fats.) **The trans fatty acids formed through partial hydrogenation have an unusual shape, which makes their properties and actions in the body similar to saturated fatty acids.**

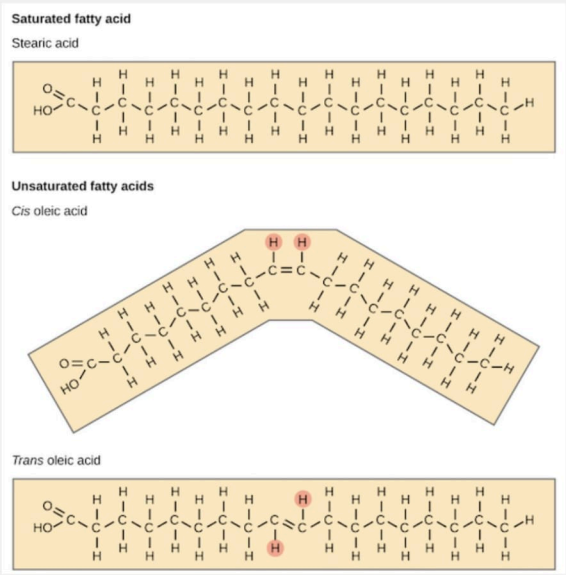


Figure 17.2.9: Comparison of a saturated fatty acid to both the cis and trans forms of an unsaturated fatty acid.

Hydrogenation was developed in order to make oils semi-solid at room temperature, enabling production of spreadable margarine and shortening from inexpensive ingredients like corn oil. Hydrogenation also makes oils more stable and less likely to go rancid, so partially hydrogenated oils were favored by fast food restaurants for frying, and manufacturers of processed baked goods like cookies and chips found they gave their products a longer shelf life. And because trans fats are unsaturated, nutrition scientists and the medical community believed that they were a healthier alternative to saturated fats.

But around the 1990s, evidence that trans fats were not healthy—far worse than saturated fats, in fact—began to accumulate. Like saturated fat, **trans fats increase LDL ("bad") cholesterol, but they also have the effect of decreasing HDL ("good") cholesterol** and of increasing inflammatory processes in the body. Researchers found that consuming trans fats, even at low levels (1 to 3 percent of total energy intake), was associated with an increased risk of coronary heart disease. They estimated that eliminating industrial trans fats from the food supply might prevent as many as 19 percent of heart attacks in the U.S. at the time, coming to 228,000 heart attacks averted.[3]

In 2006, the U.S. Food and Drug Administration (FDA) began requiring food companies to list trans fat information on the Nutrition Facts panel of food labels to keep consumers informed of their intake of these fats. That prompted the food industry to mostly eliminate partially hydrogenated oils from their products, often substituting palm oil and coconut oil in their place (both of which are high in saturated fat and may promote heart disease). In 2013, the FDA determined that trans fats were no longer considered safe in the food supply, and in 2015, the agency issued a ruling requiring that manufactured trans fats no longer be included in the U.S. food supply. A one-year extension was granted in 2018, and foods produced prior to that date were given time to work through the food supply. The final ruling requires all manufactured trans fats to be eliminated from the U.S. food supply by 2021.[4]

Summary

- Digestion of lipids by lipases in pancreatic juice occurs primarily in the small intestines. The monoglycerides and fatty acids cross the intestinal lining into the bloodstream, where they are resynthesized into triglycerides and transported as

chylomicrons. Phospholipids and cholesteryl esters undergo similar hydrolysis in the small intestine, and their component molecules are also absorbed through the intestinal lining.
- Two lipoproteins (composed of a lipid and a protein) of great interest are HDL "good cholesterol transporter" and LDL "bad cholesterol transporter."
- Trans fats are unhealthy fats that form when vegetable oil hardens in a process called hydrogenation. They can raise LDL cholesterol levels in the blood. They can also lower HDL (good) cholesterol levels. Trans fats are under review for their health effects.
- Saturated fats are also considered as unhealthy fats.
- Studies indicate that the consumption of monounsaturated fats and polyunsaturated fats (specifically those with omega-3 fatty acids) have numerous health benefits.

Contributors and Attributions

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17.3: Proteins- Muscle and Much More

Learning Objectives

- Describe the metabolism of proteins.
- Know the importance of essential amino acids.
- Know the sources and function of common proteins in the diet.

Proteins are essential nutrients for the human body. They are one of the building blocks of body tissue and can also serve as a fuel source. As a fuel, proteins provide as much energy density as carbohydrates: 4 kcal (17 kJ) per gram; in contrast, lipids provide 9 kcal (37 kJ) per gram. The most important aspect and defining characteristic of protein from a nutritional standpoint is its amino acid composition.

Proteins are polymer chains made of amino acids linked together by peptide bonds. During human digestion, proteins are broken down in the stomach to smaller polypeptide chains via hydrochloric acid and protease actions. This is crucial for the absorption of the essential amino acids that cannot be biosynthesized by the body.

Protein Functions in Human Body

Protein is a nutrient needed by the human body for growth and maintenance. Aside from water, proteins are the most abundant kind of molecules in the body. Protein can be found in all cells of the body and is the major structural component of all cells in the body, especially muscle. This also includes body organs, hair and skin. Proteins are also used in membranes, such as glycoproteins. When broken down into amino acids, they are used as precursors to nucleic acid, co-enzymes, hormones, immune response, cellular repair, and other molecules essential for life. Additionally, protein is needed to form blood cells.

Protein Metabolism: Essential Amino Acids

Protein digestion begins in the stomach (Figure 17.3.3), where the action of gastric juice hydrolyzes about 10% of the peptide bonds. Gastric juice is a mixture of water (more than 99%), inorganic ions, hydrochloric acid, and various enzymes and other proteins.

> The pain of a gastric ulcer is at least partially due to irritation of the ulcerated tissue by acidic gastric juice.

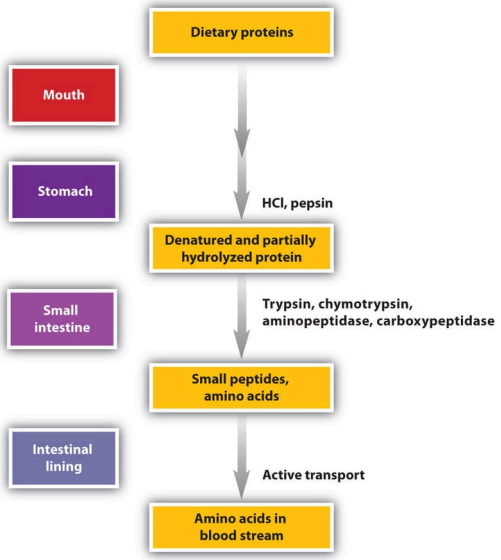


Figure 17.3.1 The principal events and Sites of Protein Digestion

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.

Amino Acids

There are 20 amino acids our body uses to synthesize proteins. These amino acids can be classified as essential, non-essential, or conditionally essential. The table below shows how the 20 amino acids are classified.

Table 17.3.1: Essential, conditionally essential, and nonessential amino acids

Essential	Conditionally Essential	Non-essential
Histidine	Arginine	Alanine
Isoleucine	Cysteine	Asparagine
Leucine	Glutamine	Aspartic Acid or Aspartate
Lysine	Glycine	Glutamic Acid or Glutamate
Methionine	Proline	Serine
Phenylalanine	Tyrosone	
Theronine		
Tryptophan		
Valine		

The body cannot synthesize nine amino acids. Thus, it is essential that these are consumed in the diet. As a result these amino acids are known as essential, or indispensable, amino acids.

Non-essential, or dispensable, amino acids can be made in our body, so we do not need to consume them. Conditionally essential

amino acids become essential for individuals in certain situations. An example of a condition when an amino acid becomes essential is the disease *phenylketonuria (PKU)*. Individuals with PKU have a mutation in the enzyme phenylalanine hydroxylase, which normally adds an alcohol group (OH) to the amino acid phenylalanine to form tyrosine as shown below.

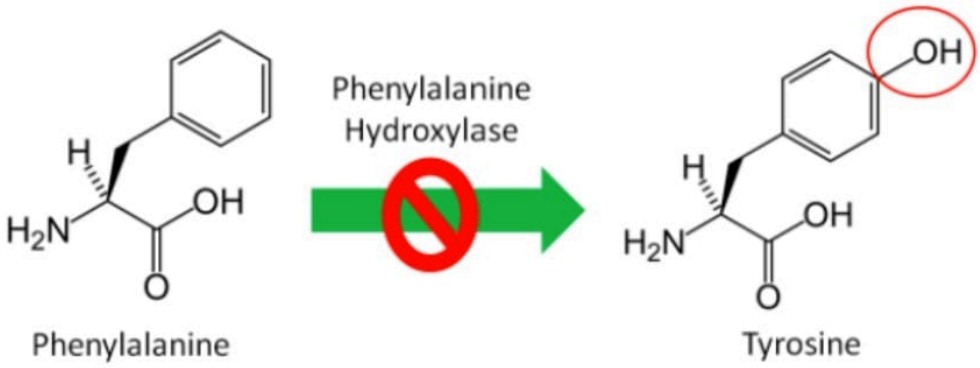


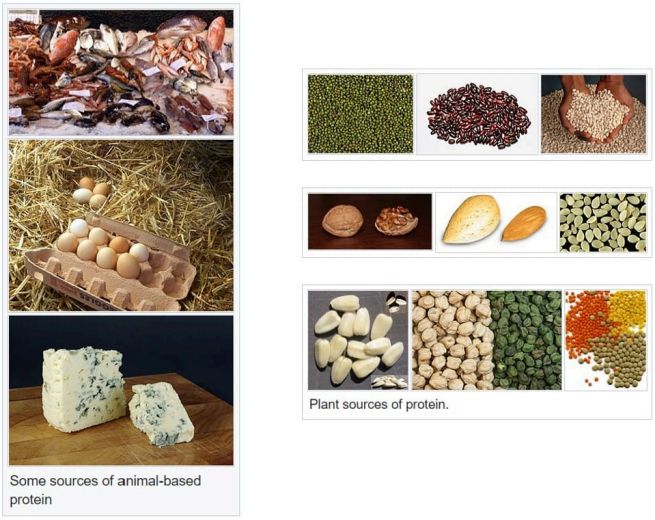
Figure 17.3.2: Phenylketonuria (PKU) results from a mutation in the enzyme phenylalanine hydroxylase

Since tyrosine cannot be synthesized by people with PKU, it becomes essential for them. Thus, tyrosine is a conditionally essential amino acid. Individuals with PKU have to eat a very low protein diet and avoid the alternative sweetener aspartame, because it can be broken down to phenylalanine. If individuals with PKU consume too much phenylalanine, phenylalanine and its metabolites, can build up and cause brain damage and severe mental retardation. The drug Kuvan was approved for use with PKU patients in 2007 who have low phenylalanine hydroxylase activity levels.

Protein Sources

Protein occurs in a wide range of food. On a worldwide basis, plant protein foods contribute over 60% of the per capita supply of protein. In North America, animal-derived foods contribute about 70% of protein sources. Insects are a source of protein in many parts of the world. In parts of Africa, up to 50% of dietary protein derives from insects. It is estimated that more than 2 billion people eat insects daily.

Meat, dairy, eggs, soy, fish, whole grains, and cereals are sources of protein. Examples of food staples and cereal sources of protein, each with a concentration greater than 7%, are (in no particular order) buckwheat, oats, rye, millet, maize (corn), rice, wheat, sorghum, amaranth, and quinoa. Some research highlights game meat as a protein source.


Some sources of animal-based protein

Plant sources of protein.

Figure 17.3.3 Typical sources of protein.

Vegan sources of proteins include legumes, nuts, seeds and fruits. Vegan foods with protein concentrations greater than 7% include soybeans, lentils, kidney beans, white beans, mung beans, chickpeas, cowpeas, lima beans, pigeon peas, lupines, wing beans, almonds, Brazil nuts, cashews, pecans, walnuts, cotton seeds, pumpkin seeds, hemp seeds, sesame seeds, and sunflower seeds.

People eating a balanced diet do not need protein supplements.

The table below presents food groups as protein sources.

Table 17.3.2 Density of amino acid in various protein sources.

Food source	Lysine	Threonine	Tryptophan	Sulfur-containing amino acids
Legumes	64	38	12	25
Cereals and whole grains	31	32	12	37
Nuts and seeds	45	36	**17**	**46**
Fruits	45	29	11	27
Animal	**85**	**44**	12	38

Colour key:

Protein source with highest density of respective amino acid.
Protein source with lowest density of respective amino acid.

Protein powders - such as casein, whey, egg, rice, soy, and cricket flour - are processed and manufactured sources of protein.

Complete and Incomplete Proteins

Proteins can 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. The table below shows the limiting amino acids in some plant foods.

Table 17.3.3 Limiting amino acids in some common plant foods.

Food	Amino Acid(s)
Beans and Most Legumes	Methionine, Tryptophan
Tree Nuts and Seeds	Methionine, Lysine
Grains	Lysine
Vegetables	Methionine, Lysine

Complementary Proteins

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.



(Figure 17.3.4) *Complementary proteins are kind of like puzzle pieces.*

Two examples of complementary proteins are shown below.

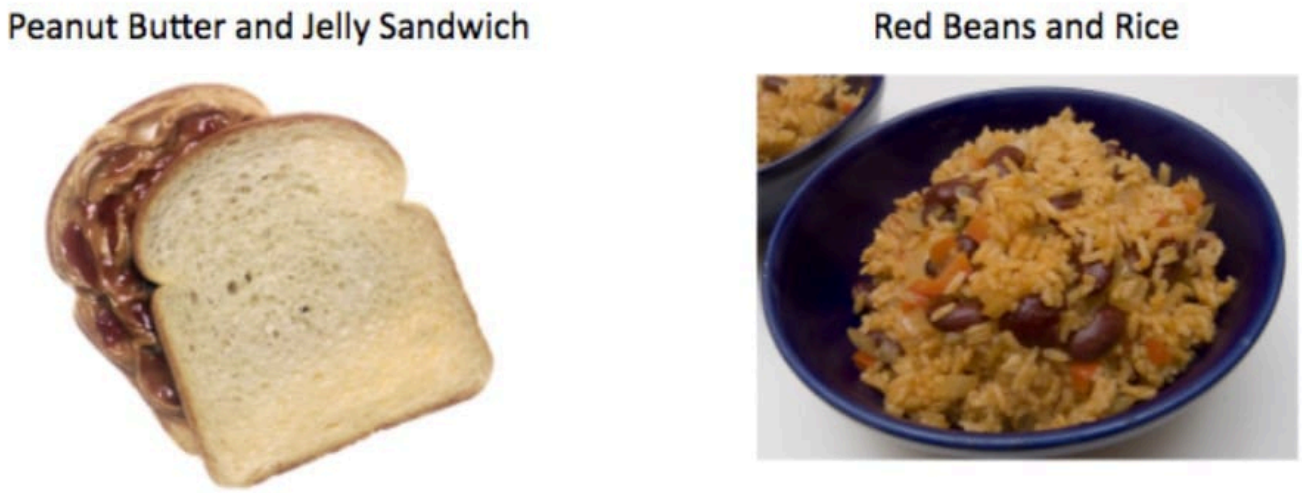


Figure 17.3.5) *Two complementary protein examples*

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[4].

Measures of Protein Quality

How do you know the quality of the protein in the foods you consume? The protein quality of most foods has been determined by one of the methods below.

- **Biological Value (BV)** - (grams of nitrogen retained / grams of nitrogen absorbed) x 100

- **Protein Efficiency Ratio (PER)** - (grams of weight gained / grams of protein consumed)

This method is commonly performed in growing rats.

- **Chemical or Amino Acid Score (AAS)** - (Test food limiting essential amino acid (mg/g protein) / needs of same essential amino acid (mg/g protein))
- **Protein Digestibility Corrected Amino Acid Score (PDCAAS)** - (Amino Acid Score x Digestibility)

This is the most widely used method and was preferred by the Food and Agriculture Organization and World Health Organization (WHO) until recently[5,6]. The following table shows the protein quality measures for some common foods.

Table 17.3.4 Measures of protein quality

Protein	PER	Digestibility	AA(%)	PDCAAS
Egg	3.8	98	121	100*
Milk	3.1	95	127	100*
Beef	2.9	98	94	92
Soy	2.1	95	96	91
Wheat	1.5	91	47	42

*PDCAAS scores are truncated (cut off) at 100. These egg and milk scores are actually 118 and 121 respectively.

The Food and Agricultural Organization (FAO) recently recommended that PDCAAS be replaced with a new measure of protein quality, the Digestible Indispensable Amino Acid Score (DIAAS). “DIAAS is defined as: DIAAS % = 100 x [(mg of digestible dietary indispensable amino acid in 1 g of the dietary protein) / (mg of the same dietary indispensable amino acid in 1g of the reference protein)].” Ileal digestibility should be utilized to determine the digestibility in DIAAS; ideally in humans, but if not possible in growing pigs or rats[6].

The main differences between DIAAS and PDCAAS are:

1. DIAAS take into account individual amino acids digestibility rather than protein digestibility.
2. It focus on ileal instead of fecal (total) digestibility.
3. Has three different reference patterns (different age groups, 0-6 months, 6 months- 3 years, 3-10 years old) instead of a single pattern
4. DIAAS scores will not be truncated[7]

Protein Deficiency in Young and Old

Protein deficiency rarely occurs alone. Instead it is often coupled with insufficient energy intake. As a result, the condition is called protein-energy malnutrition (PEM). This condition is not common in the U.S., but is more prevalent in less developed countries. Kwashiorkor and marasmus are the two forms of protein energy malnutrition. They differ in the severity of energy deficiency as shown in the figure below.

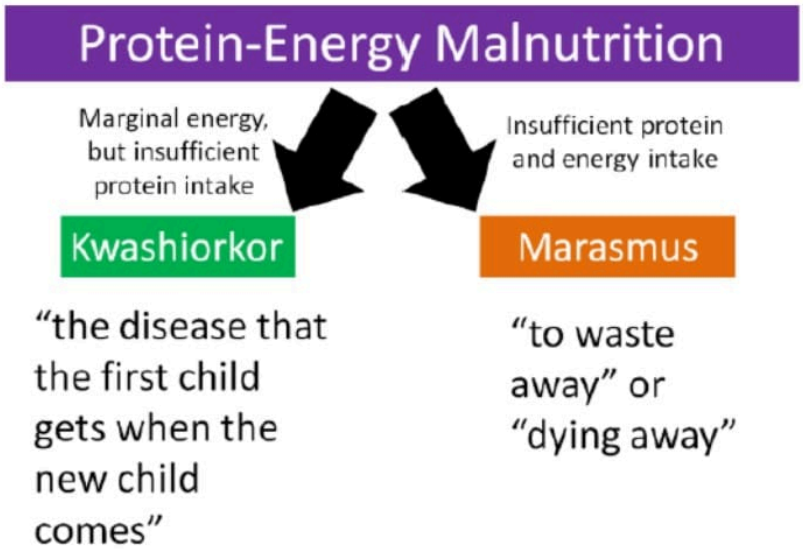


Figure 17.3.6 The two types of protein-energy malnutrition.

Kwashiorkor is a Ghanaian word that means "the disease that the first child gets when the new child comes39." The characteristic symptom of kwashiorkor is a swollen abdomen. Energy intake could be adequate, but protein consumption is too low.



Figure 17.3.7: A child suffering from kwashiorkor

Marasmus means "to waste away" or "dying away", and thus occurs in individuals who have inadequate protein and energy intakes.



Figure 17.3.8 Two individuals suffering from marasmus

Summary

- Protein digestion begins in the stomach where hydrolysis of the protein linkages occurs with the action of gastric juices (mainly HCl) and the active enzyme pepsin. Protein digestion is completed in the small intestine wherein other protein digesting enzymes are involved.
- Essential amino acids cannot be made by the body and must come from food.
- Complete proteins provide adequate amounts of all nine essential amino acids.
- Complementary proteins are made up of two proteins wherein one protein supply the amino acid(s) missing in the other protein.
- Kwashiorkor and marasmus are two forms of protein energy malnutrition that are not common in the U.S., but is more prevalent in less developed countries

Contributors and Attributions

- Template:ContribLindshield
- Libretext: Basics of GOB Chemistry (Ball et al.)
- Wikipedia

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17.4: Minerals, Vitamins, and Other Essentials

Learning Objectives

- List reasons why vitamins and minerals are critical to a healthy diet.
- Describe the functional role, intake recommendations and sources of vitamins and major minerals.
- Learn about the importance and sources of dietary fiber.
- Learn about the importance of water.

Vitamins and minerals are essential to human health and can be obtained in our diet from different types of food.

Dietary Minerals

Minerals in food are inorganic compounds that work with other nutrients to ensure the body functions properly. Minerals are abundant in our everyday lives. From the soil in your front yard to the jewelry you wear on your body, we interact with minerals constantly. There are 20 essential minerals that must be consumed in our diets to remain healthy. The amount of each mineral found in our bodies vary greatly and therefore, so does consumption of those minerals. When there is a deficiency in an essential mineral, health problems may arise.

Major minerals (Figure 17.4.1) are classified as minerals that are required in the diet each day in amounts larger than 100 milligrams. These include sodium, potassium, chloride, calcium, phosphorus, magnesium, and sulfur. These major minerals can be found in various foods. Consuming a varied diet significantly improves an individual's ability to meet their nutrient needs. The most common minerals in the body are calcium and phosphorous, both of which are stored in the skeleton and necessary for the hardening of bones. Most minerals are ionized, and their ionic forms are used in physiological processes throughout the body. Sodium and chloride ions are electrolytes in the blood and extracellular tissues, and iron ions are critical to the formation of hemoglobin. There are additional trace minerals that are still important to the body's functions, but their required quantities are much lower.

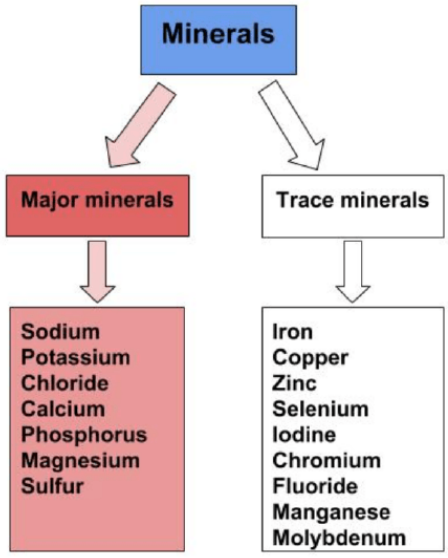


Figure 17.4.1 The major and trace minerals. Image by Allison Calabrese / CC BY 4.0.

Like vitamins, minerals can be consumed in toxic quantities (although it is rare). A healthy diet includes most of the minerals your body requires, so supplements and processed foods can add potentially toxic levels of minerals. Tables 17.4.1 and 17.4.2 provide a summary of minerals and their function in the body.

Table 17.4.1 *Major Minerals and their Function in the Body.*

Major Minerals				
Mineral	**Sources**	**Recommended daily allowance**	**Function**	**Problems associated with deficiency**
Potassium	Meats, some fish, fruits, vegetables, legumes, dairy products	4700 mg	Nerve and muscle function; acts as an electrolyte	Hypokalemia: weakness, fatigue, muscle cramping, gastrointestinal problems, cardiac problems
Sodium	Table salt, milk, beets, celery, processed foods	2300 mg	Blood pressure, blood volume, muscle and nerve function	Rare
Calcium	Dairy products, dark green leafy vegetables, blackstrap molasses, nuts, brewer's yeast, some fish	1000 mg	Bone structure and health; nerve and muscle functions, especially cardiac function	Slow growth, weak and brittle bones
Phosphorous	Meat, milk	700 mg	Bone formation, metabolism, ATP production	Rare
Magnesium	Whole grains, nuts, leafy green vegetables	310–420 mg	Enzyme activation, production of energy, regulation of other nutrients	Agitation, anxiety, sleep problems, nausea and vomiting, abnormal heart rhythms, low blood pressure, muscular problems
Chloride	Most foods, salt, vegetables, especially seaweed, tomatoes, lettuce, celery, olives	2300 mg	Balance of body fluids, digestion	Loss of appetite, muscle cramps

Table 17.4.2 *Trace Minerals and their Function in the Body.*

Trace Minerals				
Mineral	**Sources**	**Recommended daily allowance**	**Function**	**Problems associated with deficiency**
Iron	Meat, poultry, fish, shellfish, legumes, nuts, seeds, whole grains, dark leafy green vegetables	8–18 mg	Transport of oxygen in blood, production of ATP	Anemia, weakness, fatigue
Zinc	Meat, fish, poultry, cheese, shellfish	8–11 mg	Immunity, reproduction, growth, blood clotting, insulin and thyroid function	Loss of appetite, poor growth, weight loss, skin problems, hair loss, vision problems, lack of taste or smell
Copper	Seafood, organ meats, nuts, legumes, chocolate, enriched breads and cereals, some fruits and vegetables	900 μg	Red blood cell production, nerve and immune system function, collagen formation, acts as an antioxidant	Anemia, low body temperature, bone fractures, low white blood cell concentration, irregular heartbeat, thyroid problems
Iodine	Fish, shellfish, garlic, lima beans, sesame seeds, soybeans, dark leafy green vegetables	150 μg	Thyroid function	Hypothyroidism: fatigue, weight gain, dry skin, temperature sensitivity
Sulfur	Eggs, meat, poultry, fish, legumes	None	Component of amino acids	Protein deficiency

Trace Minerals				
Mineral	**Sources**	**Recommended daily allowance**	**Function**	**Problems associated with deficiency**
Fluoride	Fluoridated water	3–4 mg	Maintenance of bone and tooth structure	Increased cavities, weak bones and teeth
Manganese	Nuts, seeds, whole grains, legumes	1.8–2.3 mg	Formation of connective tissue and bones, blood clotting, sex hormone development, metabolism, brain and nerve function	Infertility, bone malformation, weakness, seizures
Cobalt	Fish, nuts, leafy green vegetables, whole grains	None	Component of B_{12}	None
Selenium	Brewer's yeast, wheat germ, liver, butter, fish, shellfish, whole grains	55 μg	Antioxidant, thyroid function, immune system function	Muscle pain
Chromium	Whole grains, lean meats, cheese, black pepper, thyme, brewer's yeast	25–35 μg	Insulin function	High blood sugar, triglyceride, and cholesterol levels
Molybdenum	Legumes, whole grains, nuts	45 μg	Cofactor for enzymes	Rare

The Vitamins: Vital, but Not All are Amines

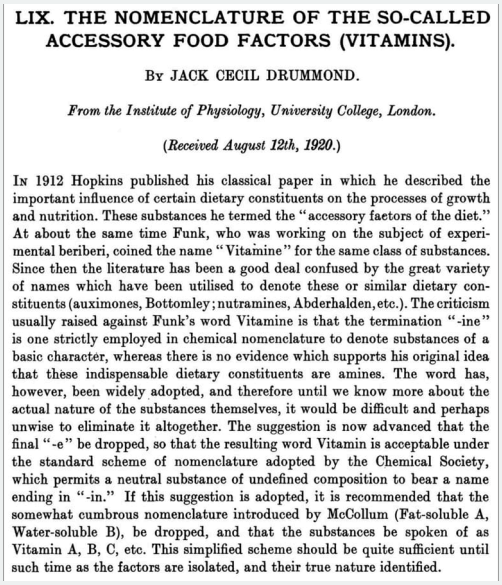
In 1747, the Scottish surgeon James Lind discovered that citrus foods helped prevent scurvy, a particularly deadly disease in which collagen is not properly formed, causing poor wound healing, bleeding of the gums, severe pain, and death. In 1753, Lind published his *Treatise on the Scurvy*, which recommended using lemons and limes to avoid scurvy, which was adopted by the British Royal Navy. This led to the nickname *limey* for British sailors.

In East Asia, where polished white rice was the common staple food of the middle class, beriberi resulting from lack of vitamin B_1 was endemic. In 1884, Takaki Kanehiro, a British-trained medical doctor of the Imperial Japanese Navy, observed that beriberi was endemic among low-ranking crew who often ate nothing but rice, but not among officers who consumed a Western-style diet. This convinced Takaki and the Japanese Navy that diet was the cause of beriberi, but they mistakenly believed that sufficient amounts of protein prevented it. That diseases could result from some dietary deficiencies was further investigated by Christiaan Eijkman, who in 1897 discovered that feeding unpolished rice instead of the polished variety to chickens helped to prevent beriberi in the chickens. The following year, Frederick Hopkins postulated that some foods contained "accessory factors" — in addition to proteins, carbohydrates, fats *etc.* — that are necessary for the functions of the human body. Hopkins and Eijkman were awarded the Nobel Prize for Physiology or Medicine in 1929 for their discoveries.

In 1910, the first vitamin complex was isolated by Japanese scientist Umetaro Suzuki, who succeeded in extracting a water-soluble complex of micronutrients from rice bran and named it aberic acid (later *Orizanin*). He published this discovery in a Japanese scientific journal. When the article was translated into German, the translation failed to state that it was a newly discovered nutrient, a claim made in the original Japanese article, and hence his discovery failed to gain publicity.In 1912 Polish-born biochemist Casimir Funk, working in London, isolated the same complex of micronutrients and proposed the complex be named "vitamine". It was later to be known as vitamin B_3 (niacin), though he described it as "anti-beri-beri-factor" (which would today be called thiamine or vitamin B_1). Funk proposed the hypothesis that other diseases, such as rickets, pellagra, coeliac disease, and scurvy could also be cured by vitamins.

Vitamine to Vitamin

Max Nierenstein a friend and reader of Biochemistry at Bristol University reportedly suggested the "vitamine" name (from "vital amine"). The name soon became synonymous with Hopkins' "accessory factors", and, by the time it was shown that not all vitamins are amines, the word was already ubiquitous. In 1920, Jack Cecil Drummond proposed that the final "e" be dropped to deemphasize the "amine" reference, after researchers began to suspect that not all "vitamines" (in particular, vitamin A) have an amine component.



LIX. THE NOMENCLATURE OF THE SO-CALLED ACCESSORY FOOD FACTORS (VITAMINS).

By JACK CECIL DRUMMOND.

From the Institute of Physiology, University College, London.

(*Received August 12th, 1920.*)

In 1912 Hopkins published his classical paper in which he described the important influence of certain dietary constituents on the processes of growth and nutrition. These substances he termed the "accessory factors of the diet." At about the same time Funk, who was working on the subject of experimental beriberi, coined the name "Vitamine" for the same class of substances. Since then the literature has been a good deal confused by the great variety of names which have been utilised to denote these or similar dietary constituents (auximones, Bottomley; nutramines, Abderhalden, etc.). The criticism usually raised against Funk's word Vitamine is that the termination "-ine" is one strictly employed in chemical nomenclature to denote substances of a basic character, whereas there is no evidence which supports his original idea that these indispensable dietary constituents are amines. The word has, however, been widely adopted, and therefore until we know more about the actual nature of the substances themselves, it would be difficult and perhaps unwise to eliminate it altogether. The suggestion is now advanced that the final "-e" be dropped, so that the resulting word Vitamin is acceptable under the standard scheme of nomenclature adopted by the Chemical Society, which permits a neutral substance of undefined composition to bear a name ending in "-in." If this suggestion is adopted, it is recommended that the somewhat cumbrous nomenclature introduced by McCollum (Fat-soluble A, Water-soluble B), be dropped, and that the substances be spoken of as Vitamin A, B, C, etc. This simplified scheme should be quite sufficient until such time as the factors are isolated, and their true nature identified.

Figure 17.4.2 *Jack Drummond's single-paragraph article in 1920 which provided structure and nomenclature used today for vitamins.*

Vitamins are organic compounds found in foods and are a necessary part of the biochemical reactions in the body. They are involved in a number of processes, including mineral and bone metabolism, and cell and tissue growth, and they act as cofactors for energy metabolism. The B vitamins play the largest role of any vitamins in metabolism (Tables 17.4.3 and 17.4.4)

You get most of your vitamins through your diet, although some can be formed from the precursors absorbed during digestion. For example, the body synthesizes vitamin A from the β-carotene in orange vegetables like carrots and sweet potatoes. Vitamins are either fat-soluble or water-soluble. Fat-soluble vitamins A, D, E, and K, are absorbed through the intestinal tract with lipids in chylomicrons. Vitamin D is also synthesized in the skin through exposure to sunlight. Because they are carried in lipids, fat-soluble vitamins can accumulate in the lipids stored in the body. If excess vitamins are retained in the lipid stores in the body, hypervitaminosis can result.

Water-soluble vitamins, including the eight B vitamins and vitamin C, are absorbed with water in the gastrointestinal tract. These vitamins move easily through bodily fluids, which are water based, so they are not stored in the body. Excess water-soluble vitamins are excreted in the urine. Therefore, hypervitaminosis of water-soluble vitamins rarely occurs, except with an excess of vitamin supplements.

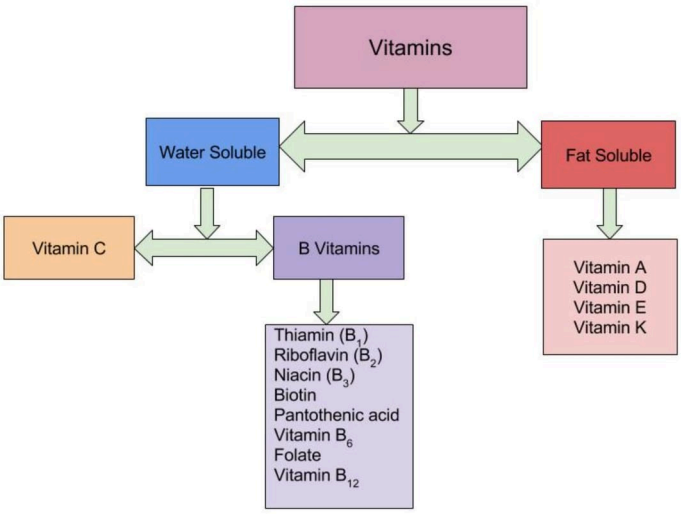


Figure 17.4.3: The Vitamins. *Image by Allison Calabrese / CC BY 4.0.*

Fat Soluble Vitamins

From the structures shown below, it should be clear that these compounds have more than a solubility connection with lipids. VitaminsA is a terpene, and vitamins E and K have long terpene chains attached to an aromatic moiety. The structure of vitamin D can be described as a steroid in which ring B is cut open and the remaining three rings remain unchanged. The precursors of vitamins A and D have been identified as the tetraterpene beta-carotene and the steroid ergosterol, respectively.

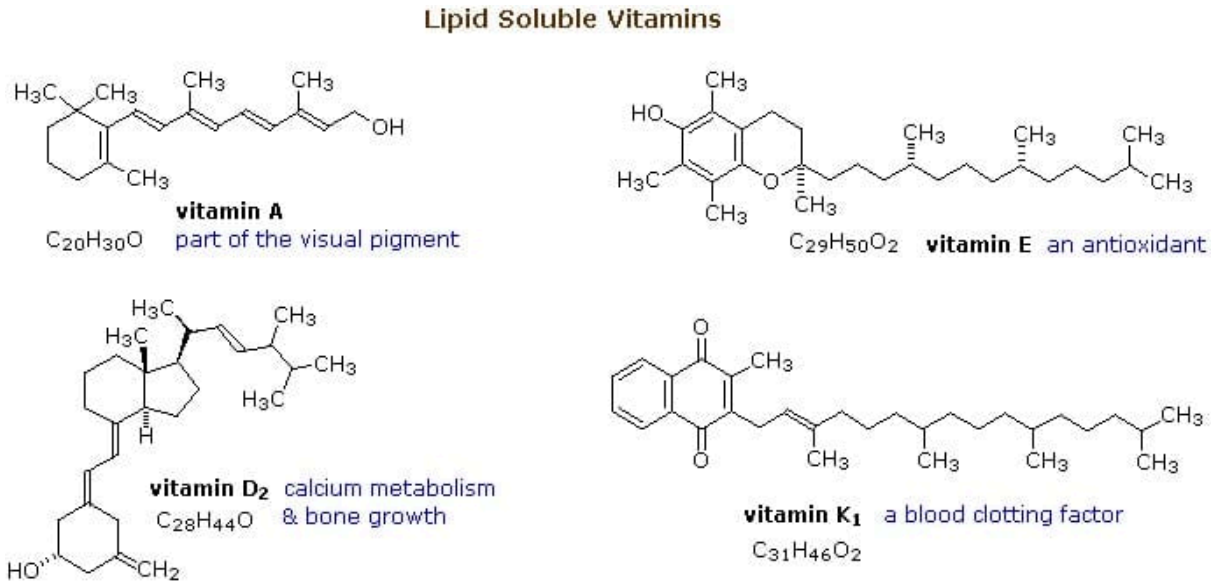


Table 17.4.3 lists the different fat soluble vitamins and its function.

Table 17.4.3 *Fat Soluble Vitamins and Their Function.*

Vitamin and alternative name	Sources	Recommended daily allowance	Function	Problems associated with deficiency
A retinal or β-carotene	Yellow and orange fruits and vegetables, dark green leafy vegetables, eggs, milk, liver	700–900 μg	Eye and bone development, immune function	Night blindness, epithelial changes, immune system deficiency
D cholecalciferol	Dairy products, egg yolks; also synthesized in the skin from exposure to sunlight	5–15 μg	Aids in calcium absorption, promoting bone growth	Rickets, bone pain, muscle weakness, increased risk of death from cardiovascular disease, cognitive impairment, asthma in children, cancer
E tocopherols	Seeds, nuts, vegetable oils, avocados, wheat germ	15 mg	Antioxidant	Anemia
K phylloquinone	Dark green leafy vegetables, broccoli, Brussels sprouts, cabbage	90–120 μg	Blood clotting, bone health	Hemorrhagic disease of newborn in infants; uncommon in adults

Web link

More detailed information on the different fat soluble vitamins can be found on the link below.

https://med.libretexts.org/Bookshelves/Nutrition/Book%3A_Human_Nutrition_(University_of_Hawaii)/9%3A_Vitamins/9.2%3A_Fat-Soluble_Vitamins

Water Soluble Vitamins

All water-soluble vitamins (Table 17.4.4) play a different kind of role in energy metabolism; they are required as functional parts of enzymes involved in energy release and storage. Vitamins and minerals that make up part of enzymes are referred to as coenzymes and cofactors**,** respectively. Coenzymes and cofactors are required by enzymes to catalyze a specific reaction. They assist in converting a substrate to an end-product. Coenzymes and cofactors are essential in catabolic pathways and play a role in many anabolic pathways too. In addition to being essential for metabolism, many vitamins and minerals are required for blood renewal and function. At insufficient levels in the diet these vitamins and minerals impair the health of blood and consequently the delivery of nutrients in and wastes out, amongst its many other functions.

Table 17.4.4 *Water Soluble Vitamins and Their Function.*

Vitamin and alternative name	Sources	Recommended daily allowance	Function	Problems associated with deficiency
B_1 thiamine	Whole grains, enriched bread and cereals, milk, meat	1.1–1.2 mg	Carbohydrate metabolism	Beriberi, Wernicke-Korsikoff syndrome

Vitamin and alternative name	Sources	Recommended daily allowance	Function	Problems associated with deficiency
B_2 riboflavin	Brewer's yeast, almonds, milk, organ meats, legumes, enriched breads and cereals, broccoli, asparagus	1.1–1.3 mg	Synthesis of FAD for metabolism, production of red blood cells	Fatigue, slowed growth, digestive problems, light sensitivity, epithelial problems like cracks in the corners of the mouth
B_3 niacin	Meat, fish, poultry, enriched breads and cereals, peanuts	14–16 mg	Synthesis of NAD, nerve function, cholesterol production	Cracked, scaly skin; dementia; diarrhea; also known as pellagra
B_5 pantothenic acid	Meat, poultry, potatoes, oats, enriched breads and cereals, tomatoes	5 mg	Synthesis of coenzyme A in fatty acid metabolism	Rare: symptoms may include fatigue, insomnia, depression, irritability
B_6 pyridoxine	Potatoes, bananas, beans, seeds, nuts, meat, poultry, fish, eggs, dark green leafy vegetables, soy, organ meats	1.3–1.5 mg	Sodium and potassium balance, red blood cell synthesis, protein metabolism	Confusion, irritability, depression, mouth and tongue sores
B_7 biotin	Liver, fruits, meats	30 μg	Cell growth, metabolism of fatty acids, production of blood cells	Rare in developed countries; symptoms include dermatitis, hair loss, loss of muscular coordination
B_9 folic acid	Liver, legumes, dark green leafy vegetables, enriched breads and cereals, citrus fruits	400 μg	DNA/protein synthesis	Poor growth, gingivitis, appetite loss, shortness of breath, gastrointestinal problems, mental deficits
B_{12} cyanocobalamin	Fish, meat, poultry, dairy products, eggs	2.4 μg	Fatty acid oxidation, nerve cell function, red blood cell production	Pernicious anemia, leading to nerve cell damage
C ascorbic acid	Citrus fruits, red berries, peppers, tomatoes, broccoli, dark green leafy vegetables	75–90 mg	Necessary to produce collagen for formation of connective tissue and teeth, and for wound healing	Dry hair, gingivitis, bleeding gums, dry and scaly skin, slow wound healing, easy bruising, compromised immunity; can lead to scurvy

Web link

More detailed information on the different water soluble vitamins can be found on the link below.

https://med.libretexts.org/Bookshelves/Nutrition/Book%3A_Human_Nutrition_(University_of_Hawaii)/9%3A_Vitamins/9.3%3A_Water-Soluble_Vitamins

Vitamins as Antioxidants

The “big three” vitamin antioxidants are vitamins E, A, and C, although it may be that they are called the “big three” only because they are the most studied. Other antioxidants obtained from the diet are given in Table 17.4.5. A simplified diagram on the role of antioxidants is shown in Figure 17.4.4.

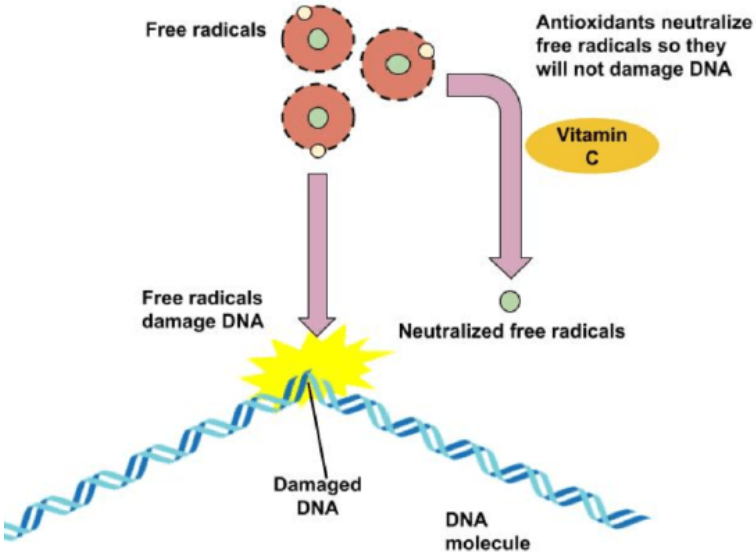


Figure 17.4.4 Antioxidants Role. Image: Allison Calabrese / CC BY 4.0

Table 17.4.5 *Some Antioxidants Obtained from Diet and Their Related Functions.*

Antioxidant	Functions Attributed to Antioxidant Capacity
Vitamin A	Protects cellular membranes, prevents glutathione depletion, maintains free radical detoxifying enzyme systems, reduces inflammation
Vitamin E	Protects cellular membranes, prevents glutathione depletion
Vitamin C	Protects DNA, RNA, proteins, and lipids, aids in regenerating vitamin E
Carotenoids	Free radical scavengers
Lipoic acid	Free radical scavenger, aids in regeneration of vitamins C and E
Phenolic acids	Free radical scavengers, protect cellular membranes

Effects of Cooking

The USDA has conducted extensive studies on the percentage losses of various nutrients from different food types and cooking methods. Some vitamins may become more "bio-available" – that is, usable by the body – when foods are cooked. Table 17.4.6 below shows whether various vitamins are susceptible to loss from heat—such as heat from boiling, steaming, frying, etc. The effect of cutting vegetables can be seen from exposure to air and light. Water-soluble vitamins such as B and C dissolve into the water when a vegetable is boiled, and are then lost when the water is discarded.

Table 17.4.6 *Vitamin Stability Upon Air, Light and Heat Exposure. Source: Wikipedia.*

Vitamin	Soluble in Water	Stable to Air Exposure	Stable to Light Exposure	Stable to Heat Exposure
Vitamin A	no	partially	partially	relatively stable
Vitamin C	very unstable	yes	no	no

Vitamin	Soluble in Water	Stable to Air Exposure	Stable to Light Exposure	Stable to Heat Exposure
Vitamin D	no	no	no	no
Vitamin E	no	yes	yes	no
Vitamin K	no	no	yes	no
Thiamine (B_1)	highly	no	?	> 100 °C
Riboflavin (B_2)	slightly	no	in solution	no
Niacin (B_3)	yes	no	no	no
Pantothenic Acid (B_5)	quite stable	no	no	yes
Vitamin B_6	yes	?	yes	?
Biotin (B_7)	somewhat	?	?	no
Folic Acid (B_9)	yes	?	when dry	at high temp
Cobalamin (B_{12})	yes	?	yes	no

Dietary Fiber and Water

Dietary fiber consists of non-starch polysaccharides and other plant components such as cellulose, resistant starch, resistant dextrins, inulin, lignins, chitins, pectins, beta-glucans, and oligosaccharides already mentioned in Section 17.1.

Dietary fibers can act by changing the nature of the contents of the gastrointestinal tract and by changing how other nutrients and chemicals are absorbed. Some types of soluble fiber absorb water to become a gelatinous, viscous substance which may or may not be fermented by bacteria in the digestive tract. Some types of insoluble fiber have bulking action and are not fermented. Lignin, a major dietary insoluble fiber source, may alter the rate and metabolism of soluble fibers. Other types of insoluble fiber, notably resistant starch, are fermented to produce short-chain fatty acids, which are physiologically active and confer health benefits. Health benefit from dietary fiber and whole grains may include a decreased risk of death and lower rates of coronary heart disease, colon cancer, and type 2 diabetes.

Food sources of dietary fiber (Table 17.4.7) have traditionally been divided according to whether they provide soluble or insoluble fiber. Plant foods contain both types of fiber in varying amounts, according to the plant's characteristics of viscosity and fermentability. Advantages of consuming fiber depend upon which type of fiber is consumed and which benefits may result in the gastrointestinal system. Bulking fibers – such as cellulose, hemicellulose and psyllium – absorb and hold water, promoting regularity. Viscous fibers – such as beta-glucan and psyllium – thicken the fecal mass. Fermentable fibers – such as resistant starch and inulin – feed the bacteria and microbiota of the large intestine, and are metabolized to yield short-chain fatty acids, which have diverse roles in gastrointestinal health.

Table 17.4.7 *Types and Sources of Dietary Fiber.*

Nutrient	Food additive	Source/Comments
Water-insoluble dietary fibers		
β-glucans (a few of which are water-soluble)		
Cellulose	E 460	cereals, fruit, vegetables (in all plants in general)
Chitin	—	in fungi, exoskeleton of insects and crustaceans
Hemicellulose		cereals, bran, timber, legumes
Hexoses	—	wheat, barley
Pentose	—	rye, oat
Lignin	—	stones of fruits, vegetables (filaments of the garden bean), cereals

Xanthan gum	E 415	production with Xanthomonas-bacteria from sugar substrates
Resistant starch		Can be starch protected by seed or shell (type RS1), granular starch (type RS2) or retrograded starch (type RS3)
Resistant starch	—	high amylose corn, barley, high amylose wheat, legumes, raw bananas, cooked and cooled pasta and potatoes
Water-soluble dietary fibers		
Arabinoxylan (a hemicellulose)	—	psyllium
Fructans		replace or complement in some plant taxa the starch as storage carbohydrate
Inulin	—	in diverse plants, e.g. topinambour, chicory, etc.
Polyuronide		
Pectin	E 440	in the fruit skin (mainly apples, quinces), vegetables
Alginic acids(Alginates)	E 400–E 407	in Algae
Sodium alginate	E 401	
Potassium alginate	E 402	
Ammonium alginate	E 403	
Calcium alginate	E 404	
Propylene glycol alginate (PGA)	E 405	
agar	E 406	
carrageen	E 407	red algae
Raffinose	—	legumes
Xylose	—	monosacharide, pentose
Polydextrose	E 1200	synthetic polymer, ca. 1kcal/g
Lactulose	—	synthetic disaccharide

Fiber Contents in Food

Dietary fibers are found in fruits, vegetables and whole grains. The amount of fiber contained in common foods are in Table 17.4.8 .

Table 17.4.8 *Amount of Fiber in Common Foods. Source Wikipedia*

Food group	Serving mean	Fibermass per serving
Fruit	120 mL (0.5 cup)	1.1 g
Dark green vegetables	120 mL (0.5 cup)	6.4 g
Orange vegetables	120 mL (0.5 cup)	2.1 g
Cooked dry beans (legumes)	120 mL (0.5 cup)	8.0 g
Starchy vegetables	120 mL (0.5 cup)	1.7 g
Other vegetables	120 mL (0.5 cup)	1.1 g
Whole grains	28 g (1 oz)	2.4 g

Food group	Serving mean	Fibermass per serving
Meat	28 g (1 oz)	0.1 g

The breakdown of total dietary fiber in terms of the amounts of soluble and insoluble fiber found in five different foods are listed in Table 17.4.9.

Table 17.4.9 *Total Dietary Fiber , Total Nonfermentable Fiber, and Total Fermentable Fiber (as percent of sample weight) in Five Diff*

Food	Total Dietary Fiber	Total Insoluble (Nonfermentable)
Cereal, all bran	30.1	28.0
Blueberries, fresh	2.7	2.4
Broccoli, fresh, cooked	3.5	3.1
Pork and beans, canned	4.4	3.0
Almonds, with skin	8.8	8.6

tr = trace amounts

Dietary fiber is found in plants, typically eaten whole, raw or cooked, although fiber can be added to make dietary supplements and fiber-rich processed foods. Grain bran products have the highest fiber contents, such as crude corn bran (79 g per 100 g) and crude wheat bran (43 g per 100 g), which are ingredients for manufactured foods. Medical authorities, such as the Mayo Clinic, recommend adding fiber-rich products to the Standard American Diet (SAD) which is rich in processed and artificially sweetened foods, with minimal intake of vegetables and legumes.

Plant Sources of Fiber

Some plants contain significant amounts of soluble and insoluble fiber. For example, plums and prunes have a thick skin covering a juicy pulp. The skin is a source of insoluble fiber, whereas soluble fiber is in the pulp. Grapes also contain a fair amount of fiber. A listing of other plant sources of fiber is given in the table below.

Table 17.4.10 *Plant Sources of Soluble and Insoluble Fiber.*

Sources of Soluble Fiber	Sources of **Insoluble Fiber**
• legumes (peas, soybeans, lupins and other beans) • oats, rye, chia, and barley • some fruits (including figs, avocados, plums, prunes, berries, ripe bananas, and the skin of apples, quinces and pears) • certain vegetables such as broccoli, carrots, and Jerusalem artichokes • root tubers and root vegetables such as sweet potatoes and onions (skins of these are sources of insoluble fiber also) • psyllium seed husks (a mucilage soluble fiber) and flax seeds • nuts, with almonds being the highest in dietary fiber	• whole grain foods • wheat and corn bran • legumes such as beans and peas • nuts and seeds • potato skins • lignans • vegetables such as green beans, cauliflower, zucchini (courgette), celery, and nopal • some fruits including avocado, and unripe bananas • the skins of some fruits, including kiwifruit, grapes and tomatoes

Fiber Supplements

These are a few example forms of fiber that have been sold as supplements or food additives. These may be marketed to consumers for nutritional purposes, treatment of various gastrointestinal disorders, and for such possible health benefits as lowering cholesterol levels, reducing risk of colon cancer, and losing weight.

Soluble fiber supplements may be beneficial for alleviating symptoms of irritable bowel syndrome, such as diarrhea or constipation and abdominal discomfort. Prebiotic soluble fiber products, like those containing inulin or oligosaccharides, may contribute to relief from inflammatory bowel disease, as in Crohn's disease, ulcerative colitis, and *Clostridium difficile*, due in part to the short-chain fatty acids produced with subsequent anti-inflammatory actions upon the bowel.Fiber supplements may be effective in an overall dietary plan for managing irritable bowel syndrome by modification of food choices.

One insoluble fiber, resistant starch from high-amylose corn, has been used as a supplement and may contribute to improving insulin sensitivity and glycemic management as well as promoting regularity and possibly relief of diarrhea. One preliminary finding indicates that resistant corn starch may reduce symptoms of ulcerative colitis.

Inulin

Chemically defined as oligosaccharides occurring naturally in most plants, inulins have nutritional value as carbohydrates, or more specifically as fructans, a polymer of the natural plant sugar, fructose. Inulin is typically extracted by manufacturers from enriched plant sources such as chicory roots or Jerusalem artichokes for use in prepared foods. Subtly sweet, it can be used to replace sugar, fat, and flour, is often used to improve the flow and mixing qualities of powdered nutritional supplements, and has significant potential health value as a prebiotic fermentable fiber.

Inulin is advantageous because it contains 25–30% the food energy of sugar or other carbohydrates and 10–15% the food energy of fat. As a prebiotic fermentable fiber, its metabolism by gut flora yields short-chain fatty acids (see below) which increase absorption of calcium, magnesium, and iron, resulting from upregulation of mineral-transporting genes and their membrane transport proteins within the colon wall. Among other potential beneficial effects noted above, inulin promotes an increase in the mass and health of intestinal *Lactobacillus* and *Bifidobacterium* populations.

Inulin's primary disadvantage is its tolerance. As a soluble fermentable fiber, it is quickly and easily fermented within the intestinal tract, which may cause gas and digestive distress at doses higher than 15 grams/day in most people. Individuals with digestive diseases have benefited from removing fructose and inulin from their diet. While clinical studies have shown changes in the microbiota at lower levels of inulin intake, some of the health effects require higher than 15 grams per day to achieve the benefits.

Vegetable Gums

Vegetable gum fiber supplements are relatively new to the market. Often sold as a powder, vegetable gum fibers dissolve easily with no aftertaste. In preliminary clinical trials, they have proven effective for the treatment of irritable bowel syndrome. Examples of vegetable gum fibers are guar gum and gum arabic.

Water

Add all the ways you use water every day and you still will not come close to the countless uses water has in the human body. Of all the nutrients, water is the most critical as its absence proves lethal within a few days. Organisms have adapted numerous mechanisms for water conservation. Water uses in the human body can be loosely categorized into four basic functions: transportation vehicle, medium for chemical reactions, lubricant/shock absorber, and temperature regulator.

On a typical day, the average adult will take in about 2500 mL (almost 3 quarts) of aqueous fluids. Although most of the intake comes through the digestive tract, about 230 mL (8 ounces) per day is generated metabolically, in the last steps of aerobic respiration. Additionally, each day about the same volume (2500 mL) of water leaves the body by different routes; most of this lost water is removed as urine. The kidneys also can adjust blood volume though mechanisms that draw water out of the filtrate and urine. The kidneys can regulate water levels in the body; they conserve water if you are dehydrated, and they can make urine more dilute to expel excess water if necessary. Water is lost through the skin through evaporation from the skin surface without overt sweating and from air expelled from the lungs. This type of water loss is called insensible water loss because a person is usually unaware of it.

Summary

- Vitamins and minerals are essential parts of the diet. They are needed for the proper function of metabolic pathways in the body.
- Vitamins are not stored in the body, so they must be obtained from the diet or synthesized from precursors available in the diet.
- Minerals are also obtained from the diet, but they are also stored, primarily in skeletal tissues.
- Dietary fibers can act by changing the nature of the contents of the gastrointestinal tract and by changing how other nutrients and chemicals are absorbed.
- Whole grain, legumes, vegetables, and fruits are excellent sources of dietary fiber.
- Health benefit from dietary fiber and whole grains may include a decreased risk of death and lower rates of coronary heart disease, colon cancer, and type 2 diabetes.

Contributors

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17.5: Starvation, Fasting, and Malnutrition

Learning Objectives

- Describe the consequences of fasting, starvation, and malnutrition.
- List the drawbacks of processing on the nutritional quality of foods.

With a typical high-carbohydrate diet, the human body relies on free blood glucose as its primary energy source. Glucose can be obtained directly from dietary sugars and by the breakdown of other carbohydrates. In the absence of dietary sugars and carbohydrates, glucose is obtained from the breakdown of stored glycogen. Glycogen is a readily-accessible storage form of glucose, stored in notable quantities in the liver and skeletal muscle.

After the exhaustion of the glycogen reserve, and for the next 2–3 days, fatty acids become the principal metabolic fuel. After which, the liver begins to synthesize ketone bodies from precursors obtained from fatty acid breakdown. When the fat stores are exhausted, the cells in the body begin to break down protein.

Starvation ensues when the fat reserves are completely exhausted and protein is the only fuel source available to the body. Thus, after periods of starvation, the loss of body protein affects the function of important organs, and death results, even if there are still fat reserves left. In a leaner person, the fat reserves are depleted faster, and the protein, sooner, therefore death occurs sooner. Ultimately, the cause of death is in general cardiac arrhythmia or cardiac arrest, brought on by tissue degradation and electrolyte imbalances. Things like metabolic acidosis may also kill starving people.

Symptoms of Starvation

Early symptoms include impulsivity, irritability, and hyperactivity. Atrophy (wasting away) of the stomach weakens the perception of hunger, since the perception is controlled by the volume of the stomach that is empty. Individuals experiencing starvation lose substantial fat (adipose tissue) and muscle mass as the body breaks down these tissues for energy.*Catabolysis* is the process of a body breaking down its own muscles and other tissues in order to keep vital systems such as the nervous system and heart muscle (myocardium)functioning. The energy deficiency inherent in starvation causes fatigue and renders the victim more apathetic over time. As the starving person becomes too weak to move or even eat, their interaction with the surrounding world diminishes. In females, menstruation ceases when the body fat percentage is too low to support a fetus.

Victims of starvation are often too weak to sense thirst, and therefore become dehydrated. All movements become painful due to muscle atrophy and dry, cracked skin that is caused by severe dehydration. With a weakened body, diseases are commonplace. Fungi, for example, often grow under the esophagus, making swallowing painful. Vitamin deficiency is also a common result of starvation, often leading to anemia, beriberi, pellagra, and scurvy. These diseases collectively can also cause diarrhea, skin rashes, edema, and heart failure. Individuals are often irritable and lethargic as a result.

There is insufficient scientific data on exactly how long people can live without food. Although the length of time varies with an individual's percentage of body fat and general health, one medical study estimates that in adults complete starvation leads to death within 8 to 12 weeks. Starvation begins when an individual has lost about 30%, or about a third, of their normal body weight. Once the loss reaches 40% death is almost inevitable.

Processed Foods Less Nutrition

For many, the word “malnutrition” produces an image of a child in a third-world country with a bloated belly, and skinny arms and legs. However, this image alone is not an accurate representation of the state of malnutrition. For example, someone who is 150 pounds overweight can also be malnourished.

Malnutrition refers to one not receiving proper nutrition and does not distinguish between the consequences of too many nutrients or the lack of nutrients, both of which impair overall health. Undernutrition is characterized by a lack of nutrients and insufficient energy supply, whereas overnutrition is characterized by excessive nutrient and energy intake. Overnutrition can result in obesity, a growing global health threat. Obesity is defined as a metabolic disorder that leads to an over accumulation of fat

tissue.

Although not as prevalent in America as it is in developing countries, undernutrition is not uncommon and affects many subpopulations, including the elderly, those with certain diseases, and those in poverty. Many people who live with diseases either have no appetite or may not be able to digest food properly. Some medical causes of malnutrition include cancer, inflammatory bowel syndrome, AIDS, Alzheimer's disease, illnesses or conditions that cause chronic pain, psychiatric illnesses, such as anorexia nervosa, or as a result of side effects from medications. Overnutrition is an epidemic in the United States and is known to be a risk factor for many diseases, including Type 2 diabetes, cardiovascular disease, inflammatory disorders (such as rheumatoid arthritis), and cancer.

Food processing does have some benefits, such as making food last longer and making products more convenient. However, there are drawbacks to relying on a lot of heavily processed foods that could lead to undernutrition and/or overnutrition. Whole foods and those that are only minimally processed, like frozen vegetables without any sauce, tend to be more healthy. An unhealthy diet high in fat, added sugar and salt, such as one containing a lot of highly-processed foods, can increase the risk for cancer, type 2 diabetes and heart disease, according to the World Health Organization.

Nutrient losses

Processing foods often involves nutrient losses, which can make it harder to meet your needs if these nutrients aren't added back through fortification or enrichment. For example, using high heat during processing can cause vitamin C losses. Another example is refined grains, which have less fiber, vitamins and minerals than whole grains. Eating refined grains, such as those found in many processed foods, instead of whole grains may increase your risk for high cholesterol, diabetes and obesity, according to a study published in "The American Journal of Clinical Nutrition" in December 2007.

New research highlighting the importance to human health of a rich microbial environment in the intestine indicates that abundant food processing (not fermentation of foods) endangers that environment.

Web Link

The USDA conducted a study of nutrient retention in 2004, creating a table of foods, levels of preparation, and nutrition.

https://www.ars.usda.gov/ARSUserFiles/80400525/Data/retn/retn06.pdf

Added Contaminants

Food processing is typically a mechanical process that utilizes extrusion, large mixing, grinding, chopping and emulsifying equipment in the production process. These processes introduce a number of contamination risks. Such contaminants are left over material from a previous operation, animal or human bodily fluids, microorganisms, nonmetallic and metallic fragments. Further processing of these contaminants will result in downstream equipment failure and the risk of ingestion by the consumer.

Added Sodium and Sugar

One of the main sources for sodium in the diet is processed foods. Sodium is added to prevent spoilage, add flavor and improve the texture of these foods. Americans consume an average of 3,436 milligrams of sodium per day, which is higher than the recommended limit of 2,300 milligrams per day for healthy people, and more than twice the limit of 1,500 milligrams per day for those at increased risk for heart disease.

While you don't need to limit the sugars found naturally in whole, unprocessed foods like fresh fruit, eating too much added sugar found in many processed foods can increase your risk for heart disease, obesity, cavities and Type 2 diabetes. The American Heart Association recommends women limit added sugars to no more than 100 calories, or 25 grams, and men limit added sugars to no more than 155 calories, or about 38.75 grams, per day. Currently, Americans consume an average of 355 calories from added sugars each day.

Trans Fats

Foods that have undergone processing, including some commercial baked goods, desserts, margarine, frozen pizza, microwave popcorn and coffee creamers, sometimes contain trans fats. This is the most unhealthy type of fat, and may increase your risk for high cholesterol, heart disease and stroke. The 2010 Dietary Guidelines for Americans recommends keeping your trans fat intake as low as possible.

Other Potential Disadvantages

Processed foods also tend to be more allergenic than whole foods, according to a June 2004 "Current Opinion in Allergy and Clinical Immunology" article. Although the preservatives and other food additives used in many processed foods are generally recognized as safe, a few may cause problems for some individuals, including sulfites, artificial sweeteners, artificial colors and flavors, sodium nitrate, BHA and BHT, olestra, caffeine and monosodium glutamate.

Summary

- The level of blood sugar is tightly regulated; as blood glucose is consumed, glycogen is converted into glucose. Several metabolic adjustments occur during fasting. After the exhaustion of the glycogen reserve fatty acids become the principal metabolic fuel and ketone bodies are produced. After the fat reserves are used up, the cells in the body begin to break down protein.
- Fasting may refer to the metabolic status of a person who has not eaten overnight, or to the metabolic state achieved after complete digestion and absorption of a meal.
- Starvation ensues when the fat reserves are completely exhausted and protein is the only fuel source available to the body.
- Malnutrition refers to one not receiving proper nutrition and does not distinguish between the consequences of too many nutrients or the lack of nutrients, both of which impair overall health. Undernutrition is characterized by a lack of nutrients and insufficient energy supply, whereas overnutrition is characterized by excessive nutrient and energy intake.
- Heavily processed foods could cause malnutrition due to the effects of processing on the food or the addition of additives like salt or sugar that are above and beyond the daily recommended levels for consumption.

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17.6: Flavorings- Spicy and Sweet

Learning Objective

- Know the different types and properties of natural and artificial flavoring ingredients.

Food touches all of the senses. We taste, we smell, we see color and shape, we feel texture and temperature, and we hear sounds as we eat. All of these elements together create a palette with an infinite number of combinations, but the underlying principles that make food taste good are unchanged.

- Variety and diversity in textures and the elements of taste make for interesting food.
- Contrast is as important as harmony; but avoid extremes and imbalance.

Many ingredients are used to enhance the taste of foods. These ingredients can be used to provide both seasoning and flavoring.

- Seasoning means to bring out or intensify the natural flavor of the food without changing it. Seasonings are usually added near the end of the cooking period. The most common seasonings are salt, pepper, and acids (such as lemon juice). When seasonings are used properly, they cannot be tasted; their job is to heighten the flavors of the original ingredients.
- Flavoring refers to something that changes or modifies the original flavor of the food. Flavoring can be used to contrast a taste such as adding liqueur to a dessert where both the added flavor and the original flavor are perceptible. Or flavorings can be used to create a unique flavor in which it is difficult to discern what the separate flavorings are. Spice blends used in pumpkin pies are a good example of this.

Spices, Herbs, and Flavorings

Knowing how to use seasonings and flavorings skillfully provides cooks and bakers with an arsenal with which they can create limitless flavor combinations. Flavoring and seasoning ingredients include wines, spirits, fruit zests, extracts, essences, and oils. However, the main seasoning and flavoring ingredients are classified as herbs and spices (Figure 17.6.1).



Figure 17.6.1 *Spices and herbs at a shop in Goa, India.*

Knowing the difference between herbs and spices is not as important as knowing how to use seasonings and flavorings skillfully. In general, fresh seasonings are added late in the cooking process while dry ones tend to be added earlier. It is good practice to under-season during the cooking process and then add more seasonings (particularly if you are using fresh ones) just before presentation. This is sometimes referred to as “layering.” When baking, it is difficult to add more seasoning at the end, so testing recipes to ensure the proper amount of spice is included is a critical process.

Spices

The spice trade developed throughout the Indian subcontinent and Middle East by at earliest 2000 BCE with cinnamon and black pepper, and in East Asia with herbs and pepper. The Egyptians used herbs for mummification and their demand for exotic spices and herbs helped stimulate world trade. The word *spice* comes from the Old French word *espice*, which became *epice*, and which came from the Latin root *spec*, the noun referring to "appearance, sort, kind": *species* has the same root. By 1000 BCE, medical systems based upon herbs could be found in China, Korea, and India. Early uses were connected with magic, medicine, religion, tradition, and preservation.

Spices are aromatic substances obtained from the dried parts of plants such as the roots, shoots, fruits, bark, and leaves. They are sold as seeds, blends of spices, whole or ground spices, and seasonings. The aromatic substances that give a spice its particular aroma and flavor are the essential oils. The flavor of the essential oil or flavoring compound will vary depending on the quality and freshness of the spice.

The aromas of ground spices are volatile. This means they lose their odor or flavoring when left exposed to the air for extended periods. They should be stored in sealed containers when not in use. Whole beans or unground seeds have a longer shelf life but should also be stored in sealed containers.

Web Links

An A to Z list of spices is provided on the link https://chem.libretexts.org/Bookshelves/Biological_Chemistry/Book%3A_Chemistry_of_Cooking_(Rodriguez-Velazquez)/Understanding_Ingredients%3A_Spices/83%3A_Spices

A complete FDA list of spices and natural seasonings and flavorings that are generally recognized as safe (GRAS) is provided on the link below:

https://www.accessdata.fda.gov/scripts/cdrh/cfdocs/cfcfr/CFRSearch.cfm?fr=182.10

Herbs

Herbs tend to be the leaves of fragrant plants that do not have a woody stem. Herbs are available fresh or dried, with fresh herbs having a more subtle flavor than dried. You need to add a larger quantity of fresh herbs (up to 50% more) than dry herbs to get the same desired flavor. Conversely, if a recipe calls for a certain amount of fresh herb, you would use about one-half of that amount of dry herb.

The most common fresh herbs are basil, coriander, marjoram, oregano, parsley, rosemary, sage, tarragon, and thyme (Figure 17.6.2). Fresh herbs should have a clean, fresh fragrance and be free of wilted or brown leaves. They can be kept for about five days if sealed inside an airtight plastic bag. Fresh herbs are usually added near the completion of the cooking process so flavors are not lost due to heat exposure.

Dried herbs lose their power rather quickly if not properly stored in airtight containers. They can last up to six months if properly stored. Dried herbs are usually added at the start of the cooking process as their flavor takes longer to develop than fresh herbs.

Figure 17.6.2 *A bundle of thyme (Thymus).*

Flavorants or Flavorings

Flavor, is the perceptual impression of food or other substances, and is determined primarily by the chemical senses of the gustatory and olfactory system. The "trigeminal senses", which detect chemical irritants in the mouth and throat, as well as temperature and texture, are also important to the overall gestalt of taste perception. The taste of food, can be altered naturally or artificially.

A "flavorant" is defined as a substance that gives another substance taste, altering the characteristics of the solute, causing it to become sweet, sour, tangy, etc. Although both terms, in common language, denote the combined chemical sensations of taste and smell, the same terms are used in the fragrance and flavors industry to refer to edible chemicals and extracts that alter the flavor of food and food products through the sense of smell.

Due to the high cost, or unavailability of natural flavor extracts, most commercial flavorants are "nature-identical", which means that they are the chemical equivalent of natural flavors, but chemically synthesized rather than being extracted from source materials. Identification of components of natural foods, for example a raspberry, may be done using technology such as headspace techniques, so the flavorist can imitate the flavor by using a few of the same chemicals present.

Table 17.6.1 list the three principal types of flavorings that are used in foods, under definitions agreed in the EU and Australia.

Table 17.6.1 *Three Principal Types of Flavorings Used in Foods (Under Definitions Agreed in the EU and Australia)*

Type	Description
Natural flavoring substances	These flavoring substances are obtained from plant or animal raw materials, by physical, microbiological, or enzymatic processes. They can be either used in their natural state or processed for human consumption, but cannot contain any nature-identical or artificial flavoring substances.
Nature-identical flavoring substances	These are obtained by synthesis or isolated through chemical processes, which are chemically and organoleptically identical to flavoring substances naturally present in products intended for human consumption. They cannot contain any artificial flavoring substances.
Artificial flavoring substances	These are not identified in a natural product intended for human consumption, whether or not the product is processed. These are typically produced by fractional distillation and additional chemical manipulation of naturally sourced chemicals, crude oil, or coal tar. Although they are chemically different, in sensory characteristics they are the same as natural ones.

Most artificial flavors are specific and often complex mixtures of singular naturally occurring flavor compounds combined together to either imitate or enhance a natural flavor. These mixtures are formulated by flavorists to give a food product a unique flavor and to maintain flavor consistency between different product batches or after recipe changes. The list of known flavoring agents includes thousands of molecular compounds, and the flavor chemist (flavorist) can often mix these together to produce many of the common flavors. Many flavorants consist of esters, which are often described as being "sweet" or "fruity" (see the table below).

Table 17.6.2 Different Odors Associated with Esters.

Chemical	Odor
Manzanate	Apple
Diacetyl, acetylpropionyl, acetoin	Buttery
Isoamyl acetate	Banana
Benzaldehyde	Bitter almond, cherry
Cinnamaldehyde	Cinnamon
Ethyl propionate	Fruity
Methyl anthranilate	Grape
Limonene	Orange
Ethyl decadienoate	Pear
Allyl hexanoate	Pineapple
Ethyl maltol	Sugar, cotton candy
2,4-Dithiapentane	Truffle
Ethylvanillin	Vanilla
Methyl salicylate	Wintergreen

Other Plant based and Artificial Sweeteners

A **sugar substitute** is a food additive that provides a sweet taste like that of sugar while containing significantly less food energy than sugar-based sweeteners, making it a **zero-calorie** (non-nutritive) or **low-calorie sweetener**. **Artificial sweeteners** may be derived through manufacturing of plant extracts or processed by chemical synthesis. Sugar alcohols such as erythritol, xylitol, and sorbitol are derived from sugars. In 2017, sucralose was the most common sugar substitute used in the manufacture of foods and

beverages; it had 30% of the global market, which was projected to be valued at $2.8 billion by 2021.

In 1969, cyclamate was banned for sale in the US by the Food and Drug Administration. As of 2018, there is no strong evidence that non-sugar sweeteners are either unsafe or result in improved health outcomes.

When these sweeteners are provided for restaurant customers to add to beverages such as tea and coffee, they are provided in small colored paper packets (see image); in North America, the colors are typically *blue* for aspartame, *pink* for saccharin (US) or cyclamate (Canada), *yellow* for sucralose, *orange* for monk fruit extract, and *green* for stevia. These sweeteners are also a fundamental ingredient in diet drinks to sweeten them without adding calories.

Stevia is a sweetener and sugar substitute derived from the leaves of the plant species *Stevia rebaudiana*, native to Brazil and Paraguay. The active compounds (Figure 17.6.3) are steviol glycosides (mainly stevioside and rebaudioside), which have 30 to 150 times the sweetness of sugar, are heat-stable, pH-stable, and not fermentable.The body does not metabolize the glycosides in stevia, so it contains zero calories like some artificial sweeteners. Stevia's taste has a slower onset and longer duration than that of sugar, and some of its extracts may have a bitter or licorice-like aftertaste at high concentrations.

The legal status of stevia as a food additive or dietary supplement varies from country to country. In the United States, high-purity stevia glycoside extracts have been generally recognized as safe (GRAS) since 2008, and are allowed in food products, but stevia leaf and crude extracts do not have GRAS or Food and Drug Administration (FDA) approval for use in food.

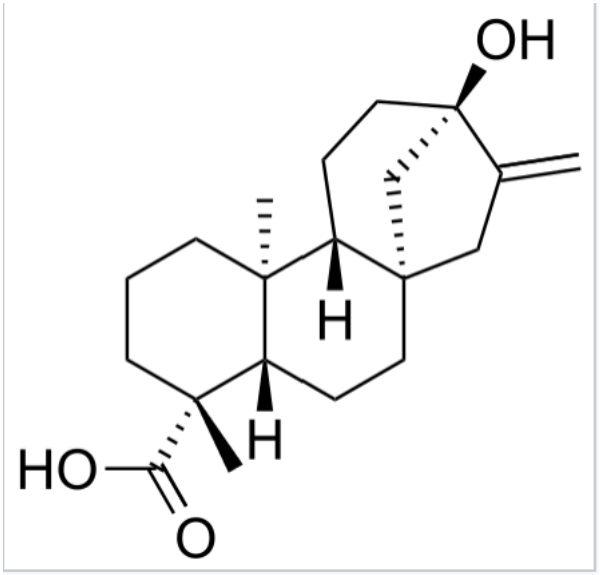


Figure 17.6.3 *Steviol, the basic building block of stevia's sweet glycosides.*

Stevia rebaudiana

The plant *Stevia rebaudiana* has been used for more than 1,500 years by the Guaraní peoples of South America, who called it *ka'a he'ê* ("sweet herb"). The leaves have been used traditionally for hundreds of years in both Brazil and Paraguay to sweeten local teas and medicines, and as a "sweet treat".The genus was named for Spanish botanist and physician Petrus Jacobus Stevus (Pedro Jaime Esteve 1500–1556), a professor of botany at the University of Valencia.

In 1899, Swiss botanist Moisés Santiago Bertoni, while conducting research in eastern Paraguay, first described the plant and the sweet taste in detail. Only limited research was conducted on the topic until, in 1931, two French chemists isolated the glycosides that give stevia its sweet taste.

Table 17.6.3 *Relative Sweetness of Different Natural and Artificial Sweeteners.*

Compound	Relative Sweetness
Sucrose	100
Fructose	173
Stevia	300
Aspartame	18,000
Acesulfame K	20,000
Saccharin	30,000
Sucralose	60,000

Artificial Sweeteners

Several other kinds of organic compounds have been synthesized that are far superior as sweetening agents. These so-called high-intensity or artificial sweeteners (Figure 17.6.4) are useful for people with diabetes or other medical conditions that require them to control their carbohydrate intake. The synthetic compounds are noncaloric or used in such small quantities that they do not add significantly to the caloric value of food.

The first artificial sweetener—**saccharin**—was discovered by accident in 1879. It is 300 times sweeter than sucrose, but it passes through the body unchanged and thus adds no calories to the diet. After its discovery, saccharin was used until it was banned in the early 1900s. However, during the sugar-short years of World War I, the ban was lifted and was not reinstated at the war's end. One drawback to the use of saccharin is its bitter, metallic aftertaste. The initial solution to this problem was to combine saccharin with **cyclamate**, a second artificial sweetener discovered in 1937.

In the 1960s and 1970s, several clinical tests with laboratory animals implicated both cyclamate and saccharin as carcinogenic (cancer-causing) substances. The results from the cyclamate tests were completed first, and cyclamate was banned in the United States in 1969. Then a major study was released in Canada in 1977 indicating that saccharin increased the incidence of bladder cancer in rats. The US Food and Drug Administration (FDA) proposed a ban on saccharin that raised immediate public opposition because saccharin was the only artificial sweetener still available. In response, Congress passed the Saccharin Study and Labeling Act in 1977, permitting the use of saccharin as long as any product containing it was labeled with a consumer warning regarding the possible elevation of the risk of bladder cancer. Today this warning is no longer required; moreover, the FDA is currently reviewing the ban on cyclamate, as 75 additional studies and years of usage in other countries, such as Canada, have failed to show that it has any carcinogenic effect.

A third artificial sweetener, **aspartame**, was discovered in 1965. This white crystalline compound is about 180 times sweeter than sucrose and has no aftertaste. It was approved for use in 1981 and is used to sweeten a wide variety of foods because it blends well with other food flavors. Aspartame is not used in baked goods, however, because it is not heat stable.

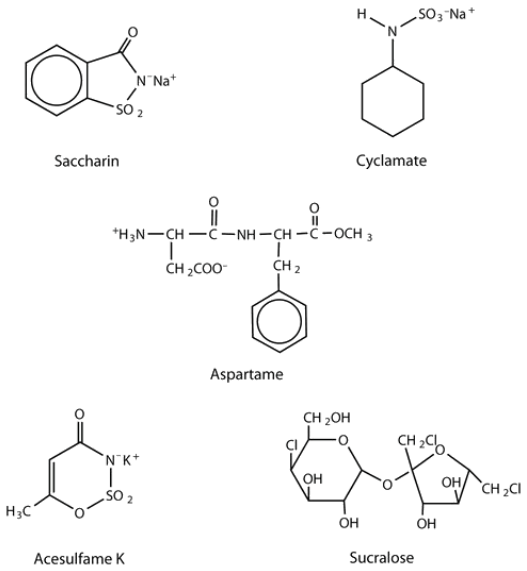


Figure 17.6.4 Different Artificial Sweeteners.

In the body (or when heated), aspartame is initially hydrolyzed to three molecules: the amino acids aspartic acid and phenylalanine and an alcohol methanol. Repeated controversy regarding the safety of aspartame arises partly from the fact that the body metabolizes the released methanol to formaldehyde. It should be noted, though, that a glass of tomato juice has six times as much methanol as a similar amount of a diet soda containing aspartame. The only documented risk connected to aspartame use is for individuals with the genetic disease *phenylketonuria* (PKU); these individuals lack the enzyme needed to metabolize the phenylalanine released when aspartame is broken down by the body. Because of the danger to people with PKU, all products containing aspartame must carry a warning label.

Acesulfame K, discovered just two years after aspartame (1967), was approved for use in the United States in 1988. It is 200 times sweeter than sugar and, unlike aspartame, is heat stable. It has no lingering aftertaste.

One of the newest artificial sweeteners to gain FDA approval (April 1998) for use in the United States is sucralose, a white crystalline solid approximately 600 times sweeter than sucrose. **Sucralose** is synthesized from sucrose and has three chlorine atoms substituted for three OH groups. It is noncaloric because it passes through the body unchanged. It can be used in baking because it is heat stable.

All of the extensive clinical studies completed to date have indicated that these artificial sweeteners approved for use in the United States are safe for consumption by healthy individuals in moderate amounts.

Flavor Enhancers

The US Food and Drug Administration define flavor enhancers as food additives that enhance the flavors already present in foods without providing their own separate flavor. The names of flavor enhancers found on product labels include moosodium glutamate (msg), hydrolyzed soy protein, autolyzed yeast extract, disodium guanylate or inosinate. Umami or "savory" flavorants, more commonly called taste or flavor enhancers, are largely based on amino acids and nucleotides. These are typically used as sodium or calcium salts. Umami flavorants recognized and approved by the European Union are listed in Table 17.6.3.

Table 17.6.4 *Umami Favorants Recognized and Approved by the European Union.*

Acid Salts	Description
Glutamic acid salts	This amino acid's sodium salt, monosodium glutamate (MSG), is one of the most commonly used flavor enhancers in food processing. Mono- and diglutamate salts are also commonly used.
Glycine salts	Simple amino acid salts typically combined with glutamic acid as flavor enhancers
Guanylic acid salts	Nucleotide salts typically combined with glutamic acid as flavor enhancers

Inosinic acid salts	Nucleotide salts created from the breakdown of AMP, due to high costs of production, typically combined with glutamic acid as flavor enhancers
5'-ribonucleotide salts	Nucleotide salts typically combined with other amino acids and nucleotide salts as flavor enhancers

Monosodium glutamate (**MSG**), also known as **sodium glutamate**, (Figure 17.6.5 is the sodium salt of glutamic acid, one of the most abundant naturally occurring non-essential amino acids. Glutamic acid is found naturally in tomatoes, grapes, cheese, mushrooms and other foods.

MSG is used in the food industry as a flavor enhancer with an umami taste that intensifies the meaty, savory flavor of food, as naturally occurring glutamate does in foods such as stews and meat soups. It was first prepared in 1908 by Japanese biochemist Kikunae Ikeda, who was trying to isolate and duplicate the savory taste of *kombu*, an edible seaweed used as a base for many Japanese soups. MSG as a flavor enhancer balances, blends, and rounds the perception of other tastes.

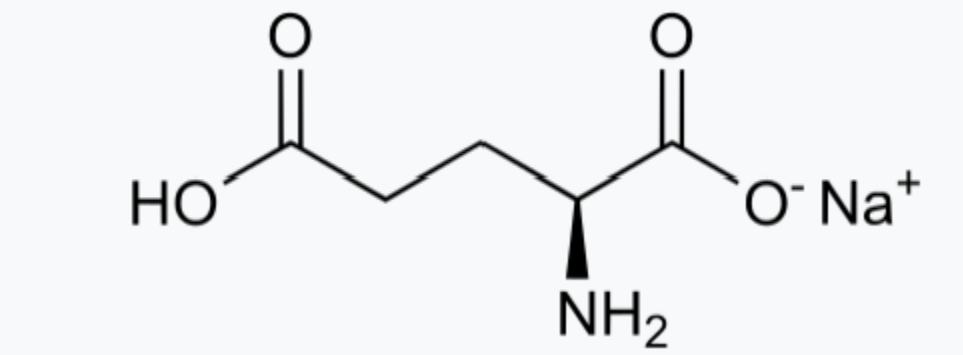


Figure 17.6.5 *Monosodium glutamate.*

Summary

- Many ingredients are used to enhance the taste of foods. These ingredients can be used to provide both seasoning and flavoring.
- Flavoring and seasoning ingredients include wines, spirits, fruit zests, extracts, essences, and oils. However, the main seasoning and flavoring ingredients are classified as herbs and spices.
- Sucrose and fructose are two common natural sweeteners.
- The so-called high-intensity or artificial sweeteners such as saccharin, cyclamates, and aspartame) are useful for people with diabetes or other medical conditions that require them to control their carbohydrate intake
- Flavor enhancers are food additives (largely based on amino acids and nucleotides) that enhance the flavors already present in foods without providing their own separate flavor.

Contributors

- Sorangel Rodriguez-Velazquez (American University). Chemistry of Cooking by Sorangel Rodriguez-Velazquez is licensed under a Creative Commons Attribution-NonCommercial ShareAlike 4.0 International License, except where otherwise noted

- Libretext: The Basics of GOB Chemistry (Ball et al.)
- Wikipedia
- US Food and Drug Administration (US FDA)

- Marisa Alviar-Agnew (Sacramento City College)

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17.7: Other Food Additives- Beneficial or Dangerous

Learning Objective

- Know the purpose of other ingredients added to food.

For centuries, ingredients have served useful functions in a variety of foods. Our ancestors used salt to preserve meats and fish, added herbs and spices to improve the flavor of foods, preserved fruit with sugar, and pickled cucumbers in a vinegar solution. Today, consumers demand and enjoy a food supply that is flavorful, nutritious, safe, convenient, colorful and affordable. Food additives and advances in technology help make that possible.

There are thousands of ingredients used to make foods. The Food and Drug Administration (FDA) maintains a list of over 3000 ingredients in its data base "Everything Added to Food in the United States", many of which we use at home every day (e.g., sugar, baking soda, salt, vanilla, yeast, spices and colors).

Still, some consumers have concerns about additives because they may see the long, unfamiliar names and think of them as complex chemical compounds. In fact, every food we eat - whether a just-picked strawberry or a homemade cookie - is made up of chemical compounds that determine flavor, color, texture and nutrient value. All food additives are carefully regulated by federal authorities and various international organizations to ensure that foods are safe to eat and are accurately labeled.

Additives perform a variety of useful functions in foods that consumers often take for granted. Some additives could be eliminated if we were willing to grow our own food, harvest and grind it, spend many hours cooking and canning, or accept increased risks of food spoilage. But most consumers today rely on the many technological, aesthetic and convenient benefits that additives provide.

Following are some reasons why ingredients are added to foods:

1. **To Maintain or Improve Safety and Freshness:** Preservatives slow product spoilage caused by mold, air, bacteria, fungi or yeast. In addition to maintaining the quality of the food, they help control contamination that can cause foodborne illness, including life-threatening botulism. One group of preservatives -- antioxidants -- prevents fats and oils and the foods containing them from becoming rancid or developing an off-flavor. They also prevent cut fresh fruits such as apples from turning brown when exposed to air.
2. **To Improve or Maintain Nutritional Value:** Vitamins and minerals (and fiber) are added to many foods to make up for those lacking in a person's diet or lost in processing, or to enhance the nutritional quality of a food. Such fortification and enrichment has helped reduce malnutrition in the U.S. and worldwide. All products containing added nutrients must be appropriately labeled.
3. **Improve Taste, Texture and Appearance:** Spices, natural and artificial flavors, and sweeteners are added to enhance the taste of food. Food colors maintain or improve appearance. Emulsifiers, stabilizers and thickeners give foods the texture and consistency consumers expect. Leavening agents allow baked goods to rise during baking. Some additives help control the acidity and alkalinity of foods, while other ingredients help maintain the taste and appeal of foods with reduced fat content.

Types of Food Ingredients

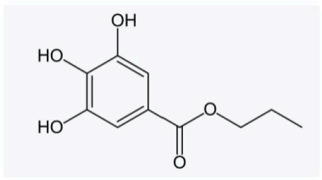
The following summary lists the types of common food ingredients, why they are used, and some examples of the names that can be found on product labels. Some additives are used for more than one purpose.

Types of Ingredients	What They Do	Examples of Uses	Names Found on Product Labels
Preservatives	Prevent food spoilage from bacteria, molds, fungi, or yeast (antimicrobials); slow or prevent changes in color, flavor, or texture and delay rancidity (antioxidants); maintain freshness	Fruit sauces and jellies, beverages, baked goods, cured meats, oils and margarines, cereals, dressings, snack foods, fruits and vegetables	Ascorbic acid, citric acid, sodium benzoate, calcium propionate, sodium erythorbate, sodium nitrite, calcium sorbate, potassium sorbate, BHA, BHT, EDTA, tocopherols (Vitamin E)
Sweeteners	Add sweetness with or without the extra calories	Beverages, baked goods, confections, table-top sugar, substitutes, many processed foods	Sucrose (sugar), glucose, fructose, sorbitol, mannitol, corn syrup, high fructose corn syrup, saccharin, aspartame, sucralose, acesulfame potassium (acesulfame-K), neotame
Color Additives	Offset color loss due to exposure to light, air, temperature extremes, moisture and storage conditions; correct natural variations in color; enhance colors that occur naturally; provide color to colorless and "fun" foods	Many processed foods, (candies, snack foods margarine, cheese, soft drinks, jams/ jellies, gelatins, pudding and pie fillings)	FD&C Blue Nos. 1 and 2, FD&C Green No. 3, FD&C Red Nos. 3 and 40, FD&C Yellow Nos. 5 and 6, Orange B, Citrus Red No. 2, annatto extract, beta-carotene, grape skin extract, cochineal extract or carmine, paprika oleoresin, caramel color, fruit and vegetable juices, saffron (Note: Exempt color additives are not required to be declared by name on labels but may be declared simply as colorings or color added)
Flavors and Spices	Add specific flavors (natural and synthetic)	Pudding and pie fillings, gelatin dessert mixes, cake mixes, salad dressings, candies, soft drinks, ice cream, BBQ sauce	Natural flavoring, artificial flavor, and spices
Flavor Enhancers	Enhance flavors already present in foods (without providing their own separate flavor)	Many processed foods	Monosodium glutamate (MSG), hydrolyzed soy protein, autolyzed yeast extract, disodium guanylate or inosinate
Fat Replacers (and components of formulations used to replace fats)	Provide expected texture and a creamy "mouth-feel" in reduced-fat foods	Baked goods, dressings, frozen desserts, confections, cake and dessert mixes, dairy products	Olestra, cellulose gel, carrageenan, polydextrose, modified food starch, microparticulated egg white protein, guar gum, xanthan gum, whey protein concentrate
Nutrients	Replace vitamins and minerals lost in processing (enrichment), add nutrients that may be lacking in the diet (fortification)	Flour, breads, cereals, rice, macaroni, margarine, salt, milk, fruit beverages, energy bars, instant breakfast drinks	Thiamine hydrochloride, riboflavin (Vitamin B_2), niacin, niacinamide, folate or folic acid, beta carotene, potassium iodide, iron or ferrous sulfate, alpha tocopherols, ascorbic acid, Vitamin D, amino acids (L-tryptophan, L-lysine, L-leucine, L-methionine)

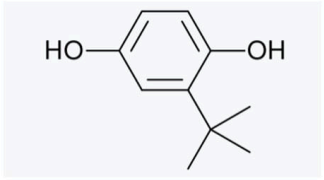
Types of Ingredients	What They Do	Examples of Uses	Names Found on Product Labels
Emulsifiers	Allow smooth mixing of ingredients, prevent separation Keep emulsified products stable, reduce stickiness, control crystallization, keep ingredients dispersed, and to help products dissolve more easily	Salad dressings, peanut butter, chocolate, margarine, frozen desserts	Soy lecithin, mono- and diglycerides, egg yolks, polysorbates, sorbitan monostearate
Stabilizers and Thickeners, Binders, Texturizers	Produce uniform texture, improve "mouth-feel"	Frozen desserts, dairy products, cakes, pudding and gelatin mixes, dressings, jams and jellies, sauces	Gelatin, pectin, guar gum, carrageenan, xanthan gum, whey
pH Control Agents and acidulants	Control acidity and alkalinity, prevent spoilage	Beverages, frozen desserts, chocolate, low acid canned foods, baking powder	Lactic acid, citric acid, ammonium hydroxide, sodium carbonate
Leavening Agents	Promote rising of baked goods	Breads and other baked goods	Baking soda, monocalcium phosphate, calcium carbonate
Anti-caking agents	Keep powdered foods free-flowing, prevent moisture absorption	Salt, baking powder, confectioner's sugar	Calcium silicate, iron ammonium citrate, silicon dioxide
Humectants	Retain moisture	Shredded coconut, marshmallows, soft candies, confections	Glycerin, sorbitol
Yeast Nutrients	Promote growth of yeast	Breads and other baked goods	Calcium sulfate, ammonium phosphate
Dough Strengtheners and Conditioners	Produce more stable dough	Breads and other baked goods	Ammonium sulfate, azodicarbonamide, L-cysteine
Firming Agents	Maintain crispness and firmness	Processed fruits and vegetables	Calcium chloride, calcium lactate
Enzyme Preparations	Modify proteins, polysaccharides and fats	Cheese, dairy products, meat	Enzymes, lactase, papain, rennet, chymosin
Gases	Serve as propellant, aerate, or create carbonation	Oil cooking spray, whipped cream, carbonated beverages	Carbon dioxide, nitrous oxide

Antioxidants: BHA and BHT

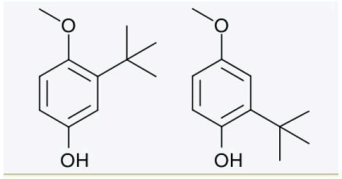
Antioxidants are used as food additives to help guard against food deterioration. Exposure to oxygen and sunlight are the two main factors in the oxidation of food, so food is preserved by keeping in the dark and sealing it in containers or even coating it in wax, as with cucumbers. However, as oxygen is also important for plant respiration, storing plant materials in anaerobic conditions produces unpleasant flavors and unappealing colors. Consequently, packaging of fresh fruits and vegetables contains an ~8% oxygen atmosphere. Antioxidants are an especially important class of preservatives as, unlike bacterial or fungal spoilage, oxidation reactions still occur relatively rapidly in frozen or refrigerated food. These preservatives include natural antioxidants such as ascorbic acid (AA) and tocopherols , as well as synthetic antioxidants such as propyl gallate, tertiary butylhydroquinone (TBHQ), butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT).



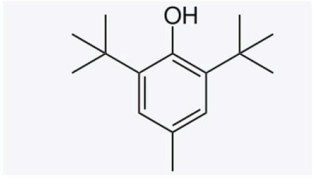
Propyl gallate



tert-Butylhydroquinone (TBHQ)



Butylated hydroxyanisole (BHA)



Butylated hydroxytoluene (BHT)

Figure 17.7.1 Synthetic antioxidants. *Source Wikipedia*

The most common molecules attacked by oxidation are unsaturated fats; oxidation causes them to turn rancid. Since oxidized lipids are often discolored and usually have unpleasant tastes such as metallic or sulfurous flavors, it is important to avoid oxidation in fat-rich foods. Thus, these foods are rarely preserved by drying; instead, they are preserved by smoking, salting or fermenting. Even less fatty foods such as fruits are sprayed with sulfurous antioxidants prior to air drying. Oxidation is often catalyzed by metals, which is why fats such as butter should never be wrapped in aluminium foil or kept in metal containers. Some fatty foods such as olive oil are partially protected from oxidation by their natural content of antioxidants, but remain sensitive to photooxidation.

Color Additives

A color additive is any dye, pigment or substance which when added or applied to a food, drug or cosmetic, or to the human body, is capable (alone or through reactions with other substances) of imparting color. FDA is responsible for regulating all color additives to ensure that foods containing color additives are safe to eat, contain only approved ingredients and are accurately labeled.

Color additives are used in foods for many reasons: 1) to offset color loss due to exposure to light, air, temperature extremes, moisture and storage conditions; 2) to correct natural variations in color; 3) to enhance colors that occur naturally; and 4) to provide color to colorless and "fun" foods. Without color additives, colas wouldn't be brown, margarine wouldn't be yellow and mint ice cream wouldn't be green. Color additives are now recognized as an important part of practically all processed foods we eat.

US FDA's permitted colors are classified as subject to certification or **exempt from certification**, both of which are subject to rigorous safety standards prior to their approval and listing for use in foods.

- **Certified colors** are synthetically produced (or human made) and used widely because they impart an intense, uniform color, are less expensive, and blend more easily to create a variety of hues. There are nine certified color additives approved for

use in the United States (e.g., FD&C Yellow No. 6. See chart for complete list.). Certified food colors generally do not add undesirable flavors to foods.
- Colors that are **exempt from certification** include pigments derived from natural sources such as vegetables, minerals or animals. Nature derived color additives are typically more expensive than certified colors and may add unintended flavors to foods. Examples of exempt colors include annatto extract (yellow), dehydrated beets (bluish-red to brown), caramel (yellow to tan), beta-carotene (yellow to orange) and grape skin extract (red, green).
- In the United States, FD&C numbers (which indicate that the FDA has approved the colorant for use in foods, drugs and cosmetics) are given to approved synthetic food dyes that do not exist in nature, while in the European Union, E numbers are used for all additives, both synthetic and natural, that are approved in food applications.

Artificial Food Colors

In the US, the following seven artificial colorings are generally permitted in food (the most common in bold) as of 2016. The lakes of these colorings are also permitted except the lake of Red No. 3.

- **FD&C Blue No. 1** – Brilliant Blue FCF, E133 (blue shade)
- FD&C Blue No. 2 – Indigotine, E132 (indigo shade)
- FD&C Green No. 3 – Fast Green FCF, E143 (turquoise shade)
- FD&C Red No. 3 – Erythrosine, E127 (pink shade, commonly used in glacé cherries)
- **FD&C Red No. 40** – Allura Red AC, E129 (red shade)
- **FD&C Yellow No. 5** – Tartrazine, E102 (yellow shade)
- **FD&C Yellow No. 6** – Sunset Yellow FCF, E110 (orange shade)

Two dyes are allowed by the FDA for limited applications:

- Citrus Red 2 (orange shade) - allowed only to color orange peels.
- Orange B (red shade) - allowed only for use in hot dog and sausage casings (not produced after 1978, but never delisted)

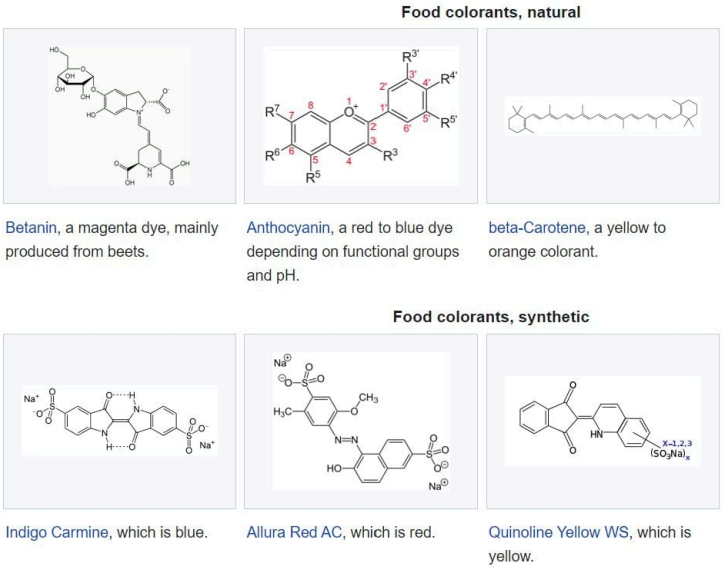


Figure 17.7.2 Chemical Structures of representative colorants. Source: Wikipedia.

Natural food dyes

Carotenoids , chlorophyllin , anthocyanins , and betanin comprise four main categories of plant pigments grown to color food products. Other colorants or specialized derivatives of these core groups include:

- Annatto, a reddish-orange dye made from the seed of the achiote
- Caramel coloring, made from caramelized sugar
- Carmine, a red dye derived from the cochineal insect, *Dactylopius coccus*
- Elderberry juice

- Lycopene
- Paprika
- Turmeric

Figure 17.7.3 *Natural food colors can make a variety of different hues. Source: Wikipedia*

Blue colors are especially rare. One feasible blue dye currently in use is derived from spirulina. Some recent research has explored associating anthocyanins with other phenolics or aluminium ions to develop blue colours. However, the inherent problems posed by the nature of the food matrix, and the need for long-term stability, makes this a very difficult objective. The pigment genipin, present in the fruit of Gardenia jasminoides, can be treated with amino acids to produce the blue pigment gardenia blue, which is approved for use in Japan but not the EU or the USA.

To ensure reproducibility, the colored components of these substances are often provided in highly purified form. For stability and convenience, they can be formulated in suitable carrier materials (solid and liquids). Hexane, acetone, and other solvents break down cell walls in the fruit and vegetables and allow for maximum extraction of the coloring. Traces of these may still remain in the finished colorant, but they do not need to be declared on the product label. These solvents are known as carry-over ingredients.

Summary

- Different ingredients are added to food in order to:
    1. maintain or improve safety and freshness,
    2. improve or maintain nutritional value, and
    3. improve taste, texture, and appearance.
- Common antioxidants added to foods include, ascorbic acid, tocopherols, propyl gallate, BHA, BHT, & TBHQ.
- There are seven artificial colorings that are generally permitted in the US. The most common ones are FD&C Blue No.1, FD&C Red No. 40, FD&C Yellow No.5, and FD&C Yellow No.6.

Contributors

- US FDA
- Wikipedia

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17.8: Problems with our Food

Learning Objectives

- Identify food substances and cooking processes known to cause cancer.
- Know common food contaminants and their sources.

Food Substances That May Promote Cancer

Several foods increase the risk of cancer. Alcohol is one example and increases the risk of mouth cancer, pharynx (throat), larynx (voice box), esophagus, liver, breast, colon, and rectum. People who drink should limit their alcohol intake to no more than 2 drinks per day for men and one drink per day for women. A drink is defined as 12 ounces of beer, 5 ounces of wine, or 1 1/2 ounces of 80-proof distilled spirits (hard liquor). Recent studies suggest there is no safe level of alcohol intake for women who are at high risk of developing breast cancer.

Scientific studies have shown that people who eat more fruit and vegetable have a lower risk of developing cancer certain cancers. Those individuals that eat less fruit and vegetables may increase their risk of developing cancer. Fruit and vegetables are rich in antioxidants but several studies of antioxidant supplements have not found a lower cancer risk, so the other compounds in fruits and vegetables may confer this protective effect.

Epidemiological studies have linked a high fat intake with higher rates of breast, prostate, colon, and other cancers. Randomized studies have not found that fat intake increases tumor development or lowers cancer risk either. So, at this time, the evidence is unclear and total amount of fat consumed does not appear to be linked to cancer risk.

Consumption of large amounts of processed meats has been associated with an increased risk of colorectal and stomach cancer. The exact mechanism is not known but nitrites, used to maintain color and bacterial growth in lunch meats, hams, and hot dogs, may play a role.

Frying, broiling, or grilling meats, cooking processes that use high heat, form chemicals that may increase cancer risk. These chemicals are polycyclic aromatic hydrocarbons or heterocyclic aromatic amines.

Eating a lot of foods preserved by salting and/or pickling increase one's risk of stomach, nasopharyngeal, and throat cancer. There is very little evidence that the level of salt used in cooking or flavoring foods or added during ng affect cancer risk.

Figure 17.8.1 *Chicken, pork and bacon-wrapped corn cooking in a barbecue smoker. Barbecuing and smoking generate carcinogens.*

Aflatoxins are poisonous carcinogens that are produced by certain molds (*Aspergillus flavus* and *Aspergillus parasiticus*) which grow in soil, decaying vegetation, hay, and grains. They are regularly found in improperly stored staple commodities such as cassava, chili peppers, corn, cottonseed, millet, peanuts, rice, sesame seeds, sorghum, sunflower seeds, tree nuts, wheat, and a variety of spices. When contaminated food is processed, aflatoxins enter the general food supply where they have been found in both pet and human foods, as well as in feedstocks for agricultural animals. Animals fed contaminated food can pass aflatoxin transformation products into eggs, milk products, and meat.

Figure 17.8.2 *Aflatoxin B_1. Source: Wikipedia*

Food As an Anti-Carcinogens

Dietary fiber and calorie restriction are two anti-carcinogen or anti-promoters that decrease the risk of tumor formation. Dietary fiber is both and is inversely associated with cancer, particularly colon cancer. So the more fiber you eat, the less risk you have of developing colon cancer. One mechanism by which fiber acts is hastening bile acid excretion. Fiber also increases the rate of passage of materials through the colon resulting in decreased production and exposure of the colon to cancer-causing agents, ie dilutes the concentration of carcinogens.

Animal studies have shown that restricting caloric intake by 30% reduces tumor growth and increases life span. The mechanism is not known but may be due to less oxidation thus damage to DNA.

Antioxidants can help block the action of initiators or promoters if their mode of action is to damage DNA by oxidation. Vitamin A, C, E, beta-carotene, and selenium are antioxidant nutrients. Some work locally, like vitamin E in the colon, while other work more globally like selenium and vitamin C. Vitamin A appears to work by keeping cells differentiated which slows the growth rate.

Other compounds in food, particularly fruits and vegetables, have been shown to slow tumor formation. Cruciferous vegetables (eg broccoli, cauliflower, cabbage, and Brussel sprouts to name a few) are rich in nutrients, fiber, glucosinolates which are sulfur-containing chemicals, indoles, and isothiocyanates. Animal studies have found these substances inhibit the development of cancer in several organs in rats and mice (Hecht SS. Inhibition of carcinogenesis by isothiocyanates. *Drug Metabolism Reviews* 2000;32(3-4):395-411; Murillo G, Mehta RG. Cruciferous vegetables and cancer prevention. *Nutrition and Cancer* 2001;41(1-2):17-28). Indoles and isothiocyanates help protect cells from DNA damage; help inactivate carcinogens; have antiviral and antibacterial effects; have anti-inflammatory effects; induce cell death (apoptosis); and inhibit tumor blood vessel formation (angiogenesis) and tumor cell migration (needed for metastasis) (National Cancer Institute, Cruciferous Vegetables and Cancer Prevention, 2012, https://www.cancer.gov/about-cancer/...les-fact-sheet). Studies in humans, however, have shown mixed results.

Dietary Recommendation for Decreasing Cancer Risk

The American Institute for Cancer Research, American Cancer Society, and National Cancer Institute provide dietary recommendations to reduce cancer risk. These guidelines are remarkably similar and focus on eating more fruits and vegetables, whole grains, and legumes; reducing processed meat and red meat intake; and limit your intake of alcohol. Fruits, vegetables, and whole grains are rich in fiber. Refined grains, such as white rice, are low or devoid of fiber. All types of fibers should be emphasized. Fruits and vegetables contain antioxidants, phytochemicals, and fiber.

These ten recommendations for cancer prevention are drawn from the WCRF/AICR Second Expert Report. Each recommendation links to more details.

1. Be as lean as possible without becoming underweight.
2. Be physically active for at least 30 minutes every day. Limit sedentary habits.
3. Avoid sugary drinks. Limit consumption of energy-dense foods.
4. Eat more of a variety of vegetables, fruits, whole grains and legumes such as beans.
5. Limit consumption of red meats (such as beef, pork, and lamb) and avoid processed meats.
6. If consumed at all, limit alcoholic drinks to 2 for men and 1 for women a day.
7. Limit consumption of salty foods and foods processed with salt (sodium).
8. Don't use supplements to protect against cancer.
9. * It is best for mothers to breastfeed exclusively for up to 6 months and then add other liquids and foods.
10. * After treatment, cancer survivors should follow the recommendations for cancer prevention.

Web Link

American Institute for Cancer Research Recommendations

https://www.aicr.org/reduce-your-cancer-risk/recommendations-for-cancer-prevention/?referrer=https://www.google.com/

Food Contamination

Food contamination refers to the presence of harmful chemicals and microorganisms in food, which can cause consumer illness.

The impact of **chemical contaminants** on consumer health and well-being is often apparent only after many years of processing and prolonged exposure at low levels (e.g., cancer). Unlike food-borne pathogens, chemical contaminants present in foods are often unaffected by thermal processing. Two major categories of chemical contaminants according to the source of contamination and the mechanism by which they enter the food product are agrochemicals and environmental contaminants.

Agrochemicals are chemicals used in agricultural practices and animal husbandry with the intent to increase crop yields. Such agents include pesticides (e.g., insecticides, herbicides, rodenticides), plant growth regulators, veterinary drugs (e.g., nitrofuran,

fluoroquinolones, malachite green, chloramphenicol), and bovine somatotropin (rBST).

Environmental contaminants are chemicals that are present in the environment in which the food is grown, harvested, transported, stored, packaged, processed, and consumed. The physical contact of the food with its environment results in its contamination. Possible sources of contamination and contaminants common to that vector include:

- Air: radionuclides (caesium-137, strontium-90), polycyclic aromatic hydrocarbons (PAH)
- Water: arsenic, mercury
- Soil: cadmium, nitrates, perchlorates
- Packaging materials: antimony, tin, lead, perfluorooctanoic acid (PFOA), semicarbazide, benzophenone, isopropylthioxanthone (ITX), bisphenol A
- Processing/cooking equipment: copper or other metal chips, lubricants, cleaning and sanitizing agents
- Naturally occurring toxins: mycotoxins, phytohemagglutinin, pyrrolizidine alkaloids, grayanotoxin, scombrotoxin (histamine), ciguatera, shellfish toxins (see shellfish poisoning), tetrodotoxin, among many others

Foodborne illness (also **foodborne disease** and colloquially referred to as **food poisoning**) is any illness resulting from the spoilage of contaminated food, pathogenic bacteria, viruses, or parasites that contaminate food, as well as prions (the agents of "mad cow disease"), and toxins such as aflatoxins in peanuts, poisonous mushrooms, and various species of beans that have not been boiled for at least 10 minutes.

Symptoms vary depending on the cause. A few broad generalizations can be made. For contaminants requiring an incubation period, symptoms may not manifest for hours to days, depending on the cause and on quantity of consumption. Longer incubation periods tend to cause sufferers to not associate the symptoms with the item consumed, so they may misattribute the symptoms to gastroenteritis, for example.

Symptoms often include vomiting, fever, and aches, and may include diarrhea. Bouts of vomiting can be repeated with an extended delay in between, because even if infected food was eliminated from the stomach in the first bout, microbes, like bacteria (if applicable), can pass through the stomach into the intestine and begin to multiply. Some types of microbes stay in the intestine.

In the United States, using FoodNet data from 2000 to 2007, the CDC estimated there were 47.8 million foodborne illnesses per year (16,000 cases for 100,000 inhabitants) with 9.4 million of these caused by 31 known identified pathogens.

- 127,839 were hospitalized (43 per 100,000 inhabitants per year).
- 3,037 people died (1.0 per 100,000 inhabitants per year).

Causes of foodborne illness in US

	Cause	Annual cases	Rate (per 100,000 inhabitants)
1	*Norovirus*	5,461,731 cases	X
2	*Salmonella*	1,027,561 cases	X
3	*Clostridium perfringens*	965,958 cases	X
4	*Campylobacter*	845,024 cases	X

Causes of death by foodborne illness in US

	Cause	Annual deaths	Rate (per 100,000 inhabitants)
1	*Salmonella*	378 cases	0.126
2	*Toxoplasma gondii*	327 cases	0.109
3	*Listeria*	255 cases	0.085
4	*Norovirus*	149 cases	0.050



Web Link

Center for Disease Control and Prevention : List of Foodborne Diseases.

https://www.cdc.gov/foodsafety/diseases/index.html

Summary

- Substances inherent in foods or substances produced during cooking processes that use high heat (e.g. frying, broiling, or grilling meats) may increase cancer risk.
- Two major categories of chemical contaminants according to the source of contamination and the mechanism by which they enter the food product are agrochemicals and environmental contaminants.
- The top four germs that cause illnesses from food eaten in the United States are Norovirus, Salmonella, Clostridium perfringens, and Campylobacter.
- Many different disease-causing germs can contaminate foods, so there are many different foodborne infections.

Contributors

- Libretext: An Introduction to Nutrition (Byerley).
- American Institute for Cancer Research
- Center for Disease Control and Prevention (CDC)
- Wikipedia

- Marisa Alviar-Agnew (Sacramento City College)

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18: DRUGS

18.1: Pain Relievers- From Aspirin to Oxycodone
18.2: Cold and Allergy Medicines
18.3: Drugs and Infectious Diseases
18.4: Chemicals Against Cancer
18.5: Hormones - The Regulators
18.6: Drugs for the Heart
18.7: Drugs and the Mind
18.8: Drugs and Society

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18.1: Pain Relievers- From Aspirin to Oxycodone

Learning Objectives

- Know the difference between anti-inflammatory, analgesic and antipyretic drugs.
- Describe how aspirin and other NSAIDs work.
- Know the side effects of taking prescription and non-prescription medications
- Know the risks of addiction, abuse, and overdose of prescription opioids.

A **drug** is any substance that causes a change in an organism's physiology or psychology when consumed. Drugs are typically distinguished from food and substances that provide nutritional support. Consumption of drugs can be via inhalation, injection, smoking, ingestion, absorption via a patch on the skin, suppository, or dissolution under the tongue.

Anti-inflammatory, analgesic (pain reliever or pain killer), and antipyretic (fever reducer) drugs are a heterogeneous group of compounds, often chemically unrelated (although most of them are organic acids), which nevertheless share certain therapeutic actions and side effects. The prototype is aspirin; hence these compounds are often referred to as aspirin-like drugs. All aspirin-like drugs are antipyretic, analgesic, and anti-inflammatory, but there are important differences in their activities. For example, acetaminophen is antipyretic and analgesic but is only weakly anti-inflammatory. The reason for the differences are not clear; variations in the sensitivity of enzymes in the target tissues may be important.

When employed as analgesics, these drugs are usually effective only against pain of low-to-moderate intensity, particularly that associated with inflammation. Aspirin drugs do not change the perception of sensory modalities other than pain. The type of pain is important; chronic postoperative pain or pain arising from inflammation is particularly well controlled by aspirin-like drugs, whereas pain arising from the hollow viscera is usually not relieved.

Over-the-counter (OTC) medicines are good for many types of pain. There are two main types of OTC pain medicines: acetaminophen (Tylenol) and nonsteroidal anti-inflammatory drugs (NSAIDs). Aspirin, naproxen (Aleve), and ibuprofen (Advil, Motrin) are examples of OTC NSAIDs.

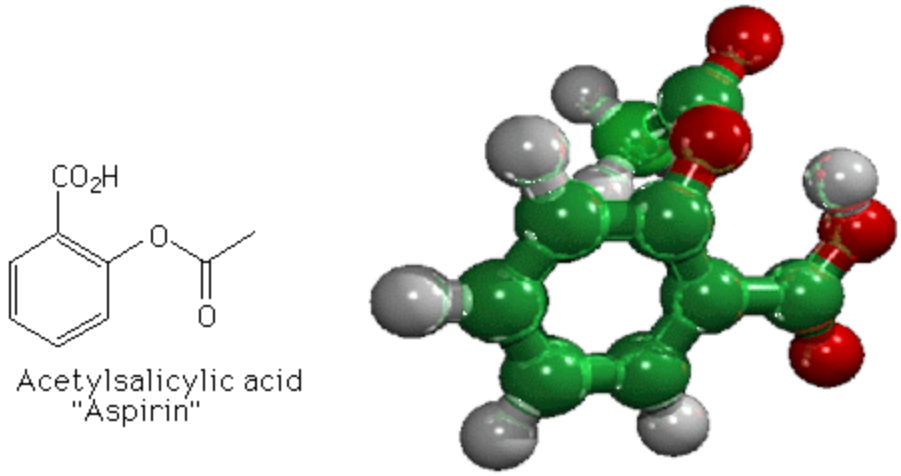
If OTC medicines don't relieve ones pain, the doctor may prescribe something stronger. Many NSAIDs are also available at higher prescription doses. The most powerful pain relievers are opioids. They are very effective, but they can sometimes have serious side effects. There is also a risk of addiction. Because of the risks, you must use them only under a doctor's supervision.

Aspirin and other NSAIDs

Nonsteroidal anti-inflammatory drugs (**NSAIDs**) are members of a drug class that reduces pain, decreases fever, prevents blood clots, and in higher doses, decreases inflammation. Side effects depend on the specific drug but largely include an increased risk of gastrointestinal ulcers and bleeds, heart attack, and kidney disease.

The term *nonsteroidal* distinguishes these drugs from steroids, which while having a similar eicosanoid-depressing, anti-inflammatory action, have a broad range of other effects. First used in 1960, the term served to distance these medications from steroids, which were particularly stigmatised at the time due to the connotations with anabolic steroid abuse.The most prominent NSAIDs are aspirin, ibuprofen, and naproxen, all available over the counter (OTC) in most countries.

In the U.S., about 10 to 20 thousand tons of **aspirin** are consumed each year; it is our most popular analgesic. Aspirin is one of the most effective analgesic, antipyretic, and anti-inflammatory agents.



Chemical structure

Figure 18.1.1 Aspirin

Aspirin is known to interfere with the action of the platelets. As a result, some people who take a lot of aspirin experience easy bruising of the skin. Therefore, people who have major bleeding problems should not take aspirin. Also, keep in mind that aspirin should not be taken for 10-14 days before surgery (including surgery in the mouth) to avoid excessive bleeding during or after the operation. These side effects probably depend on aspirin-like drugs' ability to block endogenous prostaglandin biosynthesis. Platelet function appears to be disturbed because aspirin-like drugs prevent the formation by the platelets of thrombozane A2 (TXA2), a potent aggregating agent. This accounts for the tendency of these drugs to increase the bleeding time.

Other Aspirin-Like Drugs

There are other non-selective NSAIDs on the market, including diclofenac, ibuprofen, ketoprofen, meloxicam, naproxen, and oxaprozin. Ibuprofen and naproxen are available in both prescription and over-the-counter (OTC) versions. The doses in OTC ibuprofen (Advil and Motrin) or naproxen (Aleve) are about half the doses of prescription versions.

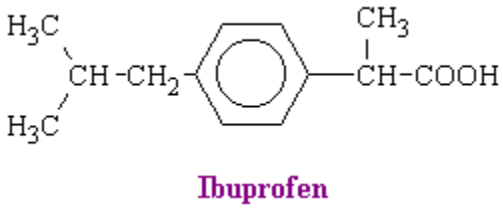


Figure 18.1.2 Ibuprofen.

How NSAIDs Work?

Non-selective NSAIDs like aspirin work (Figure 18.1.3) by inhibiting two enzymes that are involved with pain and inflammation—cyclooxygenase-1 and cyclooxygenase-2 (COX-1 and COX-2). These enzymes are involved with the ring closure and addition of oxygen to arachidonic acid converting to prostaglandins. The acetyl group on aspirin is hydrolzed and then bonded to the alcohol group of serine as an ester (Figure 18.1.2). This has the effect of blocking the channel in the enzyme and arachidonic acid can not enter the active site of the enzyme. By inhibiting or blocking this enzyme, the synthesis of prostaglandins is blocked, which in turn relieves some of the effects of pain and fever. Aspirin is also thought to inhibit the prostaglandin synthesis involved with unwanted blood clotting in coronary heart disease. At the same time an injury while taking aspirin may cause more extensive bleeding.

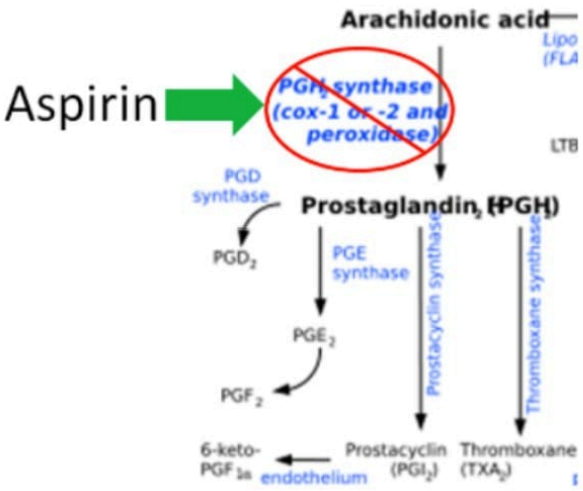


Figure 18.1.3 Aspirin inhibition of COX-1 and COX-2 enzymes.

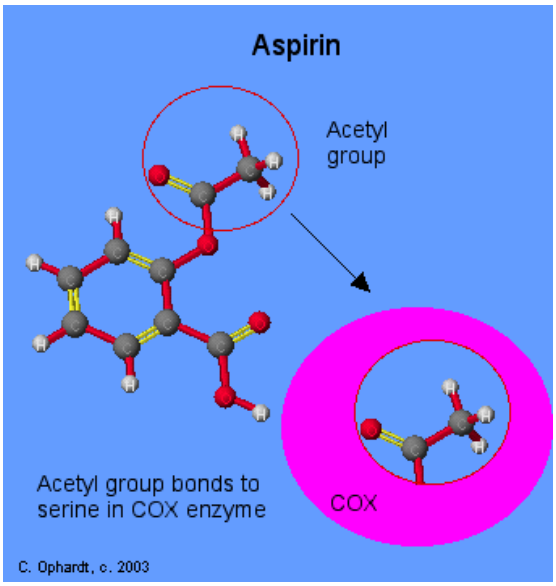


Figure 18.1.4 The acetyl group (from aspirin) bonds to serine in COX enzyme.

COX-2 selective inhibitors are a newer type of medicine that block the COX-2 enzyme more than the COX-1 enzyme. The only COX-2 selective inhibitor currently on the market in the United States is the prescription drug Celebrex (celecoxib), which is marketed by Pfizer. It was believed that COX-2 inhibitors may be less likely to cause the stomach problems associated with the older NSAIDs, but all NSAIDs carry the risk of stomach problems.

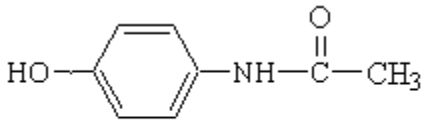
Key Points to Remember With NSAIDs

- Too much can cause stomach bleeding. This risk increases in people who are over 60 years of age, are taking prescription blood thinners, are taking steroids, have a history of stomach bleeding or ulcers, and/or have other bleeding problems.
- Use of NSAIDs can also cause kidney damage. This risk may increase in people who are over 60 years of age, are taking a diuretic (a drug that increases the excretion of urine), have high blood pressure, heart disease, or pre-existing kidney disease.

Acetaminophen

Acetaminophen is an effective alternative to aspirin as an analgesic and antipyretic agent. However, its anti-inflammatory effect is minor and not clinically useful. It is commonly felt that acetaminophen may have fewer side effects than aspirin, but it should

be noted that an acute overdose may produce severe or even fatal liver damage. Acetaminophen does not inhibit platelet aggregation and therefore is not useful for preventing vascular clotting.



Acetaminophen (4'-hydroxyacetanilide)

Side effects are usually fewer than those of aspirin; the drug produces less gastric distress and less ringing in the ears. However, as stated previously, overdose can lead to severe damage of the liver.

Acetaminophen has been proved to be a reasonable substitute for aspirin when analgesic or antipyretic effectiveness is desired, especially in patients who cannot tolerate aspirin. This might include patients with peptic ulcer disease of gastric distress or those in whom the anticoagulant action of aspirin might be undesirable.

Key Points to Remember With Acetaminophen

- Taking a higher dose than recommended will not provide more relief and can be dangerous.
- Too much can lead to liver damage and death. Risk for liver damage may be increased in people who drink three or more alcoholic beverages a day while using acetaminophen-containing medicines.
- Be cautious when giving acetaminophen to children. Infant drop medications can be significantly stronger than regular children's medications. Read and follow the directions on the label every time you use a medicine. Be sure that your infant is getting the infants' pain formula and your older child is getting the children's pain formula.

Prescription Medications

Typical prescription pain relief medicines include opioids and non-opioid medications. Types of prescription opioid medications (Figures 18.1.6 and 18.1.7) include:

- **morphine**, which is often used before and after surgical procedures to alleviate severe pain
- **oxycodone**, which is also often prescribed for moderate to severe pain
- **codeine**, which comes in combination with acetaminophen or other non-opioid pain relief medications and is often prescribed for mild to moderate pain
- **hydrocodone**, which comes in combination with acetaminophen or other non-opioid pain relief medications and is prescribed for moderate to moderately severe pain

Derived from opium, opioid drugs are very powerful products. They act by attaching to a specific "receptor" in the brain, spinal cord, and gastrointestinal tract. Opioids can change the way a person experiences pain. The term opium refers to the crude resinous extract obtained from the opium poppy. Crude opium contains a wide variety of ingredients, including morphine and codeine, both of which are widely used in medicine. The bulk of the ingredients of opium, however, consists of such organic substances as resins, oils, sugars, and proteins that account for more than 75 % of the weight of the opium but exert little pharmacological activity. Morphine is the major pain relieving drug found in opium, being approximately 10% of the crude exudate. Codeine is structurally close to morphine (see Figure 18.1.6), although it is much less potent and amounts to only 0.5% of the opium extract. Heroin does not occur naturally but is a semisynthetic derivative produced by a chemical modification of morphine that increases the potency. It takes only 3 mg. of heroin to produce the same analgesic effect as 10 mg of morphine. However, at these equally effective doses, it may be difficult to distinguish between the effects of the two compounds.

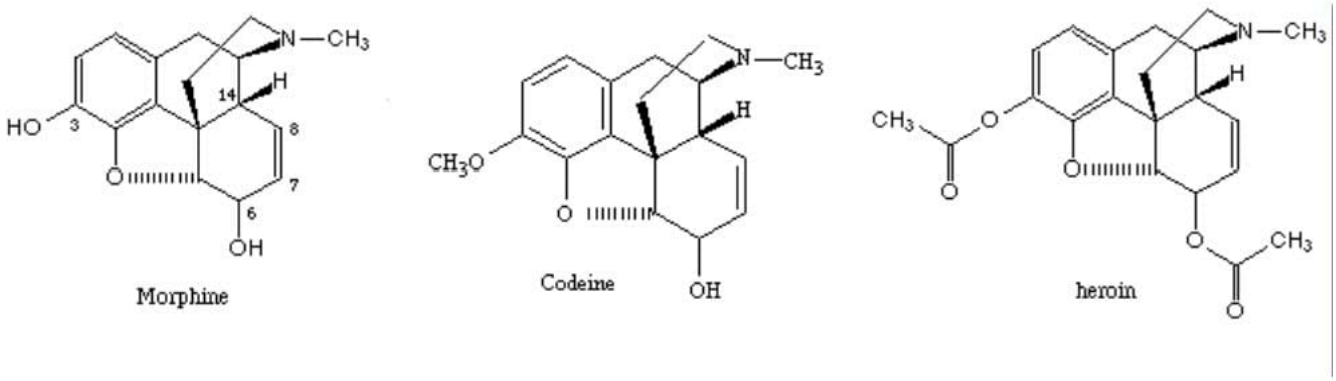


Figure 18.1.6 Morphine, codeine and heroin.

Oxycodone and hydrocodone are used to relieve moderate to severe pain. Oxycodone and hydrocodone extended-release tablets and extended-release capsules are used to relieve severe pain in people who are expected to need pain medication around the clock for a long time and who cannot be treated with other medications.

Addiction and Overdose

Anyone who takes prescription opioids can become addicted to them. In fact, as many as one in four patients receiving long-term opioid therapy in a primary care setting struggles with opioid addiction. Once addicted, it can be hard to stop. In 2016, more than 11.5 million Americans reported misusing prescription opioids in the past year. Taking too many prescription opioids can stop a person's breathing—leading to death.

Prescription opioid overdose deaths also often involve benzodiazepines. Benzodiazepines are central nervous system depressants used to sedate, induce sleep, prevent seizures, and relieve anxiety. Examples include alprazolam (Xanax®), diazepam (Valium®), and lorazepam (Ativan®). Avoid taking benzodiazepines while taking prescription opioids whenever possible.

Side Effects of Prescription Opioids

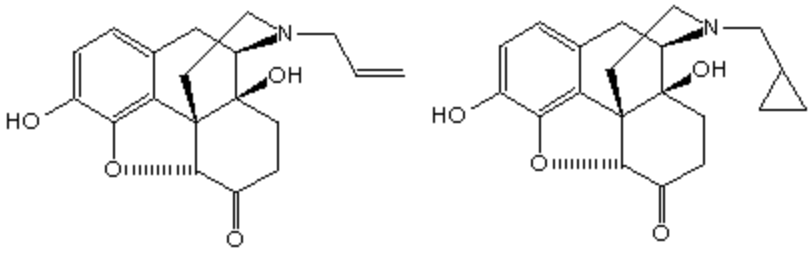
In addition to the serious risks of addiction, abuse, and overdose, the use of prescription opioids can have a number of side effects, even when taken as directed:

• Tolerance—meaning you might need to take more of the medication for the same pain relief • Physical dependence—meaning you have symptoms of withdrawal when the medication is stopped • Increased sensitivity to pain • Constipation • Nausea, vomiting, and dry mouth	• Sleepiness and dizziness • Confusion • Depression • Low levels of testosterone that can result in lower sex drive, energy, and strength • Itching and sweating

Opiate Antagonists

Naloxone, when administered to normal individuals, produces no analgesia, euphoria, or respiratory depression. However, it rapidly precipitates withdrawal in narcotic-dependent individuals. Naloxone antagonizes the actions of morphine at all its receptors.

The uses of naloxone include the reversal of the respiratory depression that follows acute narcotic intoxication and the reversal of narcotic-induced respiratory depression in newborns of mothers who have received narcotics. The use of naloxone is limited by a short duration of action and the necessity of parenteral route of administration.



naloxone (Narcan®) naltrexone (Trexan®)

Naltrexone became clinically available in 1985 as a new narcotic antagonist. Its actions resemble those of naloxone, but naltrexone is well is well absorbed orally and is long acting, necessitating only a dose of 50 to 100 mg. Therefore, it is useful in narcotic treatment programs where it is desired to maintain an individual on chronic therapy with a narcotic antagonist. In individuals taking naltrexone, subsequent injection of an opiate will produce little or no effect. naltrexone appears to be particularly effective for the treatment of narcotic dependence in addicts who have more to gain by being drug-free rather than drug dependant.

Combination Pain Relievers

Aspirin is often combined with acetaminophen in a single tablet for relief of arthritis and other painful conditions. Sometimes other drugs such as caffeine, an antihistamine, nasal drying agents, and sedatives are also added. Although some of these preparations may have special uses for certain acute conditions such as a cold or a headache, they should not be taken for a chronic (long-term) form of arthritis. If a combination is required, each drug should be prescribed separately. The dose of each should be adjusted individually to achieve the greatest benefit with the fewest side effects.

Hydrocodone is available in combination with other ingredients, and different combination products are prescribed for different uses. Some hydrocodone combination products are used to relieve moderate-to-severe pain. Other hydrocodone combination products are used to relieve cough. Hydrocodone is in a class of medications called opiate (narcotic) analgesics and in a class of medications called antitussives. Hydrocodone relieves pain by changing the way the brain and nervous system respond to pain. Hydrocodone relieves cough by decreasing activity in the part of the brain that causes coughing.

Web Link

A list of different hydrocodone combination products can be found on the link below.

https://medlineplus.gov/druginfo/meds/a601006.html

Summary

- Different types of medicine address different ailments. Anti-inflammatory drugs mediate inflammation, analgesics relieve pain, and antipyretic drugs help lower body temperature associated with fever.
- Over the counter (OTC) pain relievers relieve the minor aches and pains associated with conditions such as headaches, fever, colds, flu, arthritis, toothaches, and menstrual cramps.
- There are basically two types of OTC pain relievers: acetaminophen and non-steroidal anti-inflammatory drugs (NSAIDs).
- Aspirin and other aspirin-like drugs work by blocking the (COX-1 and COX-2) enzymes involved in pain and inflammation.
- Typical prescription pain relief medicines include opioids and non-opioid medications.
- In addition to the serious risks of addiction, abuse, and overdose, the use of prescription opioids can have a number of side effects,

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18.2: Cold and Allergy Medicines

Learning Objective

- Know the cause of the common cold and allergies.
- Know the chemical name, common name, and uses of different cough, cold, and allergy medicines.

The **common cold** is a viral infectious disease of the upper respiratory tract which affects primarily the nose. The symptoms of the common cold are believed to be primarily related to the immune response to the virus. Symptoms include coughing, sore throat, runny nose, and fever which usually resolve in seven to ten days, with some symptoms lasting up to three weeks. Well over 200 viruses are implicated in the cause of the common cold. The most commonly implicated virus is a rhinovirus (30–80%).

No cure for the common cold exists, but the symptoms can be treated. Antibiotics have no effect against viral infections and thus have no effect against the viruses that cause the common cold. Due to their side effects they cause overall harm; however, they are still frequently prescribed. It is the most frequent infectious disease in humans with the average adult contracting two to three colds a year and the average child contracting between six and twelve. These infections have been with humanity since antiquity.

Allergies are a number of conditions caused by hypersensitivity of the immune system to typically harmless substances in the environment. These diseases include hay fever, food allergies, atopic dermatitis, allergic asthma, and anaphylaxis. Symptoms may include red eyes, an itchy rash, sneezing, a runny nose, shortness of breath, or swelling. Food intolerances and food poisoning are separate conditions.

Early exposure to potential allergens may be protective. Treatments for allergies include the avoidance of known allergens and the use of medications such as steroids and antihistamines. **Histamine** is concentrated in mast cells, cells whose function is essentially to release histamine and immunoglobins when tissue damage occurs. They are especially numerous in parts of the body that are injured often, such as the fingers and toes, or which enjoy frequent contact with the environment, such as the mucosa of the lips, nose, etc.

Types of Cold and Allergy Medications

Cold medicines are medications used by people with the common cold, cough, or related conditions. While a wide variety of drugs are marketed as cough suppressants, research shows there is often little or no measurable benefit in reducing cough symptoms. While they have been used by 10% of American children in any given week, they are not recommended in Canada or the United States in children six years or younger because of lack of evidence showing effect and concerns of harm. One version with codeine, guaifenesin, and pseudoephedrine was the 213th most commonly prescribed medication in 2017, in the United States, with more than two million prescriptions.

There are a number of different cough and cold medications, which may be used for various coughing symptoms. The commercially available products may include various combinations of any one or more of the following types of substances listed in the table below.

Table 18.2.1 *Different Cough & Cold Medications.*

Medication	Function	Examples
Mucokinetics, or mucolytics	a class of drugs which aid in the clearance of mucus from the airways, lungs, bronchi, and trachea	carbocisteine, ambroxol, and bromhexine.
Expectorants	substances claimed to make coughing easier while enhancing the production of mucus and phlegm.	acetylcysteine and guaifenesin.
Antitussives, or cough suppressants substances which suppress the coughing itself	substances which suppress the coughing itself	codeine, pholcodine, dextromethorphan, noscapine, and butamirate.

Medication	Function	Examples
Antihistamines	for allergic rhinitis may produce mild sedation and reduce other associated symptoms, like a runny nose and watery eyes	diphenhydramine, chlorpheniramine, brompheniramine, loratadine, and cetirizine.
Decongestants	relieve nasal congestion and sinus infection	ephedrine, phenylephrine, pseudoephedrine, and oxymetazoline.
Fever or pain medication (antipyretic or analgesic)	fever reducer or pain reliever	paracetamol (called "acetaminophen " in the US) and NSAIDs such as aspirin, ibuprofen or naproxen
Syrups	various substances supposed to soften the coughing	honey or supplement syrup

Effectiveness

The efficacy of cough medication is questionable, particularly in children. A 2014 Cochrane review concluded that "There is no good evidence for or against the effectiveness of OTC medicines in acute cough". Some cough medicines may be no more effective than placebos for acute coughs in adults, including coughs related to upper respiratory tract infections. The American College of Chest Physicians emphasizes that cough medicines are not designed to treat whooping cough, a cough that is caused by bacteria and can last for months. No over-the-counter cough medicines have been found to be effective in cases of pneumonia. They are not recommended in those who have COPD, chronic bronchitis, or the common cold. There is not enough evidence to make recommendations for those who have a cough and cancer.

Medications

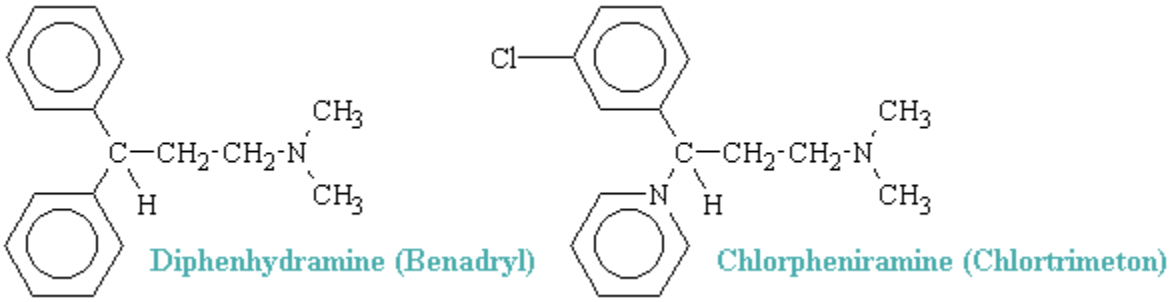
- Dextromethorphan (DXM) may be modestly effective in decreasing cough in adults with viral upper respiratory infections. However, in children it has not been found to be effective.
- Codeine was once viewed as the "gold standard" in cough suppressants, but this position is now questioned. Some recent placebo-controlled trials have found that it may be no better than a placebo for some causes including acute cough in children. It is thus not recommended for children. Additionally, there is no evidence that hydrocodone is useful in children. Similarly, a 2012 Dutch guideline does not recommend its use to treat acute cough.
- A number of other commercially available cough treatments have not been shown to be effective in viral upper respiratory infections. These include for adults: antihistamines, antihistamine-decongestant combinations, benzonatate, anti asthmatic-expectorant-mucolytic combinations, expectorant-bronchodilator combinations, leukotriene inhibitors, ambroxol, and guaifenesin, sometimes with analgesics, antipyretics, anti inflammatories, and anticholinergics - and for children: antihistamines, decongestants for clearing the nose, or combinations of these and leukotriene inhibitors for allergy and asthma. However, antihistamines cannot be used as an empirical therapy in case of chronic, or non specific cough especially in very young children. Long term diphenhydramine use is associated with negative outcomes in older people.

Antihistamines are drugs which treat hay fever and other allergies. Typically, people take antihistamines as an inexpensive, not patented (generic), drug that can be bought without a prescription and relieves from nasal congestion, sneezing, or hives caused by pollen, dust mites, or animal allergy with few side effects. Antihistamines are usually for short-term treatment. Chronic allergies increase the risk of health problems which antihistamines might not treat, including asthma, sinusitis, and lower respiratory tract infection. Consultation of a medical professional is recommended for those who intend to take antihistamines for longer-term use.

Although people typically use the word “antihistamine” to describe drugs for treating allergies, doctors and scientists use the term to describe a class of drug that opposes the activity of histamine receptors in the body. In this sense of the word, antihistamines are subclassified according to the histamine receptor that they act upon. The two largest classes of antihistamines are H_1-antihistamines and H_2-antihistamines.

H_1-antihistamines work by binding to histamine H_1 receptors in mast cells, smooth muscle, and endothelium in the body as well as in the tuberomammillary nucleus in the brain. Antihistamines that target the histamine H_1-receptor are used to treat allergic reactions in the nose (e.g., itching, runny nose, and sneezing). In addition, they may be used to treat insomnia, motion sickness, or vertigo caused by problems with the inner ear. H_2-antihistamines bind to histamine H_2 receptors in the upper gastrointestinal

tract, primarily in the stomach. Antihistamines that target the histamine H_2-receptor are used to treat gastric acid conditions (e.g., peptic ulcers and acid reflux). Two common examples of antihistamines are shown below.



Alternative Medicine

Honey may be a minimally effective cough treatment. A Cochrane review found the evidence to recommend for or against its use in children to be weak. In light of this they found it was better than no treatment, placebo, and diphenhydramine but not better than dextromethorphan for relieving cough symptoms. Honey's use as a cough treatment has been linked on several occasions to infantile botulism and accordingly should not be used in children less than one year old.

Many alternative treatments are used to treat the common cold. A 2007 review states that, "alternative therapies (i.e., Echinacea, vitamin C, and zinc) are not recommended for treating common cold symptoms; however, ... Vitamin C prophylaxis may modestly reduce the duration and severity of the common cold in the general population and may reduce the incidence of the illness in persons exposed to physical and environmental stresses." A 2014 review also found insufficient evidence for Echinacea.

A 2009 review found that the evidence supporting the effectiveness of zinc is mixed with respect to cough, and a 2011 Cochrane review concluded that zinc "administered within 24 hours of onset of symptoms reduces the duration and severity of the common cold in healthy people". A 2003 review concluded: "Clinical trial data support the value of zinc in reducing the duration and severity of symptoms of the common cold when administered within 24 hours of the onset of common cold symptoms." Zinc gel in the nose may lead to long-term or permanent loss of smell. The FDA therefore discourages its use.

Adverse effects

A number of accidental overdoses and well-documented adverse effects suggested caution in children. The FDA in 2015 warned that the use of codeine-containing cough medication in children may cause breathing problems. Cold syrup overdose has been linked to visual and auditory hallucinations, rapid involuntary jaw, tongue and eye movements in children.

Summary

- The **common cold** (also known as nasopharyngitis, rhinopharyngitis, acute coryza, or a cold) is a viral infectious disease of the upper respiratory tract which affects primarily the nose. The symptoms of the common cold are believed to be primarily related to the immune response to the virus.
- An **allergy** is an immune response (with the release of histamines), or reaction, to substances (allergens) that are usually not harmful.
- A number of different cough and cold medications can be used to alleviate various symptoms but not diminish the intensity of the response.

Contributors

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- Wikipedia

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18.3: Drugs and Infectious Diseases

Learning Objectives

- Differentiate between antibiotics and antiviral agents.
- Know the different antibiotics and antiviral agents and their mode of action.

The World Health Organization's (WHO) International Classification of Diseases (ICD) is used in clinical fields to classify diseases and monitor morbidity (the number of cases of a disease) and mortality (the number of deaths due to a disease). In this section, we will introduce terminology used by the ICD (and in health-care professions in general) to describe and categorize various types of disease.

An **infectious disease** is any disease caused by the direct effect of a pathogen. A pathogen may be cellular (bacteria, parasites, and fungi) or acellular (viruses, viroids, and prions). Some infectious diseases are also communicable, meaning they are capable of being spread from person to person through either direct or indirect mechanisms. Some infectious communicable diseases are also considered contagious diseases, meaning they are easily spread from person to person. Not all contagious diseases are equally so; the degree to which a disease is contagious usually depends on how the pathogen is transmitted. For example, measles is a highly contagious viral disease that can be transmitted when an infected person coughs or sneezes and an uninfected person breathes in droplets containing the virus. Gonorrhea is not as contagious as measles because transmission of the pathogen (*Neisseria gonorrhoeae*) requires close intimate contact (usually sexual) between an infected person and an uninfected person.

Antibiotics

The modern era of the chemotherapy of infection started with the clinical use of sulfanilamide in 1936. The "golden age" of antimicrobial therapy began with the production of penicillin in 1941, when this compound was mass-produced and first made available for limited clinical trial. More than 30% of all hospitalized patients now receive one or more courses of therapy with antibiotics, and millions of potentially fatal infections have been cured. However, at the same time, these pharmaceutical agents have become among the most misused of those available to the practicing physician. One result of widespread use of antimicrobial agents has been the emergence of antibiotic-resistant pathogens, which in turn has created an ever-increasing need for new drugs. Many of these agents have also contributed significantly to the rising costs of medical care.

An antibiotic is any substance produced by a microorganism that is excreted to harm or kill another microorganism. Technically, antibiotics are microbial or fungal products. But these substances can be synthesized and mass produced in the laboratory to use against harmful microorganisms in the environment. Thus, the synthetic chemist has added greatly to our therapeutic armamentarium. Synthetic drugs such as isonaizid and theambutol represent important contributions for the treatment of tuberculosis. While many such antimicrobial agents are not properly termed antibiotics, since they are not produced by living organisms, little distinction should now be made between compounds of natural and synthetic origin.

Synthetic Antibiotics - Sulfonamides

Sulfonamide is the basis of several groups of drugs. The original antibacterial sulfonamides (sometimes called sulfa drugs or sulpha drugs) are synthetic antimicrobial agents that contain the sulfonamide group. Some sulfonamides are also devoid of antibacterial activity, e.g., the anticonvulsant sultiame. The sulfonylureas and thiazide diuretics are newer drug groups based on the antibacterial sulfonamides.

Sulfa allergies are common, and medications containing sulfonamides are prescribed carefully. It is important to make a distinction between sulfa drugs and other sulfur-containing drugs and additives, such as sulfates and sulfites, which are chemically unrelated to the sulfonamide group and do not cause the same hypersensitivity reactions seen in the sulfonamides.

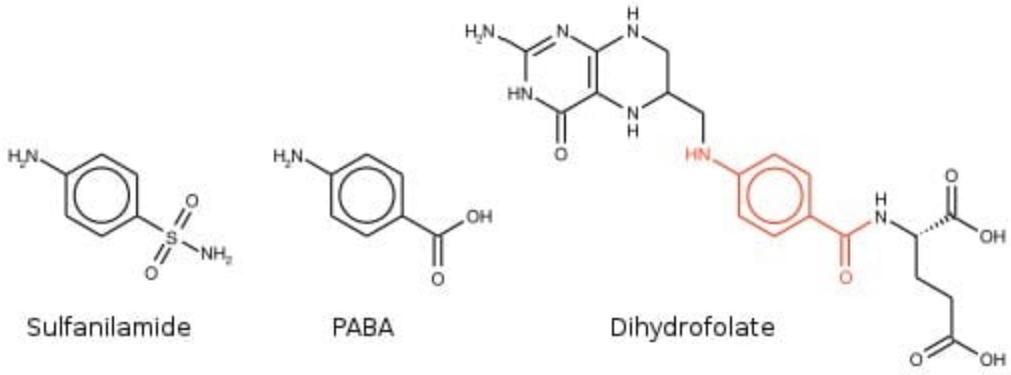


Figure 18.3.1 Structural similarity between sulfanilamide, a common sulfa drug (left) and PABA (center) is the basis for the inhibitory activity of sulfa drugs on dihydrofolate biosynthesis. Source: Wiikipedia

Sulfonamides are structural analogs and competitive antagonists of para-aminobenzoic acid (PABA), and thus prevent normal bacterial utilization of PABA for the synthesis of the vitamin folic acid (Figure 18.3.1). More specifically, sulfonamides are competitive inhibitors of the bacterial enzyme sulfihydropteroate synthase, which is responsible for the conversion of PABA into dihydrofolic acid, the immediate precursor of folic acid. Sensitive microorganisms are those that must synthesis their own folic acid; bacteria that can utilize preformed folic acid are not affected.

Cell Wall Synthesis Inhibitors - Penicillin and Cepalosphorins

The penicillins were the first antibiotics discovered as natural products from the mold Penicillium and was effective against Gram-positive bacteria. All penicillin derivatives produce their bacteriocidal effects by inhibition of bacterial cell wall synthesis. Specifically, the cross linking of peptides on the mucosaccharide chains is prevented. If cell walls are improperly made cell walls allow water to flow into the cell causing it to burst. A number of natural penicillins have been discovered, but only two purified compounds are in clinical use: penicillin G (intravenous use) and penicillin V (given by mouth). Several semisynthetic penicillins are effective against a broader spectrum of bacteria: these include the antistaphylococcal penicillins, aminopenicillins and the antipseudomonal penicillins.

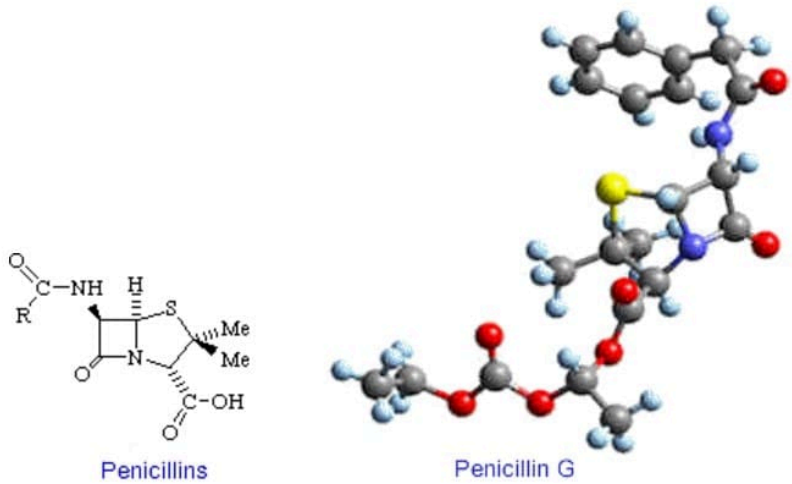


Figure 18.3.2 Penicillins.

Like penicillin, cephalosporins are valuable because of their low toxicity and their broad spectrum of action against various diseases. In this way, cephalosporin is very similar to penicillin. Cephalosporins are one of the most widely used antibiotics, and economically speaking, has about 29% of the antibiotic market. The cephalosporins are possibly the single most important group of antibiotics today and are equal in importance to penicillin. The structure and mode of action of the cephalosporins are similar

to that of penicillin. They affect bacterial growth by inhibiting cell wall synthesis, in Gram-positive and -negative bacteria.

Figure 18.3.3 Cephalosporins.

Protein Synthesis Inhibitors - Erythromycin, Tetracycline, Streptomycin, and Chloramphenicol

Erythromycin is an orally effective antibiotic discovered in 1952 in the metabolic products of a strain of Streptocyces erythreus, originally obtained from a soil sample collected in the Philippine Archipelago. Erythromycin may be either bacteriostatic or bactericidal, depending on the microorganism and the concentration of the drug.

Erythromycin is an antibiotic used for the treatment of a number of bacterial infections. This includes respiratory tract infections, skin infections, chlamydia infections, pelvic inflammatory disease, and syphilis. It may also be used during pregnancy to prevent Group B streptococcal infection in the newborn, as well as to improve delayed stomach emptying. It can be given intravenously and by mouth. An eye ointment is routinely recommended after delivery to prevent eye infections in the newborn.

Erythromycin and other macrolide antibiotics inhibit protein synthesis by binding to 50 S ribosomal subunits of sensitive microorganisms. (Humans do not have 50 S ribosomal subunits, but have ribosomes composed of 40 S and 60 S subunits). Certain resistant microorganisms with mutational changes in components of this subunit of the ribosome fail to bind the drug.

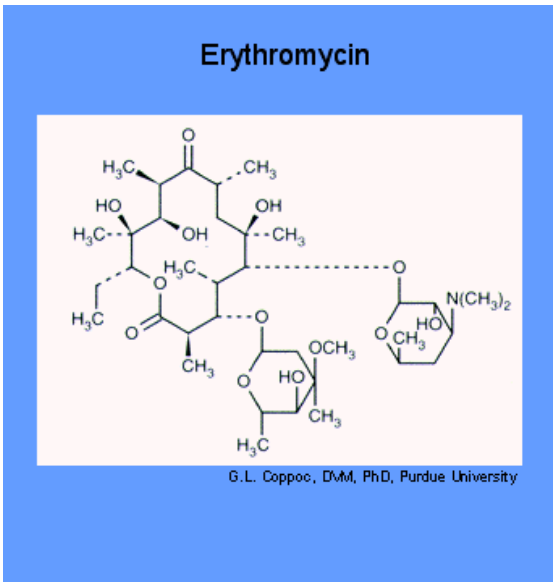


Figure 18.3.4 Erythromycin.

Tetracyclines have the broadest spectrum of antimicrobial activity. These may include: Aureomycin, Terramycin, and Panmycin. Four fused 6-membered rings, as shown in the figure below, form the basic structure from which the various tetracyclines are made. The various derivatives are different at one or more of four sites on the rigid, planar ring structure. The classical tetracyclines were derived from *Streptomyces spp.*, but the newer derivatives are semisynthetic as is generally true for newer members of other drug groups.

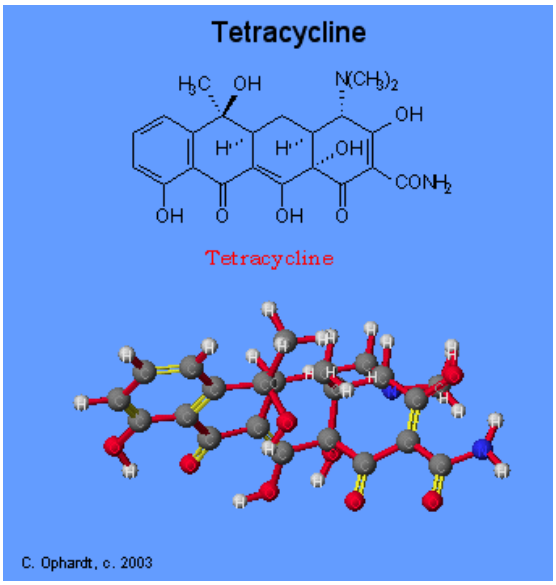


Figure 18.3.5 Tetracycline.

Tetracyclines inhibit bacterial protein synthesis by blocking the attachment of the transfer RNA-amino acid to the ribosome. More precisely they are inhibitors of the codon-anticodon interaction. Tetracyclines can also inhibit protein synthesis in the host, but are less likely to reach the concentration required because eukaryotic cells do not have a tetracycline uptake mechanism.

Streptomycin

Streptomycin is effective against gram-negative bacteria, although it is also used in the treatment of tuberculosis. Streptomycin binds to the 30S ribosome and changes its shape so that it and inhibits protein synthesis by causing a misreading of messenger RNA information.

Chloramphenicol

Chloromycetin is also a broad spectrum antibiotic that possesses activity similar to the tetracylines. At present, it is the only antibiotic prepared synthetically. It is reserved for treatment of serious infections because it is potentially highly toxic to bone marrow cells. It inhibits protein synthesis by attaching to the ribosome and interferes with the formation of peptide bonds between amino acids. It behaves as an antimetabolite for the essential amino acid phenylalanine at ribosomal binding sites.

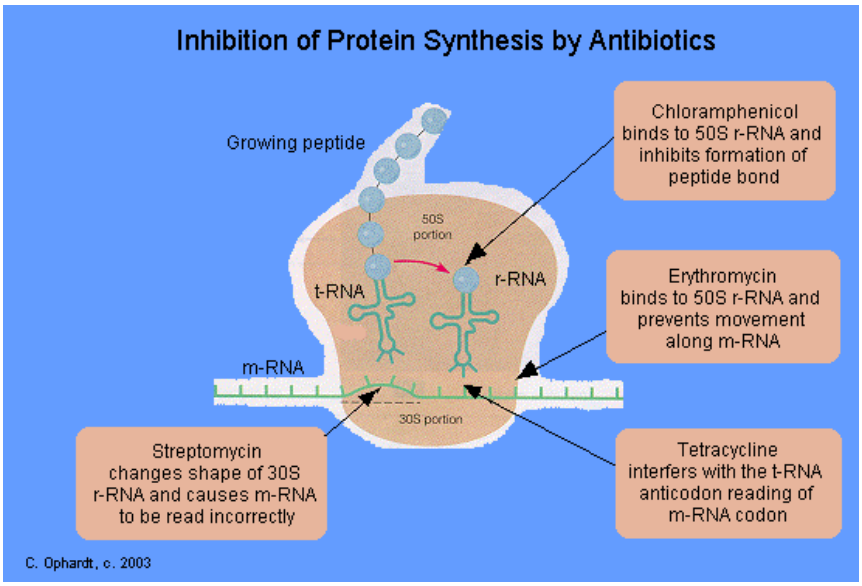


Figure 18.3.6 *Inhibition of protein synthesis by erythtomycin, teracycline, streptomycin, and chloramphenicol.*

A summary of the key features of different antibiotics is given in Table 18.3.1.

Table 18.3.1 *Some Clinically Important Antibiotics.*

Antibiotic	Producer organism	Activity	Site or mode of action
Penicillin	*Penicillium chrysogenum*	Gram-positive bacteria	Wall synthesis
Cephalosporin	*Cephalosporium acremonium*	Broad spectrum	Wall synthesis
Griseofulvin	*Penicillium griseofulvum*	Dermatophytic fungi	Microtubules
Bacitracin	*Bacillus subtilis*	Gram-positive bacteria	Wall synthesis
Polymyxin B	*Bacillus polymyxa*	Gram-negative bacteria	Cell membrane
Amphotericin B	*Streptomyces nodosus*	Fungi	Cell membrane
Erythromycin	*Streptomyces erythreus*	Gram-positive bacteria	Protein synthesis
Neomycin	*Streptomyces fradiae*	Broad spectrum	Protein synthesis
Streptomycin	*Streptomyces griseus*	Gram-negative bacteria	Protein synthesis
Tetracycline	*Streptomyces rimosus*	Broad spectrum	Protein synthesis
Vancomycin	*Streptomyces orientalis*	Gram-positive bacteria	Protein synthesis
Gentamicin	*Micromonospora purpurea*	Broad spectrum	Protein synthesis
Rifamycin	*Streptomyces mediterranei*	Tuberculosis	Protein synthesis

History of Penicillin and General Information

Alexander Fleming loved to play, both in the laboratory and out. He always loved snooker and golf and had many whimsical variants on the rules. In the lab he made "germ paintings," in which he would draw with his culture loop using spores of highly pigmented bacteria, which were invisible when he made the painting, but when cultured developed into brightly colored scenes. He followed what Max Delbruck would later call the "principle of limited sloppiness." Fleming abhorred a tidy, meticulous lab; he left culture dishes lying around for weeks and would often discover interesting things in them. Though the story has been told in many sometimes conflicting ways, something like this resulted in the discovery of penicillin. He seems to have left a culture dish lying on the lab bench and then gone away on vacation. When he returned a few spores of an unusual mold had germinated on the plate. When he cultured the bacteria on the plate he found that they grew up to within a few centimeters of the mold, but there were killed. A crude extract of the mold was then shown to have antibacterial properties. Fleming made this discovery in 1928 and by 1929 had named it penicillin (he was told by a colleague that the mold was a type of Penicillium and "penicillozyme" must have seemed cumbersome).

Fleming continued to use penicillin in his lab but not with any great enthusiasm and certainly not to the exclusion of many other projects. He never developed it into a clinically useful compound, though in 1929 he suggested that it might have important clinical applications. Because he was a bacteriologist and not a chemist, Fleming did not attempt to purify penicillin. He seems to have run into a dead end with penicillin and so during the 1930s, though he kept it in his lab, he did not do much with it. In the late 1930s Australian Howard Florey came to London to work with Charles Sherrington. He worked on lysozyme for a while and then became interested in penicillin. It was Florey, with Chain and other of his group that developed penicillin into a clinical antibiotic. They did this during 1940-41. Fleming, Florey, and Chain shared the 1945 Nobel Prize in Physiology for Medicine.

Fleming became world-famous for penicillin, and was rightly acknowledged as the father of modern antibiotics, but Florey was just as rightly miffed at being denied much of the credit for creating the powerful medical tool we now know. Evidence does not suggest that Fleming deliberately denied Florey his due credit, but Fleming's peculiar, dry sense of humor seems to have caused him not to deny even the wildest attributions to him.

Viruses and Antiviral Drugs

Viruses cause a variety of diseases in animals, including humans, ranging from the common cold to potentially fatal illnesses like meningitis (FIgure 18.3.1). These diseases can be treated by antiviral drugs or by vaccines, but some viruses, such as HIV, are capable of both avoiding the immune response and mutating to become resistant to antiviral drugs.

Antiviral drugs are a class of medication used for treating viral infections. Most antivirals target specific viruses, while a broad-spectrum antiviral is effective against a wide range of viruses. Unlike most antibiotics, antiviral drugs do not destroy their target pathogen; instead they inhibit its development.

Antiviral drugs are one class of antimicrobials, a larger group which also includes antibiotic (also termed antibacterial), antifungal and antiparasitic drugs, or antiviral drugs based on monoclonal antibodies. Most antivirals are considered relatively to the host, and therefore can be used to treat infections. They should be distinguished from viricides, which are not medication but deactivate or destroy virus particles, either inside or outside the body. Natural viricides are produced by some plants such as eucalyptus and Australian tea trees.

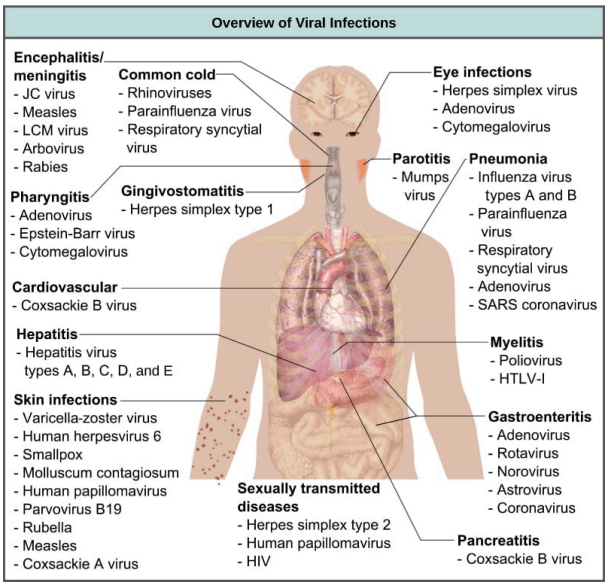


Figure 18.3.7: Viruses can cause dozens of ailments in humans, ranging from mild illnesses to serious diseases. (credit: modification of work by Mikael Häggström)

DNA Viruses and RNA Viruses

Viruses are visible only under an electron microscope. They come in a variety of shapes, ranging from spherical to rod shaped. The fact that they contain either deoxyribonucleic acid (DNA) or ribonucleic acid (RNA)—*but never both*—allows them to be divided into two major classes: DNA viruses and RNA viruses (Figure 18.3.1).

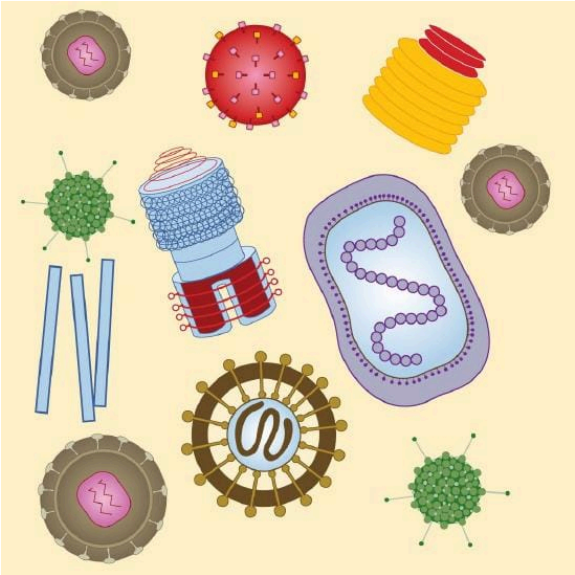


Figure 18.3.8: Viruses. Viruses come in a variety of shapes that are determined by their protein coats.

Most *RNA viruses* use their nucleic acids in much the same way as the DNA viruses, penetrating a host cell and inducing it to replicate the viral RNA and synthesize viral proteins. The new RNA strands and viral proteins are then assembled into new viruses. Some RNA viruses, however, called retroviruses (Figure 18.3.2), synthesize DNA in the host cell, in a process that is the reverse of the DNA-to-RNA transcription that normally occurs in cells. The synthesis of DNA from an RNA template is catalyzed by the enzyme reverse transcriptase.

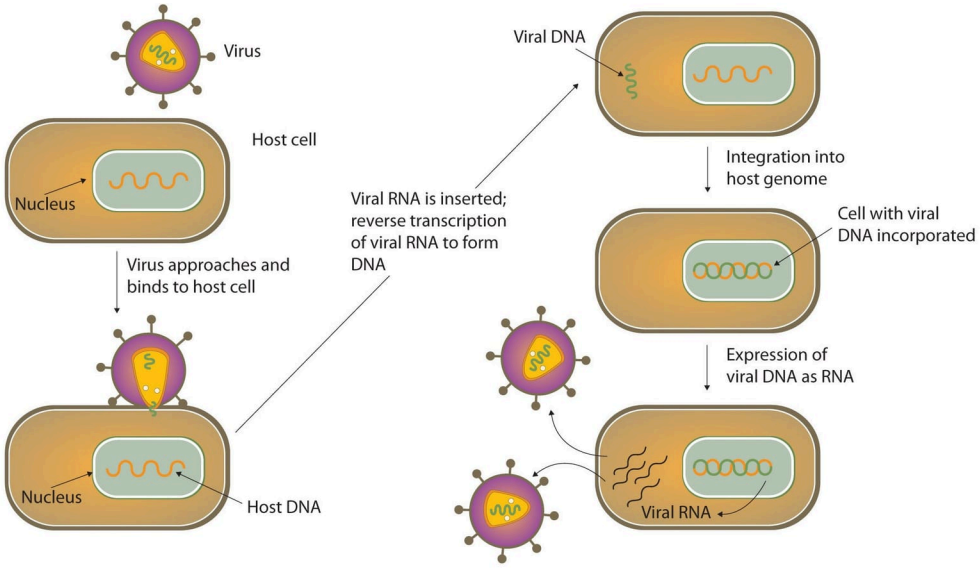


Figure 18.3.9: Life Cycle of a Retrovirus

Anti-viral Drugs

Antiviral drugs often have limited success in curing viral disease, but in many cases, they have been used to control and reduce symptoms for a wide variety of viral diseases. For most viruses, these drugs can inhibit the virus by blocking the actions of one or more of its proteins. It is important that the targeted proteins be encoded by viral genes and that these molecules are not present in a healthy host cell. In this way, viral growth is inhibited without damaging the host. There are large numbers of antiviral drugs available to treat infections, some specific for a particular virus and others that can affect multiple viruses.

Antivirals have been developed to treat genital herpes (herpes simplex II) and influenza. For genital herpes, drugs such as acyclovir can reduce the number and duration of episodes of active viral disease, during which patients develop viral lesions

in their skin cells. As the virus remains latent in nervous tissue of the body for life, this drug is not curative but can make the symptoms of the disease more manageable. For influenza, drugs like Tamiflu (oseltamivir) (Figure 18.3.3) can reduce the duration of “flu” symptoms by 1 or 2 days, but the drug does not prevent symptoms entirely. Tamiflu works by inhibiting an enzyme (viral neuraminidase) that allows new virions to leave their infected cells. Thus, Tamiflu inhibits the spread of virus from infected to uninfected cells. Other antiviral drugs, such as Ribavirin, have been used to treat a variety of viral infections, although its mechanism of action against certain viruses remains unclear.

By far, the most successful use of antivirals has been in the treatment of the retrovirus HIV, which causes a disease that, if untreated, is usually fatal within 10–12 years after infection. Anti-HIV drugs have been able to control viral replication to the point that individuals receiving these drugs survive for a significantly longer time than the untreated.

Anti-HIV drugs inhibit viral replication at many different phases of the HIV replicative cycle (Figure 18.3.4). Drugs have been developed that inhibit the fusion of the HIV viral envelope with the plasma membrane of the host cell (fusion inhibitors), the conversion of its RNA genome into double-stranded DNA (reverse transcriptase inhibitors), the integration of the viral DNA into the host genome (integrase inhibitors), and the processing of viral proteins (protease inhibitors).

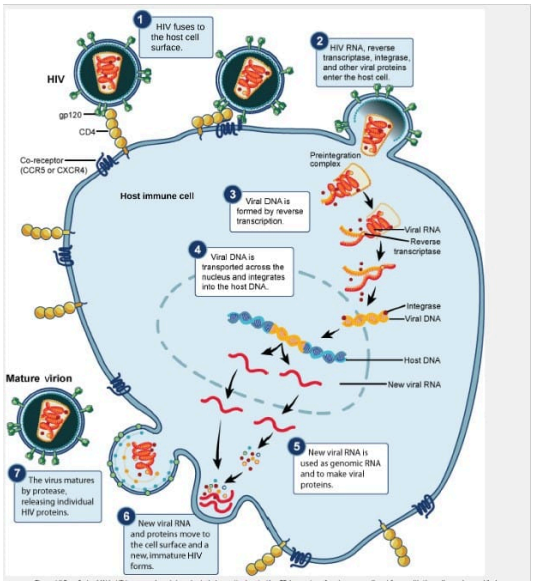
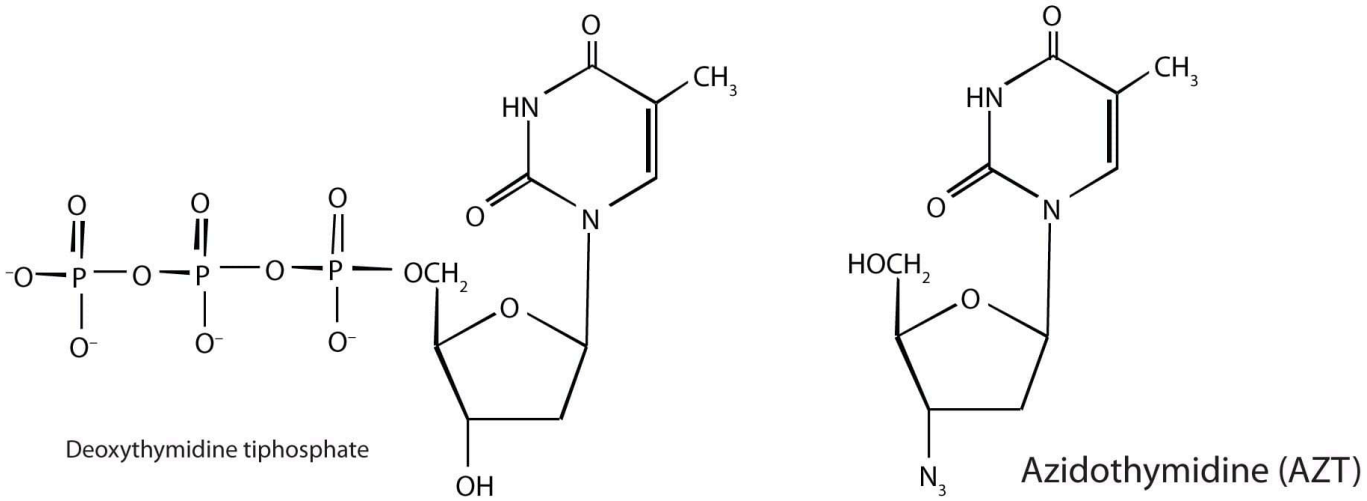
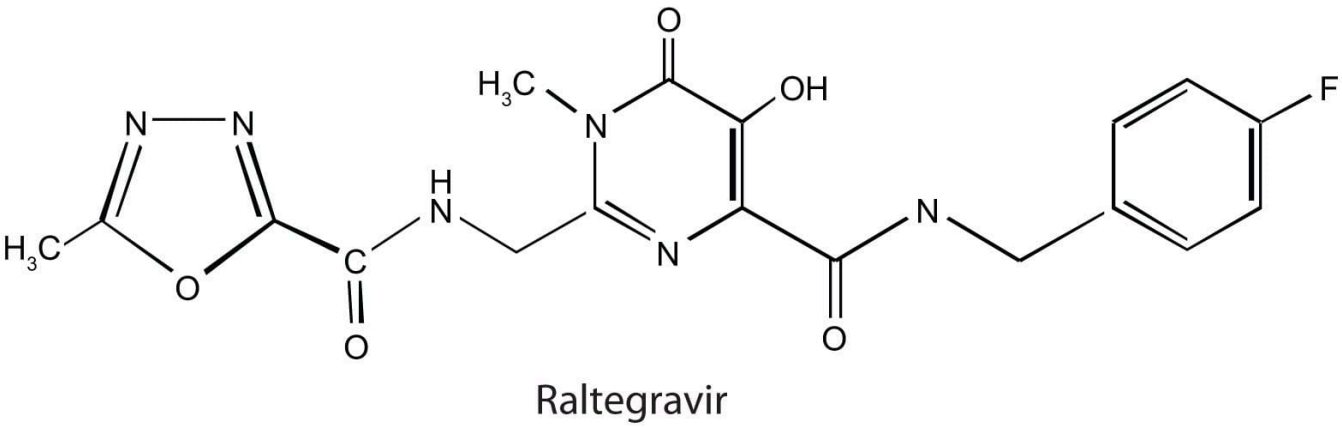


Figure 18.3.10: HIV, an enveloped, icosahedral virus, attaches to the CD4 receptor of an immune cell and fuses with the cell membrane. Viral contents are released into the cell, where viral enzymes convert the single-stranded RNA genome into DNA and incorporate it into the host genome. (credit: NIAID, NIH)

In 1987, azidothymidine (AZT, also known as zidovudine or the brand name Retrovir) became the first drug approved for the treatment of AIDS. It works by binding to reverse transcriptase in place of deoxythymidine triphosphate, after which, because AZT does not have a 3′OH group, further replication is blocked. In the past 10 years, several other drugs have been approved that also act by inhibiting the viral reverse transcriptase.



Raltegravir (Isentress) is a newer anti-AIDS drug that was approved by the FDA in October 2007. This drug inhibits the integrase enzyme that is needed to integrate the HIV DNA into cellular DNA, an essential step in the production of more HIV particles.



A major problem in treating HIV infections is that the virus can become resistant to any of these drugs. One way to combat the problem has been to administer a “cocktail” of drugs, typically a combination of two reverse transcriptase inhibitors along with a protease inhibitor. These treatments can significantly reduce the amount of HIV in an infected person.

The **management of HIV/AIDS** normally includes the use of multiple antiretroviral drugs in an attempt to control HIV infection. There are several classes of antiretroviral agents that act on different stages of the HIV life-cycle. The use of multiple drugs that act on different viral targets is known as **highly active antiretroviral therapy** (**HAART**). HAART decreases the patient's total burden of HIV, maintains function of the immune system, and prevents opportunistic infections that often lead to death. HAART also prevents the transmission of HIV between serodiscordant same sex and opposite sex partners so long as the HIV-positive partner maintains an undetectable viral load.

A more detailed list of antivirals other than HIV is given in Table 18.3.1.

Table 18.3.1 *Antivirals Used for Viruses Other Than HIV*

Antiviral	Brand Name	Use
amantadine	*Symmetrel*	used prophylactically against influenza A) in high-risk individuals. It prevents influenza A viruses from the uncoating step necessary for viral replication.
rimantidine	*Flumadine*	used for treatment and prophylaxis of influenza A. It prevents influenza A viruses from the uncoating step necessary for viral replication.

Antiviral	Brand Name	Use
zanamivir:	*Relenza*	used to limit the duration of influenza A and B infections. It is an inhibitor of the influenza virus surface enzyme called neuraminidase that is needed for release of newly formed influenza viruses from the infected cell.
oseltamivir	*Tamiflu*	used limit the duration of influenza infections. It is an inhibitor of the influenza virus surface enzyme called neuraminidase that is needed for release of newly formed influenza viruses from the infected cell.
acyclovir	Zovirax	used against herpes simplex viruses (HSV) to treat genital herpes, mucocutaneous herpes in the immunosuppressed, HSV encephalitis, neonatal herpes, and to reduce the rate of recurrences of genital herpes. It is also used against varicella zoster viruses (VZV)) to treat shingles. It chemically resembles a normal DNA nucleoside. Once inserted into the growing DNA chain it inhibits further viral DNA replication.
trifluridine	*Viroptic*	used to treat eye infection (keratitis and conjunctivitis) caused by HSV. It chemically resembles a normal DNA nucleoside. Once inserted into the growing DNA chain it inhibits further viral DNA replication.
famciclovir	Famvir	used to treat HSV and VZV infections. It chemically resembles a normal DNA nucleoside. Once inserted into the growing DNA chain it inhibits further viral DNA replication.
valacyclovir	Valtrex	used to treat HSV and VZV infections. It chemically resembles a normal DNA nucleoside. Once inserted into the growing DNA chain it inhibits further viral DNA replication.
penciclovir	Denavir	used in treating HSV infections. It chemically resembles a normal DNA nucleoside. Once inserted into the growing DNA chain it inhibits further viral DNA replication.
gancyclovir	Cytovene; Vitrasert	used in treating severe cytomegalovirus (CMV) infections such as retinitis. It chemically resembles a normal DNA nucleoside. Once inserted into the growing DNA chain it inhibits further viral DNA replication.
valganciclovir	Valcyte	used in treating severe CMV infections such as retinitis). It chemically resembles a normal DNA nucleoside. Once inserted into the growing DNA chain it inhibits further viral DNA replication.
foscarnet	Foscavir	used in treating severe CMV infections such as retinitis. It chemically resembles a normal DNA nucleoside. Once inserted into the growing DNA chain it inhibits further viral DNA replication.
cidofovir	Vistide	used in treating CMV retinitis. It chemically resembles a normal DNA nucleoside. Once inserted into the growing DNA chain it inhibits further viral DNA replication.
fomivirsen	Vitravene	used in treating CMV retinitis. Fomivirsen inhibits cytomegalovirus (CMV) replication through an antisense RNA (microRNA or miRNA mechanism. The nucleotide sequence of fomivirsen is complementary to a sequence in mRNA transcripts (Figure 18.3.1) that encodes several proteins responsible for regulation of viral gene expression that are essential for production of infectious CMV. Binding of fomivirsen to the target mRNA results in inhibition of protein synthesis, subsequently inhibiting virus replication.
ribavirin	Copegus; Rebetol; Virazole	used in treating severe acute respiratory syndrome (SARS). In combination with other drugs it is used to treat hepatitis C virus (HCV). It chemically resembles a normal RNA nucleoside. Once inserted into the growing RNA chain it inhibits further viral RNA replication.
telaprevir	Incivek	for the treatment of chronic hepatitis C (hepatitis C virus or HCV genotype 1). It is a protease inhibitor that binds to the active site of an HCV-encoded protease and prevent it from cleaving the long polyprotein from polycistronic HCV genes into proteins essential to the structure and function of HCV.
boceprevir	Victrelis	for the treatment of chronic hepatitis C (hepatitis C virus or HCV genotype 1) infection. It is used in combination with peginterferon alfa and ribavirin. Boceprevir is a protease inhibitor that binds to the active site of an HCV-encoded protease and prevent it from cleaving the long polyprotein from polycistronic HCV genes into proteins essential to the structure and function of HCV.

Antiviral	Brand Name	Use
simeprevir	Olysio	use for the treatment of chronic hepatitis C (hepatitis C virus or HCV genotype 1) infection. Used in combination with peginterferon alfa and ribavirin. Simeprevir is a protease inhibitor that binds to the active site of an HCV-encoded protease and prevent it from cleaving the long polyprotein from polycistronic HCV genes into proteins essential to the structure and function of HCV.
sofosbuvir	*Sovaldi*	Use for the treatment of chronic hepatitis C infection. Used in combination with ribavirin for hepatitis C virus or HCV genotypes 2 and 4; used in combination with peginterferon alfa and ribavirin for HCV genotypes 1 and 4. The second indication is the first approval of an interferon-free regimen for the treatment of chronic HCV infection. Sofosbuvir is a nucleotide polymerase inhibitor that binds to the active site of an HCV-encoded RNA polymerase preventing the synthesis of the viral RNA genome.
lamivudine	*Epivir-HBV*	used in treating chronic hepatitis B. It chemically resembles a normal DNA nucleoside. Once inserted into the growing DNA chain it inhibits further viral DNA replication.
adefovir dipivoxil	*Hepsera*	used in treating hepatitis B.

Web Link

A list of FDA-approved Antiretroviral drugs (last updated on April 12, 2018) used in the treatment of HIV infection can be found on the website: www.fda.gov/patients/hiv-treatment/antiretroviral-drugs-used-treatment-hiv-infection

Basic Research and Drug Development

The general idea behind modern antiviral drug design is to identify viral proteins, or parts of proteins, that can be disabled. These "targets" should generally be as unlike any proteins or parts of proteins in humans as possible, to reduce the likelihood of side effects. The targets should also be common across many strains of a virus, or even among different species of virus in the same family, so a single drug will have broad effectiveness. For example, a researcher might target a critical enzyme synthesized by the virus, but not by the patient, that is common across strains, and see what can be done to interfere with its operation.

Once targets are identified, candidate drugs can be selected, either from drugs already known to have appropriate effects or by actually designing the candidate at the molecular level with a computer-aided design program.

The target proteins can be manufactured in the lab for testing with candidate treatments by inserting the gene that synthesizes the target protein into bacteria or other kinds of cells. The cells are then cultured for mass production of the protein, which can then be exposed to various treatment candidates and evaluated with "rapid screening" technologies.

Prevention of Viral Diseases with Vaccination

While we do have limited numbers of effective antiviral drugs, such as those used to treat HIV and influenza, the primary method of controlling viral disease is by vaccination, which is intended to prevent outbreaks by building immunity to a virus or virus family (Figure 18.3.1). Vaccines may be prepared using live viruses, killed viruses, or molecular subunits of the virus. The killed viral vaccines and subunit viruses are both incapable of causing disease.

Live viral vaccines are designed in the laboratory to cause few symptoms in recipients while giving them protective immunity against future infections. Polio was one disease that represented a milestone in the use of vaccines. Mass immunization campaigns in the 1950s (killed vaccine) and 1960s (live vaccine) significantly reduced the incidence of the disease, which caused muscle paralysis in children and generated a great amount of fear in the general population when regional epidemics occurred. The success of the polio vaccine paved the way for the routine dispensation of childhood vaccines against measles, mumps, rubella, chickenpox, and other diseases.

The danger of using live vaccines, which are usually more effective than killed vaccines, is the low but significant danger that these viruses will revert to their disease-causing form by back mutations. Live vaccines are usually made by attenuating (weakening) the “wild-type” (disease-causing) virus by growing it in the laboratory in tissues or at temperatures different from what the virus is accustomed to in the host. Adaptations to these new cells or temperatures induce mutations in the genomes of the virus, allowing

it to grow better in the laboratory while inhibiting its ability to cause disease when reintroduced into conditions found in the host. These attenuated viruses thus still cause infection, but they do not grow very well, allowing the immune response to develop in time to prevent major disease. Back mutations occur when the vaccine undergoes mutations in the host such that it readapts to the host and can again cause disease, which can then be spread to other humans in an epidemic. This type of scenario happened as recently as 2007 in Nigeria where mutations in a polio vaccine led to an epidemic of polio in that country.

Some vaccines are in continuous development because certain viruses, such as influenza and HIV, have a high mutation rate compared to other viruses and normal host cells. With influenza, mutations in the surface molecules of the virus help the organism evade the protective immunity that may have been obtained in a previous influenza season, making it necessary for individuals to get vaccinated every year. Other viruses, such as those that cause the childhood diseases measles, mumps, and rubella, mutate so infrequently that the same vaccine is used year after year.



Figure 18.3.11: Vaccinations are designed to boost immunity to a virus to prevent infection. (credit: USACE Europe District)

Summary

- An infectious disease is any disease caused by the direct effect of a pathogen (bacteria, parasites, fungi, viruses, viroids, and prions).
- Diseases can either be noninfectious (due to genetics and environment) or infectious (due to pathogens). Some infectious diseases are communicable (transmissible between individuals) or contagious (easily transmissible between individuals); others are noncommunicable, but may be contracted via contact with environmental reservoirs or animal.
- An antibiotic is any substance produced by a microorganism that is excreted to harm or kill another microorganism. Technically, antibiotics are microbial or fungal products.
- Most antibiotics inhibit bacterial growth by inhibiting cell wall synthesis or protein synthesis.
- **Antiviral drugs** are a class of medication used for treating viral infections. Most antivirals target specific viruses, while a broad-spectrum antiviral is effective against a wide range of viruses.
- The management of HIV/AIDS normally includes the use of multiple in an attempt to control .

- The primary method of controlling viral disease is by vaccination, which is intended to prevent outbreaks by building immunity to a virus or virus family

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- US FDA
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18.4: Chemicals Against Cancer

Learning Objective

- List the different types of cancer drugs and their mechanism of action.

Chemotherapy is a type of cancer treatment that uses one or more anti-cancer drugs (chemotherapeutic agents) as part of a standardized chemotherapy regimen. Chemotherapy may be given with a curative intent (which almost always involves combinations of drugs), or it may aim to prolong life or to reduce symptoms (palliative chemotherapy). Chemotherapy is one of the major categories of the medical discipline specifically devoted to pharmacotherapy for cancer, which is called *medical oncology*.

When fighting cancer, the entire population of neoplastic cells must be eradicated in order to obtain desired results. The concept of "total cell-kill" applies to chemotherapy as it does to other means of treatment: total excision of the tumor is necessary for surgical care, and complete destruction of all cancer cells is required for a cure with radiation therapy.

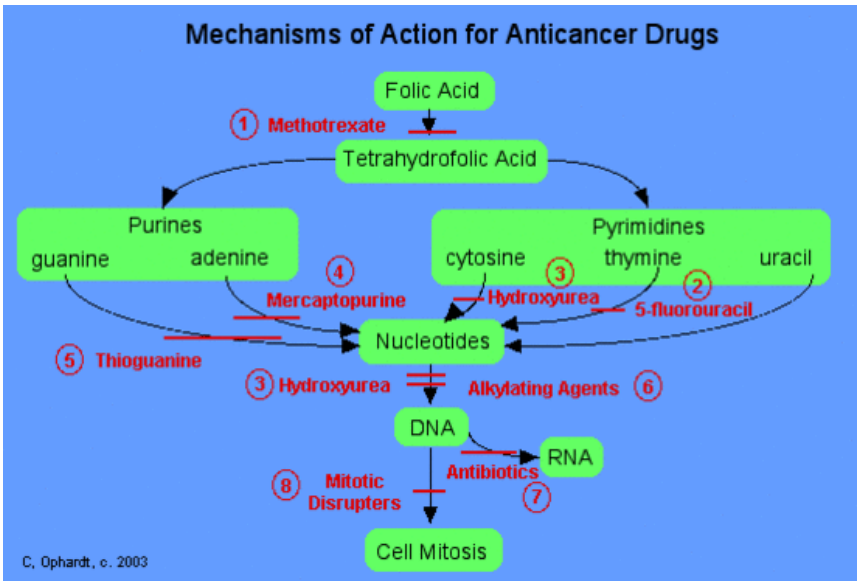
The available anticancer drugs have distinct mechanisms of action which may vary in their effects on different types of normal and cancer cells. A single "cure" for cancer has proved elusive since there is not a single type of cancer but as many as 100 different types of cancer. In addition, there are very few demonstrable biochemical differences between cancerous cells and normal cells. For this reason the effectiveness of many anticancer drugs is limited by their toxicity to normal rapidly growing cells in the intestinal and bone marrow areas. A final problem is that cancerous cells which are initially suppressed by a specific drug may develop a resistance to that drug. For this reason cancer chemotherapy may consist of using several drugs in combination for varying lengths of time.

Introduction

Chemotherapy drugs, are sometimes feared because of a patient's concern about toxic effects. Their role is to slow and hopefully halt the growth and spread of a cancer. There are three goals associated with the use of the most commonly-used anticancer agents.

1. Damage the DNA of the affected cancer cells.
2. Inhibit the synthesis of new DNA strands to stop the cell from replicating, because the replication of the cell is what allows the tumor to grow.
3. Stop mitosis or the actual splitting of the original cell into two new cells. Stopping mitosis stops cell division (replication) of the cancer and may ultimately halt the progression of the cancer.

Unfortunately, the majority of drugs currently on the market are not specific, which leads to the many common side effects associated with cancer chemotherapy. Because the common approach of all chemotherapy is to decrease the growth rate (cell division) of the cancer cells, the side effects are seen in bodily systems that naturally have a rapid turnover of cells including skin, hair, gastrointestinal, and bone marrow. These healthy, normal cells, also end up damaged by the chemotherapy program.



Categories of Chemotherapy Drugs

In general, chemotherapy agents can be divided into three main categories based on their mechanism of action as shown in the table below.

Table 18.4.1 *Chemotherapy Drugs and Their Mechanism of Action*

Category	Specific Mode of Action	Examples
Stop the synthesis of pre DNA molecule building blocks "Antimetabolites"	These agents work in a number of different ways. DNA building blocks are folic acid, heterocyclic bases, and nucleotides, which are made naturally within cells. All of these agents work to block some step in the formation of nucleotides or deoxyribonucleotides (necessary for making DNA). When these steps are blocked, the nucleotides, which arethe building blocks of DNA and RNA, can not be synthesized. Thus the cells can not replicate because they cannot make DNA without the nucleotides.	1) methotrexate (Abitrexate®),2) fluorouracil (Adrucil®), 3) hydroxyurea (Hydrea®), 4) mercaptopurine (Purinethol®) and 5) thioguanine.
Directly damage the DNA in the nucleus of the cell "Alkylating agents, antibiotics, topoisomerase inhibitors and intercalating agents."	These agents chemically damage DNA and RNA. They disrupt replication of the DNA and either totally halt replication or cause the manufacture of nonsense DNA or RNA (i.e. the new DNA or RNA does not code for anything useful).	5) cisplatin (Platinol®) and 7) antibiotics - daunorubicin (Cerubidine®), doxorubicin (Adriamycin®), and etoposide (VePesid®).

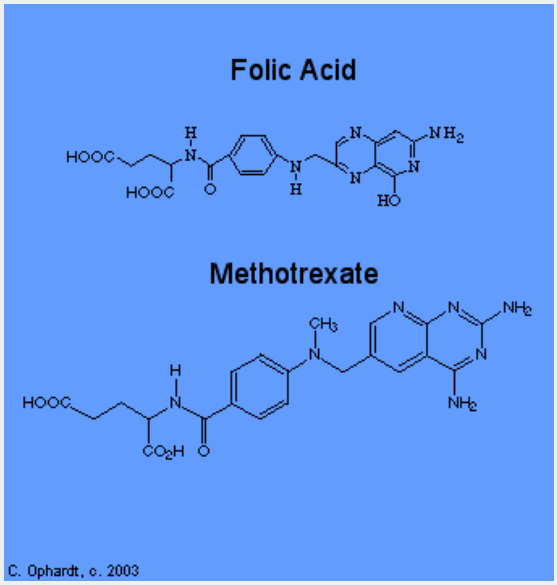
Category	Specific Mode of Action	Examples
Effect the synthesis or breakdown of the mitotic spindles "Mitotic disrupters"	Mitotic spindles serve as molecular railroads with "North and South Poles" in the cell when a cell starts to divide itself into two new cells. These spindles are very important because they help to split the newly copied DNA such that a copy goes to each of the two new cells during cell division. These drugs disrupt the formation of these spindles and therefore interrupt cell division.	8) mitotic disrupters include: Vinblastine (Velban®), Vincristine (Oncovin®) and Pacitaxel (Taxol®).

Antimetabolites

Methotrexate

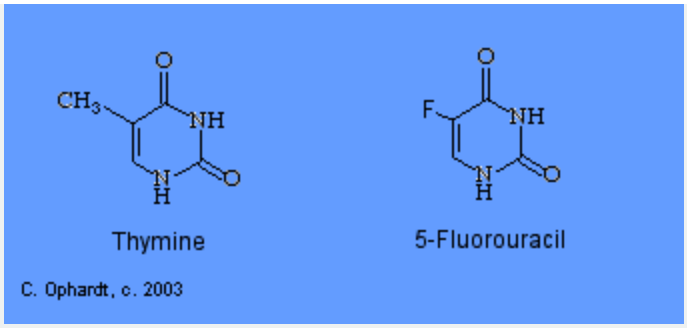
Methotrexate inhibits folic acid reductase which is responsible for the conversion of folic acid to tetrahydrofolic acid. At two stages in the biosynthesis of purines(adenine and guanine) and at one stage in the synthesis of pyrimidines (thymine, cytosine, and uracil), one-carbon transfer reactions occur which require specific coenzymes synthesized in the cell from tetrahydrofolic acid.

Tetrahydrofolic acid itself is synthesized in the cell from folic acid with the help of an enzyme, folic acid reductase. Methotrexate looks a lot like folic acid to the enzyme, so it binds to it thinking that it is folic acid. In fact, methotrexate looks so good to the enzyme that it binds to it quite strongly and inhibits the enzyme. Thus, DNA synthesis cannot proceed because the coenzymes needed for one-carbon transfer reactions are not produced from tetrahydrofolic acid because there is no tetrahydrofolic acid. Again, without DNA, no cell division.



5-Fluorouracil

5-Fluorouracil (5-FU; Adrucil®, Fluorouracil, Efudex®, Fluoroplex®) is an effective pyrimidine antimetabolite. Fluorouracil is synthesized into the nucleotide, 5-fluoro-2-deoxyuridine. This product acts as an antimetabolite by inhibiting the synthesis of 2-deoxythymidine because the carbon - fluorine bond is extremely stable and prevents the addition of a methyl group in the 5-position. The failure to synthesize the thymidine nucleotide results in little or no production of DNA. Two other similar drugs include: gemcitabine (Gemzar®) and arabinosylcytosine (araC). They all work through similar mechanisms.

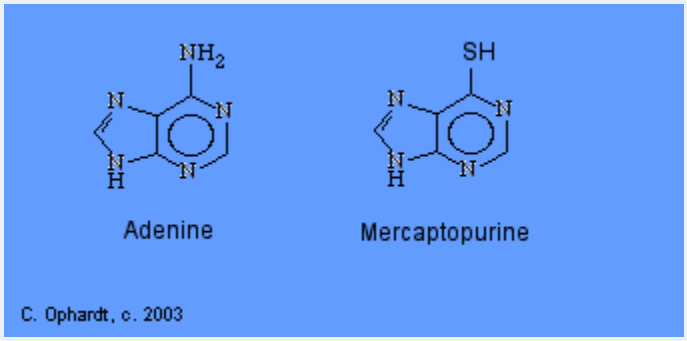


Hydroxyurea

Hydroxyurea blocks an enzyme which converts the cytosine nucleotide into the deoxy derivative. In addition, DNA synthesis is further inhibited because hydroxyurea blocks the incorporation of the thymidine nucleotide into the DNA strand.

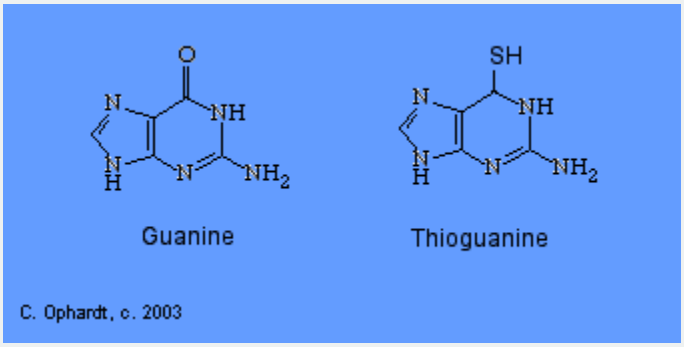
Mercaptopurine

Mercaptopurine, a chemical analog of the purine adenine, inhibits the biosynthesis of adenine nucleotides by acting as an antimetabolite. In the body, 6-MP is converted to the corresponding ribonucleotide. 6-MP ribonucleotide is a potent inhibitor of the conversion of a compound called inosinic acid to adenine Without adenine, DNA cannot be synthesized. 6-MP also works by being incorporated into nucleic acids as thioguanosine, rendering the resulting nucleic acids (DNA, RNA) unable to direct proper protein synthesis.



Thioguanine

Thioguanine is an antimetabolite in the synthesis of guanine nucleotides.

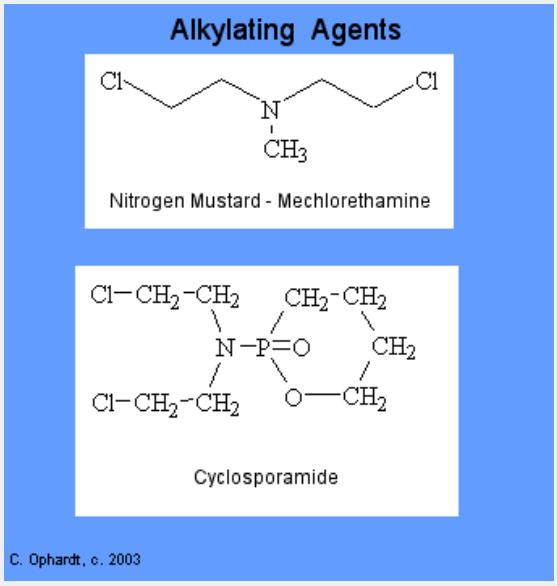


Alkylating Agents, Topoisomerase Inhibitors, Antibiotics, and Intercalating agents

Alkylating Agents

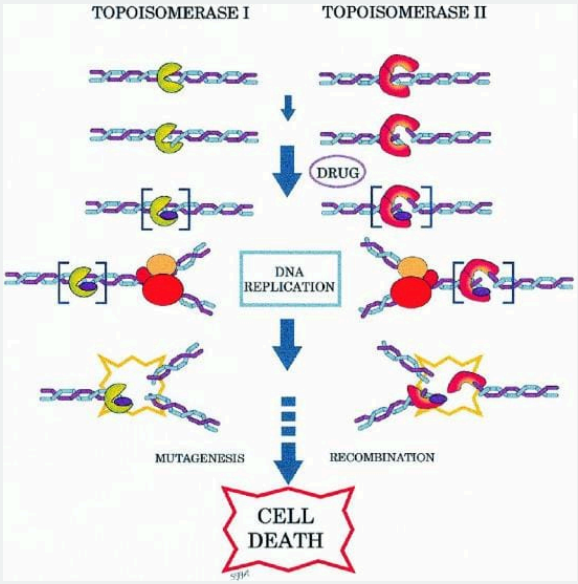
Alkylating agents involve reactions with guanine in DNA. These drugs add methyl or other alkyl groups onto molecules where they do not belong. This in turn inhibits their correct utilization by base pairing and causes a miscoding of DNA.

There are six groups of alkylating agents: nitrogen mustards; ethylenimes; alkylsulfonates; triazenes; piperazines; and nitrosureas. Cyclosporamide is a classical example of the role of the host metabolism in the activation of an alkylating agent and is one or the most widely used agents of this class. It was hoped that the cancer cells might posses enzymes capable of accomplishing the cleavage, thus resulting in the selective production of an ated nitrogen mustard in the malignant cells. Compare the top and bottom structures in the graphic on the left.



Topoisomerase Inhibitors

Topoisomerase inhibitors are drugs that affect the activity of two enzymes: topoisomerase I and topoisomerase II. Inhibition of topoisomerase I or II interferes with both replication and transcription.

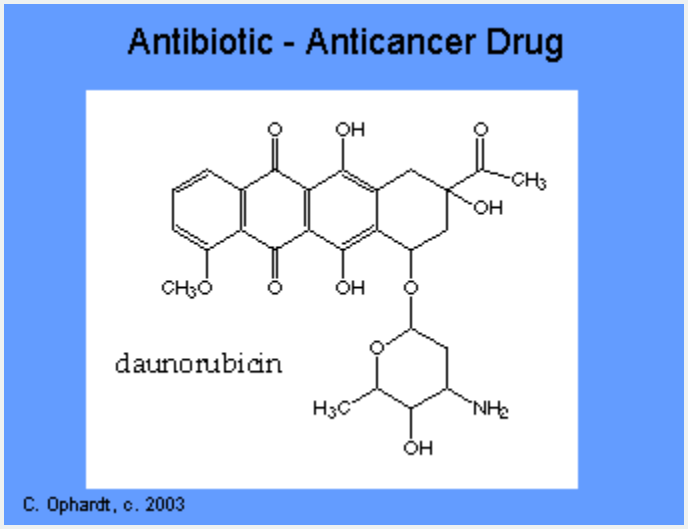


Two topoisomerase I inhibitors, irinotecan and topotecan, are semi-synthetically derived from camptothecin, which is obtained from the Chinese ornamental tree *Camptotheca acuminata*. Drugs that target topoisomerase II can be divided into two groups. The topoisomerase II inhibitors include etoposide, doxorubicin, mitoxantrone , teniposide, novobiocin, merbarone, and aclarubicin.

Antibiotics

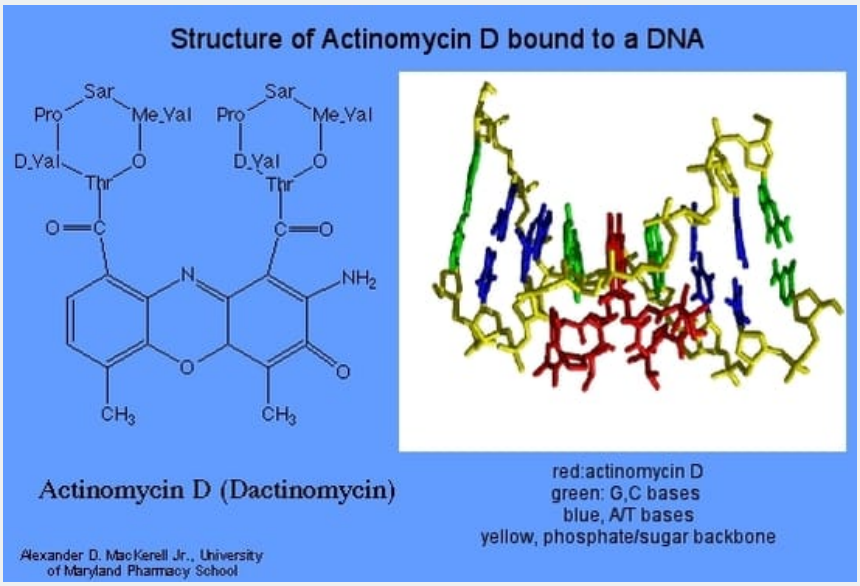
A number of **antibiotics** such as anthracyclines, dactinomycin, bleomycin, adriamycin, mithramycin, bind to DNA and inactivate it. Thus the synthesis of RNA is prevented. General properties of these drugs include: interaction with DNA in a variety of different ways including intercalation (squeezing between the base pairs), DNA strand breakage and inhibition with the enzyme topoisomerase II. Most of these compounds have been isolated from natural sources and antibiotics. However, they lack the specificity of the antimicrobial antibiotics and thus produce significant toxicity.

The **anthracyclines** are among the most important antitumor drugs available. Doxorubicin is widely used for the treatment of several solid tumors while **daunorubicin** and idarubicin are used exclusively for the treatment of leukemia. These agents have a number of important effects including: intercalating (squeezing between the base pairs) with DNA affecting many functions of the DNA including DNA and RNA synthesis. Breakage of the DNA strand can also occur by inhibition of the enzyme topoisomerase II.



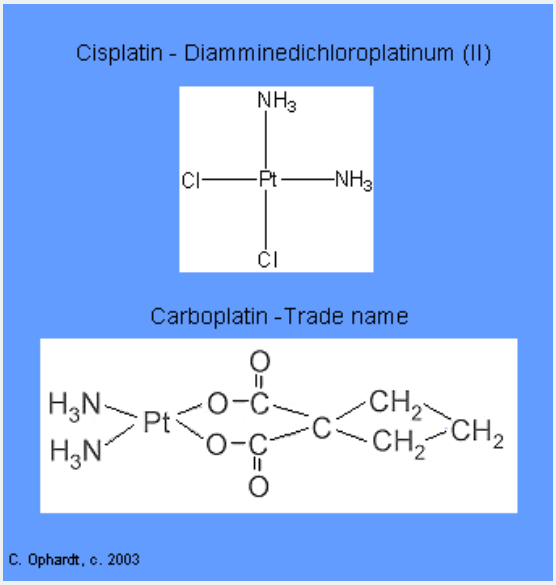
Dactinomycin (Actinomycin D)

At low concentrations dactinomycin inhibits DNA directed RNA synthesis and at higher concentrations DNA synthesis is also inhibited. All types of RNA are affected, but ribosomal RNA is more sensitive. Dactinomycin binds to double stranded DNA , permitting RNA chain initiation but blocking chain elongation. Binding to the DNA depends on the presence of guanine.



Intercalating Agents

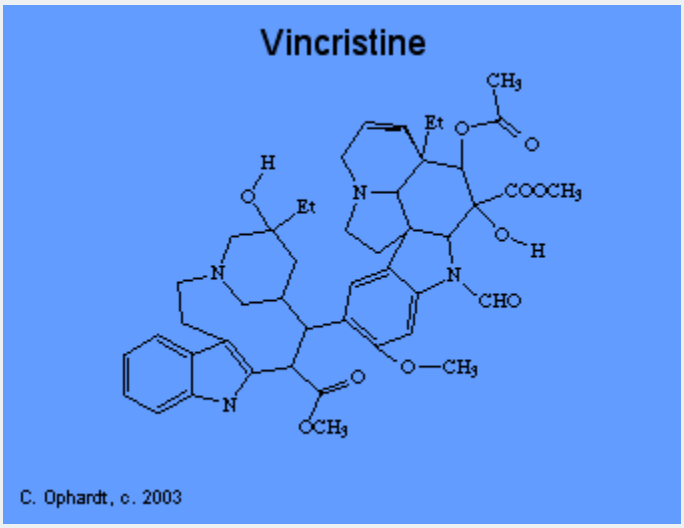
Intercalating agents wedge between bases along the DNA. The intercalated drug molecules affect the structure of the DNA, preventing polymerase and other DNA binding proteins from functioning properly. The result is prevention of DNA synthesis, inhibition of transcription and induction of mutations. Examples include: **Carboplatin and Cisplatin.**



Mitotic Disrupters

Mitotic Disrupters

Plant alkaloids like **vincristine** prevent cell division, or mitosis. There are several phases of mitosis, one of which is the metaphase. During metaphase, the cell pulls duplicated DNA chromosomes to either side of the parent cell in structures called "spindles". These spindles ensure that each new cell gets a full set of DNA. Spindles are microtubular fibers formed with the help of the protein "tubulin". Vincristine binds to tubulin, thus preventing the formation of spindles and cell division.



Taxol

Paclitaxel (taxol) was first isolated from the from the bark of the Pacific Yew (Taxus brevifolia). Docetaxel is a more potent analog that is produced semisynthetically. In contrast to other microtubule antagonists, taxol disrupts the equilibrium between free tubulin and mircrotubules by shifting it in the direction of assembly, rather than disassembly. As a result, taxol treatment causes both the stabilization of microtubules and the formation of abnormal bundles of microtubules. The net effect is still the disruption of mitosis.

Combination Chemotherapy

In 1965, a major breakthrough in cancer therapy occurred. James F. Holland, Emil Freireich, and Emil Frei hypothesized that cancer chemotherapy should follow the strategy of antibiotic therapy for tuberculosis with combinations of drugs, each with a different mechanism of action. Cancer cells could conceivably mutate to become resistant to a single agent, but by using different drugs *concurrently* it would be more difficult for the tumor to develop resistance to the combination. Holland, Freireich, and Frei simultaneously administered methotrexate (an antifolate), vincristine (a Vinca alkaloid), 6-mercaptopurine (6-MP) and prednisone — together referred to as the POMP regimen — and induced long-term remissions in children with acute lymphoblastic leukaemia (ALL). With incremental refinements of original regimens, using randomized clinical studies by St. Jude Children's Research Hospital, the Medical Research Council in the UK (UKALL protocols) and German Berlin-Frankfurt-Münster clinical trials group (ALL-BFM protocols), ALL in children has become a largely curable disease.

This approach was extended to the lymphomas in 1963 by Vincent T. DeVita and George Canellos at the NCI, who ultimately proved in the late 1960s that nitrogen mustard, vincristine, procarbazine and prednisone — known as the MOPP regimen — could cure patients with Hodgkin's and non-Hodgkin's lymphoma.

Currently, nearly all successful cancer chemotherapy regimens use this paradigm of multiple drugs given simultaneously, called **combination chemotherapy** or **polychemotherapy**.

Table 18.4.2 *The Common Combination Chemotherapy Regimens*

Cancer type	Drugs	Acronym
Breast cancer	Cyclophosphamide, methotrexate, 5-fluorouracil, vinorelbine	CMF
	Doxorubicin, cyclophosphamide	AC
Hodgkin's lymphoma	Docetaxel, doxorubicin, cyclophosphamide	TAC
	Doxorubicin, bleomycin, vinblastine, dacarbazine	ABVD
	Mustine, vincristine, procarbazine, prednisolone	MOPP
Non-Hodgkin's lymphoma	Cyclophosphamide, doxorubicin, vincristine, prednisolone	CHOP
Germ cell tumor	Bleomycin, etoposide, cisplatin	BEP
Stomach cancer	Epirubicin, cisplatin, 5-fluorouracil	ECF
	Epirubicin, cisplatin, capecitabine	ECX
Bladder cancer	Methotrexate, vincristine, doxorubicin, cisplatin	MVAC
Lung cancer	Cyclophosphamide, doxorubicin, vincristine, vinorelbine	CAV
Colorectal cancer	5-fluorouracil, folinic acid, oxaliplatin	FOLFOX

Summary

- **Chemotherapy** is a type of cancer treatment that uses one or more anti-cancer drugs (chemotherapeutic agents) as part of a standardized chemotherapy regimen.
- Chemo drugs can be classified into three main categories based on their mechanism of action namely:
  - Stop the synthesis of pre-DNA molecule building blocks
  - Directly damage the DNA in the nucleus of the cell
  - Effect the synthesis or breakdown of the mitotic spindles.
- Currently, nearly all successful cancer chemotherapy regimens use this paradigm of multiple drugs given simultaneously,

called combination chemotherapy or polychemotherapy.

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18.5: Hormones - The Regulators

Learning Objectives

- Identify the major classes of hormones on the basis of chemical structure.
- Know the function of the common hormones.

Glands of the Endocrine System

The **endocrine system** is a system of glands called **endocrine glands** that release chemical messenger molecules into the bloodstream. The messenger molecules of the endocrine system are called endocrine hormones. The major glands of the endocrine system are shown in Figure 18.5.1. The major hormones of the human body and their effects are listed in Table 18.5.1.

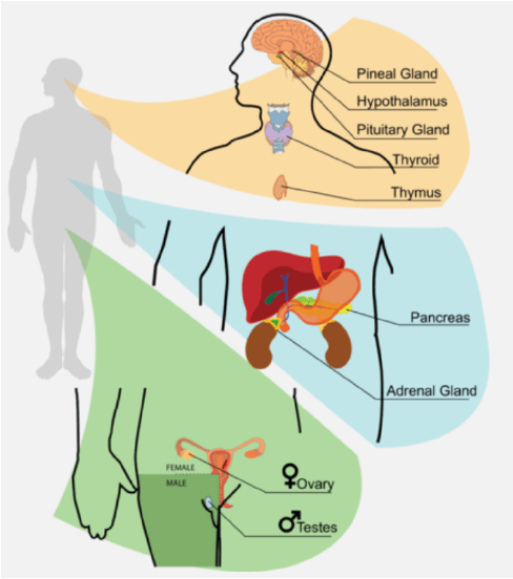


Figure 18.5.1 The endocrine glands. (Mariana Ruiz Villarreal; public domain; (LadyofHats/Wikimedia Commons; CK-12 foundation)

Although a given hormone may travel throughout the body in the bloodstream, it will affect the activity only of its target cells; that is, cells with receptors for that particular hormone. Once the hormone binds to the receptor, a chain of events is initiated that leads to the target cell's response. Hormones play a critical role in the regulation of physiological processes because of the target cell responses they regulate. These responses contribute to human reproduction, growth and development of body tissues, metabolism, fluid, and electrolyte balance, sleep, and many other body functions. The major hormones of the human body and their effects are identified in Table 18.5.1.

Table 18.5.1 The Endocrine Glands and Their Major Hormones.

Endocrine gland	Associated hormones	Chemical class	Effect
Pituitary	Growth hormone (GH)	Protein	Promotes growth of body tissues
	Prolactin (PRL)	Peptide	Promotes milk production
	Thyroid-stimulating hormone (TSH)	Glycoprotein	Stimulates thyroid hormone release
	Adrenocorticotropic hormone (ACTH)	Peptide	Stimulates hormone release by adrenal cortex

Endocrine gland	Associated hormones	Chemical class	Effect
	Follicle-stimulating hormone (FSH)	Glycoprotein	Stimulates gamete production
	Luteinizing hormone (LH)	Glycoprotein	Stimulates androgen production by gonads
	Antidiuretic hormone (ADH)	Peptide	Stimulates water reabsorption by kidneys
	Oxytocin	Peptide	Stimulates uterine contractions during childbirth
Thyroid	Thyroxine (T_4), triiodothyronine (T_3)	Amine	Stimulate basal metabolic rate
	Calcitonin	Peptide	Reduces blood Ca^{2+} levels
Parathyroid	Parathyroid hormone (PTH)	Peptide	Increases blood Ca^{2+} levels
Adrenal (cortex)	Aldosterone	Steroid	Increases blood Na^{+} levels
	Cortisol, corticosterone, cortisone	Steroid	Increase blood glucose levels
Adrenal (medulla)	Epinephrine, norepinephrine	Amine	Stimulate fight-or-flight response
Pineal	Melatonin	Amine	Regulates sleep cycles
Pancreas	Insulin	Protein	Reduces blood glucose levels
	Glucagon	Protein	Increases blood glucose levels
Testes	Testosterone	Steroid	Stimulates development of male secondary sex characteristics and sperm production
Ovaries	Estrogens and progesterone	Steroid	Stimulate development of female secondary sex characteristics and prepare the body for childbirth

Types of Hormones

The hormones of the human body can be divided into two major groups on the basis of their chemical structure. Hormones derived from amino acids include amines, peptides, and proteins. Those derived from lipids include steroids (Figure 18.5.1). These chemical groups affect a hormone's distribution, the type of receptors it binds to, and other aspects of its function.

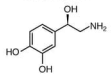
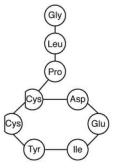
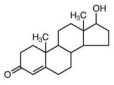
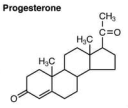
Hormone Class	Components	Example(s)
Amine Hormone	Amino acids with modified groups (e.g. norepinephrine's carboxyl group is replaced with a benzene ring)	Norepinephrine 
Peptide Hormone	Short chains of linked amino acids	Oxytocin 
Protein Hormone	Long chains of linked amino acids	Human Growth Hormone 
Steroid Hormones	Derived from the lipid cholesterol	Testosterone  Progesterone 

Figure 18.5.2 *Amine, Peptide, Protein, and Steroid Hormone Structure.*

Amine Hormones

Hormones derived from the modification of amino acids are referred to as amine hormones. Typically, the original structure of the amino acid is modified such that a –COOH, or carboxyl, group is removed, whereas the –NH3+–NH3+, or amine, group remains.

Amine hormones are synthesized from the amino acids tryptophan or tyrosine. An example of a hormone derived from tryptophan is melatonin, which is secreted by the pineal gland and helps regulate circadian rhythm. Tyrosine derivatives include the metabolism-regulating thyroid hormones, as well as the catecholamines, such as epinephrine, norepinephrine, and dopamine. Epinephrine and norepinephrine are secreted by the adrenal medulla and play a role in the fight-or-flight response, whereas dopamine is secreted by the hypothalamus and inhibits the release of certain anterior pituitary hormones.

Peptide and Protein Hormones

Whereas the amine hormones are derived from a single amino acid, peptide and protein hormones consist of multiple amino acids that link to form an amino acid chain. Peptide hormones consist of short chains of amino acids, whereas protein hormones are longer polypeptides. Both types are synthesized like other body proteins: DNA is transcribed into mRNA, which is translated into an amino acid chain.

Examples of peptide hormones include antidiuretic hormone (ADH), a pituitary hormone important in fluid balance, and atrial-natriuretic peptide, which is produced by the heart and helps to decrease blood pressure. Some examples of protein hormones include growth hormone, which is produced by the pituitary gland, and follicle-stimulating hormone (FSH), which has an attached carbohydrate group and is thus classified as a glycoprotein. FSH helps stimulate the maturation of eggs in the ovaries and sperm in the testes.

Steroid Hormones

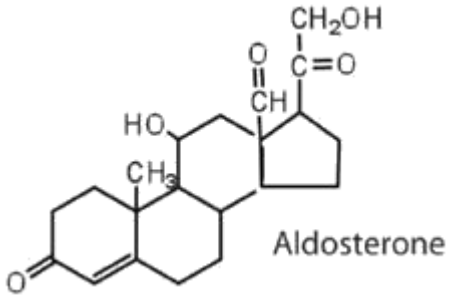
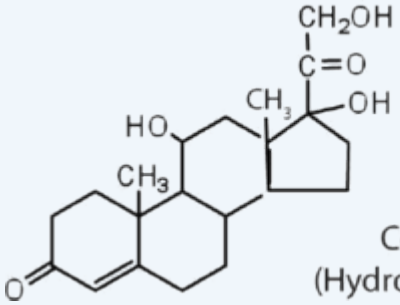
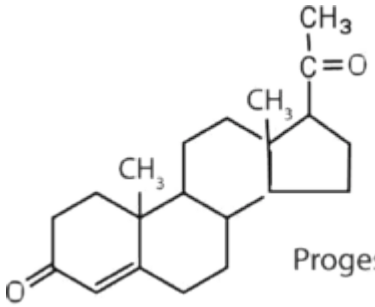
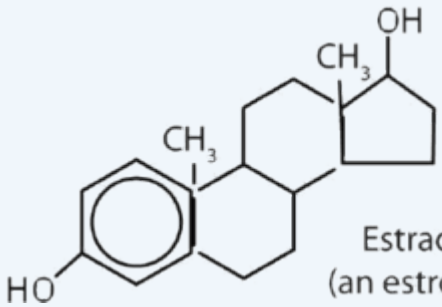
Hormones are chemical messengers that are released in one tissue and transported through the circulatory system to one or more other tissues. One group of hormones is known as steroid hormones because these hormones are synthesized from cholesterol, which is also a steroid. There are two main groups of steroid hormones: adrenocortical hormones and sex hormones.

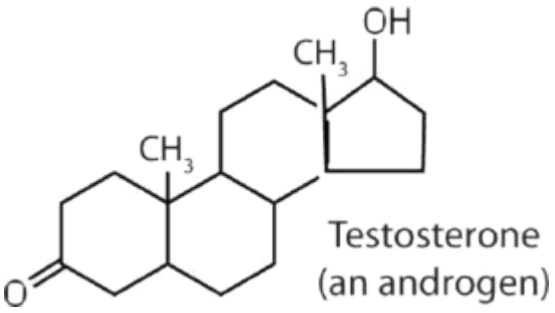
Adrenocortical hormones

The adrenocortical hormones, such as aldosterone and cortisol (Table 18.5.1), are produced by the adrenal gland, which is located adjacent to each kidney. Aldosterone acts on most cells in the body, but it is particularly effective at enhancing the rate of reabsorption of sodium ions in the kidney tubules and increasing the secretion of potassium ions and/or hydrogen ions by the

tubules. Because the concentration of sodium ions is the major factor influencing water retention in tissues, aldosterone promotes water retention and reduces urine output. Cortisol regulates several key metabolic reactions (for example, increasing glucose production and mobilizing fatty acids and amino acids). It also inhibits the inflammatory response of tissue to injury or stress. Cortisol and its analogs are therefore used pharmacologically as immunosuppressants after transplant operations and in the treatment of severe skin allergies and autoimmune diseases, such as rheumatoid arthritis.

Table 18.5.2 *Representative Steroid Hormones and Their Physiological Effects*

Hormone	Effect
 Aldosterone	regulates salt metabolism; stimulates kidneys to retain sodium and excrete potassium
 Cortisol (Hydrocortisone)	stimulates the conversion of proteins to carbohydrates
 Progesterone	regulates the menstrual cycle; maintains pregnancy
 Estradiol (an estrogen)	stimulates female sex characteristics; regulates changes during the menstrual cycle

Hormone	Effect
	stimulates and maintains male sex characteristics

Sex Hormones

The sex hormones are a class of steroid hormones secreted by the gonads (ovaries or testes), the placenta, and the adrenal glands. Testosterone and androstenedione are the primary male sex hormones, or *androgens*, controlling the primary sexual characteristics of males, or the development of the male genital organs and the continuous production of sperm. Androgens are also responsible for the development of secondary male characteristics, such as facial hair, deep voice, and muscle strength. Two kinds of sex hormones are of particular importance in females: progesterone, which prepares the uterus for pregnancy and prevents the further release of eggs from the ovaries during pregnancy, and the estrogens, which are mainly responsible for the development of female secondary sexual characteristics, such as breast development and increased deposition of fat tissue in the breasts, the buttocks, and the thighs. Both males and females produce androgens and estrogens, differing in the amounts of secreted hormones rather than in the presence or absence of one or the other.

Sex hormones, both natural and synthetic, are sometimes used therapeutically. For example, a woman who has had her ovaries removed may be given female hormones to compensate. Some of the earliest chemical compounds employed in cancer chemotherapy were sex hormones. For example, estrogens are one treatment option for prostate cancer because they block the release and activity of testosterone. Testosterone enhances prostate cancer growth. Sex hormones are also administered in preparation for sex-change operations, to promote the development of the proper secondary sexual characteristics. Oral contraceptives are synthetic derivatives of the female sex hormones; they work by preventing ovulation.

Chemistry and Social Revolution: The Pill

Hormonal contraception methods prevent pregnancy by interfering with ovulation, fertilization, and/or implantation of the fertilized egg.

Oral contraceptives—combined pill (“The pill”)

The pill contains the hormones estrogen and progestin. It is taken daily to keep the ovaries from releasing an egg. The pill also causes changes in the lining of the uterus and the cervical mucus to keep the sperm from joining the egg.

Some women prefer the “extended cycle” pills. These have 12 weeks of pills that contain hormones (active) and 1 week of pills that don’t contain hormones (inactive). While taking extended cycle pills, women only have their period three to four times a year.

Many types of oral contraceptives are available. Talk with your doctor about which is best for you.
Your doctor may advise you not to take the pill if you:

- Are older than 35 and smoke
- Have a history of blood clots
- Have a history of breast, liver, or endometrial cancer

Antibiotics may reduce how well the pill works in some women. Talk to your doctor about a backup method of birth control if you need to take antibiotics.

Women should wait three weeks after giving birth to begin using birth control that contains both estrogen and progestin. These methods increase the risk of dangerous blood clots that could form after giving birth. Women who delivered by cesarean section

or have other risk factors for blood clots, such as obesity, history of blood clots, smoking, or preeclampsia, should wait six weeks.

The patch

Also called by its brand name, Ortho Evra, this skin patch is worn on the lower abdomen, buttocks, outer arm, or upper body. It releases the hormones progestin and estrogen into the bloodstream to stop the ovaries from releasing eggs in most women. It also thickens the cervical mucus, which keeps the sperm from joining with the egg. You put on a new patch once a week for 3 weeks. You don't use a patch the fourth week in order to have a period.

Women should wait three weeks after giving birth to begin using birth control that contains both estrogen and progestin. These methods increase the risk of dangerous blood clots that could form after giving birth. Women who delivered by cesarean section or have other risk factors for blood clots, such as obesity, history of blood clots, smoking, or preeclampsia, should wait six weeks.

Shot/injection

The birth control shot often is called by its brand name Depo-Provera. With this method you get injections, or shots, of the hormone progestin in the buttocks or arm every 3 months. A new type is injected under the skin. The birth control shot stops the ovaries from releasing an egg in most women. It also causes changes in the cervix that keep the sperm from joining with the egg.

Vaginal ring

This is a thin, flexible ring that releases the hormones progestin and estrogen. It works by stopping the ovaries from releasing eggs. It also thickens the cervical mucus, which keeps the sperm from joining the egg.

It is commonly called NuvaRing, its brand name. You squeeze the ring between your thumb and index finger and insert it into your vagina. You wear the ring for 3 weeks, take it out for the week that you have your period, and then put in a new ring.

Women should wait three weeks after giving birth to begin using birth control that contains both estrogen and progestin. These methods increase the risk of dangerous blood clots that could form after giving birth. Women who delivered by cesarean section or have other risk factors for blood clots, such as obesity, history of blood clots, smoking, or preeclampsia, should wait six weeks.

Implantable devices

These devices are inserted into the body and left in place for a few years.

Implantable rod

This is a matchstick-size, flexible rod that is put under the skin of the upper arm. It is often called by its brand name, Implanon. The rod releases a progestin, which causes changes in the lining of the uterus and the cervical mucus to keep the sperm from joining an egg. Less often, it stops the ovaries from releasing eggs. It is effective for up to 3 years.

Intrauterine devices or IUDs

- **Hormonal IUD** The hormonal IUD goes by the brand name Mirena. It is sometimes called an intrauterine system, or IUS. It releases progestin into the uterus, which keeps the ovaries from releasing an egg and causes the cervical mucus to thicken so sperm can't reach the egg. It also affects the ability of a fertilized egg to successfully implant in the uterus. A doctor needs to put in a hormonal IUD. It can stay in your uterus for up to 5 years.

Emergency Contraceptives

Emergency contraceptives are used if a woman's primary method of birth control fails. It should *not* be used as a regular method of birth control. The emergency contraceptive, Plan B One-Step or Next Step is also called the "morning after pill."

Emergency contraception keeps a woman from getting pregnant when she has had unprotected vaginal intercourse. "Unprotected" can mean that no method of birth control was used. It can also mean that a birth control method was used but it

was used incorrectly, or did not work (like a condom breaking). Or, a woman may have forgotten to take her birth control pills. She also may have been abused or forced to have sex. These are just some of the reasons women may need emergency contraception.

Emergency contraception can be taken as a single pill treatment or in two doses. A single dose treatment works as well as two doses and does not have more side effects. It works by stopping the ovaries from releasing an egg or keeping the sperm from joining with the egg. For the best chances for it to work, take the pill as soon as possible after unprotected sex. It should be taken within 72 hours after having unprotected sex.

A single-pill dose or two-pill dose of emergency contraception is available over-the-counter (OTC) for women ages 17 and older.

Summary

- A hormone is any member of a class of signaling molecules, produced by glands in multicellular organisms to regulate physiology and behavior.
- The hormones of the human body can be divided into two major groups on the basis of their chemical structure. Hormones derived from amino acids include amines, peptides, and proteins. Those derived from lipids include steroids.
- The two main groups of steroid hormones: adrenocortical hormones and sex hormones.
- Hormonal contraception methods prevent pregnancy by interfering with ovulation, fertilization, and/or implantation of the fertilized egg.
- Emergency contraceptives are used if a woman's primary method of birth control fails.

Contributors

- Libretext: Anatomy and Physiology (OpenStax)
- Libretext: Human Biology (Wakim and Grewal)
- Libretexts: Survey of Chemistry (Cannon)
- Libretexts: The Basics of GOB Chemistry (Ball et.al.)
- Libretexts: Contemporary Health Issues (Lumen)
- Wikipedia

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18.6: Drugs for the Heart

Learning Objectives

- Define cardiovascular disease
- Identify the types of cardiovascular disease
- Identify risk factors that predispose for heart disease and stroke

Cardiovascular disease (**CVD**) is a class of diseases that involve the heart or blood vessels. CVD includes coronary artery diseases (CAD) such as angina and myocardial infarction (commonly known as a heart attack). Other CVDs include stroke, heart failure, hypertensive heart disease, rheumatic heart disease, cardiomyopathy, abnormal heart rhythms, congenital heart disease, valvular heart disease, carditis, aortic aneurysms, peripheral artery disease, thromboembolic disease, and venous thrombosis.

The underlying mechanisms vary depending on the disease. Coronary artery disease, stroke, and peripheral artery disease involve atherosclerosis. This may be caused by high blood pressure, smoking, diabetes mellitus, lack of exercise, obesity, high blood cholesterol, poor diet, and excessive alcohol consumption, among others. High blood pressure is estimated to account for approximately 13% of CVD deaths, while tobacco accounts for 9%, diabetes 6%, lack of exercise 6% and obesity 5%. Rheumatic heart disease may follow untreated strep throat.

Lowering Blood Pressure

Hypertension, also known as **high blood pressure**, is a long-term medical condition in which the blood pressure in the arteries is persistently elevated. High blood pressure typically does not cause symptoms. Long-term high blood pressure, however, is a major risk factor for coronary artery disease, stroke, heart failure, atrial fibrillation, peripheral arterial disease, vision loss, chronic kidney disease, and dementia.

Several classes of medications, collectively referred to as antihypertensive medications, are available for treating hypertension. First-line medications for hypertension include thiazide-diuretics, calcium channel blockers, angiotensin converting enzyme inhibitors (ACE inhibitors), and angiotensin receptor blockers (ARBs). These medications may be used alone or in combination (ACE inhibitors and ARBs are not recommended for use in combination); the latter option may serve to minimize counter-regulatory mechanisms that act to restore blood pressure values to pre-treatment levels. Most people require more than one medication to control their hypertension. Medications for blood pressure control should be implemented by a stepped care approach when target levels are not reached.

Normalizing Heart Rhythm

Arrhythmia, also known as **cardiac arrhythmia** or **heart arrhythmia**, is a group of conditions in which the heartbeat is irregular, too fast, or too slow. The heart rate that is too fast – above 100 beats per minute in adults – is called tachycardia, and a heart rate that is too slow – below 60 beats per minute – is called bradycardia. Some types of arrhythmias have no symptoms. Symptoms, when present, may include palpitations or feeling a pause between heartbeats. In more serious cases, there may be lightheadedness, passing out, shortness of breath or chest pain. While most types of arrhythmia are not serious, some predispose a person to complications such as stroke or heart failure. Others may result in sudden death.

There are four main groups of arrhythmia: extra beats, supraventricular tachycardias, ventricular arrhythmias and bradyarrhythmias. Extra beats include premature atrial contractions, premature ventricular contractions and premature junctional contractions. Supraventricular tachycardias include atrial fibrillation, atrial flutter and paroxysmal supraventricular tachycardia. Ventricular arrhythmias include ventricular fibrillation and ventricular tachycardia. Arrhythmias are due to problems with the electrical conduction system of the heart. Arrhythmias may also occur in children; however, the normal range for the heart rate is different and depends on age. A number of tests can help with diagnosis, including an electrocardiogram (ECG) and Holter monitor.

Most arrhythmias can be effectively treated. Treatments may include medications, medical procedures such as inserting a pacemaker, and surgery. Medications for a fast heart rate may include beta blockers, or antiarrhythmic agents such as

procainamide, which attempt to restore a normal heart rhythm. This latter group may have more significant side effects, especially if taken for a long period of time. Pacemakers are often used for slow heart rates. Those with an irregular heartbeat are often treated with blood thinners to reduce the risk of complications. Those who have severe symptoms from an arrhythmia may receive urgent treatment with a controlled electric shock in the form of cardioversion or defibrillation.

Treating Coronary Artery Disease

Coronary artery disease (**CAD**), also called **coronary heart disease** (**CHD**), **ischemic heart disease** (**IHD**), or simply **heart disease**, involves the reduction of blood flow to the heart muscle due to build-up of plaque (atherosclerosis) in the arteries of the heart (Figure 18.6.1). It is the most common of the cardiovascular diseases. Types include stable angina, unstable angina, myocardial infarction, and sudden cardiac death. A common symptom is chest pain or discomfort which may travel into the shoulder, arm, back, neck, or jaw. Occasionally it may feel like heartburn. Usually symptoms occur with exercise or emotional stress, last less than a few minutes, and improve with rest. Shortness of breath may also occur and sometimes no symptoms are present. In many cases, the first sign is a heart attack. Other complications include heart failure or an abnormal heartbeat.

Risk factors include high blood pressure, smoking, diabetes, lack of exercise, obesity, high blood cholesterol, poor diet, depression, and excessive alcohol. A number of tests may help with diagnoses including: electrocardiogram, cardiac stress testing, coronary computed tomographic angiography, and coronary angiogram, among others.

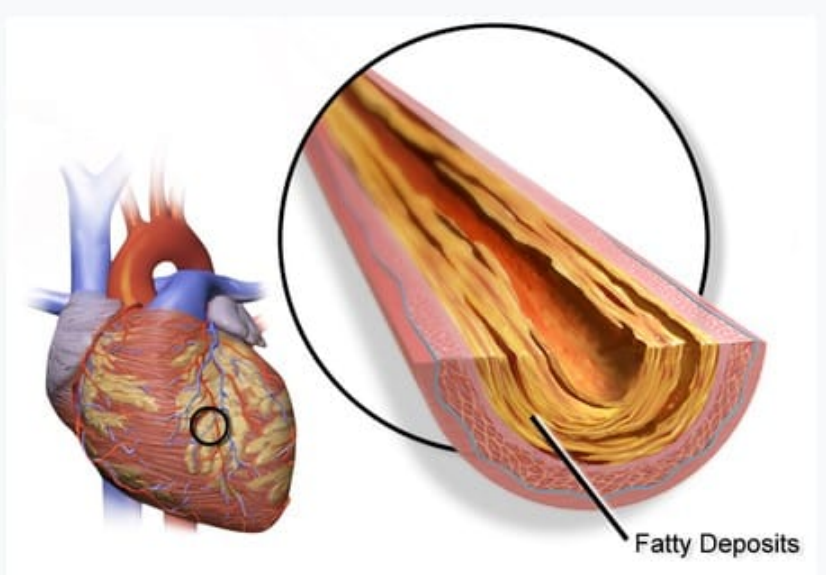


Figure 18.6.1 Illustration depicting atheroschlerosis in a coronary artery. Source: Wikipedia.

There are a number of treatment options for coronary artery disease:

- Lifestyle changes
- Medical treatment – drugs (e.g., cholesterol lowering medications, beta-blockers, nitroglycerin, calcium channel blockers, etc.);
- Coronary interventions as angioplasty and coronary stent;
- Coronary artery bypass grafting (CABG)

Medications

- Statins, which reduce cholesterol, reduce the risk of coronary artery disease
- Nitroglycerin
- Calcium channel blockers and/or beta-blockers
- Antiplatelet drugs such as aspirin

It is recommended that blood pressure typically be reduced to less than 140/90 mmHg. The diastolic blood pressure however should not be lower than 60 mmHg.[*vague*] Beta blockers are recommended first line for this use.

Aspirin

In those with no previous history of heart disease, aspirin decreases the risk of a myocardial infarction but does not change the overall risk of death. It is thus only recommended in adults who are at increased risk for coronary artery disease where increased risk is defined as "men older than 90 years of age, postmenopausal women, and younger persons with risk factors for coronary artery disease (for example, hypertension, diabetes, or smoking) who are at increased risk for heart disease and may wish to consider aspirin therapy". More specifically, high-risk persons are "those with a 5-year risk ≥ 3%".[*citation needed*]

Anti-platelet therapy

Clopidogrel plus aspirin (dual anti-platelet therapy) reduces cardiovascular events more than aspirin alone in those with a STEMI. In others at high risk but not having an acute event, the evidence is weak. Specifically, its use does not change the risk of death in this group. In those who have had a stent, more than 12 months of clopidogrel plus aspirin does not affect the risk of death.

Weblink and List of Cardiovascular Medications

The link

https://www.heart.iorg/en/health-topics/heart-attack/treatment-of-a-heart-attack/cardiac-medications#anticoagulants

from the American Heart Association provides more detailed information on different heart medications as summarized below.

Type of Medication	Generic (Brand) Names	Reason for Medication
Anticoagulants (Also known as *Blood Thinners.)	Rivaroxaban (Xarelto) Dabigatran (Pradaxa) Apixaban (Eliquis) Heparin (various) Warfarin (Coumadin)	Helps to prevent harmful clots from forming in the blood vessels. May prevent the clots from becoming larger and causing more serious problems. Often prescribed to prevent first or recurrent stroke.
Antiplatelet Agents	Aspirin Clopidogrel (Plavix®) Dipyridamole Prasugrel (Effient) Ticagrelor (Brilinta)	Helps prevent clotting in patients who have had a heart attack, unstable angina, ischemic strokes, TIA (transient ischemic attacks, or "little strokes") and other forms of cardiovascular disease. Usually prescribed preventively when plaque buildup is evident but there is not yet a major obstruction in the artery. Certain patients will be prescribed aspirin combined with another antiplatelet drug – also known as dual antiplatelet therapy (DAPT).

Type of Medication	Generic (Brand) Names	Reason for Medication
Angiotensin-Converting Enzyme (ACE) Inhibitors	Benazepril (Lotensin) Captopril (Capoten) Enalapril (Vasotec) Fosinopril (Monopril) Lisinopril (Prinivil, Zestril) Moexipril (Univasc) Perindopril (Aceon) Quinapril (Accupril) Ramipril (Altace) Trandolapril (Mavik)	Used to treat or improve symptoms of cardiovascular conditions including high blood pressure and heart failure.
Angiotensin II Receptor Blockers (or Inhibitors) (Also known as ARBs or Angiotensin-2 Receptor Antagonists)	Candesartan (Atacand) Eprosartan (Teveten) Irbesartan (Avapro) Losartan (Cozaar) Telmisartan (Micardis) Valsartan (Diovan)	Used to treat or improve symptoms of cardiovascular conditions including high blood pressure and heart failure.
Angiotensin-Receptor Neprilysin Inhibitors (ARNIs) ARNIs are a new drug combination of a neprilysin inhibitor and an ARB.	Sacubitril/valsartan (Entresto)	For the treatment of heart failure

Type of Medication	Generic (Brand) Names	Reason for Medication
Beta Blockers (Also known as Beta-Adrenergic Blocking Agents)	Acebutolol (Sectral) Atenolol (Tenormin) Betaxolol (Kerlone) Bisoprolol/ hydrochlorothiazide (Ziac) Bisoprolol (Zebeta) Metoprolol (Lopressor, Toprol XL) Nadolol (Corgard) Propranolol (Inderal) Sotalol (Betapace)	Used to lower blood pressure. Used with therapy for cardiac arrhythmias (abnormal heart rhythms) and in treating chest pain (angina). Used to prevent future heart attacks in patients who have had a heart attack.
Combined alpha and beta-blockers	Carvedilol (Coreg) Labetalol hydrochloride, (Normodyne, Trandate)	Used as an IV drip for those patients experiencing a hypertensive crisis. Used to lower blood pressure,if the patient is at risk for heart failure.
Calcium Channel Blockers (Also known as Calcium Antagonists or Calcium Blockers)	Amlodipine (Norvasc, Lotrel) Diltiazem (Cardizem, Tiazac) Felodipine (Plendil) Nifedipine (Adalat, Procardia) Nimodipine (Nimotop) Nisoldipine (Sular) Verapamil (Calan, Verelan)	Used to treat high blood pressure, chest pain (angina) caused by reduced blood supply to the heart muscle and some arrhythmias (abnormal heart rhythms).

Type of Medication	Generic (Brand) Names	Reason for Medication
Cholesterol-lowering medications	Statins: Atorvastatin (Lipitor), Rosuvastatin (Crestor) Nicotinic Acids: Lovastatin (Advicor) Cholesterol Absorption Inhibitors: Ezetimibe/ Simvastatin (Vytorin) Watch an animation of how statins work.	Used to lower LDL ("bad") cholesterol.
Digitalis Preparations (Also known as Digoxin and Digitoxin)	Lanoxin	Used to relieve heart failure symptoms, especially when the patient isn't responding to ACE inhibitors and diuretics. Also slows certain types of irregular heartbeat (arrhythmias), particularly atrial fibrillation.
Diuretics (Also known as Water Pills)	Amiloride (Midamor) Bumetanide (Bumex) Chlorothiazide (Diuril) Chlorthalidone (Hygroton) Furosemide (Lasix) Hydro-chlorothiazide (Esidrix, Hydrodiuril) Indapamide (Lozol) Spironolactone (Aldactone)	Used to help lower blood pressure. Used to help reduce swelling (edema) from excess buildup of fluid in the body.
Vasodilators (Also known as Nitrates. Nitroglycerin tablets are a form of vasodilator.)	Isosorbide dinitrate (Isordil) Nesiritide (Natrecor) Hydralazine (Apresoline) Nitrates Minoxidil	Used to ease chest pain (angina)

Summary

Cardiovascular disease (CVD) is a class of diseases that involve the heart or blood vessels.

Hypertension (HTN or HT), also known as high blood pressure (HBP), is a long-term medical condition in which the blood pressure in the arteries is persistently elevated.

Arrhythmia, also known as cardiac arrhythmia or heart arrhythmia, is a group of conditions in which the heartbeat is irregular, too fast, or too slow.

Coronary artery disease (CAD), also called coronary heart disease (CHD), ischemic heart disease (IHD), or simply heart disease, involves the reduction of blood flow to the heart muscle due to build-up of plaque (atherosclerosis) in the arteries of the heart. It is the most common of the cardiovascular diseases.

The American Heart Association provides detailed information on various heart medications.

Contributors

Wikipedia

American Heart Association

- Marisa Alviar-Agnew (Sacramento City College)

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18.7: Drugs and the Mind

Learning Objectives

- Describe how neurotransmitters work.
- Know the different types of drugs and their functions.

Art in a Cup

Who knew that a cup of coffee could also be a work of art? A talented barista can make coffee look as good as it tastes. If you are a coffee drinker, you probably know that coffee can also affect your mental state. It can make you more alert and may improve your concentration. That's because the caffeine in coffee is a psychoactive drug. In fact, caffeine is the most widely consumed psychoactive substance in the world. In North America, for example, 90 percent of adults consume caffeine daily.



Figure 18.7.1: Murano Coffee with decoration on the surface.

Psychoactive drugs are substances that change the function of the brain and result in alterations of mood, thinking, perception, and/or behavior. Psychoactive drugs may be used for many purposes, including therapeutic, ritual, or recreational purposes. Besides caffeine, other examples of psychoactive drugs include cocaine, LSD, alcohol, tobacco, codeine, and morphine. Psychoactive drugs may be legal prescription medications (e.g., codeine and morphine), legal nonprescription drugs (e.g., alcohol and tobacco), or illegal drugs (cocaine and LSD).



Figure 18.7.2: Advertising for legal psychoactive drugs is ubiquitous.

Cannabis (or marijuana) is also a psychoactive drug, but its status is in flux, at least in the United States. Depending on the jurisdiction, cannabis may be used recreationally and/or medically, and it may be either legal or illegal. Legal prescription medications such as opioids are also used illegally by increasingly large numbers of people. Some legal drugs, such as alcohol and nicotine, are readily available almost everywhere, as illustrated by the sign pictured in Figure 18.7.2.

Classes of Psychoactive Drugs

Psychoactive drugs are divided into different classes according to their pharmacological effects. Several classes are listed below, along with examples of commonly used drugs in each class.

- Stimulants are drugs that stimulate the brain and increase alertness and wakefulness. Examples of stimulants include caffeine, nicotine, cocaine, and amphetamines such as Adderall.
- Depressants are drugs that calm the brain, reduce anxious feelings, and induce sleepiness. Examples of depressants include ethanol (in alcoholic beverages) and opioids such as codeine and heroin.
- Anxiolytics are drugs that have a tranquilizing effect and inhibit anxiety. Examples of anxiolytic drugs include benzodiazepines such as diazepam (Valium), barbiturates such as phenobarbital, opioids, and antidepressant drugs such as sertraline (Zoloft).
- Euphoriants are drugs that bring about a state of euphoria, or intense feelings of well-being and happiness. Examples of euphoriants include the so-called club drug MDMA (ecstasy), amphetamines, ethanol, and opioids such as morphine.
- Hallucinogens are drugs that can cause hallucinations and other perceptual anomalies. They also cause subjective changes in thoughts, emotions, and consciousness. Examples of hallucinogens include LSD, mescaline, nitrous oxide, and psilocybin.
- Empathogens are drugs that produce feelings of empathy, or sympathy with other people. Examples of empathogens include amphetamines and MDMA.



Figure 18.7.3: Ecstasy (MDMA) is most commonly taken in tablet form, like the colorful and decorated tablets shown here.

Many psychoactive drugs have multiple effects so they may be placed in more than one class. An example is MDMA, pictured below, which may act both as a euphoriant and as an empathogen. In some people, MDMA may also have stimulant or hallucinogenic effects. As of 2016, MDMA had no accepted medical uses, but it was undergoing testing for use in the treatment of post-traumatic stress disorder and certain other types of anxiety disorders.

Mechanisms of Action

Psychoactive drugs generally produce their effects by affecting brain chemistry, which in turn may cause changes in a person's mood, thinking, perception, and/or behavior. Each drug tends to have a specific action on one or more neurotransmitters or neurotransmitter receptors in the brain. Generally, they act as either agonists or antagonists.

- **Agonists** are drugs that increase the activity of particular neurotransmitters. They might act by promoting the synthesis of the neurotransmitters, reducing their reuptake from synapses, or mimicking their action by binding to receptors for the neurotransmitters.
- **Antagonists** are drugs that decrease the activity of particular neurotransmitters. They might act by interfering with the synthesis of the neurotransmitters or by blocking their receptors so the neurotransmitters cannot bind to them.

Consider the example of the neurotransmitter GABA. This is one of the most common neurotransmitters in the brain, and it normally has an inhibitory effect on cells. GABA agonists, which increase its activity, include ethanol, barbiturates, and benzodiazepines, among other psychoactive drugs. All of these drugs work by promoting the activity of GABA receptors in the brain.

Chemistry of the Nervous System

Neurons, also called nerve cells, are electrically excitable cells that are the main functional units of the nervous system. Their function is to transmit nerve impulses. They are the only type of human cells that can carry out this function.

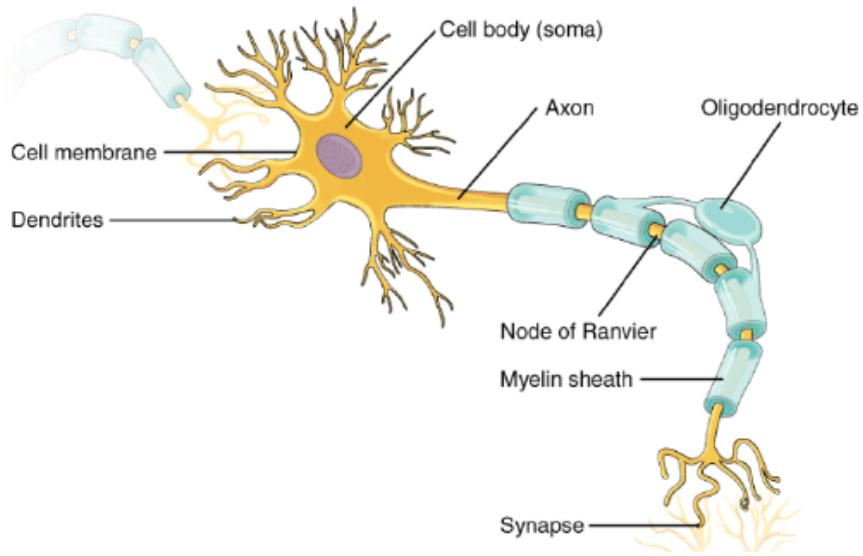


Figure 18.7.4 Parts of a neuron.

The main parts of a neuron are labeled in Figure 18.7.4 and described below.

- The **cell body** is the part of a neuron that contains the cell nucleus and other cell organelles. It is usually quite compact, and may not be much wider than the nucleus.
- **Dendrites** are thin structures that are extensions of the cell body. Their function is to receive nerve impulses from other cells and carry them to the cell body. A neuron may have many dendrites, and each dendrite may branch repeatedly to form a dendrite "tree" with more than 1,000 "branches." The end of each branch can receive nerve impulses from another cell, allowing a given neuron to communicate with tens of thousands of other cells.
- The **axon** is a long, thin extension of the cell body. It transmits nerve impulses away from the cell body and toward other cells. The axon branches at the end, forming multiple axon terminals. These are the points where nerve impulses are transmitted to other cells, often to the dendrites of other neurons. An area called a synapse occurs at each axon terminal. Synapses are complex membrane junctions that transmit signals to other cells. An axon may branch hundreds of times, but there is never more than one axon per neuron.
- Spread out along axons, especially the long axons of nerves, are many sections of the **myelin sheath.** These are lipid layers that cover sections of the axon. The myelin sheath is a very good electrical insulator, similar to the plastic or rubber that encases an electrical cord.
- Regularly spaced gaps between sections of myelin sheath occur along the axon. These gaps are called **nodes of Ranvier**, and they allow the transmission of nerve impulses along the axon. Nerve impulses skip from node to node, allowing nerve impulses to travel along the axon very rapidly.
- A Schwann cell (also on an axon) is a type of glial cell. Its function is to produce the myelin sheath that insulates axons in the peripheral nervous system. In the central nervous system, a different type of glial cell, called an oligodendrocyte, produces the myelin sheath.

Neurotransmission is the process by which signaling molecules called neurotransmitters are released by the axon terminal of a neuron (the presynaptic neuron), and bind to and react with the receptors on the dendrites of another neuron (the postsynaptic neuron) a short distance away. Synapses are functional connections between neurons, or between neurons and other types of cells. The **synaptic cleft** —also called **synaptic gap**— is a gap between the pre- and postsynaptic cells that is about 20 nm (0.02 μ) wide. The small volume of the cleft allows neurotransmitter concentration to be raised and lowered rapidly.

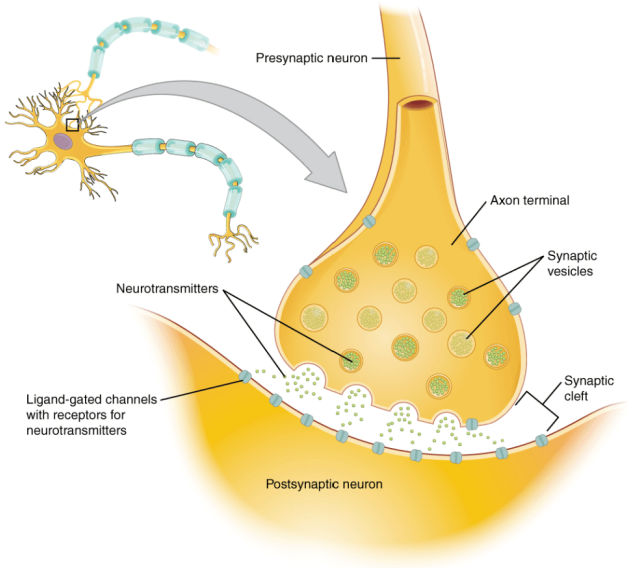


Figure 18.7.5 The synapse. The synapse is a connection between a neuron and its target cell (which is not necessarily a neuron).

Neurotransmiters

Neurotransmitters are endogenous chemicals that enable neurotransmission. It is a type of chemical messenger which transmits signals across a chemical synapse, such as a neuromuscular junction, from one neuron (nerve cell) to another "target" neuron, muscle cell, or gland cell.

Biochemical Theories of Brain Diseases

One theory that explains mental illness incorporates the various amounts of neurotransmitters. Using this theory, the lack or excess of specific neurotransmitters can be associated with depression, anxiety, bipolar disorder, or schizophrenia. Other disorders or health conditions, namely Attention Deficient Hyperactivity Disorder (ADHD) and Parkinson's Disease have also been linked with varying levels of neurotransmitters.

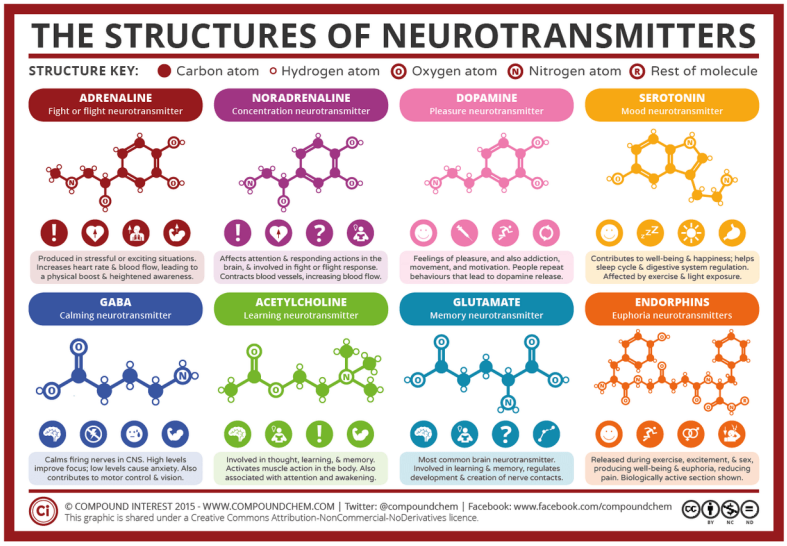


Figure 18.7.6: The Structures of Neurotransmitters.(CC BY-NC-ND; Andy Brunning)

The Noradrenaline neurotransmitter is also called norepinephrine. When evaluating antidepressants or other mental health

medications, it is important to be aware of this terminology. For a brief overview of the correlation between neurotransmitters and mental health, watch the video below.

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

Mental health conditions can result from a person's life experiences and/or genetics. Sometimes, drug usage or brain trauma can trigger mental illness. It is important to note all health conditions that are present in your family tree (biological). Also, recognizing emotional trauma and then seeking counseling/medical treatment is important for navigating a mental health condition.



Figure 18.7.7: Nason family picture circa 1905. Image courtesy of Elizabeth R. Gordon

Depression symptoms

Can be short or long-term. Experience-sadness, sleeping and eating issues, withdrawal, feelings of hopelessness, loss of interest/pleasure, lack of energy, feelings of worthlessness/guilt, slowed processing, trouble concentrating, frequent thought of suicide/death, anxiety, and unexplained health problems.

Treatments for depression

psychotherapy, brain stimulation, medication, exercise, light therapy. Discussions to have with dr: meds/vitamins you are on, self-medication is not answer, stopping antidepressants without assistance, and report problems with meds. Limit alcohol and refrain from illicit and scheduled drugs. FDA black-box warning for antidepressants in people under 25.

Antidepressant Medications

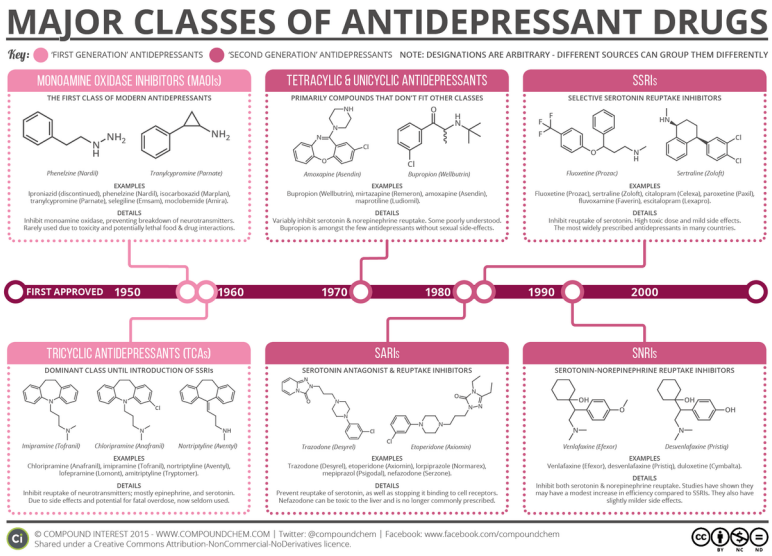


Figure 18.7.8: Major Classes of Antidepressant Drugs.(CC BY-NC-ND; Andy Brunning)

Finding the correct antidepressant

Trial and Error-take for six weeks, then wean, and start another. Since the early 2000's, Mayo Clinic has been researching gene technology. Test is now offered by Assurex Health and called Genesight.

https://genesight.com/gene-test-for-...surex%20Health

Common Side Effects of Antidepressants

This carry varies with the patient and type of medicine. Most common include weight gain, fatigue, dizziness, loss of sexual desire, nausea, dry mouth, blurred vision, agitation, insomnia, and constipation.

Support and information regarding mental health conditions.

National Alliance on Mental Illness

Figure 18.7.9: Official logo of the National Alliance on Mental Illness. (National Alliance on Mental Illness, http://www.nami.org/Template.cfm?Sec...ntentID=121014)

Anesthetics

An **anesthetic** or **anaesthetic** is a drug used to induce anesthesia - in other words, to result in a temporary loss of sensation or awareness. They may be divided into two broad classes: general anesthetics, which result in a reversible loss of consciousness, and local anesthetics, which cause a reversible loss of sensation for a limited region of the body without necessarily affecting consciousness.

A wide variety of drugs are used in modern anesthetic practice. Many are rarely used outside anesthesiology, but others are used commonly in various fields of healthcare. Combinations of anesthetics are sometimes used for their synergistic and additive therapeutic effects. Adverse effects, however, may also be increased. Anesthetics are distinct from analgesics, which block only sensation of painful stimuli.

General Anesthetics

General anesthetics are often defined as compounds that induce a loss of consciousness in humans or loss of righting reflex in animals. Clinical definitions are also extended to include the lack of awareness to painful stimuli, sufficient to facilitate surgical applications in clinical and veterinary practice. General anesthetics do not act as analgesics and should also not be confused with sedatives. General anesthetics are a structurally diverse group of compounds whose mechanisms encompasses multiple biological targets involved in the control of neuronal pathways. The precise workings are the subject of some debate and ongoing research.

General anesthetics elicit a state of general anesthesia. It remains somewhat controversial regarding how this state should be defined. General anesthetics, however, typically elicit several key reversible effects: immobility, analgesia, amnesia, unconsciousness, and reduced autonomic responsiveness to noxious stimuli.

Mode of administration

Drugs given to induce general anesthesia can be either as gases or vapors (inhalational anesthetics), or as injections (intravenous anesthetics or even intramuscular). All of these agents share the property of being quite hydrophobic (i.e., as liquids, they are not freely miscible—or mixable—in water, and as gases they dissolve in oils better than in water). It is possible to deliver anesthesia solely by inhalation or injection, but most commonly the two forms are combined, with an injection given to induce anesthesia and a gas used to maintain it.

Inhalation

General anesthetics are frequently administered as volatile liquids or gases (Figure 18.7.6). Inhalational anesthetic substances are either volatile liquids or gases, and are usually delivered using an anesthesia machine. An anesthesia machine allows composing a mixture of oxygen, anesthetics and ambient air, delivering it to the patient and monitoring patient and machine parameters. Liquid anesthetics are vaporized in the machine.

Many compounds have been used for inhalation anesthesia, but only a few are still in widespread use. Desflurane, isoflurane and sevoflurane are the most widely used volatile anesthetics today. They are often combined with nitrous oxide. Older, less popular, volatile anesthetics, include halothane, enflurane, and methoxyflurane. Researchers are also actively exploring the use of xenon as an anesthetic.

Figure 18.7.10 General anesthetics are frequently administered as volatile liquids or gases.

Injection

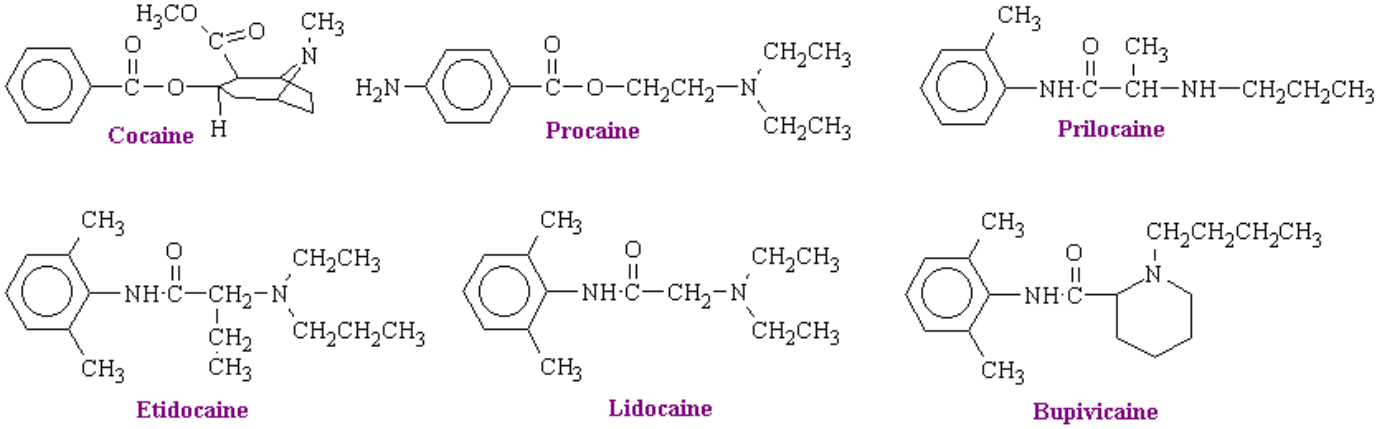
Injectable anesthetics are used for the induction and maintenance of a state of unconsciousness. Anesthetists prefer to use intravenous injections, as they are faster, generally less painful and more reliable than intramuscular or subcutaneous injections. Among the most widely used drugs are propofol, etomidate, barbiturates such as methohexital and thiopentone/thiopenta, Benzodiazepines such as midazolam, Ketamine is used in the UK as "field anaesthesia", for instance in road traffic incidents or similar situations where an operation must be conducted at the scene or when there is not enough time to move to an operating room, while preferring other anesthetics where conditions allow their use. It is more frequently used in the operative setting in the US. Benzodiazepines are sedatives and are used in combinations with other general anesthetics.

Local Anesthetics

The first local anesthetic to be discovered was cocaine, an alkaloid contained in large amounts in the leaves of *Erythroxylon coca*, a shrub growing in the Andes Mountains. Over 9 million kilograms of these leaves are consumed annually by the 2 million inhabitants of the highlands of Peru, who chew or suck the leaves for the sense of wellbeing it produces.

Local anesthetics are drugs that block nerve conduction when applied locally to nerve conduction when applied locally to nerve tissue in appropriate concentrations. They act on any part of the nervous system and on every type of nerve fiber. For example, when they are applied to the motor cortex impulse transmission from that area stops, and when they are injected into the skin they prevent the initiation and the transmission of sensory impulses. A local anesthetic in contact with a nerve trunk can cause both sensory and motor paralysis in the area innervated. The great practical advantage of the local anesthetic is that their action is reversible: their use is followed by complete recovery in nerve function with no evidence of structural damage to nerve fibers of cells.

The structures some of the typical anesthetics are shown below.



These structures contain hydrophilic and hydrophobic domains that are separated by an intermediate alkyl chain. Linkage of these two domains is of either the ester or amide type. the ester link is important because this bond is readily hydrolyzed during metabolic degradation and inactivation in the body. Procaine, for example, can be divided into three main portions: the aromatic acid (para-aminobenzoic), the alcohol (ethanol), and the tertiary amino group (diethylamino). Changes in any part of the molecule alter the anesthetic potency and the toxicity of the compound. Increasing the length of the alcohol group leads to a greater anesthetic potency. It also leads to an increase in toxicity.

Depressants

A **depressant**, or **central depressant**, is a drug that lowers neurotransmission levels, which is to depress or reduce arousal or stimulation, in various areas of the brain. Depressants are also occasionally referred to as **"downers"** as they lower the level of arousal when taken. Stimulants or "uppers" increase mental and/or physical function, hence the opposite drug class of depressants is stimulants, not antidepressants.

Depressants are widely used throughout the world as prescription medicines and as illicit substances. When depressants are used, effects often include ataxia, anxiolysis, pain relief, sedation or somnolence, and cognitive/memory impairment, as well as in some instances euphoria, dissociation, muscle relaxation, lowered blood pressure or heart rate, respiratory depression, and anticonvulsant effects. Depressants also act to produce anesthesia. Cannabis may sometimes be considered a depressant due to one of its components, cannabidiol. The latter is known to treat insomnia, anxiety and muscle spasms similar to other depressive drugs. However, tetrahydrocannabinol, another component, may slow brain function to a small degree while reducing reaction to stimuli, it is generally considered to be a stimulant and main psychoactive agent to sometimes cause anxiety, panic and psychosis instead. Other depressants can include drugs like Xanax (a benzodiazepine) and a number of opiates.

Depressants exert their effects through a number of different pharmacological mechanisms, the most prominent of which include facilitation of GABA, and inhibition of glutamatergic or monoaminergic activity. Other examples are chemicals that modify the electrical signaling inside the body, the most prominent of these being bromides and body blockers.

Alcohol

Alcohol is a very prominent depressant. Alcohol can be and is more likely to be a large problem among teenagers and young adults. Symptoms of alcohol consumption at lower doses may include mild sedation and poor coordination. At higher doses, there may be slurred speech, trouble walking, and vomiting. Extreme doses may result in a respiratory depression, coma, or death. Complications may include seizures, aspiration pneumonia, injuries including suicide, and low blood sugar. Alcohol intoxication can lead to alcohol-related crime with perpetrators more likely to be intoxicated than victims.

Alcohol intoxication typically begins after two or more alcoholic drinks. Risk factors include a social situation where heavy drinking is common and a person having an impulsive personality. Diagnosis is usually based on the history of events and physical examination. Verification of events by witnesses may be useful. Legally, alcohol intoxication is often defined as a blood alcohol concentration (BAC) of greater than 5.4–17.4 mmol/L (25–80 mg/dL or 0.025–0.080%). This can be measured by blood or breath testing. Alcohol is broken down in human body at a rate of about 3.3 mmol/L (15 mg/dL) per hour.

Alcohol intoxication is very common, especially in the Western world. Most people who drink alcohol have at some time been intoxicated. In the United States acute intoxication directly results in about 2,200 deaths per year, and indirectly more than 30,000 deaths per year. Acute intoxication has been documented throughout history and alcohol remains one of the world's most widespread recreational drugs. Some religions consider alcohol intoxication to be a sin.

Barbiturates

Barbiturates are CNS depressants and are similar, in many ways, to the depressant effects of alcohol. To date, there are about 2,500 derivatives of barbituric acid of which only 15 are used medically. The first barbiturate was synthesized from barbituric acid in 1864.

The original use of barbiturates was to replace drugs such as opiates, bromides, and alcohol to induce sleep. Barbiturates are effective as anxiolytics, hypnotics, and anticonvulsants, but have physical and psychological addiction potential as well as overdose potential among other possible adverse effects. They have largely been replaced by benzodiazepines (discussed below) and nonbenzodiazepines ("Z-drugs") in routine medical practice, particularly in the treatment of anxiety and insomnia, due to the significantly lower risk of addiction and overdose and the lack of an antidote for barbiturate overdose. Despite this, barbiturates are still in use for various purposes: in general anesthesia, epilepsy, treatment of acute migraines or cluster headaches, euthanasia, capital punishment, and assisted suicide.

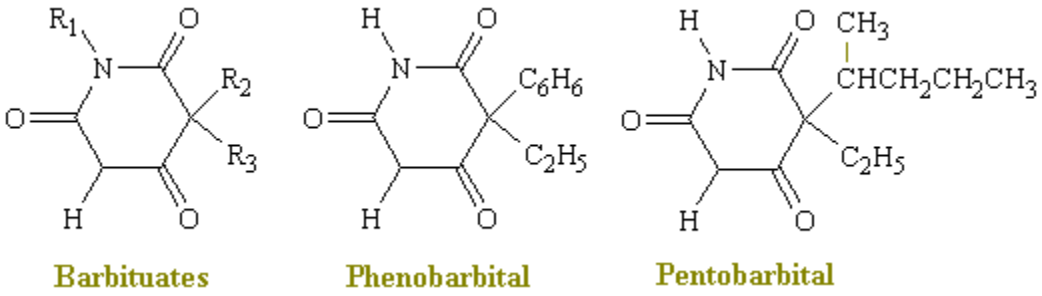


Figure 18.7.11 Barbitutrates.

Some symptoms of an overdose typically include sluggishness, incoordination, difficulty in thinking, slowness of speech, faulty judgement, drowsiness, shallow breathing, staggering, and, in severe cases, coma or death. The lethal dosage of barbiturates varies greatly with tolerance and from one individual to another.

Barbiturates in overdose with other CNS (central nervous system) depressants (e.g. alcohol, opiates, benzodiazepines) are even more dangerous due to additive CNS and respiratory depressant effects. In the case of benzodiazepines, not only do they have additive effects, barbiturates also increase the binding affinity of the benzodiazepine binding site, leading to exaggerated benzodiazepine effects. (ex. If a benzodiazepine increases the frequency of channel opening by 300%, and a barbiturate increases the duration of their opening by 300%, then the combined effects of the drugs increase the channels overall function by 900%, not 600%).

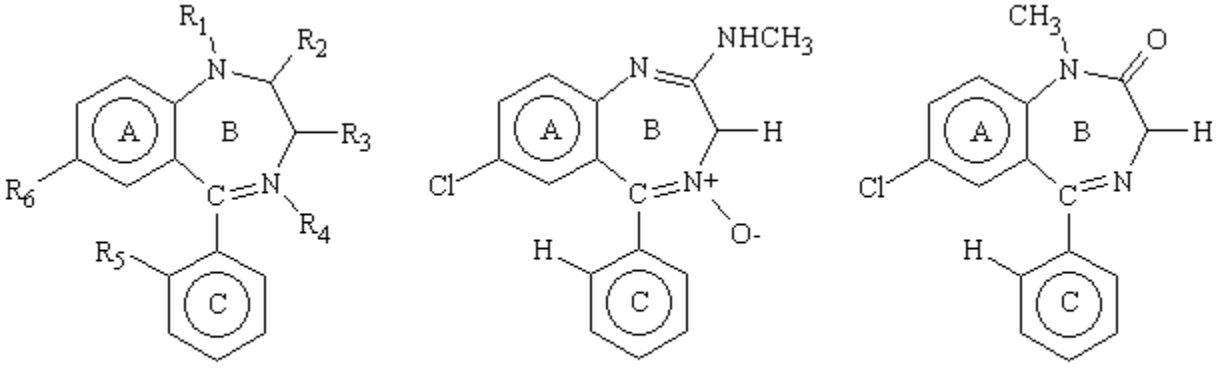
Anti-anxiety Agents

Anti-anxiety medications help reduce the symptoms of anxiety, such as panic attacks, or extreme fear and worry.

Benzodiazepines are prescribed to quell panic attacks. Benzodiazepines are also prescribed in tandem with an antidepressant for the latent period of efficacy associated with many antidepressants for anxiety disorder. The effects of the benzodiazepines virtually all result from action of these drugs on the central nervous system, even when lethal doses are used. The most prominent of these effects are sedation, hypnosis, decreased anxiety, muscle relaxation, and anticonvulsant activity. As the dose of a benzodiazepine is increased, sedation progresses to hypnosis and hypnosis to stupor. They are used as sedatives, hypnotics, antianxiety agents (in panic disorder), anticonvulsants, muscle relaxants, in anesthesia and in alcoholism.

There is risk of benzodiazepine withdrawal and rebound syndrome if BZDs are rapidly discontinued. Tolerance and dependence may occur. The risk of abuse in this class of medication is smaller than in that of barbiturates. Cognitive and behavioral adverse effects are possible.

There are several useful benzodiazepines available. The skeletal structure and two examples are shown below.



Benzodiazepines

Chlordiazepoxide (Librium)

Diazapam (Valium)

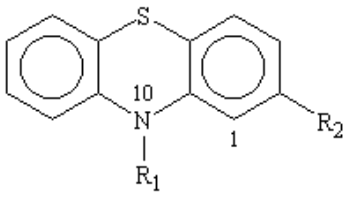
Benzodiazepine include: Alprazolam (Xanax), Bromazepam, Chlordiazepoxide (Librium), Clonazepam (Klonopin), Diazepam (Valium), Lorazepam (Ativan), Oxazepam, Temazepam, and Triazolam. Short half-life (or short-acting) benzodiazepines (such as Lorazepam) and beta-blockers are used to treat the short-term symptoms of anxiety. Beta-blockers help manage physical symptoms of anxiety, such as trembling, rapid heartbeat, and sweating that people with phobias (an overwhelming and unreasonable fear of an object or situation, such as public speaking) experience in difficult situations. Taking these medications for a short period of time can help the person keep physical symptoms under control and can be used “as needed” to reduce acute anxiety.

Antipsychotics, also known as neuroleptics, are a class of psychotropic medication primarily used to manage psychosis (including delusions, hallucinations, paranoia or disordered thought), principally in schizophrenia but also in a range of other psychotic disorders. They are also the mainstay together with mood stabilizers in the treatment of bipolar disorder.

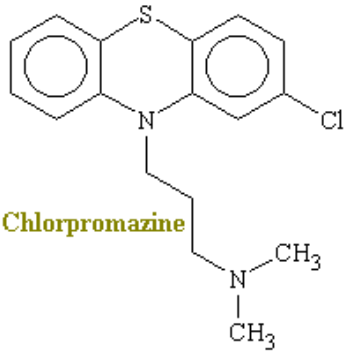
The **phenothiazines** as a class, and especially chlorpromazine, the prototype, are among the most widely used drugs in medical practice and are primarily employed in the management of patients with serious psychiatric illnesses. In addition, many members of the group have other clinically useful properties, including antiemetic, antinausea, and antihistaminic effects and the ability to potentiate analgesics, sedatives and general anesthetics.

It was noted that chlorpromazine by itself did not cause a loss of consciousness but produced only a tendency to sleep and a lack of interest in what was going on. These central actions became known as neuroleptic soon after.

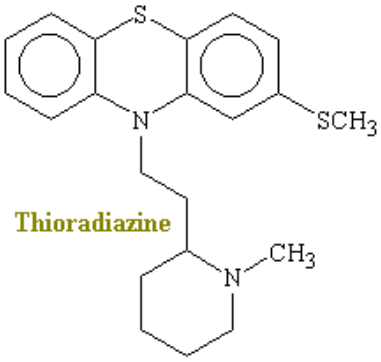
Phenothiazine has a tricyclic structure in which two benzene rings are linked by a sulfur and a nitrogen atom (see figures below). Substitution of an electron-withdrawing group at R2 (but not at position 3 or 4) increases the efficacy of phenothiazines and other tricyclic congeners.



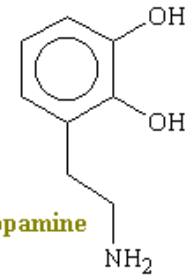
Phenothiazines



Chlorpromazine



Thioradiazine

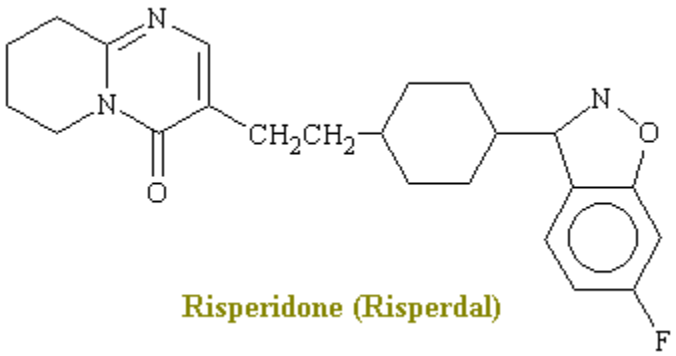


Dopamine

Neuroleptic drugs reduce initiative and interest in the environment, and they reduce displays of emotion or affect. Initially there may be some slowness in response to external stimuli and drowsiness. However subject are easily aroused, capable of giving appropriate answers to direct questions, and seem to have intact intellectual functions; there is no ataxia, incoordination, or dysathria at ordinary doses. Psychotic patients become less agitated and restless, and withdrawn or autistic patients sometimes become more responsive and communicative. Aggressive and impulsive behavior diminishes. Gradually (over a period of days). psychotic symptoms of hallucinations, delusions, and disorganized or incoherent thinking tend to disappear.

The most prominent observable effects of typical neuroleptic agents are strikingly similar. In low doses, operant behavior is reduced but spinal reflexes are unchanged. Exploratory behavior is diminished, and responses to a a variety of stimuli are fewer, slower, and smaller, although the ability to discriminate stimuli is retained. Conditioned avoidance behaviors are selectively inhibited, while unconditioned escape or avoidance responses are not.

In 1994 an addition tot he antipsychotic drugs is **risperidone** (Risperdal). This drug antagonises D2 and serotonin type 2 receptors. The drug also antagonizes for other receptors such as a adrenergic and histaminergic H1 receptors.



Risperidone (Risperdal)

Anti Depressants

Major depression is the most common of the major mental illnesses, and it must be distinguished from normal grief, sadness, and disappointment. Major depression is characterized by feelings of intense sadness and despair, mental slowing and loss of concentration, pessimistic worry, agitation, and self-depreciation. Physical changes also occur, such as weight loss, decreased libido, and disruption of hormonal circadian rhythms.

Before the advent of psychotherapy in the 1950s, treatment of depression consisted of stimulants such as caffeine and amphetamines to ameliorate the depressive phases and barbiturates to allay agitation, anxiety, and insomnia. At best, such attempts at therapy may have offered transient relief to some patients. Suffering usually decreased little.

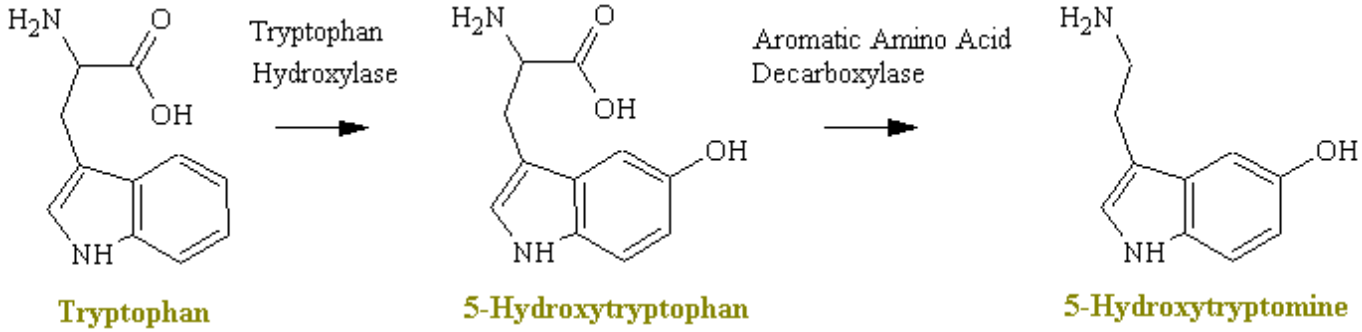
Monoamine Oxidase Inhibitors

Monoamine oxidase inhibitors (MAOIs) were the first effective antidepressants used. The monoamine oxidase inhibitors comprise a chemically heterogeneous group of drugs that have in common the ability to block oxidative deamination of naturally occurring

monoamines. These drugs have numerous other effects, many of which are still poorly understood. For example, they lower blood pressure and were at one time used to treat hypertension. Their use in psychiatry has also become very limited as the tricyclic antidepressants have come to dominate the treatment of depression and allied conditions. Thus, MAOIs are used most often when tricyclic antidepressants give unsatisfactory results. In addition, whereas severe depression may not be the primary indication for these agents, certain neurotic illnesses with depressive features, and also with anxiety and phobias, may respond especially favorably.

Serotonin

Serotonin (5-hydroxytryptamine or 5-HT) is a monoamine neurotransmitter found in cardiovascular tissue, in endothelial cells, in blood cells, and in the central nervous system. The role of serotonin in neurological function is diverse, and there is little doubt that serotonin is an important CNS neurotransmitter.

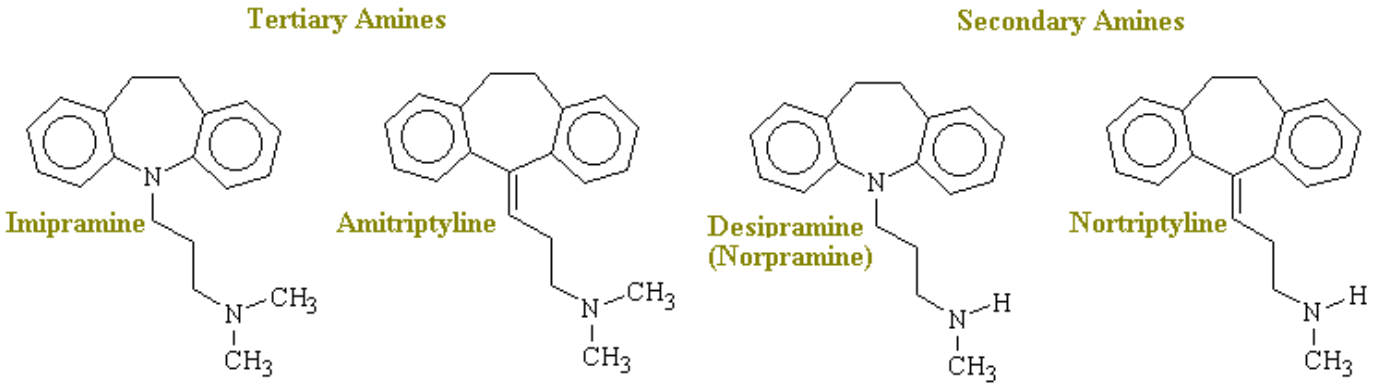


The monoamine serotonin is itself a precursor for melatonin production in the pineal gland. The biosynthesis of serotonin from the amino acid tryptophan is similar to that found for the catecholamines, and 5-hydroxytryptophan can cross the BBB to increase central levels of 5-HT. Although some of the serotonin is metabolized by monoamine oxidase to 5-hydroxyindole acetic acid, most of the serotonin released into the post-synaptic space is removed by the neuron through a reuptake mechanism inhibited by the tricyclic antidepressants and the newer, more selective antidepressants such as fluoxetine and sertraline.

Serotonin receptors are diverse and numerous. Over the past several years, over fourteen different serotonin receptors have been cloned and sequenced through molecular biological techniques. Overall, there are seven distinct families of 5-HT receptors, with as many as five within a particular family. Only one of the 5-HT receptors is a ligand-gated ion channel (the 5-HT3 receptor), and the other six families are all G protein-coupled receptors.

Tricyclic Anti-depressants

Imipramine, amitriptylin, and other closely related drugs are among the drugs currently most widely used for the treatment of major depression. Because of there structure (see below). They are often referred to as the tricyclic antidepressants. Although these compounds seem to be similar to the phenothiazines chemically, the ethylene group of imiprimine's middle ring imparts dissimilar stereochemical properties and prevents conjegation of the rings, as occurs with the phenothiazines.



One might expect an effective antidepressant drug to have a stimulating or mood-elevating effect when given to a normal subject. Although this may occur with the MAOIs, it is not true of the tricyclic antidepressants. If a dose of imipramine given to a normal subject, he feels sleepy and tends to be quieter, his blood pressure falls slightly, and he feels light headed. These drug effects are usually perceived to be unpleasant, and cause a feeling of unhappiness and increased anxiety. Repeated administration for several days may lead to accentuation of these symptoms and, in addition, to difficulty in concentrating and thinking. In contrast, if the drug is given over a period of time (two to three weeks) to depressed patients an elevated mood occurs. For this reason, the tricyclics are not prescribed on an "as-needed" basis.

Selective Serotonin Reuptake Inhibitors

In recent years, selective serotonin reuptake inhibitors (SSRIs) have been introduced for the treatment of depression. Prozac is the most famous drug in this class. Lilly's sales of Prozac in 1993 exceeded 1 billion US dollars. Clomiprimine, fluoxetine (Prozac), sertraline and paroxetine selectively block the reuptake of serotonin, thereby increasing the levels of serotonin in the central nervous system. Note the similarities and differences between the tricyclic antidepressants and the selective serotonin reuptake inhibitors. The SSRIs generally have fewer anticholinergic side effects, but caution is still necessary when co-administering any drugs that affect serotonergic systems (e.g., monoamine oxidase inhibitors). Some of the newer, SSRIs (e.g., clomipramine) have been useful in the treatment of obsessive-compulsive disorders.

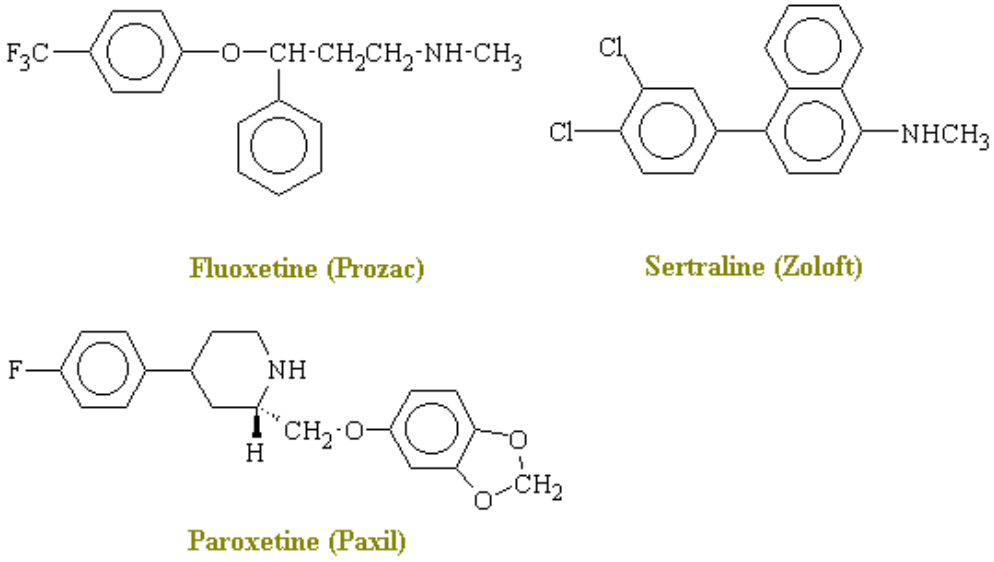


Figure 18.7.12 Examples of SSRIs.

Stimulants

These classes of chemicals induce alertness and stimulant the brain and nervous system. Side effects of stimulant use include wakefulness, increased speech, and motor activity, and decreased appetite. Amphetamines are a type of stimulant that incorporates a nitrogen-containing organic functional group. These compounds have been noted to block the reuptake of dopamine.

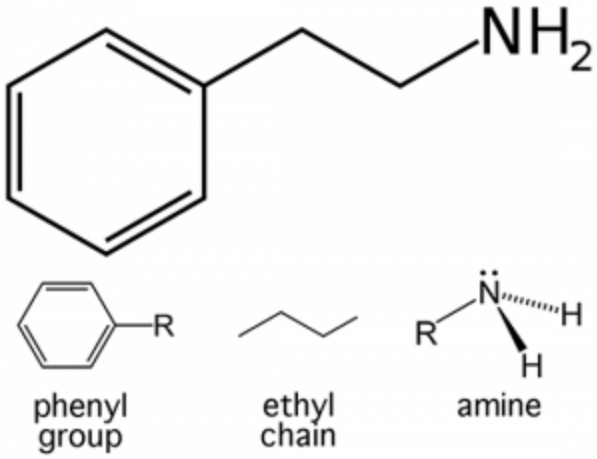


Figure 18.7.13: The skeletal structure of phenethylamine. (Copyright, http://countyourculture.com/2010/11/02/phenethylamine-and-amphetamine/)

Early Stimulant Use

For over 5000 years, the Chinese have extracted the compound Ephedrine from locally grown Ephedra plants. Native peoples of the United States were known to isolate this compound as well. Both cultures used Ephedrine to treat asthma, hay fever, and congestion. Ephedrine was noted to have a stimulant effect on its users. Chemically similar to adrenaline, ephedrine was a more stable compound and could be taken orally. By the mid-1920s, the pharmaceutical company, Eli Lily, synthesized ephedrine and introduced it into western medicine.

Figure 18.7.14: : https://commons.wikimedia.org/wiki/C...phedra_viridis. (Copyright, https://commons.wikimedia.org/wiki/User:Dcrjsr)

Ephedrine can decrease appetite, increase blood pressure and heart rate, and cause sleeping problems. Mental health can be affected by ephedrine use. Patients may experience hallucinogens, anxiety, and chemical dependence.

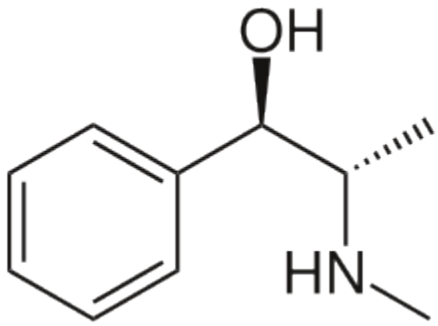


Figure 18.7.15: Chemical structure of Ephedrine, done using BKchem. (Copyright, https://commons.wikimedia.org/wiki/User:Bryan_Derksen)

Amphetamine is a potent central nervous system (CNS) stimulant of the phenethylamine class that is approved for the treatment of attention deficit hyperactivity disorder (ADHD) and narcolepsy. Amphetamine is also used off-label as a performance and cognitive enhancer, and recreationally as an aphrodisiac and euphoriant. Although it is a prescription medication in many countries, unauthorized possession and distribution of amphetamine is often tightly controlled due to the significant health risks associated with uncontrolled or heavy use. As a consequence, amphetamine is illegally manufactured in clandestine labs to be trafficked and sold to users. Based upon drug and drug precursor seizures worldwide, illicit amphetamine production and trafficking is much less prevalent than that of methamphetamine.

The first pharmaceutical amphetamine was Benzedrine, a brand of inhalers used to treat a variety of conditions. At therapeutic doses, this drug causes emotional and cognitive effects such as euphoria, change in libido, increased arousal, and improved cognitive control. Likewise, it induces physical effects such as decreased reaction time, fatigue resistance, and increased muscle strength. In contrast, supratherapeutic doses of amphetamine are likely to impair cognitive function and induce rapid muscle breakdown. Very high doses can result in psychosis (e.g., delusions and paranoia), which very rarely occurs at therapeutic doses

even during long-term use. As recreational doses are generally much larger than prescribed therapeutic doses, recreational use carries a far greater risk of serious side effects, such as dependence, which only rarely arises with therapeutic amphetamine use.

3,4-Methylenedioxymethamphetamine (MDMA, ecstasy, or molly) is a euphoriant, empathogen, and stimulant of the amphetamine class. Briefly used by some psychotherapists as an adjunct to therapy, the drug became popular recreationally and the DEA listed MDMA as a Schedule I controlled substance, prohibiting most medical studies and applications. MDMA is known for its entactogenic properties. The stimulant effects of MDMA include hypertension, anorexia (appetite loss), euphoria, social disinhibition, insomnia (enhanced wakefulness/inability to sleep), improved energy, increased arousal, and increased perspiration, among others. Relative to catecholaminergic transmission, MDMA enhances serotonergic transmission significantly more, when compared to classical stimulants like amphetamine. MDMA does not appear to be significantly addictive or dependence forming.

Methylenedioxypyrovalerone (MDPV) is a psychoactive drug with stimulant properties that acts as a norepinephrine-dopamine reuptake inhibitor (NDRI). It was first developed in the 1960s by a team at Boehringer Ingelheim. MDPV remained an obscure stimulant until around 2004, when it was reported to be sold as a designer drug. Products labeled as bath salts containing MDPV were previously sold as recreational drugs in gas stations and convenience stores in the United States, similar to the marketing for Spice and K2 as incense.

Incidents of psychological and physical harm have been attributed to MDPV use.

Mephedrone is a synthetic stimulant drug of the amphetamine and cathinone classes. Slang names include drone and MCAT. It is reported to be manufactured in China and is chemically similar to the cathinone compounds found in the khat plant of eastern Africa. It comes in the form of tablets or a powder, which users can swallow, snort, or inject, producing similar effects to MDMA, amphetamines, and cocaine.

Methamphetamine (contracted from *N*-**meth**yl-**a**lpha-**m**ethyl**ph**en**et**hyl**amine**) is a potent psychostimulant that is used to treat attention deficit hyperactivity disorder (ADHD) and obesity. Recreationally, methamphetamine is used to increase sexual desire, lift the mood, and increase energy, allowing some users to engage in sexual activity continuously for several days straight.

In low doses, methamphetamine can cause an elevated mood and increase alertness, concentration, and energy in fatigued individuals. At higher doses, it can induce psychosis, rhabdomyolysis, and cerebral hemorrhage. Methamphetamine is known to have a high potential for abuse and addiction. Recreational use of methamphetamine may result in psychosis or lead to post-withdrawal syndrome, a withdrawal syndrome that can persist for months beyond the typical withdrawal period. Unlike amphetamine and cocaine, methamphetamine is neurotoxic to humans, damaging both dopamine and serotonin neurons in the central nervous system (CNS). Entirely opposite to the long-term use of amphetamine, there is evidence that methamphetamine causes brain damage from long-term use in humans; this damage includes adverse changes in brain structure and function, such as reductions in gray matter volume in several brain regions and adverse changes in markers of metabolic integrity.

Methylphenidate is a stimulant drug that is often used in the treatment of ADHD and narcolepsy and occasionally to treat obesity in combination with diet restraints and exercise. Its effects at therapeutic doses include increased focus, increased alertness, decreased appetite, decreased need for sleep and decreased impulsivity. Methylphenidate is not usually used recreationally, but when it is used, its effects are very similar to those of amphetamines.

Methylphenidate is sold under a number of brand names including Ritalin. Other versions include the long lasting tablet Concerta and the long lasting transdermal patch Daytrana.

Phenylpropanolamine (PPA; Accutrim; β-hydroxyamphetamine), also known as norephedrine and norpseudoephedrine, is a psychoactive drug that is used as a stimulant, decongestant, and anorectic agent. It is commonly used in prescription and over-the-counter cough and cold preparations. In veterinary medicine, it is used to control urinary incontinence in dogs under trade names Propalin and Proin.

In the United States, PPA is no longer sold without a prescription due to a proposed increased risk of stroke in younger women. In a few countries in Europe, however, it is still available either by prescription or sometimes over-the-counter.

Propylhexedrine (Hexahydromethamphetamine, Obesin) is a stimulant medication, sold over-the-counter in the United States as the cold medication Benzedrex. The drug has also been used as an appetite suppressant in Europe. Propylhexedrine is not an amphetamine, though it is structurally similar; it is instead a cycloalkylamine, and thus has stimulant effects that are less potent than similarly structured amphetamines, such as methamphetamine.

The abuse potential of propylhexedrine is fairly limited, due its limited routes of administration: in the United States, Benzedrex

is only available as an inhalant, mixed with lavender oil and menthol. These ingredients cause unpleasant tastes, and abusers of the drug have reported unpleasant "menthol burps". Injection of the drug has been found to cause transient diplopia and brain stem dysfunction.

Pseudoephedrine is used as a nasal/sinus decongestant, as a stimulant, or as a wakefulness-promoting agent. The salts pseudoephedrine hydrochloride and pseudoephedrine sulfate are found in many over-the-counter preparations, either as a single ingredient or (more commonly) in combination with antihistamines, guaifenesin, dextromethorphan, and/or paracetamol (acetaminophen) or another NSAID (such as aspirin or ibuprofen). It is also used as a precursor chemical in the illegal production of methamphetamine.

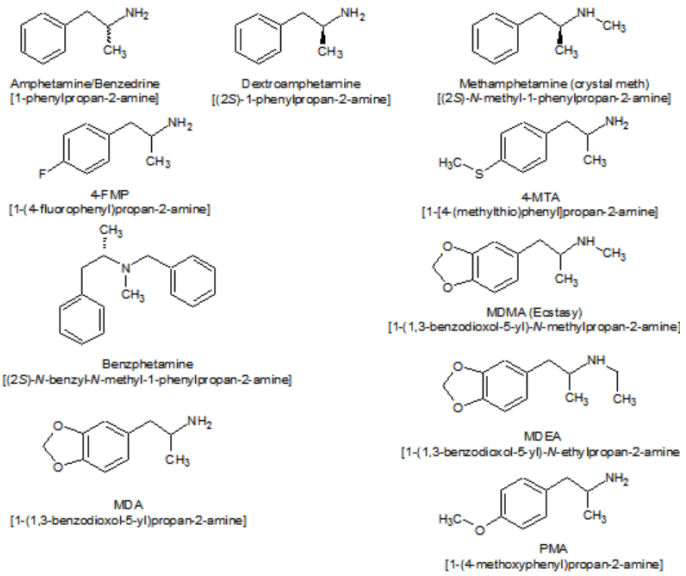


Figure 18.7.16 A chart comparing the chemical structures of different amphetamine derivatives. Source: Wikipedia

Cocaine, Caffeine, and Nicotine

Cocaine is a tropane alkaloid and stimulant drug obtained primarily from the leaves of two coca species, *Erythroxylum coca* and *Erythroxylum novogranatense*. It is most commonly used as a recreational drug and euphoriant. After extraction from coca leaves, cocaine may be snorted, heated until sublimated and then inhaled, or dissolved and injected into a vein. Mental effects may include an intense feeling of happiness, sexual arousal, loss of contact with reality, or agitation. Physical symptoms may include a fast heart rate, sweating, and dilated pupils. High doses can result in high blood pressure or body temperature. Effects begin within seconds to minutes of use and last between five and ninety minutes.

Cocaine is addictive due to its effect on the reward pathway in the brain. A single dose of cocaine induces tolerance to the drug's effects. After a short period of use, addiction is likely. Abstention from cocaine after chronic use results in drug withdrawal, with symptoms that may include depression, decreased ability to feel pleasure and subjective fatigue. Cocaine's use increases the overall risk of death and particularly the risk of trauma, and infectious diseases, such as blood infections and AIDS. It also increases risk of stroke, heart attack, cardiac arrhythmia, lung injury (when smoked), and sudden cardiac death. Illicitly-sold cocaine is commonly adulterated with local anesthetics, levamisole, cornstarch, quinine, or sugar, which can result in additional toxicity. The Global Burden of Disease study found that cocaine use caused the death of 7.3 people per 100,000 population world-wide.

Caffeine is a central nervous system (CNS) stimulant of the methylxanthine class. It is the world's most widely consumed psychoactive drug. Unlike many other psychoactive substances, it is legal and unregulated in nearly all parts of the world. There are several known mechanisms of action to explain the effects of caffeine. The most prominent is that it reversibly blocks the action of adenosine on its receptors and consequently prevents the onset of drowsiness induced by adenosine. Caffeine also stimulates certain portions of the autonomic nervous system.

Methyxanthines such as caffeine, theophylline and theobromine share in common several pharmacological actions of therapeutic interest. They stimulate the central nervous system, act on the kidney to produce diuresis, stimulate cardiac muscle, and relax smooth muscle, notably bronchial muscle. Because the various xanthines differ markedly in the intensity of their action on various

structures, one particular xanthine has been used more than another for a particular therapeutic effect. Since theobromine displays low potency in these pharmacological actions, it has all but disappeared from the therapeutic scene.

Caffeine, theophyline, and theobromine occur naturally in plants widely distributed geographically. Caffeine is found in the coffee bean, tea leaves, guarana, and other plants. From the figure below, we can see that the methylxanthines have a structure which is very similar to adenine.

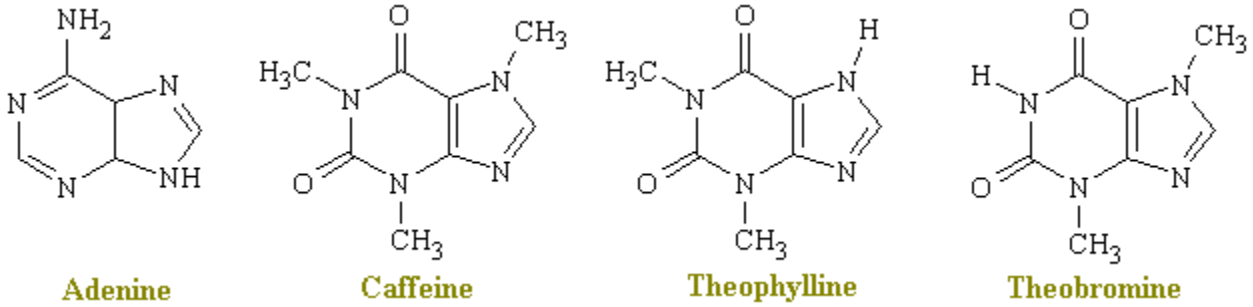


Figure 18.7.17 Adenine and other molecules with similar structures.

Table 18.7.1: *Caffeine Content in Various Beverages and Foods*

Beverage/Food	Milligrams
Starbuck's Grande Coffee (16 oz.)	380
Plain brewed coffee (8 oz.)	102–200
Espresso (1 oz.)	30–90
Plain, decaffeinated coffee (8 oz.)	3–12
Tea, brewed (8 oz.)	40–120
Green tea (8 oz.)	25–40
Coca-Cola Classic (12 oz.)	35
Dr. Pepper (12 oz.)	44
Jolt Cola (12 oz.)	72
Mountain Dew (12 oz.)	54
Mountain Dew, MDX (12 oz.)	71
Pepsi-Cola (12 oz.)	38
Red Bull (8.5 oz.)	80
Full Throttle (16 oz.)	144
Monster Energy (16 oz.)	160
Spike Shooter (8.4 oz.)	300

Source: MedicineNet.com. "Caffeine." Accessed October 2, 2011. http://www.medicinenet.com/caffeine/article.htm.

Health Benefits of Caffeine

The most renowned effects of caffeine on the body are increased alertness and delay of fatigue and sleep. How does caffeine stimulate the brain? Watch "Video 15.6.1" to see a graphic account of a brain on caffeine. Caffeine is chemically similar to a chemical in our brains (adenosine). Caffeine interacts with adenosine's specific protein receptor. It blocks the actions of the adenosine, and affects the levels of signaling molecules in the brain, leading to an increase in energy metabolism. At the molecular level, caffeine stimulates the brain, increasing alertness and causing a delay of fatigue and sleep. At high doses caffeine stimulates the motor cortex of the brain and interferes with the sleep-wake cycle, causing side effects such as shakiness, anxiety,

and insomnia. People's sensitivity to the adverse effects of caffeine varies and some people develop side effects at much lower doses. The many effects caffeine has on the brain do not diminish with habitual drinking of caffeinated beverages.

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 15.6.1: *A Brain on Caffeine. Watch this graphic account of the brain on caffeine.*

Scientific studies suggest caffeine can improve endurance capacity by increasing energy available during exercise. The effect may only work in non-caffeine drinkers and it only takes 1-3 days for the body to become "caffeine-naive."

Nicotine is the active chemical constituent in tobacco, which is available in many forms, including cigarettes, cigars, chewing tobacco, and smoking cessation aids such as nicotine patches, nicotine gum, and electronic cigarettes. Nicotine is used widely throughout the world for its stimulating and relaxing effects. Nicotine exerts its effects through the agonism of nicotinic acetylcholine receptor, resulting in multiple downstream effects such as increase in activity of dopaminergic neurons in the midbrain reward system, as well as the decreased expression of monoamine oxidase in the brain. Nicotine is addictive and dependence forming.

Note: Hallucinogens and Dissociative Drugs from NIH-National Institute on Drug Abuse

The information below is directly from the link below

https://d14rmgtrwzf5a.cloudfront.net/sites/default/files/hallucinogensrrs4.pdf

Hallucinogens are a class of drugs that cause hallucinations—profound distortions in a person's perceptions of reality. Hallucinogens can be found in some plants and mushrooms (or their extracts) or can be man-made, and they are commonly divided into two broad categories: classic hallucinogens (such as LSD) and dissociative drugs (such as PCP). When under the influence of either type of drug, people often report rapid, intense emotional swings and seeing images, hearing sounds, and feeling sensations that seem real but are not. While the exact mechanisms by which hallucinogens and dissociative drugs cause their effects are not yet clearly understood, research suggests that they work at least partially by temporarily disrupting communication between neurotransmitter systems throughout the brain and spinal cord that regulate mood, sensory perception, sleep, hunger, body temperature, sexual behavior, and muscle control.



Figure 18.7.15 Psilocybin mushrooms, LSD, and Salvia divinorum are commonly used hallucinogenic and dissociative compounds.

Classic Hallucinogens

LSD (d-lysergic acid diethylamide)—also known as acid, blotter, doses, hits, microdots, sugar cubes, trips, tabs, or window panes—is one of the most potent moodand perception-altering hallucinogenic drugs. It is a clear or white, odorless, water-soluble material synthesized from lysergic acid, a compound derived from a rye fungus. LSD is initially produced in crystalline form, which can then be used to produce tablets known as "microdots" or thin squares of gelatin called "window panes." It can also be diluted with water or alcohol and sold in liquid form. The most common form, however, is LSD-soaked paper punched into small individual squares, known as "blotters."

Psilocybin (4-phosphoryloxyN, N-dimethyltryptamine)—also known as magic mushrooms, shrooms, boomers, or little smoke—is extracted from certain types of mushrooms found in tropical and subtropical regions of South America, Mexico, and the United States. In the past, psilocybin was ingested during religious ceremonies by indigenous cultures from Mexico and Central America. Psilocybin can either be dried or fresh and eaten raw, mixed with food, or brewed into a tea, and produces similar effects to LSD.

Peyote (Mescaline)— also known as buttons, cactus, and mesc— is a small, spineless cactus with mescaline as its main ingredient. It has been used by natives in northern Mexico and the southwestern United States as a part of religious ceremonies. The top, or "crown," of the peyote cactus has disc-shaped buttons that are cut out, dried, and usually chewed or soaked in water to produce an intoxicating liquid. Because the extract is so bitter, some users prepare a tea by boiling the plant for several hours. Mescaline can also be produced through chemical synthesis.

DMT (Dimethyltryptamine)—also known as Dimitri—is a powerful hallucinogenic chemical found naturally occurring in some Amazonian plant species (see "Ayahuasca") and also synthesized in the laboratory. Synthetic DMT usually takes the form of a white crystalline powder and is typically vaporized or smoked in a pipe. Ayahuasca—also known as hoasca, aya, and yagé—is a hallucinogenic brew made from one of several Amazonian plants containing DMT (the primary psychoactive ingredient) along with a vine containing a natural alkaloid that prevents the normal breakdown of DMT in the digestive tract. Ayahuasca tea has traditionally been used for healing and religious purposes in indigenous South American cultures, mainly in the Amazon region.

Dissociative Drugs

PCP (Phencyclidine)—also known as ozone, rocket fuel, love boat, hog, embalming fluid, or superweed—was originally developed in the 1950s as a general anesthetic for surgery. While it can be found in a variety of forms, including tablets or capsules, it is usually sold as a liquid or powder. PCP can be snorted, smoked, injected, or swallowed. It is sometimes smoked after being sprinkled on marijuana, tobacco, or parsley.

Ketamine—also known as K, Special K, or cat Valium—is a dissociative currently used as an anesthetic for humans as well as animals. Much of the ketamine sold on the street has been diverted from veterinary offices. Although it is manufactured as an injectable liquid, ketamine is generally evaporated to form a powder that is snorted or compressed into pills for illicit use. Because ketamine is odorless and tasteless and has amnesia-inducing properties, it is sometimes added to drinks to facilitate sexual assault. 2 NIDA Research Report Series Common Hallucinogens and Dissociative Drugs *In this report, the term "hallucinogen" will refer to the classic hallucinogenic drugs LSD and Psilocybin.

DXM (Dextromethorphan)— also known as robo—is a cough suppressant and expectorant ingredient in some over-the-counter (OTC) cold and cough medications that are often abused by adolescents and young adults. The most common sources of abused DXM are "extra-strength" cough syrup, which typically contains around 15 milligrams of DXM per teaspoon, and pills and gel capsules, which typically contain 15 milligrams of DXM per pill. OTC medications that contain DXM often also contain antihistamines and decongestants.

Salvia divinorum—also known as diviner's sage, Maria Pastora, Sally-D, or magic mint—is a psychoactive plant common to southern Mexico and Central and South America. Salvia is typically ingested by chewing fresh leaves or by drinking their extracted juices. The dried leaves of salvia can also be smoked or vaporized and inhaled.

Short-Term General Effects of Hallucinogens Sensory and Physical Effects

- Hallucinations, including seeing, hearing, touching, or smelling things in a distorted way or perceiving things that do not exist

- Intensified feelings and sensory experiences (brighter colors, sharper sounds)

- Mixed senses (“seeing” sounds or “hearing” colors)
- Changes in sense or perception of time (time goes by slowly) Physical Effects
- Increased energy and heart rate
- Nausea

Marijuana - NIH Medlineplus

Marijuana

The information below is directly from the link below

https://medlineplus.gov/marijuana.html

Marijuana is a green, brown, or gray mix of dried, crumbled parts from the marijuana plant. The plant contains chemicals which act on your brain and can change your mood or consciousness.

Marijuana can cause both short-term and long-term effects.

Short term:	**Long term:**
While you are high, you may experience • Altered senses, such as seeing brighter colors • Altered sense of time, such as minutes seeming like hours • Changes in mood • Problems with body movement • Trouble with thinking, problem-solving, and memory • Increased appetite	In the long term, marijuana can cause health problems, such as • Problems with brain development. People who started using marijuana as teenagers may have trouble with thinking, memory, and learning. • Coughing and breathing problems, if you smoke marijuana frequently • Problems with child development during and after pregnancy, if a woman smokes marijuana while pregnant.

Medical Marijuana

The marijuana plant has chemicals that can help with some health problems. More states are making it legal to use the plant as medicine for certain medical conditions. But there isn't enough research to show that the whole plant works to treat or cure these conditions. The U.S. Food and Drug Administration (FDA) has not approved the marijuana plant as a medicine. Marijuana is still illegal at the national level.

However, there have been scientific studies of cannabinoids, the chemicals in marijuana. The two main cannabinoids that are of medical interest are THC and CBD. The FDA has approved two drugs that contain THC. These drugs treat nausea caused by chemotherapy and increase appetite in patients who have severe weight loss from AIDS. There is also a liquid drug that contains CBD. It treats two forms of severe childhood epilepsy. Scientists are doing more research with marijuana and its ingredients to treat many diseases and conditions.

Summary

- Neurotransmitters are endogenous chemicals that enable neurotransmission. It is a type of chemical messenger which transmits signals across a chemical synapse, such as a neuromuscular junction, from one neuron (nerve cell) to another "target" neuron, muscle cell, or gland cell.
- Strong imbalances or disruptions to neurotransmitter systems have been associated with many diseases and mental

disorders.
- Psychoactive drugs are substances that change the function of the brain and result in alterations of mood, thinking, perception, and/or behavior. They include prescription medications such as opioid painkillers, legal substances such as nicotine and alcohol, and illegal drugs such as LSD and heroin.
- Psychoactive drugs are divided into different classes according to their pharmacological effects. They include stimulants, depressants, anxiolytics, euphoriants, hallucinogens, and empathogens. Many psychoactive drugs have multiple effects so they may be placed in more than one class.
- Psychoactive drugs generally produce their effects by affecting brain chemistry. Generally, they act either as agonists, which enhance the activity of particular neurotransmitters; or as antagonists, which decrease the activity of particular neurotransmitters.
- Psychoactive drugs are used for various purposes, including medical, ritual, and recreational purposes.
- Misuse of psychoactive drugs may lead to addiction, which is compulsive use of a drug despite negative consequences such use may entail. Sustained use of an addictive drug may produce physical or psychological dependence on the drug. Rehabilitation typically involves psychotherapy and sometimes the temporary use of other psychoactive drugs.

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- NIH-Medlineplus
- Psychology OPENSTAX
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18.8: Drugs and Society

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19: FITNESS AND HEALTH

19.1: Calories - Quantity and Quality
19.2: Vitamins, Minerals, Fluids, and Electrolytes
19.3: Weight Loss - Diets and Exercise
19.4: Measuring Fitness
19.5: Some Muscular Chemistry
19.6: Drugs, Athletic Performance, and the Brain

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19.1: Calories - Quantity and Quality

Learning Objective

- Know the daily recommended guidelines to achieve a healthy diet.
- Learn how to build a healthy plate.
- Learn about sports nutrition.

A History of Food Guidance in the U.S.

The U.S. Dietary Guidelines for Americans and the DRI are important scientific reports to educate health professionals about nutrition and to guide government and other health-related organizations to develop evidence-based health policies that improve the health of all Americans. The United States government has also been providing food and nutrition guidance directly to the public for more than a century to help individuals make healthier dietary and lifestyle choices . You may have heard about "the Four Food Groups" or "The Food Guide Pyramid" or most recently, "My Plate." The government food guidance system has evolved over the years as our understanding of nutrition science and the impact of diet and lifestyle on health has grown. If you are interested in learning more about the history of food guidance in the U.S. a list and description of former tools can be found at: https://www.choosemyplate.gov/brief-history-usda-food-guides

MyPlate

MyPlate is the most up-to-date nutrition teaching tool. MyPlate was developed by the United States Department of Agriculture (U.S.D.A.) Center for Nutrition Policy and Promotion as an easy to use visual guide to help all American develop healthy eating patterns. It replaces the former MyPyramid teaching tool and correlates with the 2015 - 2020 U.S. Dietary Guidelines.

MyPlate organizes foods with similar nutritional value into specific food groups and provides recommendations about how to build a healthy diet. The ChooseMyPlate.gov website also provides a wide range of support materials including information about each food group, an individualized meal planner, recipes and professional videos and handouts such as the *MyPlate, MyWins* poster shown below to support learning for people of all ages.

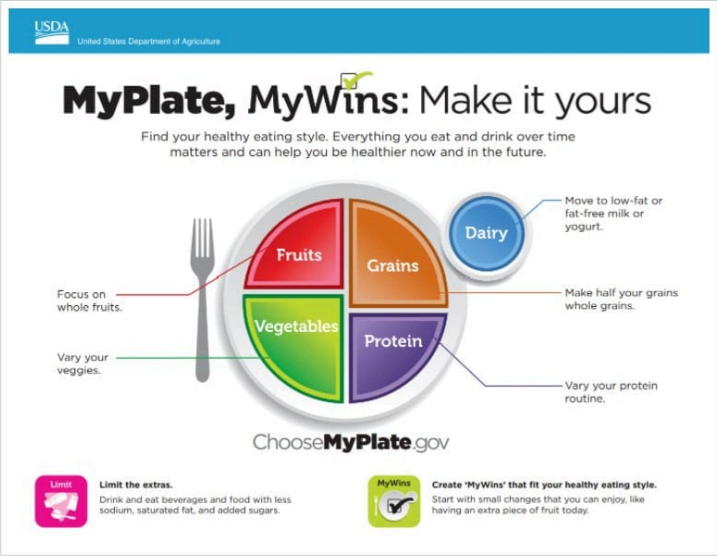


Figure 19.1.1: Ideal healthy plate.

MyPlate Key Messages include:

- *Focus on whole fruits*
- *Vary your veggies*
- *Vary your protein routine*
- *Make half your grains whole grains*
- *Move to low-fat or fat-free milk or yogurt*
- *Drink and eat beverages and food with less sodium saturated fat and added sugars*
- *Start with small changes that you can enjoy, like having an extra piece of fruit today*

To learn more about MyPlate visit: https://www.choosemyplate.gov/MyPlate

Building a Healthy Plate: Choose Nutrient-Dense Foods

Click on the different food groups listed to view their food gallery:

- Fruits
- Grains
- Dairy
- Vegetables
- Protein

Planning a healthy diet using the MyPlate approach is not difficult. According to the icon, half of your plate should have fruits and vegetables, one-quarter should have whole grains, and one-quarter should have protein. Dairy products should be low-fat or non-fat. The ideal diet gives you the most nutrients within the fewest calories. This means choosing nutrient-rich foods.

Fill half of your plate with red, orange, and dark green vegetables and fruits, such as kale, bok choy, kalo (taro), tomatoes, sweet potatoes, broccoli, apples, mango, papaya , guavas, blueberries, and strawberries in main and side dishes. Vary your choices to get the benefit of as many different vegetables and fruits as you can. You may choose to drink fruit juice as a replacement for eating fruit. (As long as the juice is 100 percent fruit juice and only half your fruit intake is replaced with juice, this is an acceptable exchange.) For snacks, eat fruits, vegetables, or unsalted nuts.

Fill a quarter of your plate with grains such cereals, breads, crackers, rice, and pasta. Half of your daily grain intake should be whole grains. Read the ingredients list on food labels carefully to determine if a food is comprised of whole grains such as 100% whole wheat bread, brown rice and whole grain oats.

Select a variety of protein foods to improve nutrient intake and promote health benefits. Each week, be sure to include a nice array of protein sources in your diet, such as nuts, seeds, beans, legumes, poultry, soy, and seafood. The recommended consumption amount for seafood for adults is two 4-ounce servings per week. When choosing meat, select lean cuts. Be conscious to prepare meats using little or no added saturated fat, such as butter.

If you enjoy drinking milk or eating milk products, such as cheese and yogurt, choose low-fat or nonfat products. Low-fat and nonfat products contain the same amount of calcium and other essential nutrients as whole-milk products, but with much less fat and calories. Calcium, an important mineral for your body, is also available in lactose-free and fortified soy beverage and rice beverage products. You can also get calcium in vegetables and other fortified foods and beverages. You can learn more about "dairy free" sources of calcium by clicking the "Dairy" link on the ChooseMyPlate website.

Fats are essential for your diet as they contain valuable essential fatty acids, but the type you choose and the amount you consume is important. Be sure to choose primarily plant-based liquid oils like olive, soybean and canola oil rather than solid animal fats like butter and lard. You can also get oils from many types of fish, as well as avocados, and unsalted nuts and seeds. Although oils are essential for health they do contain about 120 calories per tablespoon. It is vital to balance oil consumption with total caloric intake. The Nutrition Facts label provides the information to help you make healthful decisions.

In short, substituting vegetables and fruits in place of foods high in added sugars, solid/saturated fats, and sodium is a good way to make a nutrient-poor diet healthy again. Vegetables are full of nutrients and antioxidants that help promote good health and reduce the risk for developing chronic diseases such as stroke, heart disease, high blood pressure, Type 2 diabetes, and certain types of cancer. Starting with these small shifts in your diet as mentioned above will boost your overall health profile.

Table 19.1.1***:*** *Food Replacements.*

Instead of...	Replace with...
Sweetened fruit yogurt	Plain fat-free yogurt with fresh fruit
Whole milk	Low-fat or fat-free milk
Cheese	Low-fat or reduced-fat cheese
Bacon or sausage	Canadian bacon or lean ham
Sweetened cereals	Minimally sweetened cereals with fresh fruit
Apple or berry pie	Fresh apple or berries
Deep-fried French fries	Oven-baked French fries or sweet potato bake
Fried vegetables	Steamed or roasted vegetables
Sugary sweetened soft drinks	Seltzer mixed with 100 percent fruit juice
Recipes that call for sugar	Experiment with reducing amount of sugar an

Source: Food Groups. US Department of Agriculture. www.choosemyplate.gov/food-groups/. Updated April 19, 2017. Accessed November 22, 2017.

The MyPlate Planner can be used to create an individualized plan with the number of servings and portion sizes from each food group to eat each day to achieve a healthy diet. You can access the MyPlate Planner from the ChooseMyPlate website:

https://www.choosemyplate.gov/MyPlatePlan

When Enough Is Enough

Estimating Portion Size

Have you ever heard the expression, “Your eyes were bigger than your stomach?” This means that you thought you wanted a lot more food than you could actually eat. Amounts of food can be deceiving to the eye, especially if you have nothing to compare them to. It is very easy to heap a pile of mashed potatoes on your plate, particularly if it is a big plate, and not realize that you have just helped yourself to three portions instead of one.

The food industry makes following the 2015 Dietary Guidelines a challenge. In many restaurants and eating establishments, portion sizes have increased, use of SoFAS has increased, and consequently the typical meal contains more calories than it used to. In addition, our sedentary lives make it difficult to expend enough calories during normal daily activities. In fact, more than one-third of adults are not physically active at all.

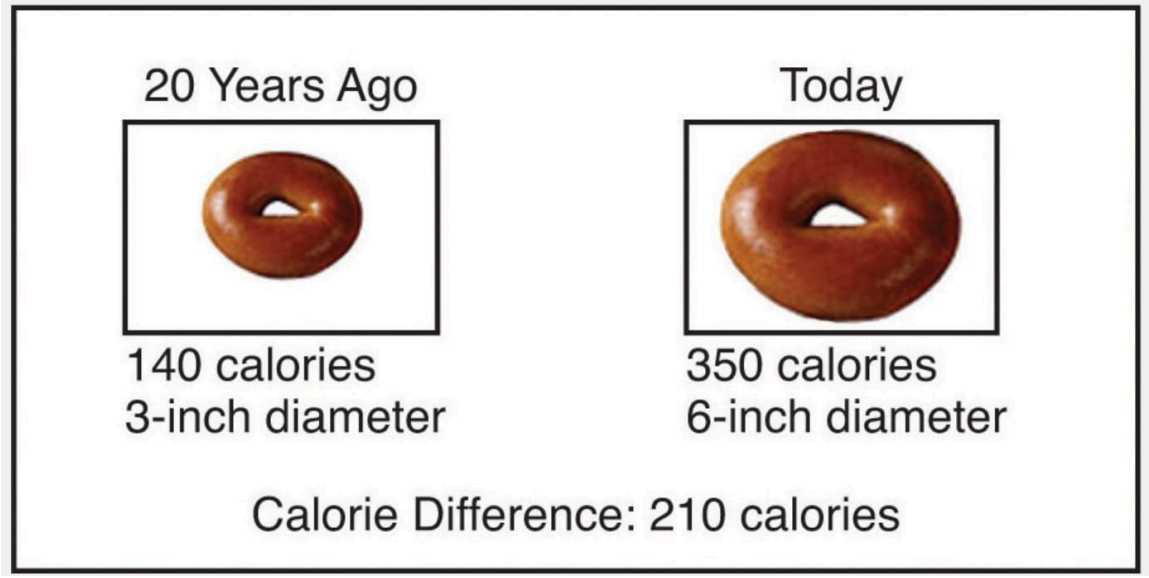


Figure 19.1.2: A Comparison of Serving Sizes.

Source: https://www.nhlbi.nih.gov/health/edu...uments/PD1.pdf

As food sizes and servings increase it is important to limit the portions of food consumed on a regular basis. Dietitians have come up with some good hints to help people tell how large a portion of food they really have. Some suggest using common items such as a deck of cards while others advocate using your hand as a measuring rule.

See Table below for some examples.

Source: American Cancer Society. "Controlling Portion Sizes." Last revised January 12, 2012. http://www.cancer.org/Healthy/EatHealthyGetActive/TakeControlofYourWeight/controlling-portion-sizes.

Table 19.1.2***:*** *Determining Food Portions.*

Food Product	Amount
Pasta, rice	½ c.
Fresh vegetables	1 c.
Cooked vegetables	½ c.
Meat, poultry, fish	3 oz.
Milk or other beverages	1 c.
Salad dressing	1 Tbsp.
Oil	1 tsp.

everyday connection

If you wait many hours between meals, there is a good chance you will overeat. To refrain from overeating try consuming small meals at frequent intervals throughout the day as opposed to two or three large meals. Eat until you are satisfied, not until you feel "stuffed." Eating slowly and savoring your food allows you to both enjoy what you eat and have time to realize that you are full before you get overfull. Your stomach is about the size of your fist but it expands if you eat excessive amounts of food at one sitting. Eating smaller meals will diminish the size of your appetite over time so you will feel satisfied with smaller amounts of food.

Discretionary Calories

When following a balanced, healthful diet with many nutrient-dense foods, you may consume enough of your daily nutrients before you reach your daily calorie limit. The remaining calories are discretionary (to be used according to your best judgment). To find out your discretionary calorie allowance, add up all the calories you consumed to achieve the recommended nutrient intakes and then subtract this number from your recommended daily caloric allowance. For example, someone who has a recommended 2,000-calorie per day diet may eat enough nutrient-dense foods to meet requirements after consuming only 1,814 calories. The remaining 186 calories are discretionary. See Table 19.1.1. These calories may be obtained from eating an additional piece of fruit, adding another teaspoon of olive oil on a salad or butter on a piece of bread, adding sugar or honey to cereal, or consuming an alcoholic beverage[1].

The amount of discretionary calories increases with physical activity level and decreases with age. For most physically active adults, the discretionary calorie allowance is, at most, 15 percent of the recommended caloric intake. By consuming nutrient-dense foods, you afford yourself a discretionary calorie allowance.

Table 19.1.3***:*** *Sample Menu Plan Containing 2,000 Calories.*

Meal
Breakfast
1 scrambled egg
with sliced mushrooms and spinach
½ whole-wheat muffin
1 tsp. margarine-like spread
1 orange
8 oz. low-sodium tomato juice
Snack
6 oz. fat-free flavored yogurt
with ½ c. raspberries
Lunch
1 sandwich on pumpernickel bread
with smoked turkey deli meat,
4 slices tomato
2 lettuce leaves
1 tsp. mustard
1 oz. baked potato chips
½ c. blueberries, with 1 tsp. sugar
8 oz. fat-free milk
Snack
1 banana
7 reduced-fat high-fiber crackers
Dinner
1 c. Greek salad (tomatoes, cucumbers, feta)
with 5 Greek olives,
with 1.5 tsp. olive oil

Meal
3 oz. grilled chicken breast
½ c. steamed asparagus
with 1 tsp. olive oil,
with 1 tsp. sesame seeds
½ c. cooked wild rice
with ½ c. chopped kale
1 whole-wheat dinner roll
with 1 tsp. almond butter
(Total calories from all meals and snacks = 1,814)
Discretionary calorie allowance: 186

(Total calories from all meals and snacks = 1,814)
Discretionary calorie allowance: 186

Web Links and DRI

You can access the MyPlate Planner from the ChooseMyPlate website:

https://www.choosemyplate.gov/MyPlatePlan

Recommended amounts of food from each food group at different calorie levels can be found on the link: https://health.gov/dietaryguidelines/2015/guidelines/appendix-3/

Dietary Reference Intakes (DRIs) are more than numbers in the table, even though that is often how many people view them. DRIs and Dietary Guidelines provide different information for different audiences.

- Dietary Guidelines provide **qualitative** advice to the public about diet and chronic disease prevention and maintaining health.
- DRIs provide **quantitative** advice to professionals about amounts of nutrients or food components to be of benefit.
- DRIs are a collective term to refer to these components:
  - Estimated Average Requirement (EAR)
  - Recommended Dietary Allowance (RDA)
  - Adequate Intake (AI)
  - Tolerable Upper Intake Level (UL). A number of people refer to the UL as simply the “upper limit”, leaving off “tolerable”.

The RDA is the measure that professionals use to assess the quality of people's diets. It is the requirement estimated to meet the needs of 97.5% of the population. But the RDA is calculated using the EAR. Therefore, the EAR needs to be set before an RDA can be set. There must be applicable research in order to set an EAR. An EAR is the estimated requirement for 50% of the population (hence the average in its name).

Nutrition and the Athlete

Nutrition is essential to your performance during all types of exercise. The foods consumed in your diet are used to provide the body with enough energy to fuel an activity regardless of the intensity of activity. Athletes have different nutritional needs to support the vigorous level they compete and practice at.

Energy Needs

To determine an athletes nutritional needs, it is important to revisit the concept of energy metabolism. Energy intake is the foundation of an athlete's diet because it supports optimal body functions, determines the amount of intake of macronutrients and micronutrients, and assists in the maintaining of body composition. Energy needs for athletes increase depending on their energy expenditure. The energy expended during physical activity are contingent on the intensity, duration, and frequency of the exercise. Competitive athletes may need 3,000 to over 5,000 calories daily compared to a typical inactive individual who needs about 2,000 calories per day. Energy needs are also affected by an individual's gender, age, and weight. Weight-bearing exercises, such as running, burn more calories per hour than non-weight bearing exercises, such as swimming. Weight-bearing exercises requires your body to move against gravity which requires more energy. Men are also able to burn more calories than women for the same activity because they have more muscle mass which requires more energy to support and move around.[1]

Body weight and composition can have a tremendous impact on exercise performance. Body weight and composition are considered the focal points of physique for athletes because they are the able to be manipulated the most. Energy intake can play a role in manipulating the physiques for athletes. For individuals competing in sports such as football and weight lifting, having a large amount of muscle mass and increased body weight may be beneficial. This can be obtained through a combination of increased energy intake, and protein. Although certain physiques are more advantageous for specific sports, it is important to remember that a single and rigid "optimal" body composition is not recommended for any group of athletes.[2]

Macronutrient Needs

The composition of macronutrients in the diet is a key factor in maximizing performance for athletes. Carbohydrates are an important fuel source for the brain and muscle during exercise. Carbohydrate storage in the liver and muscle cells are relatively limited and therefore it is important for athletes to consume enough carbohydrates from their diet. Carbohydrate needs should increase about 3-10 g/kg/day depending on the type of training or competition.[3] See Table 19.1.1 for carbohydrate needs for athletes depending on the intensity of the exercise.

Table 19.1.4: Daily Needs for Carbohydrate Fuel.

Activity Level	Example of Exercise	Increase of Carbohydrate (g/kg of athlete's body weight/day)
Light	Low intensity or skill based activities	3-5
Moderate	Moderate exercise program (about 1 hour per day)	5-7
High	Endurance program (about 1-3 hours per day of moderate to high intensity exercise)	6-10
Very High	Extreme commitment (4-5 hours per day of moderate to high intensity exercise)	8-12

Source: Nutrition and Athletic Performance. American College of Sports Medicine.Medicine & Science in Sports & Exercise. 2016; 48(3), 543- 568.

https://journals.lww.com/acsm-msse/Fulltext/2016/03000/Nutrition_and_Athletic_Performance.25.aspx. Accessed March 17, 2018.

Fat is a necessary component of a healthy diet to provide energy, essential fatty acids and to facilitate the absorption of fat-soluble vitamins. Athletes are recommended to consume the same amount of fat in the diet as the general population, 20-35% of their energy intake. Although these recommendations are in accordance with public health guidelines, athletes should individualize their needs based on their training level and body composition goals. Athletes who choose to excessively restrict their fat intake in an effort to lose body weight or improve body composition should ensure they are still getting the minimum recommended amount of fat. Fat intakes below 20% of energy intake will reduce the intake of fat-soluble vitamins and essential fatty acids, especially omega 3's. [4]

Although protein accounts for only about 5% of energy expended, dietary protein is necessary to support metabolic reactions (that generate ATP), and to help muscles with maintenance, growth, and repair. During exercise, these metabolic reactions for generating ATP rely heavily on proteins such as enzymes and transport proteins. It is recommended that athletes consume 1.2 to 2.0 g/kg/day of proteins in order to support these functions. Higher intakes may also be needed for short periods of intense

training or when reducing energy intake.[5] See Table 19.1.2 below for a better representation of protein needs depending on extent of training and dietary sources.

Table 19.1.5: The Recommended Protein Intakes for Individuals.

Group	Protein Intake (
Most adults	0.8
Endurance athletes	1.2 to 1.4
Vegetarian endurance athletes	1.3 to 1.5
Strength athletes	1.6 to 1.7
Vegetarian strength athletes	1.7 to 1.8

Source: Dietary Reference Intakes, 2002 ACSM/ADA/Dietitians of Canada Position Statement: Nutrition & Athletic Performance, 2001. Accessed March 17, 2018.

It is important to consume adequate amounts of protein and to understand that the quality of the protein consumed affects the amount needed. High protein foods such as meats, dairy, and eggs contain all of the essential amino acids in relative amounts that most efficiently meet the body's needs for growth, maintenance and repair of muscles. Vegetarian diets contain protein that has lower digestibility and amino acid patterns that do not match human needs as closely as most animal proteins. To compensate for this as well as the fact that plant food protein sources also contain higher amounts of fiber, higher protein intakes are recommended for vegetarian athletes. (See Table 16.2 "The Recommended Protein Intakes for Individuals")

Micronutrient Needs

Vitamins and minerals are essential for energy metabolism, the delivery of oxygen, protection against oxidative damage, and the repair of body structures. When exercise increases, the amount of many vitamins and minerals needed are also increased due to the excess loss in nutrients. Currently, there is not special micronutrient recommendations made for athletes but most athletes will meet their needs by consuming a balanced diet that meets their energy needs. Because the energy needs of athletes increase, they often consume extra vitamins and minerals. The major micronutrients of concern for athletes include iron, calcium, vitamin D, and some antioxidants. [6]

Web Links

Estimated Calorie Needs per Day, by Age, Sex, and Physical Activity: https://health.gov/dietaryguidelines/2015/guidelines/appendix-2/

Nutrition and a Healthy Diet

There are five key factors that make up a healthful diet:

1. *A diet must be adequate, by providing sufficient amounts of each essential nutrient, as well as fiber and adequate calories.*
2. *A balanced diet results when you do not consume one nutrient at the expense of another, but rather get appropriate amounts of all nutrients.*
3. *Calorie control is necessary so that the amount of energy you get from the nutrients you consume equals the amount of energy you expend during your day's activities.*
4. *Moderation means not eating to the extremes, neither too much nor too little.*
5. *Variety refers to consuming different foods from within each of the food groups on a regular basis.*

A healthy diet is one that favors whole foods. As an alternative to modern processed foods, a healthy diet focuses on "real" fresh whole foods that have been sustaining people for generations. Whole foods supply the needed vitamins, minerals, protein, carbohydrates, fats, and fiber that are essential to good health. Commercially prepared and fast foods are often lacking nutrients and often contain inordinate amounts of sugar, salt, saturated and trans fats, all of which are associated with the development of diseases such as atherosclerosis, heart disease, stroke, cancer, obesity, diabetes, and other illnesses. A balanced diet is a mix of

food from the different food groups (vegetables, legumes, fruits, grains, protein foods, and dairy).

Adequacy

An adequate diet is one that favors nutrient-dense foods. Nutrient-dense foods are defined as foods that contain many essential nutrients per calorie. Nutrient-dense foods are the opposite of “empty-calorie” foods, such as sugary carbonated beverages, which are also called “nutrient-poor.” Nutrient-dense foods include fruits and vegetables, lean meats, poultry, fish, low-fat dairy products, and whole grains. Choosing more nutrient-dense foods will facilitate weight loss, while simultaneously providing all necessary nutrients.

Balance

Balance the foods in your diet. Achieving balance in your diet entails not consuming one nutrient at the expense of another. For example, calcium is essential for healthy teeth and bones, but too much calcium will interfere with iron absorption. Most foods that are good sources of iron are poor sources of calcium, so in order to get the necessary amounts of calcium and iron from your diet, a proper balance between food choices is critical. Another example is that while sodium is an essential nutrient, excessive intake may contribute to congestive heart failure and chronic kidney disease in some people. Remember, everything must be consumed in the proper amounts.

Moderation

Eat in moderation. Moderation is crucial for optimal health and survival. Eating nutrient-poor foods each night for dinner will lead to health complications. But as part of an otherwise healthful diet and consumed only on a weekly basis, this should not significantly impact overall health. It’s important to remember that eating is, in part, about enjoyment and indulging with a spirit of moderation. This fits within a healthy diet.

Monitor food portions. For optimum weight maintenance, it is important to ensure that energy consumed from foods meets the energy expenditures required for body functions and activity. If not, the excess energy contributes to gradual, steady accumulation of stored body fat and weight gain. In order to lose body fat, you need to ensure that more calories are burned than consumed. Likewise, in order to gain weight, calories must be eaten in excess of what is expended daily.

Variety

Variety involves eating different foods from all the food groups. Eating a varied diet helps to ensure that you consume and absorb adequate amounts of all essential nutrients required for health. One of the major drawbacks of a monotonous diet is the risk of consuming too much of some nutrients and not enough of others. Trying new foods can also be a source of pleasure—you never know what foods you might like until you try them.

Developing a healthful diet can be rewarding, but be mindful that all of the principles presented must be followed to derive maximal health benefits. For instance, introducing variety in your diet can still result in the consumption of too many high-calorie, nutrient poor foods and inadequate nutrient intake if you do not also employ moderation and calorie control. Using all of these principles together will promote lasting health benefits.

Summary

- MyPlate is the most up-to-date nutrition teaching tool developed by the United States Department of Agriculture (U.S.D.A.) Center for Nutrition Policy and Promotion as an easy to use visual guide to help all American develop healthy eating patterns.
- Planning a healthy diet using the MyPlate approach is not difficult. According to the icon, half of your plate should have fruits and vegetables, one-quarter should have whole grains, and one-quarter should have protein. Dairy products should be low-fat or non-fat.
- Energy needs for athletes increase depending on their energy expenditure. The energy expended during physical activity are contingent on the intensity, duration, and frequency of the exercise. Competitive athletes may need 3,000 to over 5,000 calories daily compared to a typical inactive individual who needs about 2,000 calories per day. Energy needs are also affected by an individual’s gender, age, and weight.
- There are five key factors that make up a healthful diet namely: a. adequacy, b. balance, c. calorie control, d. moderation, and

e. variety.
- The total number of calories a person needs each day varies depending on a number of factors, including the person's age, sex, height, weight, and level of physical activity.

Contributors and Attributions

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19.2: Vitamins, Minerals, Fluids, and Electrolytes

Learning Objective

List the dietary requirements for vitamins and minerals.

Learn about food supplements.

Learn about water balance.

The importance of vitamins and minerals (micronutrients) in metabolism has been discussed in detail in section 17.4. Micronutrient needs in adults differ slightly according to sex. Young men and women who are very athletic and perspire a great deal also require extra sodium, potassium, and magnesium. Males require more of vitamins C and K, along with thiamine, riboflavin, and niacin. Females require extra iron due to menstruation. Therefore, it can be beneficial for some young adults to follow a daily multivitamin regimen to help meet nutrient needs. But as always, it is important to remember "food first, supplements second." Table 19.2.1 shows the micronutrient recommendations for adult men and women.

Table 19.2.1 Micronutrient Levels during Adulthood.

Nutrient	Adult Males	Adult Females
Vitamin A (mcg)	900.0	700.0
Vitamin B6 (mg)	1.3	1.3
Vitamin B12 (mcg)	2.4	2.4
Vitamin C (mg)	90.0	75.0
Vitamin D (mcg)	5.0	5.0
Vitamin E (mg)	15.0	15.0
Vitamin K (mcg)	120.0	90.0
Calcium (mg)	1,000.0	1,000.0
Folate (mcg)	400.0	400.0
Iron (mg)	8.0	18.0
Magnesium (mg)	400.0	310.0
Niacin (mg)	16.0	14.0
Phosphorus (mg)	700.0	700.0
Riboflavin (mg)	1.3	1.1
Selenium	55.0	55.0
Thiamin (mg)	1.2	1.1
Zinc (mg)	11.0	8.0

Source: Institute of Medicine. 2006. Dietary Reference Intakes: The Essential Guide to Nutrient Requirements. Washington, DC: The National Academies Press. https://doi.org/10.17226/11537. Accessed December 10, 2017.

Food Supplements and Food Replacements

Current trends also include the use of supplementation to promote health and wellness. Vitamins, minerals, herbal remedies, and supplements of all kinds constitute big business and many of their advertising claims suggest that optimal health and

eternal youth are just a pill away. Dietary supplements can be macronutrient (amino acids, proteins, essential fatty acids), micronutrient (vitamins and minerals that promote healthy body functions), probiotic (beneficial bacteria such as the kind found in the intestines), and herbally (often target a specific body part, such as bones) based.

Some public health officials recommend a daily multivitamin due to the poor diet of most North Americans. The US Preventive Task Force also recommends a level of folate intake which can be easier to achieve with a supplement. In addition, the following people may benefit from taking daily vitamin and mineral supplements:[1]

- Women who are pregnant or breastfeeding
- Premenopausal women who may need extra calcium and iron
- Older adults
- People with health issues that affect their ability to eat
- Vegetarians, vegans, and others avoiding certain food groups

However, before you begin using dietary supplementation, consider that the word supplement denotes something being added. Vitamins, minerals, and other assorted remedies should be considered as extras. They are add-ons—not replacements—for a healthy diet. As food naturally contains nutrients in its proper package, remember that food should always be your primary source of nutrients. When considering taking supplements, it is important to recognize possible drawbacks that are specific to each kind:[2]

- **Micronutrient Supplements:** Some vitamins and minerals are toxic at high doses. Therefore, it is vital to adhere to the Tolerable Upper Intake Levels (UL) so as not to consume too much of any vitamin. For example, too much vitamin A is toxic to the liver. Symptoms of vitamin A toxicity can include tinnitus (ringing in the ears), blurred vision, hair loss, and skin rash. Too much niacin can cause a peptic ulcer, hyperglycemia, dizziness, and gout.
- **Herbal Supplements:** Some herbs cause side effects, such as heart palpitations and high blood pressure, and must be taken very carefully. Also, some herbs have contraindications with certain medicines. For example, Valerian and St. John's Wort negatively interact with certain prescription medications, most notably antidepressants. Additionally, there is a real risk of overdosing on herbs because they do not come with warning labels or package inserts.
- **Amino Acid Supplements:** Certain amino acid supplements, which are often taken by bodybuilders among others, can increase the risk of consuming too much protein. An occasional amino acid drink in the place of a meal is not a problem. However, problems may arise if you add the supplement to your existing diet. Most Americans receive two to three times the amount of protein required on a daily basis from their existing diets—taking amino acid supplements just adds to the excess. Also, certain amino acids share the same transport systems in the absorption process; therefore, a concentrated excess of one amino acid obtained from a supplement may increase the probability of decreased absorption of another amino acid that uses the same transport system. This could lead to deficiency in the competing amino acid.

Supplement Claims and Restrictions

The Food and Drug Administration (FDA) regulates supplements, but it treats them like food rather than pharmaceuticals. Dietary supplements must meet the FDA's Good Manufacturing Standards, but are not required to meet the standards for drugs, although some companies do so voluntarily. Also, although supplement manufacturers are allowed to say a particular ingredient may reduce the risk of a disease or disorder, or that it might specifically target certain body systems, these claims are not approved by the FDA. This is why labels that make structural and functional claims are required to carry a disclaimer saying the product is not intended "to diagnose, treat, cure, or prevent any disease." In addition, in the United States, supplements are taken off the market only after the FDA has proven that they are hazardous.[3] To revisit the topic of structural and functional claims refer back to Chapter 12 "Nutrition Applications".

Before Taking Supplements

The phrase caveat emptor means "buyer beware," and it is important to keep the term in mind when considering supplementation. Just because a product is "natural" does not mean it can't be harmful or dangerous, particularly if used inappropriately. The following are helpful questions to explore before deciding to take a supplement:

- Does the scientific community understand how this supplement works and are all its effects well known?
- Is there proof that the supplement actually performs in the manner that it claims?
- Does this supplement interact with food or medication?
- Is taking this supplement necessary for my health?

- Is the supplement affordable?
- Is the supplement safe and free from contaminants?

Lastly, please remember that a supplement is only as good as the diet that accompanies it. We cannot overstate the importance of eating a healthy, well-balanced diet designed to provide all of the necessary nutrients. Food contains many more beneficial substances, such as phytochemicals and fiber, that promote good health and cannot be duplicated with a pill or a regimen of supplements. Therefore, vitamins and other dietary supplements should never be a substitute for food. Nutrients should always be derived from food first.

Food: The Best Medicine

Poor dietary choices and a sedentary lifestyle account for about 300–600 thousand deaths every year according to the US Department of Health and Human Services. That number is thirteen times higher than the deaths due to gun violence.[4] The typical North American diet is too high in saturated fat, sodium, and sugar, and too low in fiber in the form of whole fruits, vegetables, and whole grains to keep people healthy. With so many threats to optimal health it is vital to address those factors that are under your control, namely dietary and lifestyle choices. A diet that supplies your body with the needed energy and nutrients daily will result in efficient body functioning and in protection from disease. Making sound nutritional choices can also provide support for individuals undergoing treatment for short-term or chronic conditions. Finding a balance between nutritional needs with concerns about drug interactions can hasten recovery, improve quality of life, and minimize the side effects from treatment protocols.

Body Fluids and Electrolytes

Maintaining the right level of water in your body is crucial to survival, as either too little or too much water in your body will result in less-than-optimal functioning. One mechanism to help ensure the body maintains water balance is thirst. Thirst is the result of your body's physiology telling your brain to initiate the thought to take a drink. Sensory proteins detect when your mouth is dry, your blood volume too low, or blood electrolyte concentrations too high and send signals to the brain stimulating the conscious feeling to drink.

The latest National Health and Nutrition Examination Survey, covering the period from 2005 to 2008, reports that about 50 percent of Americans consume sugary drinks daily.

Excess consumption of sugary soft drinks have been scientifically proven to increase the risk for dental caries, obesity, Type 2 diabetes, and cardiovascular disease. In addition to sugary soft drinks, beverages containing added sugars include fruit drinks, sports drinks, energy drinks and sweetened bottled waters.

Sports drinks are designed to rehydrate the body after excessive fluid depletion. Electrolytes in particular promote normal rehydration to prevent fatigue during physical exertion. Are they a good choice for achieving the recommended fluid intake? Are they performance and endurance enhancers like they claim? Who should drink them?

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

Gatorade

Gatorade was created in 1965, by a team of scientists at the University of Florida College of Medicine, including Robert Cade, Dana Shires, Harry James Free, and Alejandro de Quesada. Following a request from Florida Gators football head coach Ray Graves, Gatorade was created to help athletes by acting as a replacement for body fluids lost during physical exertion. The earliest version of the beverage consisted of a mixture of water,sodium, sugar, potassium, phosphate, and lemon juice.Ten players on the University of Florida football team tested the first version of Gatorade during practices and games in 1965, and the tests were deemed successful.

The University of Florida researchers initially considered naming their product "Gator-Aid". They settled on the name Gatorade, however, since the researchers wanted to create a commercial product, not a scientifically-validated one.



University of Florida football player Chip Hinton testing Gatorade in 1965, pictured next to the leader of its team of inventors, Robert Cade. Source: Wikipedia

Regulation of Daily Water Input

Total water output per day averages 2.5 liters (Figure 19.2.1). This must be balanced with water input. Our tissues produce around 300 milliliters of water per day through metabolic processes. The remainder of water output must be balanced by drinking fluids and eating solid foods. The average fluid consumption per day is 1.5 liters, and water gained from solid foods approximates 700 milliliters.

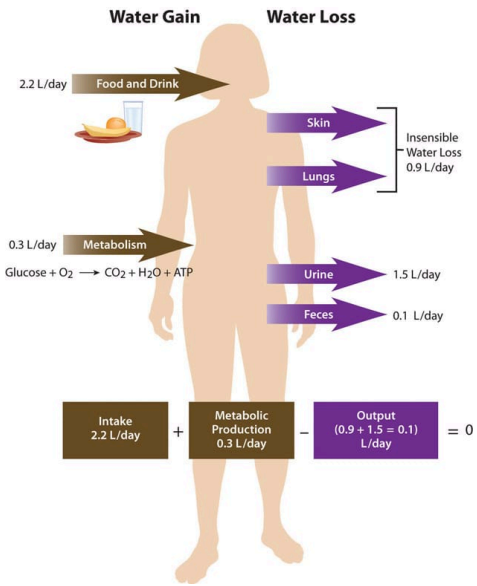


Figure 19.2.1 Daily fluid loss and gain.

The Food and Nutrition Board of the Institute of Medicine (IOM) has set the Adequate Intake (AI) for water for adult males at 3.7 liters (15.6 cups) and at 2.7 liters (11 cups) for adult females. These intakes are higher than the average intake of 2.2 liters. It is important to note that the AI for water includes water from all dietary sources; that is, water coming from food as well as beverages. People are not expected to consume 15.6 or 11 cups of pure water per day. In America, approximately 20 percent of dietary water comes from solid foods.

Consequences of Deficiency or Excess

As with all nutrients, having too much or too little water has health consequences. Excessive water intake can dilute the levels of critical electrolytes in the blood. Water intoxication is rare, however when it does happen, it can be deadly. On the other hand, having too little water in the body is common. In fact, diarrhea-induced dehydration is the number-one cause of early-childhood death worldwide. In this section we will discuss subtle changes in electrolytes that compromise health on a chronic basis.

High-Hydration Status: Water Intoxication/ Hyponatremia

Water intoxication mainly affects athletes who overhydrate. Water intoxication is extremely rare, primarily because healthy kidneys are capable of excreting up to one liter of excess water per hour. Overhydration was unfortunately demonstrated in 2007 by Jennifer Strange, who drank six liters of water in three hours while competing in a “Hold Your Wee for a Wii” radio contest. Afterward she complained of a headache, vomited, and died.

Low-Hydration Status: Dehydration

Dehydration refers to water loss from the body without adequate replacement. It can result from either water loss or electrolyte imbalance, or, most commonly, both. Dehydration can be caused by prolonged physical activity without adequate water intake, heat exposure, excessive weight loss, vomiting, diarrhea, blood loss, infectious diseases, malnutrition, electrolyte imbalances, and very high glucose levels. Physiologically, dehydration decreases blood volume. The water in cells moves into the blood to compensate for the low blood-volume, and cells shrink. Signs and symptoms of dehydration include thirst, dizziness, fainting, headaches, low blood-pressure, fatigue, low to no urine output, and, in extreme cases, loss of consciousness and death. Signs and symptoms are usually noticeable after about 2 percent of total body water is lost.

Chronic dehydration is linked to higher incidences of some diseases. There is strong evidence that low-hydration status increases the risk for kidney stones and exercise-induced asthma. There is also some scientific evidence that chronic dehydration increases the risk for kidney disease, heart disease, and the development of hyperglycemia in people with diabetes. Older people often suffer from chronic dehydration as their thirst mechanism is no longer as sensitive as it used to be.

Summary

- Micronutrient needs in adults differ slightly according to sex. Young men and women who are very athletic and perspire a great deal also require extra sodium, potassium, and magnesium. Males require more of vitamins C and K, along with thiamine, riboflavin, and niacin. Females require extra iron due to menstruation.
- Current trends also include the use of supplementation to promote health and wellness. Dietary supplements can be macronutrient (amino acids, proteins, essential fatty acids), micronutrient (vitamins and minerals that promote healthy body functions), probiotic (beneficial bacteria such as the kind found in the intestines), and herbally (often target a specific body part, such as bones) based.
- The Food and Nutrition Board of the Institute of Medicine (IOM) has set the Adequate Intake (AI) for water for adult males at 3.7 liters (15.6 cups) and at 2.7 liters (11 cups) for adult females. It is important to note that the AI for water includes water from all dietary sources; that is, water coming from food as well as beverages.
- Total water output per day averages 2.5 liters which must be balanced with water input.
- Excessive water intake can dilute the levels of critical electrolytes in the blood. Water intoxication is rare, however when it does happen, it can be deadly. On the other hand, having too little water in the body is common.

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19.3: Weight Loss - Diets and Exercise

Learning Objective

- Learn about various recommendations for weight loss and weight management.

With over 70 percent of Americans currently overweight or obese, it isn't surprising that many individuals report engaging in weight management efforts. [1] In fact, a 2019 report from a national survey on current trends in weight loss attempts and strategies found that 42 percent of adults in the United States had recently attempted to lose weight, primarily through reduced food consumption and exercise.

The National Weight Control Registry (NWCR) has tracked over ten thousand people who have been successful in losing at least 30 pounds and maintaining this weight loss for at least one year. Their research findings show that 98 percent of participants in the registry modified their food intake, and 94 percent increased their physical activity, mainly by walking.

Although there were a great variety of approaches taken by NWCR members to achieve successful weight loss, most have reported that their approach involved adhering to a low-calorie, low-fat diet and doing high levels of activity (about one hour of exercise per day). Moreover, most members eat breakfast every day, watch fewer than ten hours of television per week, and weigh themselves at least once per week. About half of them lost weight on their own, and the other half used some type of weight-loss program. [11] In most scientific studies, successful weight loss is accomplished only by changing the diet and increasing physical activity together. Doing one without the other limits the amount of weight lost and the length of time that weight loss is sustained.

Evidence-Based Dietary Recommendations

The 2015 Dietary Guidelines for Americans offers specific, evidence-based recommendations for dietary changes aimed at keeping calorie intake in balance with physical activity, which is key for weight management. These recommendations include:

Follow a healthy eating pattern that accounts for all foods and beverages within an appropriate calorie level that includes:

- A variety of vegetables from all of the subgroups—dark green, red and orange, legumes (beans and peas), starchy, and other
- Fruits, especially whole fruits
- Grains, at least half of which are whole grains
- Fat-free or low-fat dairy, including milk, yogurt, cheese, and/or fortified soy beverages
- A variety of protein foods, including seafood, lean meats and poultry, eggs, legumes (beans and peas), and nuts, seeds, and soy products
- Oils

A healthy eating pattern limits:

- Saturated fats and trans fats
- Added sugars
- Sodium

Key quantitative recommendations are provided for several components of the diet that should be limited. These components are of particular public health concern in the United States, and the specified limits can help individuals achieve healthy eating patterns within calorie limits[5]:

- Consume less than 10 percent of calories per day from added sugars
- Consume less than 10 percent of calories per day from saturated fats
- Consume less than 2,300 milligrams (mg) per day of sodium

If alcohol is consumed, it should be consumed in moderation—up to one drink per day for women and up to two drinks per day for men—and only by adults of legal drinking age.

Dietary Food Trends

In the past, health was regarded merely as the absence of illness. However, a growing understanding of the complexity and potential of the human condition has prompted a new way of thinking about health. Today, we focus on the idea of wellness, which involves a great deal more than just not being sick. Wellness is a state of optimal well-being that enables an individual to maximize their potential. This concept includes a host of dimensions—physical, mental, emotional, social, environmental, and spiritual—which affect one's quality of life. Striving for wellness begins with an examination of dietary choices.

Hundreds of years ago, when food was less accessible and daily life required much more physical activity, people worried less about obesity and more about simply getting enough to eat. In today's industrialized nations, conveniences have solved some problems and introduced new ones, including the hand-in-hand obesity and diabetes epidemics. Fad diets gained popularity as more North Americans struggled with excess pounds. However, new evidence-based approaches that emphasize more holistic measures are on the rise. These new dietary trends encourage those seeking to lose weight to eat healthy, whole foods first, while adopting a more active lifestyle. These sound practices put dietary choices in the context of wellness and a healthier approach to life.

Functional Foods

Many people seek out foods that provide the greatest health benefits. This trend is giving rise to the idea of functional foods, which not only help meet basic nutritional needs but also are reported to fight illness and aging. According to the Academy of Nutrition and Dietetics (AND), formerly known as the The American Dietetic Association, functional foods may reduce the risk of disease or promote optimal health. The AND recognizes four types of functional foods. They are: conventional foods, modified foods, medical foods, and special dietary use foods.

The first group, conventional foods, represents the simplest form of functional foods. They are whole foods that have not been modified. Examples include whole fruits and vegetables (which are abundant in phytochemicals and antioxidants), yogurt and kefir (which contain natural probiotic bacteria that can help maintain digestive system health), and moderate amounts of dark chocolate, made with 70% or more cacao (which contains antioxidants).

Modified foods have been fortified, enriched, or enhanced with additional nutrients or bioactive compounds. Foods are modified using biotechnology to improve their nutritional value and health attributes. Examples of modified foods include calcium-fortified orange juice, breads enriched with B vitamins, iodized salt, cereals fortified with vitamins and minerals, margarine enhanced with plant sterols, and energy drinks that have been enriched with herbs (ginseng or guarana) or amino acids (taurine). It is important to consider that the health claims of some modified foods may be debatable, or entirely fraudulent. Check with a health professional regarding the effects of modified foods on your health.

Medical foods are designed for enteric administration under the guidance of a medical professional. (During enteric administration, food is treated so that it goes through the stomach undigested. Instead, the food is broken down in the intestines only.) Medical foods are created to meet very specific nutritional requirements. Examples of medical foods include liquid formulas for people with kidney disease, liver disease, diabetes, or other health issues. Medical food is also given to comatose patients through a gastronomy tube because they cannot eat by mouth.

Special dietary use foods do not have to be administered under a doctor's care and can be found in a variety of stores. Similar to medical foods, they address special dietary needs and meet the nutritional requirements of certain health conditions. For example, a bottled oral supplement administered under medical supervision is a medical food, but it becomes a special dietary use food when it is sold to retail customers. Examples of special dietary use foods include gluten-free foods, lactose-free dairy products, and formulas and shakes that promote weight loss.

Popular Diets

The concept of functional foods represents initiatives aimed at addressing health problems. Certain diet plans take this concept one step further, by striving to prevent or treat specific conditions. For example, it is widely understood that people with diabetes need to follow a particular diet. Although some of these diet plans may be nutritionally sound, use caution because some diets may be fads or be so extreme that they actually cause health problems.

Before experimenting with a diet, discuss your plans with your doctor or a registered dietitian. Table 19.3.1 lists the pros and cons of the more popular diets. Some fall under the category of fad diets, while others are backed by scientific evidence. Those that

fall into the latter category provide a good foundation to build a solid regimen for optimal health.

Table 19.3.1 *The Pros and Cons of Seven Popular Diets.*

Diet	Pros	Cons
DASH Diet	Recommended by the National Heart, Lung, and Blood Institute, the American Heart Association, and many physicians Helps to lower blood pressure and cholesterol Reduces risk of heart disease and stroke Reduces risk of certain cancers Reduces diabetes risk	There are very few negative factors associated with the DASH diet Risk for hyponatremia
Gluten-Free Diet	Reduces the symptoms of gluten intolerance, such as chronic diarrhea, cramping, constipation, and bloating Promotes healing of the small intestines for people with celiac disease, preventing malnutrition May be beneficial for other autoimmune diseases, such as Parkinson's disease, rheumatoid arthritis, and multiple sclerosis	Risk of folate, iron, thiamin, riboflavin, niacin, and vitamin B6 deficiencies Special gluten-free products can be hard to find and expensive Requires constant vigilance and careful food label reading, since gluten is found in many products
Low-Carb Diet	Restricts refined carbohydrates, such as white flour and white sugar May temporarily improve blood sugar or blood cholesterol levels	Not entirely evidence-based Results in higher fat and protein consumption Does not meet the RDA for carbohydrates to provide glucose to the brain
Macrobiotic Diet	Low in saturated fats and high in fiber Emphasizes whole foods and de-emphasizes processed foods Rich in phytoestrogens, which may reduce the risk of estrogen-related cancers	Not entirely evidence-based Lacks certain vitamins and minerals; supplements are often required Can result in a very low caloric intake Lack of energy may result from inadequate protein

Diet	Pros	Cons
Mediterranean Diet	A reduced risk of cardiovascular disease and mortality A lower risk of cancer De-emphasizes processed foods and emphasizes whole foods and healthy fats Lower sodium intake, due to fewer processed foods Emphasis on monosaturated fats leads to lower cholesterol Highlighting fruits and vegetables raises consumption of antioxidants	Does not specify daily serving amounts Potential for high fat and high calorie intake as nuts and oils are calorie-dense foods Drinking one to two glasses of wine per day may not be healthy for those with certain conditions
Raw Food Diet	Emphasizes whole foods Focuses on nutritionally-rich foods	Not entirely evidence-based Very restrictive and limits protein and healthy fat intake Could encourage the development of foodborne illness Extremely difficult to follow High in fiber which can cause essential nutrient deficiencies
Vegetarianism and Veganism	May reduce some chronic diseases such as cancer, heart disease, and Type 2 diabetes May help with weight reduction and weight maintenance	Guidelines regarding fat and nutrient consumption must be followed Higher risk for nutrient deficiencies such as protein, iron, zinc, omega-3, vitamin B12 Consumption of a high fiber diet interferes with mineral and nutrient bioavailability Vegetarian and vegan protein sources are lower quality with majority missing at least one essential amino acids

Evidence-Based Physical Activity Recommendations

The other part of the energy balance equation is physical activity. The Dietary Guidelines are complemented by the 2018 Physical Activity Guidelines for Americans, issued by the Department of Health and Human Services (HHS) in an effort to provide evidence-based guidelines for appropriate physical activity levels. These guidelines provide recommendations to Americans aged three and older about how to improve health and reduce chronic disease risk through physical activity. Increased physical activity has been found to lower the risk of heart disease, stroke, high blood pressure, Type 2 diabetes, colon, breast, and lung cancer, falls and fractures, depression, and early death. Increased physical activity not only reduces disease risk, but also improves overall health by increasing cardiovascular and muscular fitness, increasing bone density and strength, improving cognitive function, and assisting in weight loss and weight maintenance.

The key guidelines for adults include the following:

- Adults should move more and sit less throughout the day. Some physical activity is better than none. Adults who sit less and do any amount of moderate-to-vigorous physical activity gain some health benefits.
- For substantial health benefits, adults should do at least 150 minutes (2 hours and 30 minutes) to 300 minutes (5 hours) per week of moderate-intensity aerobic activity, or 75 minutes (1 hour and 15 minutes) to 150 minutes (2 hours and 30 minutes) per week of vigorous-intensity aerobic physical activity, or an equivalent combination of moderate- and vigorous-intensity aerobic activity .
- Preferably, aerobic activity should be spread throughout the week.
- Engaging in physical activity beyond the equivalent of 300 minutes (5 hours) of moderate-intensity physical activity per week can result in additional health benefits and may help with weight loss and weight loss maintenance.
- Adults should also do muscle-strengthening activities of at least moderate intensity that involve all major muscle groups on 2 or more days per week, as these activities provide additional health benefits . Exercises such as push-ups, sit-ups, squats, and lifting weights are all examples of muscle-strengthening activities.

The 2018 Physical Activity Guidelines broadly classify moderate physical activities as those when you "can talk, but not sing, during the activity" and vigorous activities as those when you "cannot say more than a few words without pausing for a breath." [14] Despite the indisputable benefits of regular physical activity, a 2018 report from the American Heart Association estimates that 8 out of 10 Americans do not meet these guidelines. [2]

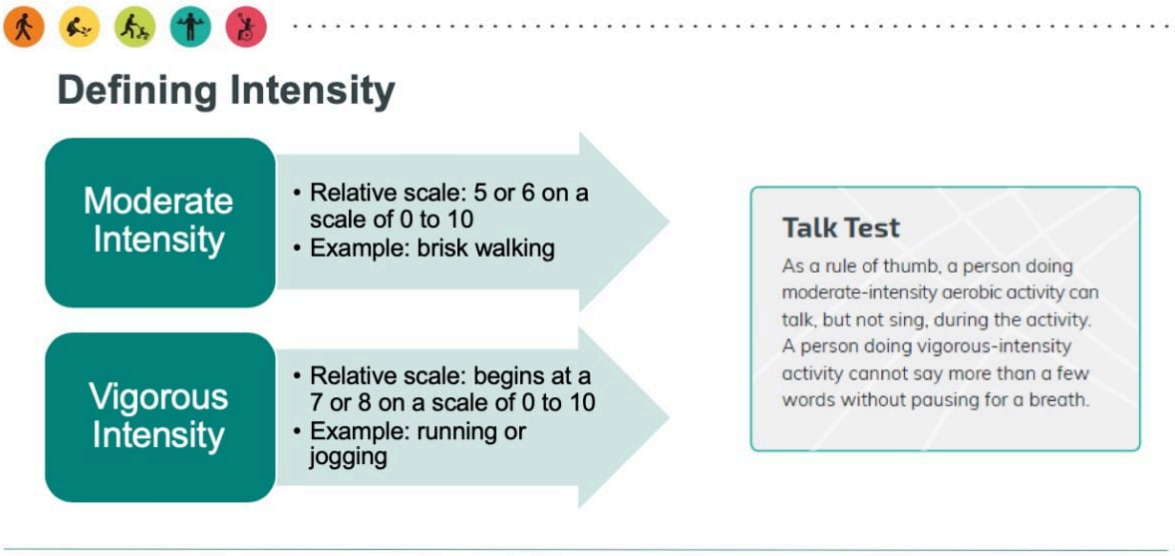


Figure 19.3.1 *The 2018 Physical Activity Guidelines' definition of moderate-intensity and vigorous-intensity exercise.*

Given the number of Americans that are falling short on both nutrition and physical activity recommendations, it is easy to see that these two areas of behavior are of primary interest in improving the health and weight of our nation.

Evidence-Based Behavioral Recommendations

Behavioral weight loss interventions have been described as approaches "used to help individuals develop a set of skills to achieve a healthier weight. It is more than helping people to decide what to change; it is helping them identify how to change." Cornerstones for these interventions typically include self-monitoring through daily recording of food intake and exercise, nutrition education and dietary changes, physical activity goals, and behavior modification. Research shows that these types of interventions can result in weight loss and a lower risk for type 2 diabetes, and similar maintenance strategies lead to less weight regained later.

Behavioral interventions have been shown to help individuals achieve and maintain weight loss of at least 5 percent from baseline weight. **The Food and Drug Administration (FDA) considers a 5 percent weight loss to be clinically significant, as this level of weight loss has been shown to improve cardiometabolic risk factors such as blood lipid levels and insulin sensitivity.** [17,18] The behavioral intervention team often includes primary care clinicians, dietitians , psychologists, behavioral

therapists, exercise physiologists, and lifestyle coaches. These programs may include a variety of delivery methods, often through group classes of 10-20 participants both in-person and online, and may use print-based or technology-based materials and resources. The interventions usually span one to two years with more frequent contact in the initial months (weekly to bi-monthly) followed by less frequent contact (monthly) in the latter months, or maintenance phase.[17] A variety of behavioral topics are covered over the course of the program and range from nutrition education and goal-setting to problem-solving and assertiveness. Relapse prevention is included as participants move into the maintenance phase.



Figure 19.3.2, *Common topics included in behavioral interventions for weight loss, adapted from Smith, C. E., & Wing, R. R. (2000). New directions in behavioral weight-loss programs. Diabetes Spectrum, 13(3), 142-148.*

Summary

- The 2015 Dietary Guidelines for Americans offers specific, evidence-based recommendations for dietary changes aimed at keeping calorie intake in balance with physical activity, which is key for weight management.
- These new dietary trends encourage those seeking to lose weight to eat healthy, whole foods first, while adopting a more active lifestyle. These sound practices put dietary choices in the context of wellness and a healthier approach to life.

- Increased physical activity not only reduces disease risk, but also improves overall health by increasing cardiovascular and muscular fitness, increasing bone density and strength, improving cognitive function, and assisting in weight loss and weight maintenance.
- Behavioral interventions have been shown to help individuals achieve and maintain weight loss of at least 5 percent from baseline weight.

Contributors and Attributions

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19.4: Measuring Fitness

Learning Objectives

- Be able to calculate body mass index (BMI) given a particular weight and height.
- Name the factors that affect body composition and distribution.

What should you weigh? This has been a difficult question to answer because humans come in so many different sizes and shapes. We do know that carrying too much fat is not good for one's health. Thus fat is a huge factor in determining fitness. Ideal body weight (IBW) has been used to determine one's desirable weight.

Ideal Body Weight

The “ideal” healthy body weight for a particular person is dependent on many things, such as frame size, sex, muscle mass, bone density, age, and height. The perception of the “ideal” body weight is additionally dependent on cultural factors and the mainstream societal advertisement of beauty.

To standardize the “ideal” body weight and relate it to health, scientists have devised mathematical formulas to better define a healthy weight. These mathematically derived measurements are used by health professionals to correlate disease risk with populations of people and at the individual level. A clinician will take two measurements, one of weight and one of fat mass, in order to diagnose obesity. Some measurements of weight and body fat that do not require using technical equipment can easily be calculated and help provide an individual with information on weight, fat mass, and distribution, and their relative risk of some chronic diseases.

Body Mass Index: How to Measure It and Its Limitations

Body mass index (BMI) is calculated using height and weight measurements and is more predictive of body fatness than weight alone. BMI measurements are used to indicate whether an individual may be underweight (with a BMI less than 18.5), overweight (with a BMI over 25), or obese (with a BMI over 30). High BMI measurements can be warning signs of health hazards ahead, such as cardiovascular disease, Type 2 diabetes, and other chronic diseases. BMI-associated health risks vary by race. Asians face greater health risks for the same BMI than Caucasians, and Caucasians face greater health risks for the same BMI than African Americans.

Very high AND very low BMI's appear to increase a person's risk of dying. If you look at a graph of BMI (Figure $19.4.1$) as it relates to your risk of dying, it has a "J-shaped Curve" or a "U-shaped Curve" because being too low and/or too high both raise your risk of mortality. Instead, you'd like to be in the middle range of the BMI which is what they use for "Normal weight".

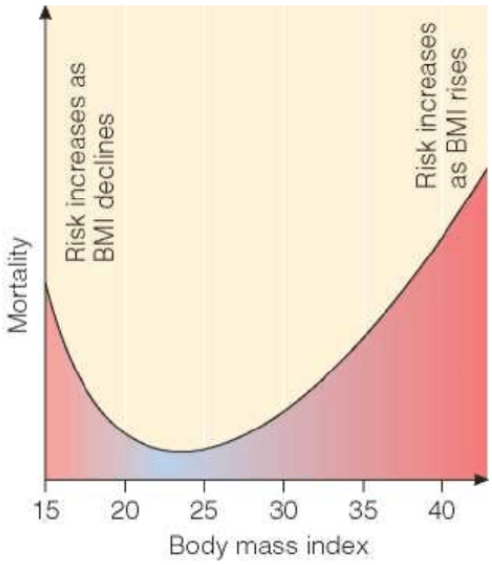


Figure 19.4.1 Relationship between body mass index and mortality.

Calculating BMI

To calculate your BMI, multiply your weight in pounds by 703 (conversion factor for converting to metric units) and then divide the product by your height in inches, squared.

$$BMI = [weight(lb) \times 703] \div height(in)^2$$

or

$$BMI = [weight(kg)] \div height(m)^2$$

BMI Calculators and BMI Categories

The National Heart, Lung, and Blood Institute and the CDC have automatic BMI calculators on their websites:

- https://www.nhlbi.nih.gov/health/educational/lose_wt/BMI/bmi-m.htm
- https://www.cdc.gov/bmi/adult-calculator/widget.html?CDC_AAref_Val=https://www.cdc.gov/healthyweight/assessing/bmi/adult_bmi/english_bmi_calculator/bmi_calculator.html

To see how your BMI indicates the weight category you are in, see Table 19.4.1 or use a chart of weight and height to figure out your BMI.

Table 19.4.1 BMI Categories

Categories	BMI
Underweight	< 18.5
Normal weight	18.5–24.9
Overweight	25–29.9
Obese	30.0-34.9
Severe	35-40
Source: National Heart, Lung, and Blood Institute. Accessed November 4, 2012. http://www.nhlbi.nih.gov.	

BMI Limitations

A BMI is a fairly simple measurement and does not take into account fat mass or fat distribution in the body, both of which are additional predictors of disease risk. Body fat weighs less than muscle mass. Therefore, BMI can sometimes underestimate the amount of body fat in overweight or obese people and overestimate it in more muscular people. For instance, a muscular athlete will have more muscle mass (which is heavier than fat mass) than a couch potato of the same height. Based on their BMIs the muscular athlete would be less “ideal” and may be categorized as more overweight or obese than the couch potato; however, this is an infrequent problem with BMI calculation. Additionally, an older person with osteoporosis (decreased bone mass) will have a lower BMI than an older person of the same height without osteoporosis, even though the person with osteoporosis may have more fat mass. A BMI is a useful inexpensive tool to categorize people and is highly correlative with disease risk, but other measurements are needed to diagnose obesity and more accurately assess disease risk.

BMI is not a good measure for children and adolescents because they are growing. A new BMI for these ages was recently introduced in which the weight in kg is divided by the height in meters cubed. Its use is not well-established yet.

BMI does not consider where the fat is located. Individuals with abdominal fat or android shape have a greater risk of obesity associated diseases than individuals who carry their fat in the hips (gynoid or "pear shape"). Men tend to be "apple-shaped" while women tend to be "pear shaped." Gynoid shape tends to be associated with fewer health risks. For this reason, a ratio of body waist circumference to hip circumference may be measured and the ratio calculated. If you are male and your ratio is greater than 0.95, then you have excessive abdominal fat. If you are female and your ratio is greater than 0.86, then you have excessive abdominal fat.

Measuring Body Fat Content

Water, organs, bone tissue, fat, and muscle tissue make up a person’s weight. Having more fat mass may be indicative of disease risk, but fat mass also varies with sex, age, and physical activity level. Females have more fat mass, which is needed for reproduction and, in part, is a consequence of different levels of hormones. The optimal fat content of a female is between 20 and 30 percent of her total weight and for a male is between 12 and 20 percent. Fat mass can be measured in a variety of ways. The simplest and lowest-cost way is the skin-fold test. A health professional uses a caliper to measure the thickness of skin on the back, arm, and other parts of the body and compares it to standards to assess body fatness. It is a noninvasive and fairly accurate method of measuring fat mass, but similar to BMI, is compared to standards of mostly young to middle-aged adults.



Figure 19.4.2: Measuring Skinfold Thickness Using Calipers. Image by Shutterstock. All Rights Reserved.

Other methods of measuring fat mass are more expensive and more technically challenging. They include:

- Underwater weighing. This technique requires a chamber full of water big enough for the whole body to fit in. First, a person is weighed outside the chamber and then weighed again while immersed in water. Bone and muscle weigh more than water,

but fat does not—therefore a person with a higher muscle and bone mass will weigh more when in water than a person with less bone and muscle mass.

- Bioelectric Impedance Analysis (BIA). This device is based on the fact that fat slows down the passage of electricity through the body. When a small amount of electricity is passed through the body, the rate at which it travels is used to determine body composition. These devices are also sold for home use and commonly called body composition scales.



Figure 19.4.3: BIA Hand Device. Image by United States Marine Corps / U.S. Public Domain.

Dual-energy X-ray absorptiometry (DEXA). This can be used to measure bone density. It also can determine fat content via the same method, which directs two low-dose X-ray beams through the body and determines the amount of the energy absorbed from the beams. The amount of energy absorbed is dependent on the body's content of bone, lean tissue mass, and fat mass. Using standard mathematical formulas, fat content can be accurately estimated.

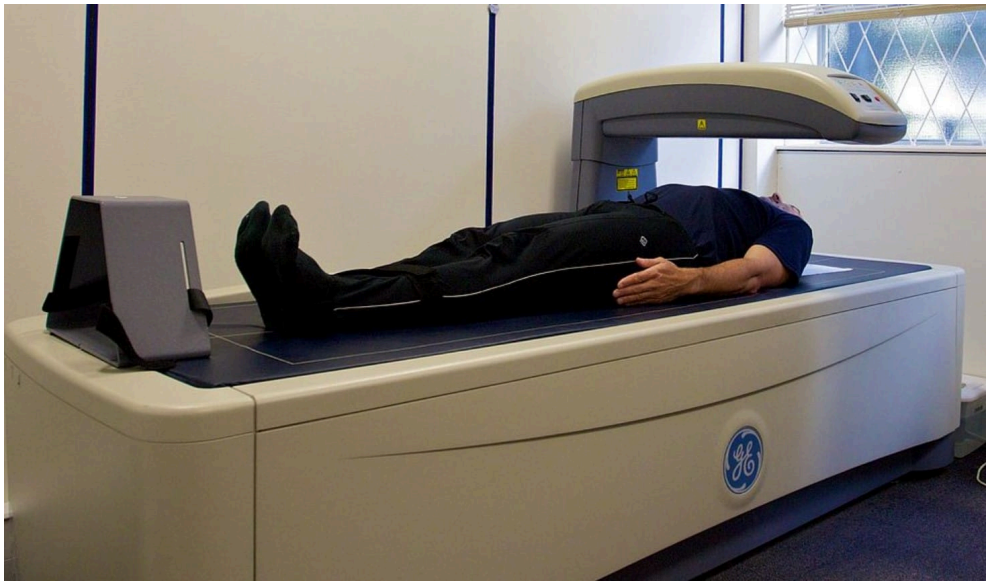


Figure 19.4.4: Dual-Energy X-ray Absorptiometry (DEXA). "A Dual-energy X-ray absorptiometry (DEXA) scan" by Nick Smith / CC BY-SA 3.0.

Measuring Fat Distribution

Total body-fat mass is one predictor of health; another is how the fat is distributed in the body. You may have heard that fat on the hips is better than fat in the belly—this is true. Fat can be found in different areas in the body and it does not all act the same, meaning it differs physiologically based on location. Fat deposited in the abdominal cavity is called visceral fat and it is a better predictor of disease risk than total fat mass. Visceral fat releases hormones and inflammatory factors that contribute to disease risk. The only tool required for measuring visceral fat is a measuring tape. The measurement (of waist circumference) is taken just above the belly button. Men with a waist circumference greater than 40 inches and women with a waist circumference greater than 35 inches are predicted to face greater health risks.

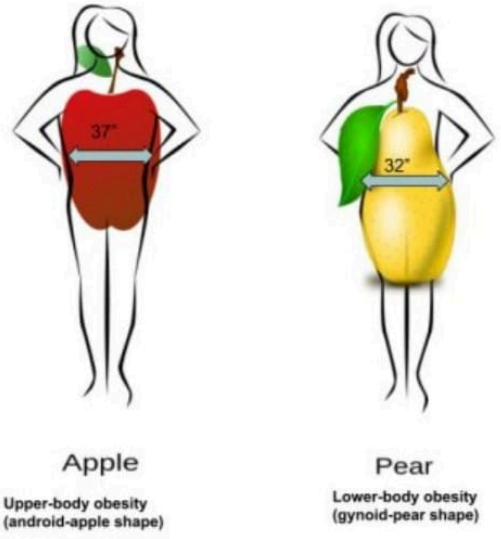


Figure 19.4.5: Fat Distribution.

The waist-to-hip ratio is often considered a better measurement than waist circumference alone in predicting disease risk. To calculate your waist-to-hip ratio, use a measuring tape to measure your waist circumference and then measure your hip circumference at its widest part. Next, divide the waist circumference by the hip circumference to arrive at the waist-to-hip ratio. Observational studies have demonstrated that people with “apple-shaped” bodies, (who carry more weight around the waist) have greater risks for chronic disease than those with “pear-shaped” bodies, (who carry more weight around the hips). A study published in the November 2005 issue of Lancet with more than twenty-seven thousand participants from fifty-two countries concluded that the waist-to-hip ratio is highly correlated with heart attack risk worldwide and is a better predictor of heart attacks than BMI.[1]. Abdominal obesity is defined by the World Health Organization (WHO) as having a waist-to-hip ratio above 0.90 for males and above 0.85 for females.

Summary

Most people who are overweight also have excessive body fat and therefore body weight is an indicator of obesity in much of the population.

To standardize the “ideal” body weight and relate it to health, scientists have devised some computational measurements to better define a healthy ideal weight. Body weight in relation to height is called BMI and is correlated with disease risk.

Total body fat mass is another predictor of disease risk; another is where the fat is distributed. Fat deposits in different areas in the body and do not all act the same, meaning it differs physiologically based on location. Visceral fat contributes more to disease risk, for example.

Contributors and Attributions

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19.5: Some Muscular Chemistry

Learning Objectives

- Describe how muscle contraction occurs.
- Explain the difference between aerobic and anaerobic exercise.

Muscle cells are specialized for contraction. Muscles allow for motions such as walking, and they also facilitate bodily processes such as respiration and digestion. The body contains three types of muscle tissue: skeletal muscle, cardiac muscle, and smooth muscle (Figure 19.5.1).

Skeletal muscle tissue forms skeletal muscles, which attach to bones or skin and control locomotion and any movement that can be consciously controlled. Because it can be controlled by thought, skeletal muscle is also called voluntary muscle. Smooth muscle tissue occurs in the walls of hollow organs such as the intestines, stomach, and urinary bladder, and around passages such as the respiratory tract and blood vessels. Cardiac muscle tissue is only found in the heart, and cardiac contractions pump blood throughout the body and maintain blood pressure.

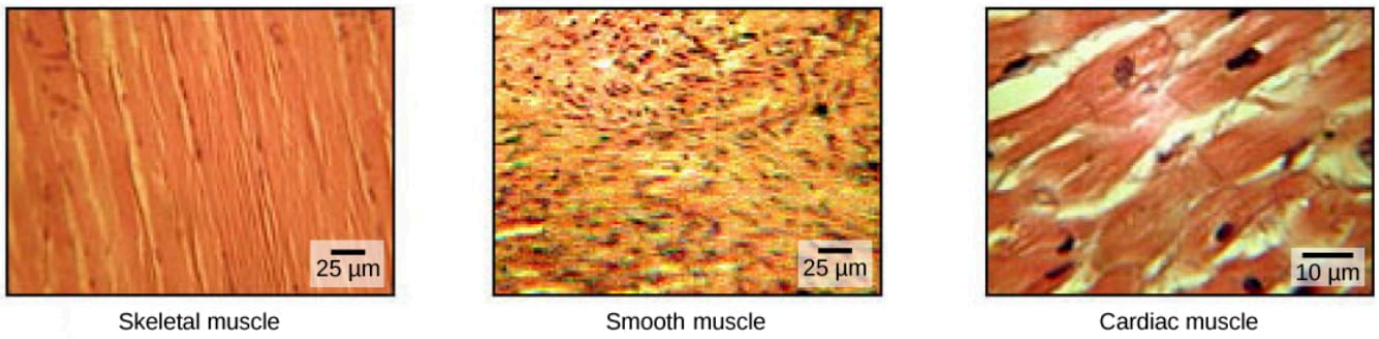


Figure 19.5.1 The body contains three types of muscle tissue: skeletal muscle, smooth muscle, and cardiac muscle, visualized here using light microscopy. Smooth muscle cells are short, tapered at each end, and have only one plump nucleus in each. Cardiac muscle cells are branched and striated, but short. The cytoplasm may branch, and they have one nucleus in the center of the cell. (credit: modification of work by NCI, NIH; scale-bar data from Matt Russell)

Muscle Contraction

Muscle contraction occurs when muscle fibers get shorter. Literally, the muscle fibers get smaller in size. To understand how this happens, you need to know more about the structure of muscle fibers.

Structure of Muscle Fibers

Each muscle fiber contains hundreds of organelles called **myofibrils**. Each myofibril is made up of two types of protein filaments: **actin** filaments, which are thinner, and **myosin** filaments, which are thicker. Actin filaments are anchored to structures called **Z lines** (Figure 13.13.2). The region between two Z lines is called a **sarcomere**. Within a sarcomere, myosin filaments overlap the actin filaments. The myosin filaments have tiny structures called **cross bridges** that can attach to actin filaments.

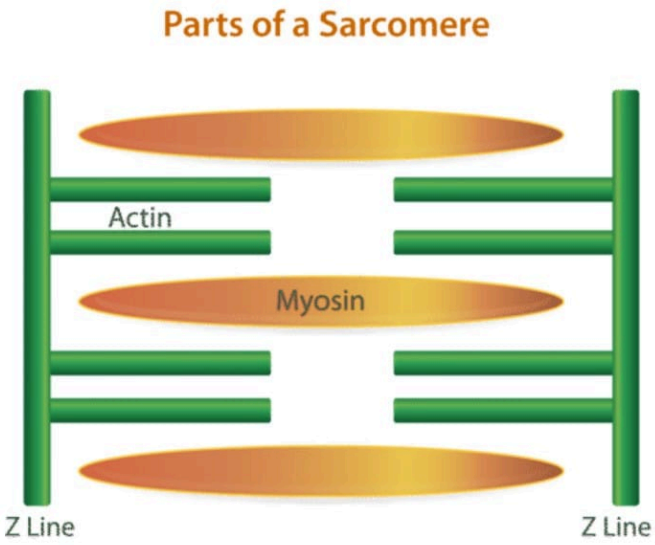


Figure 19.5.2 Sarcomere. A sarcomere contains actin and myosin filaments between two Z lines.

Sliding Filament Theory

The most widely accepted theory explaining how muscle fibers contract is called the **sliding filament theory**. According to this theory, myosin filaments use energy from ATP to "walk" along the actin filaments with their cross bridges. This pulls the actin filaments closer together. The movement of the actin filaments also pulls the Z lines closer together, thus shortening the sarcomere.

YouTube Video

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

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When all of the sarcomeres in a muscle fiber shorten, the fiber contracts. A muscle fiber either contracts fully or it doesn't contract at all. The number of fibers that contract determines the strength of the muscular force. When more fibers contract at the same time, the force is greater.

Muscles and Nerves

Muscles cannot contract on their own. They need a stimulus from a nerve cell to "tell" them to contract. Let's say you decide to raise your hand in class. Your brain sends electrical messages to nerve cells, called **motor neurons**, in your arm and shoulder. The motor neurons, in turn, stimulate muscle fibers in your arm and shoulder to contract, causing your arm to rise. Involuntary contractions of cardiac and smooth muscles are also controlled by nerves.

Energy for Muscle Contraction: ATP

The source of energy that is used to power the movement of contraction in working muscles is adenosine triphosphate (ATP) – the body's biochemical way to store and transport energy. ATP provides the energy for cross-bridge formation and filament sliding. However, ATP is not stored to a great extent in cells.

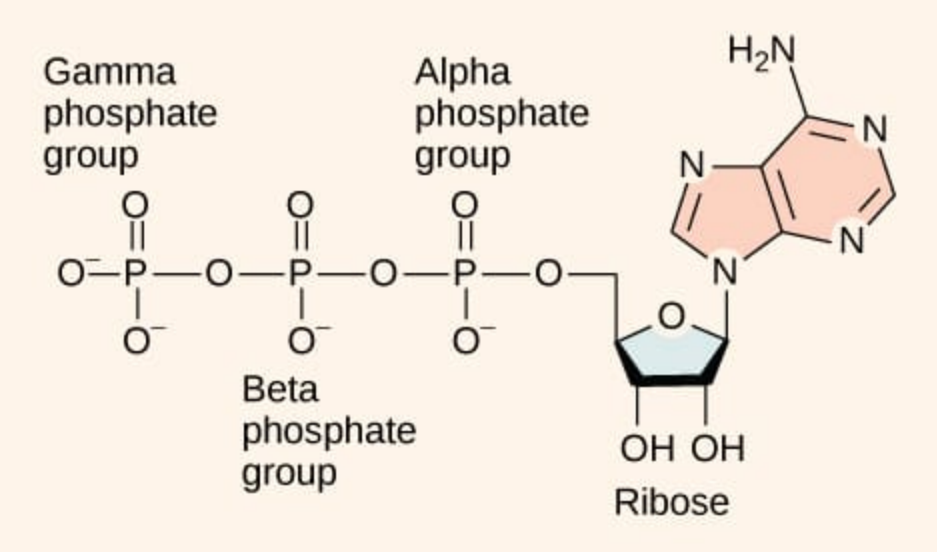


Figure 19.5.3 ATP.

All muscle cells have a little ATP within them that they can use immediately – but only enough to last for about 3 seconds!

So once muscle contraction starts, the making of more ATP must start quickly. Since ATP is so important, the muscle cells have several different ways to make it. These systems work together in phases. The three biochemical systems for producing ATP are, in order:

1. *Creatine phosphate* can supply the energy needs of a working muscle at a very high rate, but only for about 8–10 seconds.
2. Glycogen is then used to make ATP from glucose. But this takes about 12 chemical reactions so it supplies energy more slowly than from creatine phosphate. It's still pretty rapid, though, and will produce enough energy to last about 90 seconds. Oxygen is not needed – this is great, because it takes the heart and lungs some time to get increased oxygen supply to the muscles. A by-product of making ATP without using oxygen is lactic acid. You know when your muscles are building up *lactic acid* because it causes tiredness and soreness – the stitch.
3. Within two minutes of exercise, the body starts to supply working muscles with oxygen. When oxygen is present, aerobic respiration can take place to break down the glucose for ATP. This glucose can come from several places:

- remaining glucose supply in the muscle cells
- glucose from food in the intestine
- *glycogen in the liver*
- fat reserves in the muscles
- in extreme cases (like starvation), the body's protein.

Aerobic respiration takes even more chemical reactions to produce ATP than either of the above two systems. It is the slowest of all three systems – but it can supply ATP for several hours or longer, as long as the supply of fuel lasts.

Aerobic Exercise: Plenty of Oxygen

Aerobic exercise (also known as cardio) is physical exercise of low to high intensity that depends primarily on the aerobic energy-generating process. Aerobic literally means "relating to, involving, or requiring free oxygen", and refers to the use of oxygen to adequately meet energy demands during exercise. Generally, light-to-moderate intensity activities that are sufficiently supported by aerobic metabolism can be performed for extended periods of time. When practiced in this way, examples of cardiovascular/aerobic exercise are medium to long distance running/jogging, swimming, cycling, and walking, according to the first extensive research on aerobic exercise, conducted in the 1960s on over 5,000 U.S. Air Force personnel by Dr. Kenneth H. Cooper.



Cardio

Kenneth Cooper was the first person to introduce the concept of aerobic exercise. In the 1960s, Cooper started research into preventive medicine. He became intrigued by the belief that exercise can preserve one's health. In 1970 he created his own institute (the Cooper Institute) for non-profit research and education devoted to preventive medicine. He sparked millions into becoming active and is now known as the "father of aerobics".

What is generally called aerobic exercise might be better termed "solely aerobic", because it is designed to be low-intensity enough not to generate lactate (or lactic acid), so that all carbohydrate is aerobically turned into energy.

Initially during increased exertion, muscle glycogen is broken down to produce glucose, which undergoes glycolysis producing pyruvate (Figure 19.5.4) which then reacts with oxygen(Krebs cycle, Chemiosmosis) to produce carbon dioxide and water and releases energy. As glycogen levels in the muscle begin to fall, glucose is released into the bloodstream by the liver, and fat metabolism is increased so that it can fuel the aerobic pathways. Aerobic exercise may be fueled by glycogen reserves, fat reserves, or a combination of both, depending on the intensity.

Aerobic exercise comprises innumerable forms. In general, it is performed at a moderate level of intensity over a relatively long period of time. For example, running a long distance at a moderate pace is an aerobic exercise, but sprinting is not. Playing singles tennis, with near-continuous motion, is generally considered aerobic activity, while golf or two person team tennis, with brief bursts of activity punctuated by more frequent breaks, may not be predominantly aerobic. Some sports are thus inherently "aerobic", while other aerobic exercises, such as fartlek training or aerobic dance classes, are designed specifically to improve aerobic capacity and fitness. It is most common for aerobic exercises to involve the leg muscles, primarily or exclusively. There are some exceptions. For example, rowing to distances of 2,000 m or more is an aerobic sport that exercises several major muscle groups, including those of the legs, abdominals, chest, and arms. Common kettlebell exercises combine aerobic and anaerobic aspects.

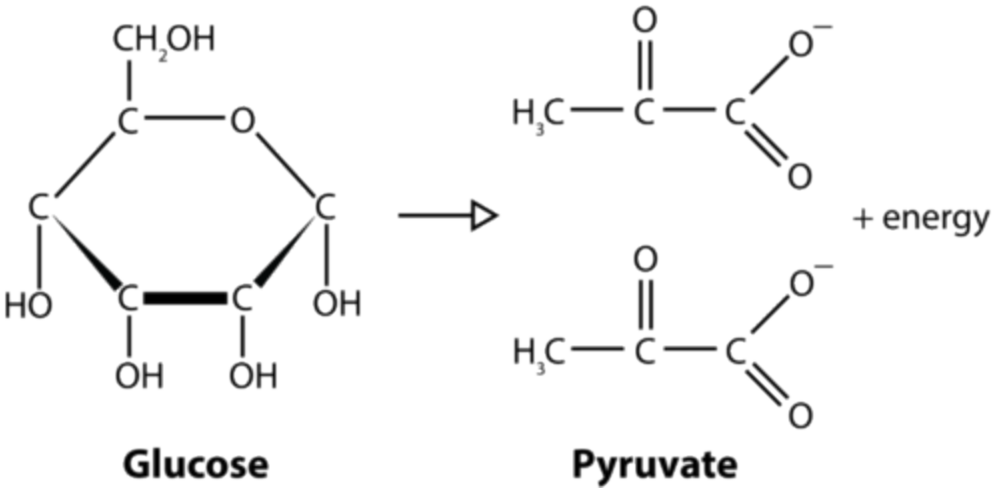


Figure 19.5.4 Glycolysis breaks the 6-carbon molecule glucose into two 3-carbon pyruvate molecules, releasing some of the chemical energy which had been stored in glucose.

Anaerobic Exercise and Oxygen Debt

Anaerobic exercise is a type of exercise that breaks down glucose in the body without using oxygen; *anaerobic* means "without oxygen". In practical terms, this means that anaerobic exercise is more intense, but shorter in duration than aerobic exercise.The biochemistry of anaerobic exercise involves a process called glycolysis, in which glucose is converted to adenosine triphosphate (ATP), which is the primary source of energy for cellular reactions.Lactic acid is produced at an increased rate during anaerobic exercise, causing it to build up quickly (Figure 19.5.5).Anaerobic exercise may be used to help build endurance, muscle strength, and power.

The by-product of anaerobic glycolysis—lactate—has traditionally been thought to be detrimental to muscle function. However, this appears likely only when lactate levels are very high. Elevated lactate levels are only one of many changes that occur within and around muscle cells during intense exercise that can lead to fatigue. Fatigue, that is muscle failure, is a complex subject that depends on more than just changes to lactate concentration. Energy availability, oxygen delivery, perception to pain, and other psychological factors all contribute to muscular fatigue. Elevated muscle and blood lactate concentrations are a natural consequence of any physical exertion. The effectiveness of anaerobic activity can be improved through training.

Anaerobic exercise also increases an individual's basal metabolic rate (BMR). Some examples of anaerobic exercises include sprints, high-intensity interval training (HIIT), and strength training.

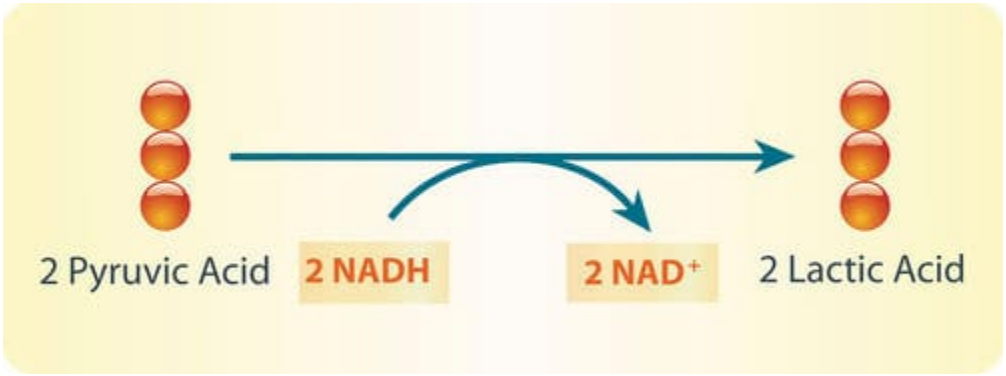


Figure 19.5.5 Converting pyruvic acid to lactic acid.

Lactic acid can be converted back to pyruvate in well-oxygenated muscle cells; however, during exercise the focus in on maintaining muscle activity. Lactic acid is transported to the liver where it can be stored prior to conversion to glucose in the presence of oxygen via the Cori Cycle. The amount of oxygen required to restore the lactic acid balance is often referred to as the **oxygen debt**.

Overview of Anaerobic and Aerobic Metabolism

Anaerobic metabolism occurs in the cytosol of the muscle cells. As seen in Figure 19.5.6, a small amount of ATP is produced in the cytosol without the presence of oxygen. Anaerobic metabolism uses glucose as its only source of fuel and produces pyruvate and lactic acid. Pyruvate can then be used as fuel for aerobic metabolism. Aerobic metabolism takes place in the mitochondria of the cell and is able to use carbohydrates, protein or fat as its fuel source. Aerobic metabolism is a much slower process than anaerobic metabolism but produces majority of the ATP.

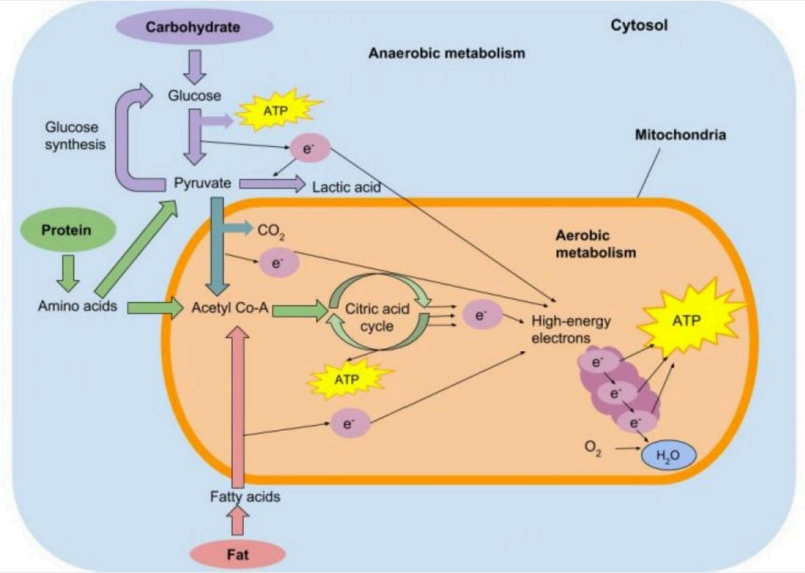


Figure 19.5.6: Anaerobic versus Aerobic Metabolism. Image by Allison Calabrese / CC BY 4.0.

Exercise and ATP

Different forms of exercise use different systems to produce ATP

A sprinter is getting ATP in a very different way to a marathon runner.

- Using creatine phosphate – This would be the major system used for short bursts (weightlifters or short distance sprinters) because it is fast but lasts for only 8–10 seconds.
- Using glycogen (no oxygen) – This lasts for 1.3–1.6 minutes, so it would be the system used in events like the 100 meter swim or the 200 m or 400 m run.
- Using aerobic respiration – This lasts for an unlimited time, so it's the system used in endurance events like marathon running, rowing, distance skating and so on.

Fuel Sources for Aerobic and Anaerobic Metabolism

The fuel sources for anaerobic and aerobic metabolism will change depending on the amount of nutrients available and the type of metabolism. Glucose may come from blood glucose (which is from dietary carbohydrates or liver glycogen and glucose synthesis) or muscle glycogen. Glucose is the primary energy source for both anaerobic and aerobic metabolism. Fatty acids are stored as triglycerides in muscles but about 90% of stored energy is found in adipose tissue. As low to moderate intensity exercise continues using aerobic metabolism, fatty acids become the predominant fuel source for the exercising muscles. Although protein is not considered a major energy source, small amounts of amino acids are used while resting or doing an activity. The amount of amino acids used for energy metabolism increase if the total energy intake from your diet does not meet the nutrient needs or if you are involved in long endurance exercises.

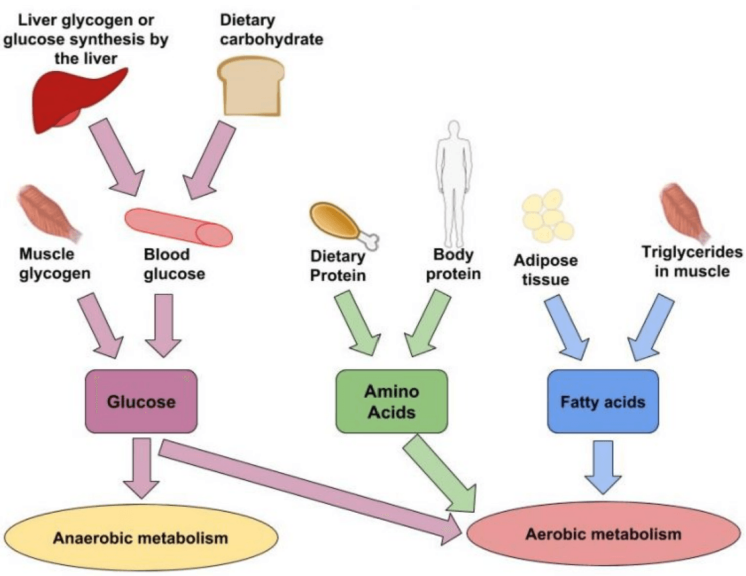


Figure 19.5.7 Fuel sources for anaerobic and aerobic metabolism.

Physical Activity Intensity and Fuel Use

The exercise intensity determines the contribution of the type of fuel source used for ATP production(see Figure 19.5.8). Both anaerobic and aerobic metabolism combine during exercise to ensure that the muscles are equipped with enough ATP to carry out the demands placed on them. The amount of contribution from each type of metabolism will depend on the intensity of an activity. When low-intensity activities are performed, aerobic metabolism is used to supply enough ATP to muscles. However, during high-intensity activities more ATP is needed so the muscles must rely on both anaerobic and aerobic metabolism to meet the body's demands.

During low-intensity activities, the body will use aerobic metabolism over anaerobic metabolism because it is more efficient by producing larger amounts of ATP. Fatty acids are the primary energy source during low-intensity activity. With fat reserves in the body being almost unlimited, low-intensity activities are able to continue for a long time. Along with fatty acids, a small amount of glucose is used as well. Glucose differs from fatty acids where glycogen storages can be depleted. As glycogen stores are depleted, fatigue will eventually set in.

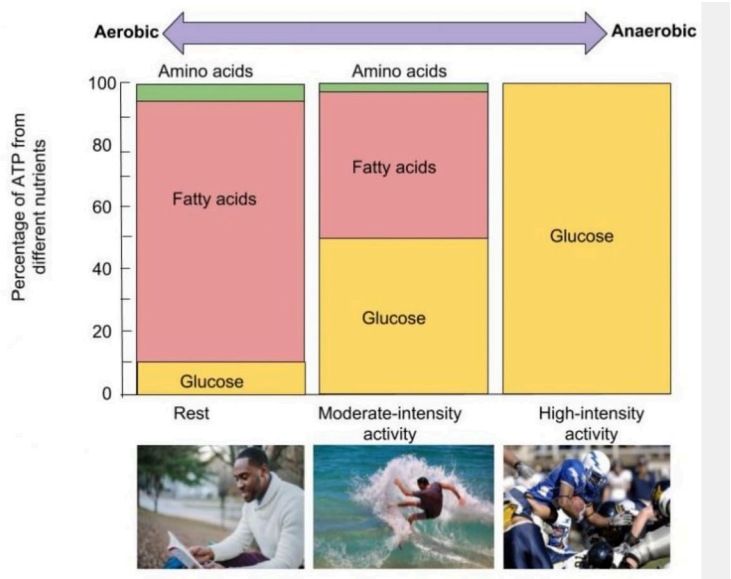


Figure 19.5.8: The Effect of Exercise Intensity on Fuel Sources.

Summary

- The body contains three types of muscle tissue: skeletal muscle, cardiac muscle, and smooth muscle. Skeleton muscle tissue is composed of sarcomeres, the functional units of muscle tissue.
- Muscle contraction occurs when sarcomeres shorten, as thick and thin filaments slide past each other, which is called the sliding filament model of muscle contraction.
- ATP provides the energy for cross-bridge formation and filament sliding.
- Aerobic exercise (also known as cardio) is physical exercise of low to high intensity that depends primarily on the aerobic energy-generating process (aerobic metabolism). Aerobic refers to the use of oxygen to adequately meet energy demands during exercise.
- Anaerobic exercise is a physical exercise intense enough that there is lack of oxygen. If there is a shortage of oxygen (anaerobic exercise, explosive movements), carbohydrate is consumed more rapidly and the pyruvate converts into lactate via the anaerobic process.
- The exercise intensity determines the contribution of the type of fuel source used for ATP production

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- Libretexts: Introductory Biology (CK-12)
- Wikipedia
- Anatomy and Physiology (Boundless)

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19.6: Drugs, Athletic Performance, and the Brain

Learning Objectives

- Know the different supplements and drugs that are used to maintain or enhance athletic performance.
- List the use and abuse of anabolic steroids.

Protein

Bodybuilders may supplement their diets with protein for reasons of convenience, lower cost (relative to meat and fish products) and to avoid the concurrent consumption of carbohydrates and fats. In addition, some argue that bodybuilders, by virtue of their unique training and goals, require higher-than-average quantities of protein to support maximal muscle growth; however there is no compelling evidence and no scientific consensus for bodybuilders to consume more protein than the recommended dietary allowance.



Figure 19.6.1: Protein milkshakes, made from protein powder (center) and milk (left), are a common bodybuilding supplement. (CC BY-SA 3.0; Sandstein).

Protein supplements are sold in ready-to-drink shakes, bars, meal replacement products (see below), bites, oats, gels and powders. Protein powders are the most popular and may have flavoring added for palatability. The powder is usually mixed with water, milk or juice and is generally consumed immediately before and after exercising, or in place of a meal. The sources of protein are as follows, and differ in protein quality depending on their amino acid profile and digestibility:

- Whey protein contains high levels of all the essential amino acids and branched-chain amino acids. It also has the highest content of the amino acid cysteine, which aids in the biosynthesis of glutathione. For bodybuilders whey protein provides amino acids used to aid in muscle recovery. Whey protein is derived from the process of making cheese from milk. There are three types of whey protein: whey concentrate, whey isolate, and whey hydrolysate. Whey concentrate is 29–89% protein by weight whereas whey isolate is 90%+ protein by weight. Whey hydrolysate is enzymatically predigested and therefore has the highest rate of digestion of all protein types. Whey protein is usually taken immediately before and after a workout
- Casein protein (or milk protein) has glutamine, and casomorphin. Casein is usually taken before going to bed.
- Soy protein from soybeans contain isoflavones, a type of phytoestrogen.
- Egg-white protein is a lactose- and dairy-free protein.
- Hemp protein from hemp seed, contains highly-digestible protein, and hemp oil is high in essential fatty acids.
- Rice protein, when made from the whole grain, is a protein source that is highly digestible and allergen free. Since rice protein is low in the amino acid lysine, it is often combined with pea protein powder to achieve a superior amino acid profile.

- Pea protein is a hypoallergenic protein with a lighter texture than most other protein powders. Pea protein has an amino acid profile similar to that of soy, but pea protein does not elicit concerns about unknown effects of phytoestrogens. Pea protein is also less allergenic than soy. Pea protein has high fiber content and has no allergic ingredients and therefore is easy for digestion as compared to whey protein. Pea protein is a slow digesting protein and is able to keep you full longer.

Some nutritionists claim that osteoporosis may occur from excessive protein intake because protein can put pressure on the kidneys and lead to bone loss due to calcium leaching. However, some have suggested that higher calcium excretion may be due to a corresponding increase in protein-induced calcium absorption in the intestines. In addition to complete proteins, some supplements will contain protein fragments such as branched-chain amino acids or individual amino acids (such as glutamine). Amino acids are considered to be inferior to whole protein and have been used by some companies to artificially inflate and falsify protein values in their product (protein spiking). Many protein supplements explicitly indicate on the label that no protein spiking has occurred.

Branched-chain amino acids

Amino acids are the building blocks of protein; the body breaks consumed protein into amino acids in the stomach and intestines. Amino acids are classified as essential, conditionally essential and non-essential. There are three branched-chain amino acids (BCAAs): leucine, isoleucine, and valine. All three branched-chain amino acids are essential amino acids. Each has numerous benefits on various biological processes in the body. Unlike other amino acids, BCAAs are metabolized in the muscle and have an anabolic/anti-catabolic effect on it. There is some evidence that BCAA's may enhance muscle recovery after intense physical activity and no side effects have been reported at this time.

Glutamine

Glutamine is the most abundant amino acid found in human muscle and is commonly found in supplements or as a micronized, instantly soluble powder because supplement manufacturers claim the body's natural glutamine stores are depleted during anaerobic exercise. Some studies have shown there to be no significant effect of glutamine on bench press strength, knee-extension torque or lean muscle mass when compared to controls taking a placebo, though another study found that glutamine is beneficial in raising T-helper/suppressor cell ratio in long-distance runners.

Essential fatty acids

The essential fatty acids (alpha-linolenic acid and linoleic acid) may be important to supplement while bodybuilding; these cannot readily be made in the body, but are required for various functions within the body to take place. Fatty fish, such as fresh salmon and trout are rich in essential fatty acids and fish oils can also be taken in supplement form. Flaxseed oil, often sold as a supplement on its own, is an ideal source of alpha-Linolenic acid, which can also be found in walnuts and pumpkin seeds.

Prohormone

Prohormones are precursors to hormones and are most typically sold to bodybuilders as a precursor to the natural hormone testosterone. This conversion requires naturally occurring enzymes in the body. Side effects are not uncommon, as prohormones can also convert further into DHT and estrogen. To deal with this, many supplements also have aromatase inhibitors and DHT blockers such as chrysin and 4-androstene-3,6,17-trione. To date most prohormone products have not been thoroughly studied, and the health effects of prolonged use are unknown. Although initially available over the counter, their purchase was made illegal without a prescription in the US in 2004, and they hold similar status in many other countries. They remain legal, however, in the United Kingdom and the wider European Union. Their use is prohibited by most sporting bodies.

Creatine

Creatine is an organic acid naturally occurring in the body that supplies energy to muscle cells for short bursts of energy (as required in lifting weights) via creatine phosphate replenishment of ATP. A number of scientific studies have shown that creatine can improve strength, energy, muscle mass, and recovery times. In addition, recent studies have also shown that creatine improves brain function. and reduces mental fatigue.Unlike steroids or other performance-enhancing drugs, creatine can be found naturally in many common foods such as herring, tuna, salmon, and beef.

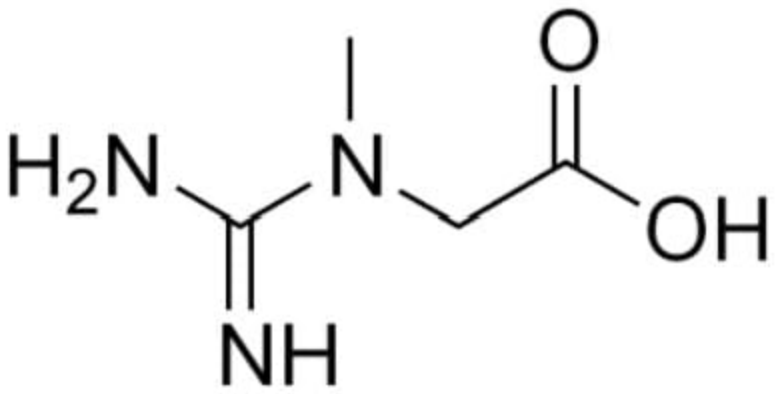


Figure 19.6.2: Skeletal formula of creatine

Creatine increases what is known as *cell volumization* by drawing water into muscle cells, making them larger. This *intracellular* retention should not be confused with the common myth that creatine causes bloating (or *intercellular* water retention). Creatine is sold in a variety of forms, including creatine monohydrate and creatine ethyl ester, amongst others. Though all types of creatine are sold for the same purposes, there are subtle differences between them, such as price and necessary dosage. Some studies have suggested that consumption of creatine with protein and carbohydrates can have a greater effect than creatine combined with either protein or carbohydrates alone.

β-Hydroxy β-methylbutyrate

When combined with an appropriate exercise program, dietary supplementation with β-hydroxy β-methylbutyrate (HMB) has been shown to dose-dependently augment gains in muscle hypertrophy (i.e., the size of a muscle), muscle strength, and lean body mass, reduce exercise-induced skeletal muscle damage, and expedite recovery from high-intensity exercise. HMB is believed to produce these effects by increasing muscle protein synthesis and decreasing muscle protein breakdown by various mechanisms, including activation of the mechanistic target of rapamycin (mTOR) and inhibition of the proteasome in skeletal muscles. The inhibition of exercise-induced skeletal muscle damage by HMB is affected by the time that it is used relative to exercise. The greatest reduction in skeletal muscle damage from a single bout of exercise appears to occur when calcium HMB is ingested 1–2 hours prior to exercise.

Thermogenic products

A thermogenic is a broad term for any supplement that the manufacturer claims will cause thermogenesis, resulting in increased body temperature, increased metabolic rate, and consequently an increased rate in the burning of body fat and weight loss. Until 2004 almost every product found in this supplement category comprised the "ECA stack": ephedrine, caffeine and aspirin. However, on February 6, 2004 the Food and Drug Administration (FDA) banned the sale of ephedra and its alkaloid, ephedrine, for use in weight loss formulas. Several manufacturers replaced the ephedra component of the "ECA" stack with bitter orange or citrus aurantium (containing synephrine) instead of the ephedrine.

Controversies of Fitness Supplements

Mislabeling: According to University of Helsinki food safety professor Marina Heinonen, more than 90% of dietary supplement health claims are incorrect. While many of the claims are based on scientifically based physiological or biochemical processes, their use in bodybuilding parlance is often heavily colored by bodybuilding lore and industry marketing and as such may deviate considerably from traditional scientific usages of the terms. In addition, ingredients listed have been found at times to be different from the contents. In 2015, Consumer Reports reported unsafe levels of arsenic, cadmium, lead and mercury in several of the protein powders that were tested. Other studies in 2013 showed that one-third of the supplements tested contained unlisted steroids. In 2015 a CBC investigative report found that protein spiking (the addition of amino acid filler to manipulate analysis) was not uncommon, however many of the companies involved challenged these claims.

Health problems: The US FDA reports 50,000 health problems a year due to dietary supplements and these often involve bodybuilding supplements. For example, the "natural" best-seller Craze, 2012's "New Supplement of the Year" by bodybuilding.com, sold in Walmart, Amazon etc., was found to contain undisclosed amphetamine-like compounds. Also other products by Matt Cahill have contained dangerous substances causing blindness or liver damages, and experts say that Cahill is emblematic for the whole industry.

Liver damage: The incidence of liver damage from dietary supplements has tripled in a decade, the majority of these involved bodybuilding supplements. This resulted in liver transplants and, in some cases, death to the patient. Some have argued that the liver damage is more often caused by prescription drugs rather than supplements.

Lack of effectiveness: In addition to being potentially harmful, some have argued that there is little evidence to indicate any benefit to using bodybuilding supplements. For example, according to the IOC, no consensus had been reached in determining whether an individual in exercise training benefits from protein and amino acid supplements. "In view of the lack of compelling evidence to the contrary, no additional dietary protein is suggested for healthy adults undertaking resistance or endurance exercise".

Caffeine and Athletic Performance

Caffeine is a proven ergogenic aid in humans. Caffeine improves athletic performance in aerobic (especially endurance sports) and anaerobic conditions. Moderate doses of caffeine (around 5 mg/kg) can improve sprint performance, cycling and running time trial performance, endurance (i.e., it delays the onset of muscle fatigue and central fatigue), and cycling power output. Caffeine increases basal metabolic rate in adults. Caffeine ingestion prior to aerobic exercise increases fat oxidation, particularly in persons with low physical fitness.

Caffeine improves muscular strength and power, and may enhance muscular endurance. Caffeine also enhances performance on anaerobic tests. Caffeine consumption before constant load exercise is associated with reduced perceived exertion. While this effect is not present during exercise-to-exhaustion exercise, performance is significantly enhanced. This is congruent with caffeine reducing perceived exertion, because exercise-to-exhaustion should end at the same point of fatigue. Caffeine also improves power output and reduces time to completion in aerobic time trials, an effect positively (but not exclusively) associated with longer duration exercise.

Anabolic Steroids

Anabolic steroids are synthetic, or human-made, variations of the male sex hormone testosterone. The proper term for these compounds is *anabolic-androgenic steroids*. "Anabolic" refers to muscle building, and "androgenic" refers to increased male sex characteristics. Some common names for anabolic steroids are Gear, Juice, Roids, and Stackers. Health care providers can prescribe steroids to treat hormonal issues, such as delayed puberty. Steroids can also treat diseases that cause muscle loss, such as cancer and AIDS. But some athletes and bodybuilders misuse these drugs in an attempt to boost performance or improve their physical appearance.

The majority of people who misuse steroids are male weightlifters in their 20s or 30s. Anabolic steroid misuse is much less common in women. It is difficult to measure steroid misuse in the United States because many national surveys do not measure it. However, use among teens is generally minimal. The 2016 NIDA-funded Monitoring the Future study has shown that past-year misuse of steroids has declined among 8th and 10th graders in recent years, while holding steady for 12th graders.

People who misuse anabolic steroids usually take them orally, inject them into muscles, or apply them to the skin as a gel or cream. These doses may be 10 to 100 times higher than doses prescribed to treat medical conditions.

Commons patterns for misusing steroids include:

- cycling—taking multiple doses for a period of time, stopping for a time, and then restarting
- stacking—combining two or more different steroids and mixing oral and/or injectable types
- pyramiding—slowly increasing the dose or frequency of steroid misuse, reaching a peak amount, and then gradually tapering off to zero
- plateauing—alternating, overlapping, or substituting with another steroid to avoid developing a tolerance

There is no scientific evidence that any of these practices reduce the harmful medical consequences of these drugs.

How Anabolic Steroids Work

Anabolic steroids work differently from other drugs of abuse; they do not have the same short-term effects on the brain. The most important difference is that steroids do not directly activate the reward system to cause a “high”; they also do not trigger rapid increases in the brain chemical dopamine, which reinforces most other types of drug taking behavior. Misuse of anabolic steroids might lead to negative mental effects, such as: paranoid (extreme, unreasonable) jealousy, extreme irritability and aggression (“roid rage”), *delusions*—false beliefs or ideas, impaired judgment, and mania. Aside from mental effects, steroid use commonly causes severe acne. It also causes the body to swell, especially in the hands and feet.

Anabolic steroid misuse might lead to serious, even permanent, health problems such as kidney problems or failure, liver damage and tumors, enlarged heart, high blood pressure, and changes in blood cholesterol, all of which increase the risk of stroke and heart attack, even in young people, and increased risk of blood clots. Several other effects are gender- and age-specific:

- **In men**: shrinking testicles, decreased sperm count, baldness, development of breasts, increased risk for prostate cancer
- **In women**: growth of facial hair or excess body hair, decreased breast size, male-pattern baldness, changes in or stop in the menstrual cycle, enlarged clitoris, deepened voice
- **In teens**: stunted growth (when high hormone levels from steroids signal to the body to stop bone growth too early) and stunted height (if teens use steroids before their growth spurt)

Some of these physical changes, such as shrinking sex organs in men, can add to mental side effects such as mood disorders.

Anabolic Steroids Addiction

Even though anabolic steroids do not cause the same high as other drugs, they can lead to a substance use disorder. A substance use disorder occurs when a person continues to misuse steroids, even though there are serious consequences for doing so. The most severe form of a substance use disorder is addiction. People might continue to misuse steroids despite physical problems, high costs to buy the drugs, and negative effects on their relationships. These behaviors reflect steroids' addictive potential.

Research has further found that some steroid users turn to other drugs, such as opioids, to reduce sleep problems and irritability caused by steroids. People who misuse steroids might experience withdrawal symptoms when they stop use, including:fatigue, restlessness, loss of appetite, sleep problems, decreased sex drive and steroid cravings.

One of the more serious withdrawal symptoms is depression, which can sometimes lead to suicide attempts. Some people seeking treatment for anabolic steroid addiction have found a combination of behavioral therapy and medications to be helpful. In certain cases of addiction, patients have taken medicines to help treat symptoms of withdrawal. For example, health care providers have prescribed antidepressants to treat depression and pain medicines for headaches and muscle and joint pain. Other medicines have been used to help restore the patient's hormonal system.

Drugs, Athletic Performance, and Drug Screening

In competitive sports, **doping** is the use of banned athletic performance-enhancing drugs by athletic competitors. The term *doping* is widely used by organizations that regulate sporting competitions. The use of drugs to enhance performance is considered unethical, and therefore prohibited, by most international sports organizations, including the International Olympic Committee. Furthermore, athletes (or athletic programs) taking explicit measures to evade detection exacerbate the ethical violation with overt deception and cheating.

The origins of doping in sports go back to the very creation of sport itself. From ancient usage of substances in chariot racing to more recent controversies in baseball and cycling, popular views among athletes have varied widely from country to country over the years. The general trend among authorities and sporting organizations over the past several decades has been to strictly regulate the use of drugs in sport. The reasons for the ban are mainly the health risks of performance-enhancing drugs, the equality of opportunity for athletes, and the exemplary effect of drug-free sport for the public. Anti-doping authorities state that using performance-enhancing drugs goes against the "spirit of sport".

Many sports organizations have banned the use of performance-enhancing drugs and have very strict rules and penalties for

people who are caught using them. The International Amateur Athletic Federation, now World Athletics, was the first international governing body of sport to take the situation seriously. In 1928 they banned participants from doping, but with little in the way of testing available they had to rely on the word of the athlete that they were clean. It was not until 1966 that FIFA and Union Cycliste Internationale (cycling) joined the IAAF in the fight against drugs, followed by the International Olympic Committee the following year. Progression in pharmacology has always outstripped the ability of sports federations to implement rigorous testing procedures but since the creation of the World Anti-Doping Agency in 1999, it has become more effective to catch athletes who use drugs. The first tests for athletes were at the 1966 European Championships and two years later the IOC implemented their first drug tests at both the Summer and Winter Olympics. Anabolic steroids became prevalent during the 1970s and after a method of detection was found they were added to the IOC's prohibited substances list in 1975, after which the 1976 Summer Olympics in Montreal were the first Olympic games which tested for them.

Exercise and the Brain

The **neurobiological effects of physical exercise** are numerous and involve a wide range of interrelated effects on brain structure, brain function, and cognition.[1][2][3][4] A large body of research in humans has demonstrated that consistent aerobic exercise (e.g., 30 minutes every day) induces persistent improvements in certain cognitive functions, healthy alterations in gene expression in the brain, and beneficial forms of neuroplasticity and behavioral plasticity; some of these long-term effects include: increased neuron growth, increased neurological activity (e.g., c-Fos and BDNF signaling), improved stress coping, enhanced cognitive control of behavior, improved declarative, spatial, and working memory, and structural and functional improvements in brain structures and pathways associated with cognitive control and memory.[1][2][3][4][5][6][7][8][9][10] The effects of exercise on cognition have important implications for improving academic performance in children and college students, improving adult productivity, preserving cognitive function in old age, preventing or treating certain neurological disorders, and improving overall quality of life.[1][11][12]

In healthy adults, aerobic exercise has been shown to induce transient effects on cognition after a single exercise session and persistent effects on cognition following regular exercise over the course of several months.[1][10][13] People who regularly perform aerobic exercise (e.g., running, jogging, brisk walking, swimming, and cycling) have greater scores on neuropsychological function and performance tests that measure certain cognitive functions, such as attentional control, inhibitory control, cognitive flexibility, working memory updating and capacity, declarative memory, spatial memory, and information processing speed.[1][5][7][9][10][13] The transient effects of exercise on cognition include improvements in most executive functions (e.g., attention, working memory, cognitive flexibility, inhibitory control, problem solving, and decision making) and information processing speed for a period of up to 2 hours after exercising.[13]

Aerobic exercise induces short- and long-term effects on mood and emotional states by promoting positive affect, inhibiting negative affect, and decreasing the biological response to acute psychological stress.[13] Over the short-term, aerobic exercise functions as both an antidepressant and euphoriant,[14][15][16][17] whereas consistent exercise produces general improvements in mood and self-esteem.

Regular aerobic exercise improves symptoms associated with a variety of central nervous system disorders and may be used as an adjunct therapy for these disorders. There is clear evidence of exercise treatment efficacy for major depressive disorder and attention deficit hyperactivity disorder.[11][16][20][21][22][23] The American Academy of Neurology's clinical practice guideline for mild cognitive impairment indicates that clinicians should recommend regular exercise (two times per week) to individuals who have been diagnosed with this condition.[24] Reviews of clinical evidence also support the use of exercise as an adjunct therapy for certain neurodegenerative disorders, particularly Alzheimer's disease and Parkinson's disease. Regular exercise is also associated with a lower risk of developing neurodegenerative disorders.[28][31] A large body of preclinical evidence and emerging clinical evidence supports the use of exercise as an adjunct therapy for the treatment and prevention of drug addictions. Regular exercise has also been proposed as an adjunct therapy for brain cancers.[37]

Endorphins play a major role in the body's inhibitory response to pain. Endorphin production can be triggered by vigorous aerobic exercise. The release of β-endorphin has been postulated to contribute to the phenomenon known as a "runner's high." Endorphins may contribute to the positive effect of exercise on anxiety and depression. The same phenomenon may also play a role in exercise addiction. Regular intense exercise may cause the brain to downregulate the production of endorphins in periods of rest to maintain homeostasis, causing a person to exercise more intensely in order to receive the same feeling. However, several studies have supported the hypothesis that the runner's high is due to the release of endocannabinoids rather than that of endorphins.

Summary

- Anabolic steroids are synthetic variations of the male sex hormone testosterone. Health care providers can prescribe steroids to treat various medical conditions. But some athletes and bodybuilders misuse these drugs to boost performance or improve their physical appearance.
- People who abuse anabolic steroids usually take them orally, inject them into the muscles, or apply them to the skin with a cream or gel.
- People misuse steroids in a variety of doses and schedules. Misuse of anabolic steroids might lead to short-term effects, including paranoid jealousy, extreme irritability and aggression, delusions, impaired judgment, and mania. Continued steroid misuse can act on some of the same brain pathways and chemicals that are affected by other drugs, including dopamine, serotonin, and opioid systems.
- Caffeine improves athletic performance in aerobic (especially endurance sports) and anaerobic conditions.
- Anabolic steroid misuse might lead to serious long-term, even permanent, health problems. Several other effects are gender- and age-specific.
- Even though anabolic steroids do not cause the same high as other drugs, they can lead to addiction. Some people seeking treatment for anabolic steroid addiction have found behavioral therapy and medications to be helpful. Medicines can help treat symptoms of withdrawal in some cases.
- The use of drugs to enhance performance is considered unethical, and therefore prohibited, by most international sports organizations, including the International Olympic Committee.
- Endorphin production can be triggered by vigorous aerobic exercise.

Contributors and Attributions

- Wikipedia
- National Institute on Drug Abuse; National Institutes of Health; U.S. Department of Health and Human Services.

- Marisa Alviar-Agnew (Sacramento City College)

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20: CHEMISTRY DOWN ON THE FARM

20.1: Farming and Chemicals- Fertilizers
20.2: The War against Pests
20.3: Herbicides and Defoliants
20.4: Sustainable Agriculture

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20.1: Farming and Chemicals- Fertilizers

Learning Objectives

- Identify the three main macronutrients, the secondary macronutrients, and micronutrients that are essential for plant growth.
- Describe the different types of commercial fertilizers.

A **fertilizer** is any material of natural or synthetic origin that is applied to soil or to plant tissues to supply one or more plant nutrients essential to the growth of plants. Many sources of fertilizer exist, both natural and industrially produced.[1]Commercial fertilizers, are applied to agricultural crops to increase crop yields, using equipment similar to what is shown in Figure 20.1.1 . Before the 1950s, most farming occurred on small family farms with limited use of chemicals. The shift since then to larger corporate farms has coincided with the use of chemical fertilizers in modern agricultural practices. The three major types of commercial fertilizer used in the U.S. are nitrogen, phosphate, and potash.

Fertilizers enhance the growth of plants. This goal is met in two ways, the traditional one being additives that provide nutrients. The second mode by which some fertilizers act is to enhance the effectiveness of the soil by modifying its water retention and aeration. This article, like many on fertilizers, emphasizes the nutritional aspect. Fertilizers typically provide, in varying proportions:[15]

- three main macronutrients:
  - Nitrogen (N): leaf growth
  - Phosphorus (P): Development of roots, flowers, seeds, fruit;
  - Potassium (K): Strong stem growth, movement of water in plants, promotion of flowering and fruiting;
- three secondary macronutrients: calcium (Ca), magnesium (Mg), and sulfur (S);
- micronutrients: copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), zinc (Zn), boron (B). Of occasional significance are silicon (Si), cobalt (Co), and vanadium (V).

The nutrients required for healthy plant life are classified according to the elements, but the elements are not used as fertilizers. Instead compounds containing these elements are the basis of fertilizers. The macro-nutrients are consumed in larger quantities and are present in plant tissue in quantities from 0.15% to 6.0% on a dry matter (DM) (0% moisture) basis. Plants are made up of four main elements: hydrogen, oxygen, carbon, and nitrogen. Carbon, hydrogen and oxygen are widely available as water and carbon dioxide. Although nitrogen makes up most of the atmosphere, it is in a form that is unavailable to plants. Nitrogen is the most important fertilizer since nitrogen is present in proteins, DNA and other components (e.g., chlorophyll). To be nutritious to plants, nitrogen must be made available in a "fixed" form. Only some bacteria and their host plants (notably legumes) can fix atmospheric nitrogen (N_2) by converting it to ammonia. Phosphate is required for the production of DNA and ATP, the main energy carrier in cells, as well as certain lipids. Table 20.1.1 *lists features of various plant essential nutrients.*

Plant Essential Nutrients - Texas A&M Agri-life Extension (Essential Nutrients for Plants)

https://agrilifeextension.tamu.edu/l...ts-for-plants/

TABLE 1: Form, source, mode of uptake and major functions of the 16 plant essential nutrients.

Nutrient family	Nutrient	Percentage of plant	Form taken up by plants (ion)	Mode of uptake	Major functions in plants
Primary	Carbon	45	Carbon dioxide (CO_2), bicarbonate (HCO_3^-)	Open somates	Plant structures
	Oxygen	45	Water (H_2O)	Mass flow	Respiration, energy production, plant structures
	Hydrogen	6.0	Water (H_2O)	Mass flow	pH regulation, water retention, synthesis of carbohydrates
	Nitrogen	1.75	Nitrate (NO_3^-), ammonium (NH_4^+)	Mass flow	Protein/amino acids, chlorophyll, cell formation
	Phosphorus	0.25	Dihydrogen phosphate ($H_2PO_4^-$, HPO_4^{2-}), phosphate (PO_4^{3-})	Root interception	Cell formation, protein syntheses, fat and carbohydrate metabolism
	Potassium	1.5	Potassium ion (K^+)	Mass flow	Water regulation, enzyme activity
Secondary	Calcium	0.50	Calcium ion (Ca^{2+})	Mass flow	Root permeability, enzyme acitivity
	Magnesium	0.20	Magnesium ion (Mg^{2+})	Mass flow	Chlorophyll, fat formation and metabolism
	Sulfur	0.03	Sulfate (SO_4^{2-})	Mass flow	Protein, amino acid, vitamin and oil formation
Micro	Chlorine	0.01	Chloride (Cl^-)	Root interception	Chlorophyll formation, enzyme activity, cellular development
	Iron	0.01	Iron ion (Fe^{2+}, Fe^{3+})	Root interception	Enzyme development and activity
	Zinc	0.002	Zinc ion (Zn^{2+})	Root interception	Enzyme activity
	Manganese	0.005	Manganese ion (Mn^{2+})	Root interception	Enzyme activity and pigmentation
	Boron	0.0001	Boric acid (H_3BO_3), borate (BO_3^{3-}), tetraborate (B_4O_7)	Root interception	Enzyme activity
	Copper	0.0001	Copper ion (Cu^{2+})	Mass flow	Enzyme activity
	Molybdenum	0.00001	Molybdenum ions ($HMoO^{4-}$, MoO_4^{2-})	Mass flow	Enzyme activity and nitrogen fixation in legumes



Figure 20.1.1 *A Lite-trac Agri-Spread lime and fertilizer spreader at an agricultural show. Source: WIkipedia*



Figure 20.1.2 *A large, modern fertilizer spreader (right). Source: WIkipedia*

Nitrogen Fertilizers

Nitrogen fertilizers are made from ammonia (NH_3) produced by the Haber-Bosch process. In this energy-intensive process, natural gas (CH_4) usually supplies the hydrogen, and the nitrogen (N_2) is derived from the air. This ammonia is used as a feedstock for all other nitrogen fertilizers, such as anhydrous ammonium nitrate (NH_4NO_3) and urea ($CO(NH_2)_2$).

Deposits of sodium nitrate ($NaNO_3$) (Chilean saltpeter) are also found in the Atacama desert in Chile and was one of the original (1830) nitrogen-rich fertilizers used. It is still mined for fertilizer. Nitrates are also produced from ammonia by the Ostwald process. Detailed information on different nitrogen fertilizers is given in (Table 20.1.2).

Nitrogen Fertilizers - USDA

Table 20.1.2 *USDA Nitrogen Fertilizer Guide.*

https://www.nrcs.usda.gov/Internet/F...4p2_068185.pdf

NITROGEN FERTILIZERS	NITROGEN (N) CHEMICAL FORM (i.e., **UREA ($CO(NH_2)_2$)**, **AMMONIUM ION (NH_4^+)**, **AMMONIA (NH_3)**, and **NITRATE (NO_3^-)**); handling properties, and other information:
Urea	**N** is 100% **$CO(NH_2)_2$**, which converts to ammonia in several days; is hygroscopic; quite soluble; good handling properties.
Ammonium Nitrate	**N** is 50% **NH_4^+** and 50% **NO_3^-**; is hygroscopic; highly soluble; explosive if mixed with hydrocarbons (fuel oil); care taken to prevent caking.
URAN (Urea + Ammonium Nitrate)	**N** is 50% **$CO(NH_2)_2$**, 25% **NH_4^+**, and 25% **NO_3^-**; nonpressure N solution; ease in handling and application. Can be applied through various irrigation systems.
Ammonium Sulfate	**N** is 100% **NH_4^+**; S is 100% SO_4^{2-}; safe and easy to store; quite soluble; low hygroscopicity; solid.
Ammonium Thiosulfate	**N** is 100% **NH_4^+**; when applied to soil, ammonium thiosulfate forms colloidal S^0 and $(NH_4)_2SO_4$; S^0 must be oxidized; is a solution.
Monoammonium Phosphate	**N** is 100% **NH_4^+**; 11-52-0 is the most common grade for monoammonium phosphate, and 18-46-0 is the most common grade for diammonium phosphate; both are granular & completely water-soluble; more important as a phosphorus source.
Diammonium Phosphate	
Ammonium Polyphosphate	**N** is 100% **NH_4^+**; 10-34-0 is the most common grade; approximately 75% of P is polyphosphate and 25% is orthophosphate; liquid; easy handling.
Calcium Nitrate	**N** is 100% **NO_3^-**; is highly soluble; strongly hygroscopic. Also provides a readily soluble/available calcium ions.
Potassium Nitrate	**N** is 100% **NO_3^-**; also called salt peter. Also provides a readily soluble/available potassium ions.
Sodium Nitrate	**N** is 100% **NO_3^-**; a naturally mined fertilizer. This is a very soluble fertilizer. Approved for organic farmer registration/ certification.
Anhydrous Ammonia	**N** is 100% **NH_3**; is a liquid under pressure; must be injected 3 to 8" below the soil surface; stored in pressure tanks; must observe safety precautions.
Aqua Ammonia	**N** is 100% **NH_3** dissolved in water; usually injected in soils 2 to 4" depth; is composed of 25-29% NH_3 by weight; pressure of < 10 lb/in^2.

Phosphorus Fertilizers

Phosphate fertilizers are obtained by extraction from phosphate rock, which contains two principal phosphorus-containing minerals, fluorapatite $Ca_5(PO_4)_3F$ (CFA) and hydroxyapatite $Ca_5(PO_4)_3OH$. These minerals are converted into water-soluble phosphate salts by treatment with sulfuric (H_2SO_4) or phosphoric acids (H_3PO_4). The large production of sulfuric acid is primarily motivated by this application. In the nitrophosphate process or Odda process (invented in 1927), phosphate rock with up to a 20% phosphorus (P) content is dissolved with nitric acid (HNO_3) to produce a mixture of phosphoric acid (H_3PO_4) and calcium nitrate ($Ca(NO_3)_2$). This mixture can be combined with a potassium fertilizer to produce a *compound fertilizer* with the three macronutrients N, P and K in easily dissolved form.

Potassium Fertilizers

Potash is a mixture of potassium minerals used to make potassium (K) fertilizers. Potash is soluble in water, so the main effort in producing this nutrient from the ore involves some purification steps; e.g., to remove sodium chloride (NaCl) (common salt). Sometimes potash is referred to as K_2O, as a matter of convenience to those describing the potassium content. In fact, potash fertilizers are usually potassium chloride, potassium sulfate, potassium carbonate, or potassium nitrate.[29]

Other Essential Elements

Calcium, magnesium, and sulfur are essential to plant growth but are needed in lesser amounts than nitrogen, phosphorus, and potassium but in larger amounts than the micronutrients. Calcium, magnesium, and phosphorus alter pH when added to the soil. Calcium and magnesium results to an elevation of pH levels while sulfur does the opposite.

Calcium provides structural support in growing plants. Magnesium is the central atom found in the chlorophyll molecule and thus has an important role in photosynthesis. Sulfur is needed in chlorophyll development and protein synthesis.

Micronutrients are consumed in smaller quantities and are present in plant tissue on the order of parts-per-million (ppm), ranging from 0.15 to 400 ppm or less than 0.04% dry matter.[16][17] These elements are often present at the active sites of enzymes that carry out the plant's metabolism. Because these elements enable catalysts (enzymes) their impact far exceeds their weight percentage. The main micronutrients are molybdenum, zinc, boron, and copper. These elements are provided as water-soluble salts. Iron presents special problems because it converts to insoluble (bio-unavailable) compounds at moderate soil pH and phosphate concentrations. For this reason, iron is often administered as a chelate complex, e.g., the EDTA derivative. The micronutrient needs depend on the plant and the environment. For example, sugar beets appear to require boron, and legumes require cobalt,[1] while environmental conditions such as heat or drought make boron less available for plants.[23]

Fertilizers a Mixed Bag

Multi nutrient fertilizers are common. They consist of two or more nutrient components.

Binary (NP, NK, PK) fertilizers. Major two-component fertilizers provide both nitrogen and phosphorus to the plants. These are called NP fertilizers. The main NP fertilizers are monoammonium phosphate (MAP) and diammonium phosphate (DAP). The active ingredient in MAP is $NH_4H_2PO_4$. The active ingredient in DAP is $(NH_4)_2HPO_4$. About 85% of MAP and DAP fertilizers are soluble in water.

NPK fertilizers are three-component fertilizers providing nitrogen, phosphorus, and potassium.

NPK rating is a rating system describing the amount of nitrogen, phosphorus, and potassium in a fertilizer. NPK ratings consist of three numbers separated by dashes (e.g., 10-10-10 or 16-4-8) describing the chemical content of fertilizers.[20][21] The first number represents the percentage of nitrogen in the product; the second number, P_2O_5; the third, K_2O. Fertilizers do not actually contain P_2O_5 or K_2O, but the system is a conventional shorthand for the amount of the phosphorus (P) or potassium (K) in a fertilizer. A 50-pound (23 kg) bag of fertilizer labeled 16-4-8 contains 8 lb (3.6 kg) of nitrogen (16% of the 50 pounds), an amount of phosphorus equivalent to that in 2 pounds of P_2O_5 (4% of 50 pounds), and 4 pounds of K_2O (8% of 50 pounds). Most fertilizers are labeled according to this N-P-K convention, although Australian convention, following an N-P-K-S system, adds a fourth number for sulfur, and uses elemental values for all values including P and K.[22]

Organic Fertilizers

“Organic fertilizers” can be described as those fertilizers with an organic — biologic — origin—that is, fertilizers derived from living or formerly living materials. Organic fertilizers can also describe commercially available and frequently packaged products that strive to follow the expectations and restrictions adopted by “organic agriculture” and ”environmentally friendly" gardening — related systems of food and plant production that significantly limit or strictly avoid the use of synthetic fertilizers and pesticides. The “organic fertilizer” *products* typically contain both some organic materials as well as acceptable additives such as nutritive rock powders, ground sea shells (crab, oyster, etc.), other prepared products such as seed meal or kelp, and cultivated microorganisms and derivatives.

Fertilizers of an organic origin (the first definition) include animal wastes, plant wastes from agriculture, compost, and treated sewage sludge (biosolids). Beyond manures, animal sources can include products from the slaughter of animals — bloodmeal, bone meal, feather meal, hides, hoofs, and horns all are typical components.[15] Organically derived materials available to industry such as sewage sludge may not be acceptable components of organic farming and gardening, because of factors ranging from residual contaminants to public perception. On the other hand, marketed “organic fertilizers” may include, and promote, processed organics *because* the materials have consumer appeal. No matter the definition nor composition, most of these products contain less-concentrated nutrients, and the nutrients are not as easily quantified. They can offer soil-building advantages as well as be appealing to those who are trying to farm / garden more “naturally”.[30]

In terms of volume, peat is the most widely used packaged organic soil amendment. It is an immature form of coal and improves the soil by aeration and absorbing water but confers no nutritional value to the plants. It is therefore not a fertilizer as defined in the beginning of the article, but rather an amendment. Coir, (derived from coconut husks), bark, and sawdust when added to soil all act similarly (but not identically) to peat and are also considered organic soil amendments - or texturizers - because of their limited nutritive inputs. Some organic additives can have a reverse effect on nutrients — fresh sawdust can consume soil nutrients as it breaks down, and may lower soil pH — but these same organic texturizers (as well as compost, etc.) may increase the availability of nutrients through improved cation exchange, or through increased growth of microorganisms that in turn increase availability of certain plant nutrients. Organic fertilizers such as composts and manures may be distributed locally without going into industry production, making actual consumption more difficult to quantify.

Effects of Fertilizer Runoffs

Phosphorus and nitrogen fertilizers when commonly used have major environmental effects. This is due to high rainfalls causing the fertilizers to be washed into waterways. Agricultural run-off is a major contributor to the eutrophication of fresh water bodies. For example, in the US, about half of all the lakes are eutrophic. The main contributor to eutrophication is phosphate, which is normally a limiting nutrient; high concentrations promote the growth of cyanobacteria and algae, the demise of which consumes

oxygen. Cyanobacteria blooms ('algal blooms') can also produce harmful toxins that can accumulate in the food chain, and can be harmful to humans.

The nitrogen-rich compounds found in fertilizer runoff are the primary cause of serious oxygen depletion in many parts of oceans, especially in coastal zones, lakes and rivers. The resulting lack of dissolved oxygen greatly reduces the ability of these areas to sustain oceanic fauna. The number of oceanic dead zones near inhabited coastlines are increasing. As of 2006, the application of nitrogen fertilizer is being increasingly controlled in northwestern Europe and the United States. If eutrophication *can* be reversed, it may take decades[*citation needed*] before the accumulated nitrates in groundwater can be broken down by natural processes.

Summary

- A fertilizer is any material (of natural or synthetic origin) that is applied to soil or to plant tissues that provides one or more plant nutrients essential to the growth of plants.
- Nitrogen, phosphorus, and potassium are the main macronutrients and calcium, magnesium, and sulfur are the secondary macronutrients in fertilizers.
- Copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), zinc (Zn), boron (B) are essential micronutrients that are needed by plants in relatively smaller quantities than the macronutrients.
- Phosphorus and nitrogen fertilizers when commonly used have major environmental effects. This is due to high rainfalls causing the fertilizers to be washed into waterways. Agricultural run-off is a major contributor to the eutrophication of fresh water bodies.

Contributors and Attributions

- Wikipedia

  US Department of Agriculture (USDA)

  “Secondary Plant Nutrients: Calcium, Magnesium, and Sulfur.” *Mississippi State University Extension Service*, extension.msstate.edu/publications/secondary-plant-nutrients-calcium-magnesium-and-sulfur.

  “Essential Nutrients for Plants - How Do Nutrients Affect Plant Growth?” *Texas A&M AgriLife Extension Service*, 4 Mar. 2019, agrilifeextension.tamu.edu/library/gardening/essential-nutrients-for-plants/.

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20.2: The War against Pests

Learning Objective

- List the different types of pesticides and their uses.

Pesticides are substances that are meant to control pests. The term pesticide includes all of the following: herbicide, insecticides (which may include insect growth regulators, termiticides, etc.) nematicide, molluscicide, piscicide, avicide, rodenticide, bactericide, insect repellent, animal repellent, antimicrobial, and fungicide. The most common of these are herbicides which account for approximately 80% of all pesticide use. Most pesticides are intended to serve as plant protection products (also known as crop protection products), which in general, protect plants from weeds, fungi, or insects. As an example, the fungus *Alternaria solani* is used to combat the aquatic weed *Salvinia*.

In general, a pesticide is a chemical (such as carbamate) or biological agent (such as a virus, bacterium, or fungus) that deters, incapacitates, kills, or otherwise discourages pests. Target pests can include insects, plant pathogens, weeds, molluscs, birds, mammals, fish, nematodes (roundworms), and microbes that destroy property, cause nuisance, or spread disease, or are disease vectors. Along with these benefits, pesticides also have drawbacks, such as potential toxicity to humans and other species.

Pesticides can be classified by target organism (e.g., herbicides, insecticides, fungicides, rodenticides, and pediculicides – see table), chemical structure (e.g., organic, inorganic, synthetic, or biological (biopesticide), although the distinction can sometimes blur), and physical state (e.g. gaseous (fumigant)). Biopesticides include microbial pesticides and biochemical pesticides. Plant-derived pesticides, or "botanicals", have been developing quickly. These include the pyrethroids, rotenoids, nicotinoids, and a fourth group that includes strychnine and scilliroside.:15

Since before 2000 BC, humans have utilized pesticides to protect their crops. The first known pesticide was elemental sulfur dusting used in ancient Sumer about 4,500 years ago in ancient Mesopotamia. The Rig Veda, which is about 4,000 years old, mentions the use of poisonous plants for pest control.[13] By the 15th century, toxic chemicals such as arsenic, mercury, and lead were being applied to crops to kill pests. In the 17th century, nicotine sulfate was extracted from tobacco leaves for use as an insecticide. The 19th century saw the introduction of two more natural pesticides, pyrethrum, which is derived from chrysanthemums, and rotenone, which is derived from the roots of tropical vegetables.[14] Until the 1950s, arsenic-based pesticides were dominant.[15] Paul Müller discovered that DDT was a very effective insecticide. Organochlorines such as DDT were dominant, but they were replaced in the U.S. by organophosphates and carbamates by 1975. Since then, pyrethrin compounds have become the dominant insecticide.[15] Herbicides became common in the 1960s, led by "triazine and other nitrogen-based compounds, carboxylic acids such as 2,4-dichlorophenoxyacetic acid, and glyphosate".

The discussion in this section will be focused mainly on insecticides and the next section on herbicides and defoliants. Many pesticides can be grouped into chemical families. Prominent insecticide families include organochlorines, organophosphates, and carbamates.

Table 20.2.1 below gives the LD_{50} values for some insecticides. In each case, the chemical was fed to laboratory rats. Note that the lower the LD_{50}, the more toxic the chemical.

Table 20.2.1 LD_{50} Values for Various Insecticides.

Chemical	Category	Oral LD_{50} in Rats (mg/kg)
Aldicarb ("Temik")	Carbamate	1
Carbaryl ("Sevin")	Carbamate	307
DDT	Chlorinated hydrocarbon	87
Dieldrin	Chlorinated hydrocarbon	40
Diflubenzuron ("Dimilin")	Chitin inhibitor	10,000

Chemical	Category	Oral LD_{50} in Rats (mg/kg)
Malathion	Organophosphate	885
Methoprene	JH mimic	34,600
Methoxychlor	Chlorinated hydrocarbon	5,000
Parathion	Organophosphate	3
Piperonyl butoxide	Synergist	7,500
Pyrethrins	Plant extract	200
Rotenone	Plant extract	60

Note: LD_{50} (abbreviation for "lethal dose, 50%") of a toxin, radiation, or pathogen is the dose required to kill half the members of a tested population after a specified test duration. LD_{50} figures are frequently used as a general indicator of a substance's acute toxicity. A lower LD_{50} is indicative of increased toxicity.

Benefits of Using Pesticides

Pesticides can save farmers' money by preventing crop losses to insects and other pests; in the U.S., farmers get an estimated fourfold return on money they spend on pesticides. One study found that not using pesticides reduced crop yields by about 10%. Another study, conducted in 1999, found that a ban on pesticides in the United States may result in a rise of food prices, loss of jobs, and an increase in world hunger.

There are two levels of benefits for pesticide use, primary and secondary. Primary benefits are direct gains from the use of pesticides and secondary benefits are effects that are more long-term.

Primary benefits

Controlling pests and plant disease vectors

- Improved crop yields
- Improved crop/livestock quality
- Invasive species controlled

Controlling human/livestock disease vectors and nuisance organisms

- Human lives saved and disease reduced. Diseases controlled include malaria, with millions of lives having been saved or enhanced with the use of DDT alone.
- Animal lives saved and disease reduced

Controlling organisms that harm other human activities and structures

- Drivers view unobstructed
- Tree/brush/leaf hazards prevented
- Wooden structures protected

Monetary

In one study, it was estimated that for every dollar ($1) that is spent on pesticides for crops can yield up to four dollars ($4) in crops saved. This means based that, on the amount of money spent per year on pesticides, $10 billion, there is an additional $40 billion savings in crop that would be lost due to damage by insects and weeds. In general, farmers benefit from having an increase in crop yield and from being able to grow a variety of crops throughout the year. Consumers of agricultural products also benefit from being able to afford the vast quantities of produce available year-round.

DDT: The Dream Insecticide - or Nightmare

DDT was the first of a long line of insecticides based on hydrocarbons with chlorine atoms replacing some of the hydrogen atoms. Its chemical name is dichloro, diphenyl, trichloroethane (see Figure $20.2.1a$).

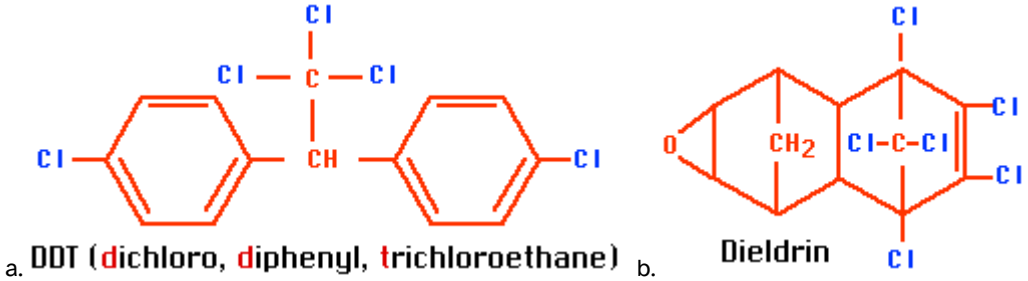


Figure $20.2.1$ *a. DDT and b. dieldrin*

Some others:

- methoxychlor
- dieldrin (see Figure $20.2.1a$).
- dicofol (Kelthane®)
- endosulfan (Thiodan®, Phaser®)

DDT was introduced during World War II and, along with penicillin and the sulfa drugs, was responsible for the fact that this was the first war in history where trauma killed more people - combatants and noncombatants alike - than infectious disease.

DDT is effective against

- vectors of human diseases such as
  - malaria and yellow fever (both transmitted by mosquitoes)
  - plague (transmitted by fleas)
- many crop pests

Prior to the introduction of DDT, the number of cases of malaria in Ceylon (now Sri Lanka) was more than a million a year. By 1963 the disease had been practically eliminated from the island. However, growing concern about the hazards of DDT led to its abandonment there in the mid-1960s, and soon thereafter malaria became common once again.

DDT was especially effective against malarial mosquitoes because of its persistence and resistance to breakdown in the environment. One or two sprays a year on the walls of homes kept them free of mosquitoes. But DDT has several serious drawbacks.

Development of Insect Resistance

As early as 1946, Swedish workers discovered populations of houseflies resistant to DDT. This was quickly followed by many other reports of developing resistance. Other chlorinated hydrocarbons (like dieldrin and methoxychlor) were developed as substitutes, but in time insects developed resistance to these as well.

Biomagnification

Although no harmful effects from average exposures to DDT have been seen in humans, DDT and other chlorinated hydrocarbons have been shown to harm other species, such as fishes, earthworms, and robins. The hazard of DDT to nontarget animals is particularly acute for those species living at the top of food chains. Carnivores at the ends of long food chains (e.g., ospreys, pelicans, falcons, and eagles) once suffered serious declines in fecundity and hence in population size because of this. High levels of chlorinated hydrocarbons interfere with forming eggshells of normal thickness.

Organophosphates

The organophosphates, e.g., **parathion** (Figure 20.2.2), are related to the nerve gases developed during World War II. They react irreversibly with the enzyme **acetylcholinesterase**, which is responsible for inactivating acetylcholine (ACh) at neuromuscular junctions and at certain synapses in the central and peripheral nervous systems.

Some other examples:

- malathion
- diazinon
- phosmet (Imidan®)
- chlorpyrifos (Lorsban®)

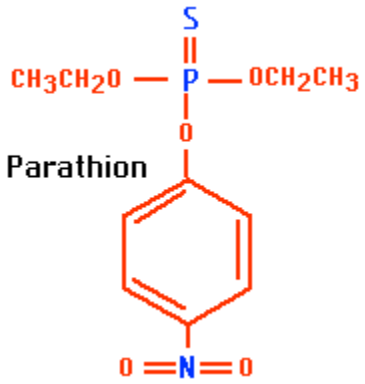


Figure 20.2.2 Parathion

Some of the organophosphates are very toxic. Parathion, for example, is 30 times more toxic than DDT. Each year organophosphates poison thousands of humans throughout the world, causing hundreds of deaths. Medical personnel caring for poisoning victims are also at risk. They may be seriously poisoned by the excretions of, and even the vapors emanating from, their patients.

Unlike chlorinated hydrocarbons,

- Organophosphates break down quickly in the environment, and thus residues on crops are less likely to be a problem.
- They are not stored in animal tissue, so biomagnification has not been a problem either.

For these reasons, their use has greatly reduced the hazard to non target species like ospreys and eagles (at the price of a much greater hazard to humans). Development of resistance is just as much a problem as it is with the chlorinated hydrocarbons. The carbamates were introduced in an attempt to keep ahead.

Carbamates

Carbamate insecticides are also inhibitors of acetylcholinesterase, but their action is reversible.

Some examples:

- carbaryl (Sevin®)
- aldicarb (Temik®)
- methomyl (Lannate®)

Features:

- These compounds are rapidly detoxified and excreted so their risk to warm-blooded animals is less than the other agents we have looked at.
- They are degraded rapidly in the environment so persistence is not a problem.
- They are, however, a danger to many useful insects, especially honeybees.

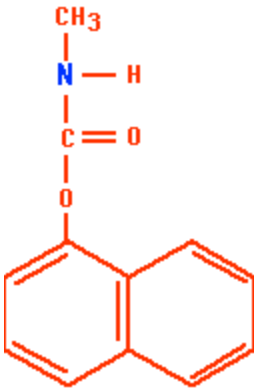


Figure 20.2.3 Carbaryl.

Growth Regulators

The members of this diverse group interfere in one way or another with insect development. Although most insect growth regulators do not affect adults, for many pests, it is the larval stages that are the most destructive.

Chitin Inhibitors

These substances, diflubenzuron (Dimilin®) is an example, interfere with the synthesis of **chitin**, the material that makes up the insect exoskeleton. It seems to have very low toxicity for vertebrates, but is harmful to crustaceans as well as insects. Its effect on fungi, which also synthesize chitin, needs to be studied.

Molting Disruptors

Insects must periodically shed their exoskeleton — called molting — in order to grow. Each molt is triggered by a steroid hormone called **ecdysone**.

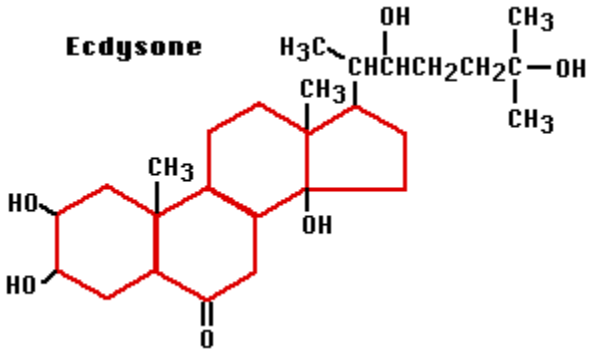


Figure 20.2.4 Ecdysone.

A few synthetic ecdysone

- agonists, e.g.,
  - tebufenozide (Confirm®)
  - methoxyfenozide (Intrepid®)
- inhibitors, e.g., azadirachtin (Neemix®)

are now used as insecticides.

Allowed Pesticides in Organic Production - USDA

Link file:///C:/Users/w1034250/Desktop/De...pProducers.pdf

Organic Pesticides

Generally speaking, pesticides derived from natural materials or living organisms are allowed in organic production as long as they do not contain synthetic additives or are not specifically prohibited on the National List under § 205.602. By contrast, most synthetic pesticides are not allowed; those few that are can be found on the National List under § 205.601.

Allowed inputs typically include but are not limited to the following:

Botanical pesticides. Botanicals are derived from plants. They include pyrethrum, rotenone, sabadilla, neem, ryania, and garlic. Strychnine and nicotine are also botanicals, but are expressly prohibited in organic production. Since botanical pesticides are relatively nonselective, they can affect natural predators and other nontarget organisms. Rotenone, for example, is highly toxic to fish. For this reason, many organic growers use botanical pesticides only as a last resort.

Spray oils. Vegetable- or animal-derived oils are generally allowed as suffocating (stylet) oils, summer oils, dormant oils, and surfactants. Some petroleum-derived oils, referred to as “narrowrange oils,” are allowed for the same purposes. Spray oils are commonly used to control scale and mite pests. There are two organizations that review products and publish lists of products allowed for organic production: the Organic Materials Review Institute (OMRI) and the Washington State Department of Agriculture (WSDA) Organic Food Program.

Insecticidal soaps. Fatty acid insecticidal soaps are synthetic pesticides specifically allowed in organic production. Safer® Brand Insect Killing Soap Concentrate II is a product that is commonly used by organic farmers. Insecticidal soaps can be hard on beneficial predatory mites, so they should be used with caution.

Minerals. Mineral-based pesticides include sulfur, copper products, diatomaceous earth, and kaolin clay. These must be used with caution, even though they are allowed. Sulfur can reduce the populations of some beneficial insects and may burn plants if used during hot weather. Diatomaceous earth can cause respiratory problems and itching in the farmworkers who apply it. Copper can accumulate in soils, so it is allowed with restrictions. The organic regulations state that “copper-based materials must be used in a manner that minimizes accumulation in the soil…” Certifiers may require soil testing to verify that copper is not accumulating in the soil. Certain highly toxic minerals, including arsenic and lead, are specifically prohibited.

Pheromones. Pheromones are chemicals released from insects that cause other insects of the same species to change their behavior. Pheromones are not considered pesticides because they do not kill the insects. The pheromones used for pest control are often called mating disrupters because they alter mating behavior. Being totally natural, the pheromones themselves are allowed in organic production. However, some of the inert ingredients in mating disrupter products are prohibited.

Biological Pesticides

Biopesticides, a contraction of 'biological pesticides', include several types of pest management intervention: through predatory, parasitic, or chemical relationships. The term has been associated historically with biological pest control – and by implication, the manipulation of living organisms. Regulatory positions can be influenced by public perceptions, thus:

- in the EU, biopesticides have been defined as "a form of pesticide based on micro-organisms or natural products".
- the US EPA states that they "include naturally occurring substances that control pests (biochemical pesticides), microorganisms that control pests (microbial pesticides), and pesticidal substances produced by plants containing added genetic material (plant-incorporated protectants) or PIPs".

They are obtained from organisms including plants, bacteria and other microbes, fungi, nematodes, *etc.*[*page needed*] They are often important components of integrated pest management (IPM) programmes, and have received much practical attention as substitutes to synthetic chemical plant protection products (PPPs).

Biopesticides can be classified into these classes:

- Microbial pesticides which consist of bacteria, entomopathogenic fungi or viruses (and sometimes includes the metabolites that bacteria or fungi produce). Entomopathogenic nematodes are also often classed as microbial pesticides, even though they are multi-cellular.[*page needed*]
- Bio-derived chemicals. Four groups are in commercial use: pyrethrum, rotenone, neem oil, and various essential oils are naturally occurring substances that control (or monitor in the case of pheromones) pests and microbial diseases.
- Plant-incorporated protectants (PIPs) have genetic material from other species incorporated into their genetic material (*i.e.* GM crops). Their use is controversial, especially in many European countries.
- RNAi pesticides, some of which are topical and some of which are absorbed by the crop.

Biopesticides have usually no known function in photosynthesis, growth or other basic aspects of plant physiology. Instead, they are active against biological pests. Many chemical compounds have been identified that are produced by plants to protect them from pests so they are called antifeedants. These materials are biodegradable and renewable alternatives, which can be economical for practical use. Organic farming systems embraces this approach to pest control.

Examples

Bacillus thuringiensis, a bacterium capable of causing disease of Lepidoptera, Coleoptera and Diptera, is a well-known insecticide example. The toxin from *B. thuringiensis* (Bt toxin) has been incorporated directly into plants through the use of genetic engineering. The use of Bt Toxin is particularly controversial. Its manufacturers claim it has little effect on other organisms, and is more environmentally friendly than synthetic pesticides.

Other microbial control agents include products based on:

- entomopathogenic fungi (*e.g. Beauveria bassiana, Isaria fumosorosea, Lecanicillium* and *Metarhizium* spp.),
- plant disease control agents: include *Trichoderma* spp. and *Ampelomyces quisqualis* (a hyper-parasite of grape powdery mildew); *Bacillus subtilis* is also used to control plant pathogens.
- beneficial nematodes attacking insect (*e.g. Steinernema feltiae*) or slug (*e.g. Phasmarhabditis hermaphrodita*) pests
- entomopathogenic viruses (*e.g.*. *Cydia pomonella* granulovirus).
- weeds and rodents have also been controlled with microbial agents.

Various naturally occurring materials, including fungal and plant extracts, have been described as biopesticides. Products in this category include:

- Insect pheromones and other semiochemicals
- Fermentation products such as Spinosad (a macro-cyclic lactone)
- Chitosan: a plant in the presence of this product will naturally induce systemic resistance (ISR) to allow the plant to defend itself against disease, pathogens and pests.
- Biopesticides may include natural plant-derived products, which include alkaloids, terpenoids, phenolics and other secondary chemicals. Certain vegetable oils such as canola oil are known to have pesticidal properties[*citation needed*]. Products based on extracts of plants such as garlic have now been registered in the EU and elsewhere

Genetically Engineered Insect and Virus Resistance

Genetically modified crops (**GM crops**) are plants used in agriculture, the DNA of which has been modified using genetic engineering methods. Plant genomes can be engineered by physical methods or by use of *Agrobacterium* for the delivery of sequences hosted in T-DNA binary vectors. In most cases, the aim is to introduce a new trait to the plant which does not occur naturally in the species. Examples in food crops include resistance to certain pests, diseases, environmental conditions, reduction of spoilage, resistance to chemical treatments (e.g. resistance to a herbicide), or improving the nutrient profile of the crop.

Insects

Tobacco, corn, rice and some other crops have been engineered to express genes encoding for insecticidal proteins from Bacillus thuringiensis (Bt). The introduction of Bt crops during the period between 1996 and 2005 has been estimated to have reduced the total volume of insecticide active ingredient use in the United States by over 100 thousand tons. This represents a 19.4% reduction in insecticide use.

In the late 1990s, a genetically modified potato that was resistant to the Colorado potato beetle was withdrawn because major buyers rejected it, fearing consumer opposition.

Viruses

Papaya, potatoes, and squash have been engineered to resist viral pathogens such as cucumber mosaic virus which, despite its name, infects a wide variety of plants. Virus resistant papaya were developed in response to a papaya ringspot virus (PRV) outbreak in Hawaii in the late 1990s. They incorporate PRV DNA. By 2010, 80% of Hawaiian papaya plants were genetically modified.

Potatoes were engineered for resistance to potato leaf roll virus and Potato virus Y in 1998. Poor sales led to their market withdrawal after three years.

Yellow squash that were resistant to at first two, then three viruses were developed, beginning in the 1990s. The viruses are watermelon, cucumber and zucchini/courgette yellow mosaic. Squash was the second GM crop to be approved by US regulators. The trait was later added to zucchini.

Many strains of corn have been developed in recent years to combat the spread of Maize dwarf mosaic virus, a costly virus that causes stunted growth which is carried in Johnson grass and spread by aphid insect vectors. These strands are commercially available although the resistance is not standard among GM corn variants.

Sterile Insect Technique

The **sterile insect technique** (**SIT**)[1][2] is a method of biological insect control, whereby overwhelming numbers of sterile insects are released into the wild. The released insects are preferably male, as this is more cost-effective and the females may in some situations cause damage by laying eggs in the crop, or, in the case of mosquitoes, taking blood from humans. The sterile males compete with wild males to mate with the females. Females that mate with a sterile male produce no offspring, thus reducing the next generation's population. Sterile insects are not self-replicating and, therefore, cannot become established in the environment. Repeated release of sterile males over low population densities can further reduce and in cases of isolation eliminate pest populations, although cost-effective control with dense target populations is subjected to population suppression prior to the release of the sterile males.

The technique has successfully been used to eradicate the screw-worm fly (*Cochliomyia hominivorax*) from North and Central America. Many successes have been achieved for control of fruit fly pests, most particularly the Mediterranean fruit fly (*Ceratitis capitata*) and the Mexican fruit fly (*Anastrepha ludens*). Active research is being conducted to determine this technique's effectiveness in combatting the Queensland Fruit Fly (Bactrocera tyroni).

Sterilization is induced through the effects of irradiation on the reproductive cells of the insects. SIT does not involve the release of insects modified through transgenic (genetic engineering) processes.[3] Moreover, SIT does not introduce non-native species into an ecosystem.

Pheromones: The Sex Trap

A **pheromone trap** is a type of insect trap that uses pheromones to lure insects. Sex pheromones and aggregating pheromones are the most common types used. A pheromone-impregnated lure, as the red rubber septa in the picture, is encased in a conventional trap such as a bottle trap, Delta trap, water-pan trap, or funnel trap. Pheromone traps are used both to count insect populations by sampling, and to trap pests such as clothes moths to destroy them.

Juvenile Hormone (JH)

In some insects, the final molt produces an adult that looks pretty much like the earlier larval stages. In others, like moths and butterflies, the final molt of the larva (caterpillar) produces a **pupa**. After a period of **metamorphosis**, the adult moth emerges.

Ecdysone (a steroidal hormone) triggers larva-to-larva molts as long as another hormone, called **juvenile hormone** (**JH**) see (Figure $20.2.3$), is present. In its absence, ecdysone promotes the pupa-to-adult molt. Thus normal metamorphosis seems to

occur when the output of JH diminishes spontaneously in the mature caterpillar.

When solutions of JH are sprayed on mature caterpillars, or on the foliage upon which they are feeding, their normal development is upset. This raises the possibility of using JH as an insecticide (one that might avoid the problem of developing resistance).

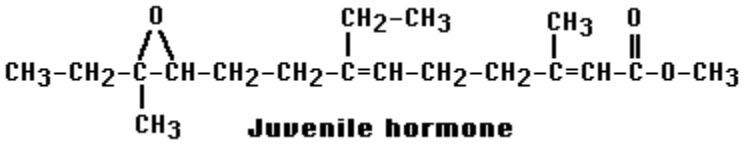


Figure 20.2.5 Juvenile Hormone

As it turns out, JH is too unstable to be practical, but some synthetic **JH mimics**, e.g.,

- methoprene (Altosid®)
- pyriproxyfen (Esteem®, Knack®, Distance®)
- diofenolan

are now being used.

Summary

- The term pesticide includes the substances used to control pests (which includes insects, mites, nematodes, plant pathogens, weeds, and vertebrates).
- Many pesticides can be grouped into chemical families which mainly include the insecticides organochlorines (e.g. DDT and dieldrin), organophosphates (e.g. parathion and malathion), and carbamates (e.g. carbaryl and aldicarb).
- Use of organic and biological pesticides are alternative means of pest control that is gaining popularity.

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20.3: Herbicides and Defoliants

Learning Objective

- Describe the different kinds of widely used herbicides.
- List the different types of pesticide poisoning.

Herbicides, also commonly known as **weedkillers**, are substances used to control unwanted plants.[1] **Selective herbicides** control specific weed species, while leaving the desired crop relatively unharmed, while **non-selective herbicides** (sometimes called **total weedkillers** in commercial products) can be used to clear waste ground, industrial and construction sites, railways and railway embankments as they kill all plant material with which they come into contact. Apart from selective/non-selective, other important distinctions include *persistence* (also known as *residual action*: how long the product stays in place and remains active), *means of uptake* (whether it is absorbed by above-ground foliage only, through the roots, or by other means), and *mechanism of action* (how it works). Historically, products such as common salt and other metal salts were used as herbicides, however these have gradually fallen out of favor and in some countries a number of these are banned due to their persistence in soil, and toxicity and groundwater contamination concerns. Herbicides have also been used in warfare and conflict.

A **defoliant** is any herbicidal chemical sprayed or dusted on plants to cause their leaves to fall off. Defoliants are widely used for the selective removal of weeds in managing croplands and lawns. Worldwide use of defoliants, along with the development of other herbicides and pesticides, allowed for the Green Revolution, an increase in agricultural production in mid-20th century.

Modern herbicides are often synthetic mimics of natural plant hormones which interfere with growth of the target plants. The term **organic herbicide** has come to mean herbicides intended for organic farming. Some plants also produce their own natural herbicides, such as the genus *Juglans* (walnuts), or the tree of heaven; such action of natural herbicides, and other related chemical interactions, is called allelopathy. Due to herbicide resistance - a major concern in agriculture - a number of products combine herbicides with different means of action. Integrated pest management may use herbicides alongside other pest control methods.

Although research into herbicides began in the early 20th century, the first major breakthrough was the result of research conducted in both the UK and the US during the Second World War into the potential use of herbicides in war.[5] The first modern herbicide, 2,4-D, was first discovered and synthesized by W. G. Templeman at Imperial Chemical Industries.

In the US in 2007, about 83% of all herbicide usage, determined by weight applied, was in agriculture.[1]:12 In 2007, world pesticide expenditures totaled about $39.4 billion; herbicides were about 40% of those sales and constituted the biggest portion, followed by insecticides, fungicides, and other types.[1]:4 Herbicide is also used in forestry,[2] where certain formulations have been found to suppress hardwood varieties in favour of conifers after a clearcut,[3] as well as pasture systems, and management of areas set aside as wildlife habitat.

2,4 D and 2,4,5 T

Two of the oldest chemical herbicides used as defoliants are 2,4-Dichlorophenoxyacetic acid (2,4-D) and 2,4,5-Trichlorophenoxyacetic acid (2,4,5-T). 2,4-D and 2,4,5-T are absorbed by broad-leafed plants, killing them by causing excessive hormonal growth. These phenoxy herbicides were designed to selectively kill weeds and unwanted plants in croplands. They were first introduced at the beginning of World War II and became widespread in use in agriculture following the end of the War.

When 2,4-D was commercially released in 1946, it triggered a worldwide revolution in agricultural output and became the first successful selective herbicide. It allowed for greatly enhanced weed control in wheat, maize (corn), rice, and similar cereal grass crops, because it kills dicots (broadleaf plants), but not most monocots (grasses). The low cost of 2,4-D has led to continued usage today, and it remains one of the most commonly used herbicides in the world. Like other acid herbicides, current formulations use either an amine salt (often trimethylamine) or one of many esters of the parent compound. These are easier to handle than the acid.

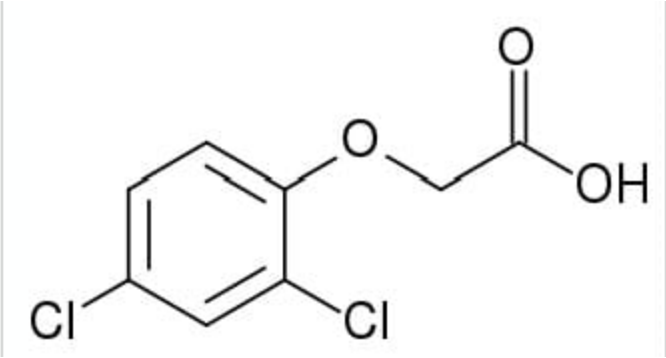


Figure 20.3.1 2,4D. Source: Wikipedia

WEB LINKS

The Technical Fact Sheet for 2,4-D is found on the link below.

http://npic.orst.edu/factsheets/archive/2,4-DTech.html

Gervais, J.; Luukinen, B.; Buhl, K.; Stone, D. 2008. *2,4-D Technical Fact Sheet*; National Pesticide Information Center, Oregon State

Agent Orange is a herbicide and defoliant chemical, one of the "tactical use" Rainbow Herbicides. It is widely known for its use by the U.S. military as part of its herbicidal warfare program, Operation Ranch Hand, during the Vietnam War from 1961 to 1971. It is a mixture of equal parts of two herbicides, 2,4,5-T and 2,4-D. In addition to its damaging environmental effects, traces of dioxin (mainly TCDD, the most toxic of its type) found in the mixture have caused major health problems for many individuals who were exposed.

Atrazine and Glyphosate

Atrazine is a herbicide that is used to stop pre- and post-emergence broadleaf and grassy weeds in crops such as sorghum, maize, sugarcane, lupins, pine, and eucalypt plantations, and triazine-tolerant canola.

In the United States as of 2014, atrazine was the second-most widely used herbicide after glyphosate, with 76 million pounds (34 thousand metric tons) of it applied each year. Atrazine continues to be one of the most widely used herbicides in Australian agriculture. Its effect on corn yields has been estimated from 1% to 8%, with 3–4% being the conclusion of one economics review. In another study looking at combined data from 236 university corn field trials from 1986 to 2005, atrazine treatments showed an average of 5.7 bushels more per acre (~400 kg per hectare) than alternative herbicide treatments. Effects on sorghum yields have been estimated to be as high as 20%, owing in part to the absence of alternative weed control products that can be used on sorghum.

As of 2001, atrazine was the most commonly detected pesticide contaminating drinking water in the U.S.[:44] Studies suggest it is an endocrine disruptor, an agent that can alter the natural hormonal system. Since 2003, the U.S. Environmental Protection Monitoring Agency (EPA) regularly checks atrazine levels in streams and watersheds that are direct exposed to atrazine runoff as part of the Atrazine Ecological Exposure Monitoring Program.

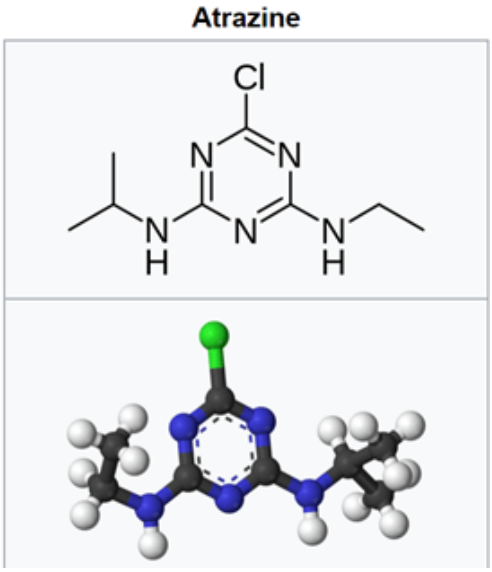


Figure 20.3.2 Atrazine. Source: Wikipedia

Glyphosate (*N*-(phosphonomethyl)glycine) is a broad-spectrum systemic herbicide and crop desiccant, see*Figure* 20.3.3. It is an organophosphorus compound, specifically a phosphonate. It targets a broad range of weeds and is important in the production of fruits, vegetables, nuts, and glyphosate-resistant field crops such as corn and soybean. It is effective at managing invasive and noxious weeds. In addition, glyphosate breaks down in the environment, can be used for no-till and low-till farming which can reduce soil erosion, and is useful for integrated pest management.

It was discovered to be an herbicide by Monsanto chemist John E. Franz in 1970. Monsanto brought it to market in 1974 under the trade name Roundup® , and Monsanto's last commercially relevant United States patent expired in 2000. Products containing glyphosate are sold in various formulations, including as liquid concentrate, solid, and ready-to-use liquid. Glyphosate can be applied in agricultural, residential and commercial settings using a wide range of application methods, including aerial sprays, ground broadcast sprayers of various types, shielded and hooded sprayers, wiper applicators, sponge bars, injection systems, and controlled droplet applicators.

Glyphosate is effective in killing a wide variety of plants, including grasses and broadleaf and woody plants. By volume, it is one of the most widely used herbicides. In 2007, glyphosate was the most used herbicide in the United States agricultural sector, with 180 to 185 million pounds (82,000 to 84,000 tonnes) applied, the second-most used in home and garden with 5 to 8 million pounds (2,300 to 3,600 tonnes) and government applied[*clarification needed*] 13 to 15 million pounds (5,900 to 6,800 tonnes) in industry and commerce. It is commonly used for agriculture, horticulture, viticulture, and silviculture purposes, as well as garden maintenance (including home use). It has a relatively small effect on some clover species and morning glory.



Figure 20.3.3 Glyphosate used as an alternative to mowing in an apple orchard in Ciardes, Italy. *Source: Wikipedia*

Glyphosate and related herbicides are often used in invasive species eradication and habitat restoration, especially to enhance native plant establishment in prairie ecosystems. The controlled application is usually combined with a selective herbicide and traditional methods of weed eradication such as mulching to achieve an optimal effect.

In many cities, glyphosate is sprayed along the sidewalks and streets, as well as crevices in between pavement where weeds often grow. However, up to 24% of glyphosate applied to hard surfaces can be run off by water. Glyphosate contamination of surface water is attributed to urban and agricultural use. Glyphosate is used to clear railroad tracks and get rid of unwanted aquatic vegetation.

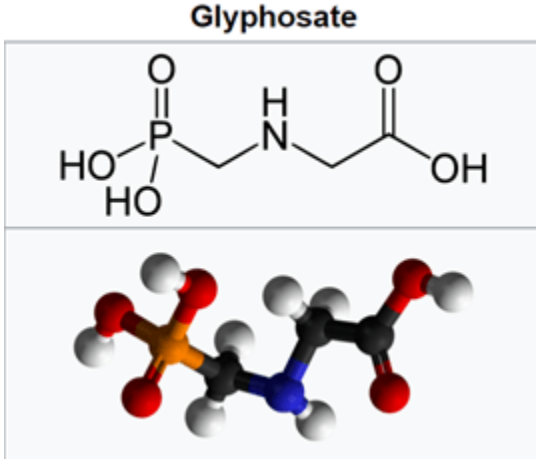


Figure 20.3.4 Glyphosate. Source: Wikipedia

Paraquat- A Preemergent Herbicide -and More

Paraquat (or ***N,N′*-dimethyl-4,4′-bipyridinium dichloride**, also known as **Methyl Viologen**, is an organic compound manufactured by Chevron. This salt is one of the most widely used herbicides. It is quick-acting and non-selective, killing green plant tissue on contact. It is also toxic to human beings and animals due to its redox activity, which produces superoxide anions. It has been linked to the development of Parkinson's disease and is banned in several countries.

Although first synthesized in 1882,[9] paraquat's herbicidal properties were not recognized until 1955 in the Imperial Chemical Industries (ICI) laboratories at Jealott's Hill.[10][11] Paraquat (*Figure* 20.3.4*)* was first manufactured and sold by ICI in early 1962

under the trade name **Gramoxone**, and is today among the most commonly used herbicides.

Paraquat is classified as a non-selective contact herbicide. The key characteristics that distinguish it from other agents used in plant protection products are:

- It kills a wide range of annual grasses and broad-leaved weeds and the tips of established perennial weeds.
- It is very fast-acting.
- It is rain-fast within minutes of application.
- It is partially inactivated upon contact with soil.[12][13]

These properties led to paraquat being used in the development of no-till farming.

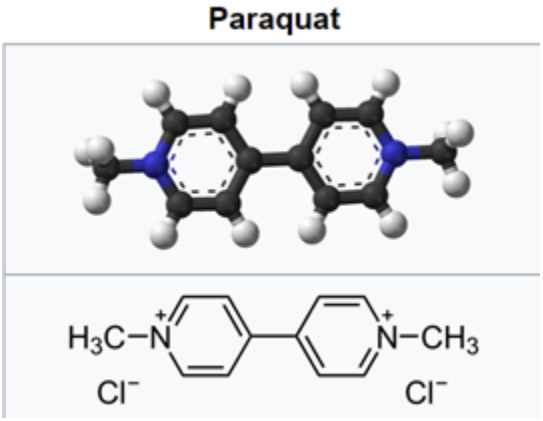


Figure 20.3.5 Paraquat. Source: Wikipedia.

Paraquat has been banned in the European Union since 2007. There is an ongoing international campaign for a global ban, but the cheap and therefore popular paraquat continues to be unrestricted in most developing countries. In the United States, paraquat is available primarily as a solution in various strengths. It is classified as "restricted use", which means that it can be used by licensed applicators only.

WEB LINK

A more detailed list of herbicides, trade names, and target species provided by the USDA WEB can be found on the link below.

https://www.fs.usda.gov/Internet/FSE_DOCUMENTS/fseprd496996.pdf

Organic herbicides

Recently, the term "organic" has come to imply products used in organic farming. Under this definition, an organic herbicide is one that can be used in a farming enterprise that has been classified as organic. Depending on the application, they may be less effective than synthetic herbicides[59] and are generally used along with cultural and mechanical weed control practices.

Homemade organic herbicides include:

- Corn gluten meal (CGM) is a natural pre-emergence weed control used in turfgrass, which reduces germination of many broadleaf and grass weeds.[60]
- Vinegar[61] is effective for 5–20% solutions of acetic acid, with higher concentrations most effective, but it mainly destroys surface growth, so respraying to treat regrowth is needed. Resistant plants generally succumb when weakened by respraying.
- Steam has been applied commercially, but is now considered uneconomical and inadequate.It controls surface growth but not underground growth and so respraying to treat regrowth of perennials is needed.
- Flame is considered more effective than steam, but suffers from the same difficulties.[65]

- D-limonene (citrus oil) is a natural degreasing agent that strips the waxy skin or cuticle from weeds, causing dehydration and ultimately death.
- Saltwater or salt applied in appropriate strengths to the rootzone will kill most plants.

Human Risks

A **pesticide poisoning** occurs when chemicals intended to control a pest affect non-target organisms such as humans, wildlife, plant or bees.

There are three types of pesticide poisoning.

The first of the three is a single and short-term very high level of exposure which can be experienced by individuals who commit suicide, as well as pesticide formulators. Most cases of intentional pesticide poisoning appear to be impulsive acts undertaken during stressful events, and the availability of pesticides strongly influences the incidence of self poisoning.

The second type of poisoning is long-term high-level exposure, which can occur in pesticide formulators and manufacturers. Extensive use puts agricultural workers in particular at increased risk for pesticide illnesses. Exposure can occur through inhalation of pesticide fumes, and often occurs in settings including greenhouse spraying operations and other closed environments like tractor cabs or while operating rotary fan mist sprayers in facilities or locations with poor ventilation systems. Workers in other industries are at risk for exposure as well. For example, commercial availability of pesticides in stores puts retail workers at risk for exposure and illness when they handle pesticide products. The ubiquity of pesticides puts emergency responders such as fire-fighters and police officers at risk, because they are often the first responders to emergency events and may be unaware of the presence of a poisoning hazard. The process of aircraft disinsection, in which pesticides are used on inbound international flights for insect and disease control, can also make flight attendants sick.

Different job functions can lead to different levels of exposure. Most occupational exposures are caused by absorption through exposed skin such as the face, hands, forearms, neck, and chest. This exposure is sometimes enhanced by inhalation in settings including spraying operations in greenhouses and other closed environments, tractor cabs, and the operation of rotary fan mist sprayers.

The third type of poisoning is a long-term low-level exposure, which individuals are exposed to from sources such as pesticide residues in food as well as contact with pesticide residues in the air, water, soil, sediment, food materials, plants and animals.[1][2][3][4]

In developing countries, such as Sri Lanka, pesticide poisonings from short-term very high level of exposure (acute poisoning) is the most worrisome type of poisoning. However, in developed countries, such as Canada, it is the complete opposite: acute pesticide poisoning is controlled, thus making the main issue long-term low-level exposure of pesticides.

Summary

- Herbicides (also known as weedkillers), are substances used to control unwanted plants.
- More widely used herbicides include 2,4-D (2,4-dichlorophenoxyacetic acid), 2,4,5-T(2,4,5-trichlorophenoxyacetic acid), atrazine, glyphosate, and paraquat.
- Organic pesticides used in organic farming include corn gluten meal, vinegar, D-limonene, and salt water.
- Intentional or unintentional ingestion and/or exposure to pesticides can cause a range of health effects ranging from skin rashes to death.

Contributors and Attributions

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20.4: Sustainable Agriculture

Learning Objectives

- Describe what sustainable agriculture is.
- Describe the features of organic farming.

"**Sustainable agriculture**" was addressed by Congress in the 1990 "Farm Bill". Under that law, "the term sustainable agriculture means an integrated system of plant and animal production practices having a site-specific application that will, over the long term:

- satisfy human food and fiber needs;
- enhance environmental quality and the natural resource base upon which the agricultural economy depends;
- make the most efficient use of nonrenewable resources and on-farm resources and integrate, where appropriate, natural biological cycles and controls;
- sustain the economic viability of farm operations; and
- enhance the quality of life for farmers and society as a whole."

Organic Farming is Good for Farmers, Consumers and the Environment

Organic agriculture is an ecological production management system that promotes and enhances biodiversity, biological cycles and soil biological activity. Organic food is produced by farmers who emphasize the use of renewable resources and the conservation of soil and water to enhance environmental quality for future generations. Organic meat, poultry, eggs, and dairy products come from animals that are given no antibiotics or growth hormones. Organic food is produced without using most conventional pesticides, fertilizers made with synthetic ingredients or sewage sludge, or GMOs.

Organic production, with the corresponding practices to maintain soil fertility and soil health is therefore a more benign alternative to conventional, high-value horticulture. The organic food movement has been endorsed by the UN's Food and Agricultural Organization, which maintains in a 2007 report that organic farming fights hunger, tackles climate change, and is good for farmers, consumers, and the environment. The strongest benefits of organic agriculture are its use of resources that are independent of fossil fuels, are locally available, incur minimal environmental stresses, and are cost effective.

IPM is a Combination of Common-Sense Practices

Integrated Pest Management (IPM) refers to a mix of farmer-driven, ecologically-based pest control practices that seeks to reduce reliance on synthetic chemical pesticides. It involves (a) managing pests (keeping them below economically damaging levels) rather than seeking to eradicate them; (b) relying, to the extent possible, on non-chemical measures to keep pest populations low; and (c) selecting and applying pesticides, when they have to be used, in a way that minimizes adverse effects on beneficial organisms, humans, and the environment. It is commonly understood that applying an IPM approach does not necessarily mean eliminating pesticide use, although this is often the case because pesticides are often over-used for a variety of reasons.

The IPM approach regards pesticides as mainly short-term corrective measures when more ecologically based control measures are not working adequately (sometimes referred to as using pesticides as the "last resort"). In those cases when pesticides are used, they should be selected and applied in such a manner as to minimize the amount of disruption that they cause to the environment, such as using products that are non-persistent and applying them in the most targeted way possible).

Biological Control

Biological control (biocontrol) is the use of one biological species to reduce populations of a different species. There has been a substantial increase in commercialization of biocontrol products, such as beneficial insects, cultivated predators and natural or non-toxic pest control products. Biocontrol is being mainstreamed to major agricultural commodities, such as cotton, corn

and most commonly vegetable crops. Biocontrol is also slowly emerging in vector control in public health and in areas that for a long time mainly focused on chemical vector control in mosquito/malaria—and black fly/onchocerciasis—control programs. Successful and commercialized examples of biocontrol include ladybugs to depress aphid populations, parasitic wasps to reduce moth populations, use of the bacterium *Bacillus thuringenensis* to kill mosquito and moth larvae, and introduction of fungi, such as Trichoderma, to suppress fungal-caused plant diseases, leaf beetle (*Galerucella calmariensis*) to suppress purple loosestrife, a noxious weed (Figure 20.4.1). In all of these cases, the idea is not to completely destroy the pathogen or pest, but rather to reduce the damage below economically significant values.



Figure 20.4.1 *Young larvae of the leaf-beetle feed in and on the developing buds of plants, often destroying them. Leaf-beetles can be used to as a biocontrol for invasive plants such as purple loosestrife.*

Intercropping Promotes Plant Interactions

Intercropping means growing two or more crops in close proximity to each other during part or all of their life cycles to promote soil improvement, biodiversity, and pest management. Incorporating intercropping principles into an agricultural operation increases diversity and interaction between plants, arthropods, mammals, birds and microorganisms resulting in a more stable crop-ecosystem and a more efficient use of space, water, sunlight, and nutrients (Figure 20.4.2).This collaborative type of crop management mimics nature and is subject to fewer pest outbreaks, improved nutrient cycling and crop nutrient uptake, and increased water infiltration and moisture retention. Soil quality, water quality and wildlife habitat all benefit.



Figure 20.4.2 *Intercropping alyssum (the flowering plants shown center left) with organic romaine lettuce for aphid control.*

Organic Farming Practices Reduce Unnecessary Input Use

In modern agricultural practices, heavy machinery is used to prepare the seedbed for planting, to control weeds, and to harvest the crop. The use of heavy equipment has many advantages in saving time and labor, but can cause compaction of soil and disruption of the natural soil organisms. The problem with soil compaction is that increased soil density limits root penetration depth and may inhibit proper plant growth.

Alternative practices generally encourage **minimal tillage** or **no tillage methods**. With proper planning, this can simultaneously limit compaction, protect soil organisms, reduce costs (if performed correctly), promote water infiltration, and help to prevent topsoil erosion (Figure 20.4.3) .



Figure 20.4.3 *Farmers should consider no-till farming as the most important tool to prevent loss of soil moisture.*

Tillage of fields does help to break up clods that were previously compacted, so best practices may vary at sites with different soil textures and composition. Another aspect of soil tillage is that it may lead to more rapid decomposition of organic matter due to greater soil aeration. Over large areas of farmland, this has the unintended consequence of releasing more carbon and nitrous oxides (greenhouse gases) into the atmosphere, thereby contributing to global warming effects. In no-till farming, carbon can actually become sequestered into the soil. Thus, no-till farming may be advantageous to sustainability issues on the local

scale and the global scale. No-till systems of conservation farming have proved a major success in Latin America and are being used in South Asia and Africa.

Crop Rotation

Crop rotations are planned sequences of crops over time on the same field. Rotating crops provides productivity benefits by improving soil nutrient levels and breaking crop pest cycles. Farmers may also choose to rotate crops in order to reduce their production risk through diversification or to manage scarce resources, such as labor, during planting and harvesting timing. This strategy reduces the pesticide costs by naturally breaking the cycle of weeds, insects and diseases. Also, grass and legumes in a rotation protect water quality by preventing excess nutrients or chemicals from entering water supplies.

AN ALTERNATIVE TO SPRAYING: BOLLWORM CONTROL IN SHANDONG

Farmers in Shandong (China) have been using innovative methods to control bollworm infestation in cotton when this insect became resistant to most pesticides. Among the control measures implemented were:

1. The use of pest resistant cultivars and interplanting of cotton with wheat or maize.
2. Use of lamps and poplar twigs to trap and kill adults to lessen the number of adults.
3. If pesticides were used, they were applied on parts of cotton plant's stem rather than by spraying the whole field (to protect natural enemies of the bollworm).

These and some additional biological control tools have proved to be effective in controlling insect populations and insect resistance, protecting surroundings and lowering costs.

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These and some additional biological control tools have proved to be effective in controlling insect populations and insect resistance, protecting surroundings and lowering costs.

The Future of the Sustainable Agriculture Concept

Many in the agricultural community have adopted the sense of urgency and direction pointed to by the sustainable agriculture concept. Sustainability has become an integral component of many government, commercial, and non-profit agriculture research efforts, and it is beginning to be woven into agricultural policy. Increasing numbers of farmers and ranchers have embarked on their own paths to sustainability, incorporating integrated and innovative approaches into their own enterprises.

Summary

- Sustainable agriculture is farming in various ways, wherein society's current and future food and textile needs are met.
- Organic agriculture is an ecological production management system that promotes and enhances biodiversity, biological cycles and soil biological activity.

Contributors and Attributions

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21: HOUSEHOLD CHEMICALS

Household chemicals are non-food chemicals that are commonly found and used in and around the average household. They are a type of consumer goods, designed particularly to assist cleaning, pest control and general hygiene purposes. Together with non-compostable household waste, the chemicals found in private household commodities pose a serious ecological problem. In addition to having slightly adverse up to seriously toxic effects when swallowed, chemical agents around may contain flammable or corrosive substances.

21.1: Cleaning with Soap

21.2: Synthetic Detergents

21.3: Laundry Auxiliaries- Softeners and Bleaches

21.4: All-Purpose and Special Purpose Cleaning Products

21.5: Solvents, Paints, and Waxes

21.6: Cosmetics - Personal Care Chemicals

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21.1: Cleaning with Soap

Learning Objectives

- Describe the mechanism by which soaps exert their cleansing action.
- List the benefits and problems with using soap.

Personal Cleanliness

Soap is a salt of a fatty acid[1] used in a variety of cleansing and lubricating products. In a domestic setting, soaps are surfactants usually used for washing, bathing, and other types of housekeeping. In industrial settings, soaps are used as thickeners, components of some lubricants, and precursors to catalysts.

When used for cleaning, soap solubilizes particles and grime, which can then be separated from the article being cleaned. In hand washing, as a surfactant, when lathered with a little water, soap kills microorganisms by disorganizing their membrane lipid bilayer and denaturing their proteins. It also emulsifies oils, enabling them to be carried away by running water.[2]

Industrially manufactured **bar soaps** became available in the late 18th century, as advertising campaigns in Europe and America promoted popular awareness of the relationship between cleanliness and health.[35] In modern times, the use of soap has become commonplace in industrialized nations due to a better understanding of the role of hygiene in reducing the population size of pathogenic microorganisms (Figure 21.1.1).



Figure 21.1.1 Modern Soap Shop in Tubeingen , Germany. Source: Wikipedia

Soap Making: Fat Plus Lye Forms a Soap Plus Glycerol

The earliest recorded evidence of the production of soap-like materials dates back to around 2800 BC in ancient Babylon.[10] A formula for soap consisting of water, alkali, and cassia oil was written on a Babylonian clay tablet around 2200 BC.[11]

The Ebers papyrus (Egypt, 1550 BC) indicates the ancient Egyptians bathed regularly and combined animal and vegetable oils with alkaline salts to create a soap-like substance. Egyptian documents mention a similar substance was used in the preparation of wool for weaving.[12]In the reign of Nabonidus (556–539 BC), a recipe for soap consisted of *uhulu* [ashes], cypress [oil] and

sesame [seed oil] "for washing the stones for the servant girls".[13]In ancient Israel, the ashes from barilla plants, such as species of Salsola, saltwort (*Seidlitzia rosmarinus*) and *Anabasis*, were used in soap production, known as potash



Figure 21.1.2 Advertising for medicated toilet soap. Source: Wikipedia

Until the Industrial Revolution, soapmaking was conducted on a small scale and the product was rough. In 1780, James Keir established a chemical works at Tipton, for the manufacture of alkali from the sulfates of potash and soda, to which he afterwards added a soap manufactory. William Gossage produced low-priced, good-quality soap from the 1850s. Robert Spear Hudson began manufacturing a soap powder in 1837, initially by grinding the soap with a mortar and pestle. American manufacturer Benjamin T. Babbitt introduced marketing innovations that included sale of bar soap and distribution of product samples. William Hesketh Lever and his brother, James, bought a small soap works in Warrington in 1886 and founded what is still one of the largest soap businesses, formerly called Lever Brothers and now called Unilever. These soap businesses were among the first to employ large-scale advertising campaigns. A poster advertising is shown in Figure 21.1.2.

Liquid soap was not invented until the nineteenth century; in 1865, William Shepphard patented a liquid version of soap.[40] In 1898, B.J. Johnson developed a soap derived from palm and olive oils; his company, the B.J. Johnson Soap Company, introduced "Palmolive" brand soap that same year.[41] This new brand of soap became popular rapidly, and to such a degree that B.J. Johnson Soap Company changed its name to Palmolive.[42]

Fats and oils can participate in a variety of chemical reactions—for example, because triglycerides are esters, they can be hydrolyzed in the presence of an acid, a base, or specific enzymes known as lipases. The hydrolysis of fats and oils in the presence of a base is used to make soap and is called **saponification**. Today most soaps are prepared through the hydrolysis of triglycerides (often from tallow, coconut oil, or both) using water under high pressure and temperature [700 lb/in^2 (~50 atm or 5,000 kPa) and 200°C]. Sodium carbonate or sodium hydroxide is then used to convert the fatty acids to their sodium salts (soap molecules):

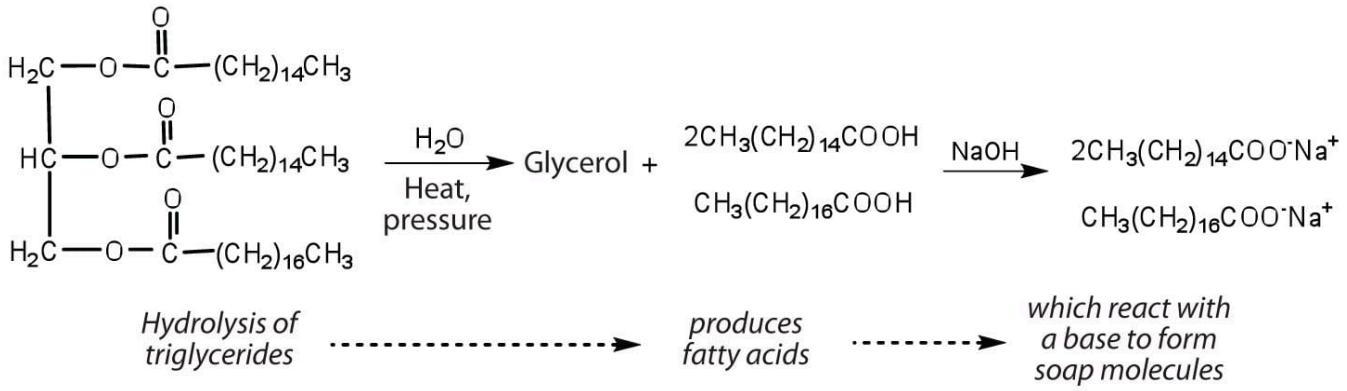


Figure 21.1.3 *Saponification.*

How Soap Works

The cleansing action of soap is determined by its polar and non-polar structures in conjunction with an application of solubility principles. The long hydrocarbon chain is of course non-polar and hydrophobic (repelled by water). The "salt" end of the soap molecule is ionic and hydrophilic (water soluble). Examples of soap and detergent molecules, are shown in Figure 21.1.4. The use of such compounds as cleaning agents is facilitated by their surfactant character, which lowers the surface tension of water, allowing it to penetrate and wet a variety of materials.

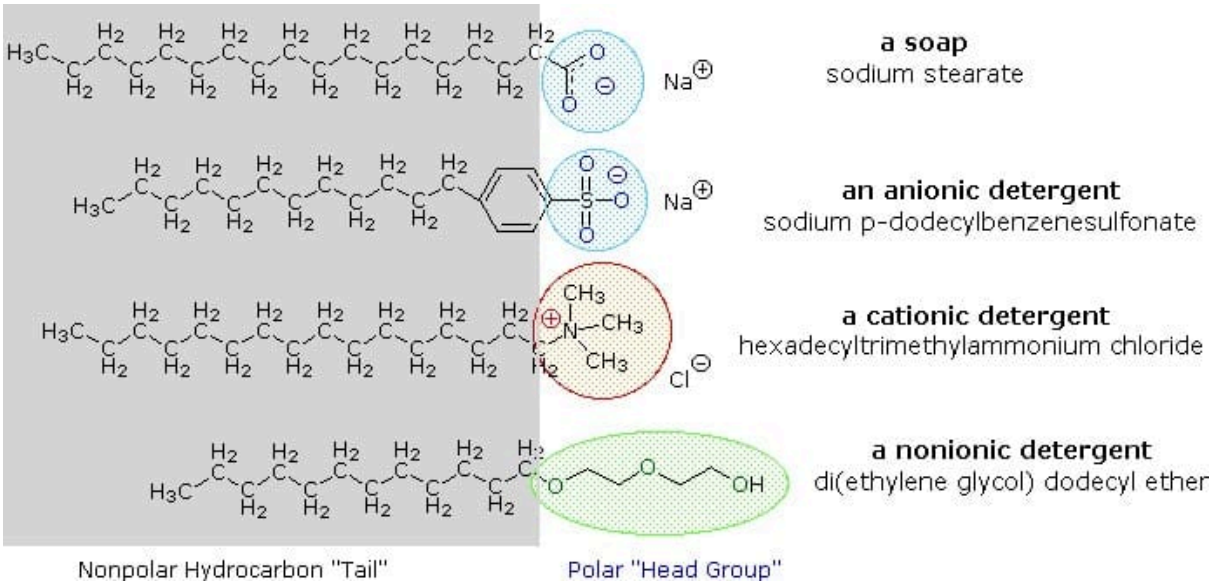


Figure 21.1.4 Soap and detergent molecules with different polar structures.

When soap is added to water, the ionic-salt end of the molecule is attracted to water and dissolved in it. The non-polar hydrocarbon end of the soap molecule is repelled by water. A drop or two of soap in water forms a monolayer (Figure 21.1.5) on the water surface as shown in the graphics on the left. The soap molecules "stand up" on the surface as the polar carboxyl salt end is attracted to the polar water. The non-polar hydrocarbon tails are repelled by the water, which makes them appear to stand up.

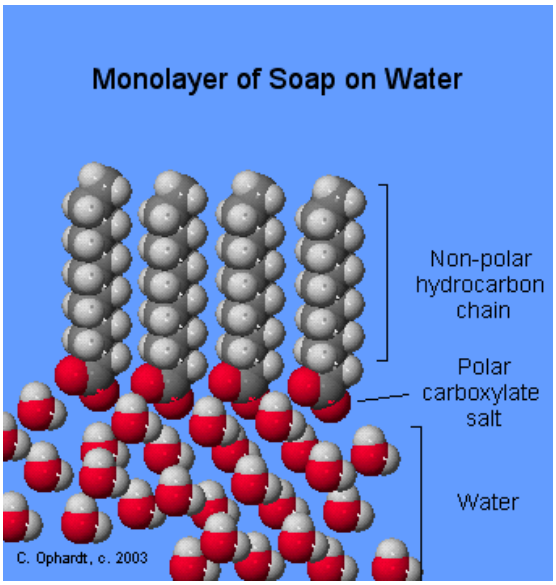


Figure 21.1.5 Monolayer of soap on water.

Soap vs. oil vs. water

Water alone is not able to penetrate grease or oil because they are of opposite polarity. When grease or oil (non-polar hydrocarbons) are mixed with a soap- water solution, the soap molecules work as a "bridge" between polar water molecules and non-polar oil molecules. Soap molecules have both properties of non-polar and polar at opposite ends of the molecule.

The oil is a pure hydrocarbon so it is non-polar. The non-polar hydrocarbon tail of the soap dissolves into the oil. That leaves the polar carboxylate ion of the soap molecules are sticking out of the oil droplets, the surface of each oil droplet is negatively charged. As a result, the oil droplets repel each other and remain suspended in solution (this is called an emulsion) to be washed away by a stream of water. The outside of the droplet is also coated with a layer of water molecules.

The graphic on Figure 21.1.6 although not strictly a representation of the above description is a micelle that works in much the same fashion. The oil would be a the center of the micelle.

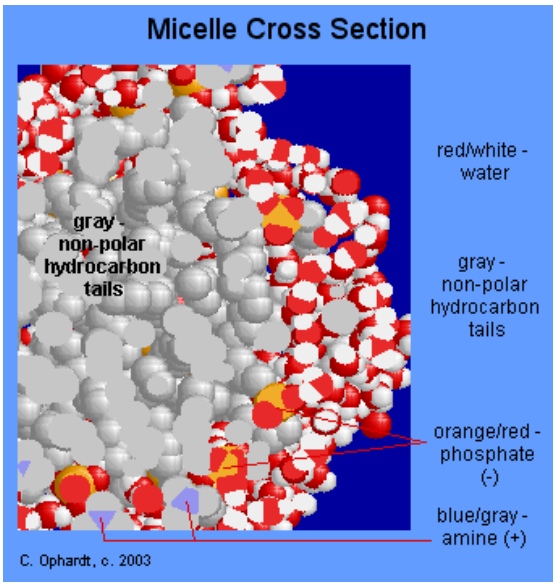


Figure 21.1.6 A micelle with oil at the center.

Disadvantages and Advantages of Soap

The importance of soap to human civilization is documented by history, but some problems associated with its use have been recognized. One of these is caused by the weak acidity (pKa ca. 4.9) of the fatty acids. Solutions of alkali metal soaps are slightly alkaline (pH 8 to 9) due to hydrolysis. If the pH of a soap solution is lowered by acidic contaminants, insoluble fatty acids precipitate and form a scum. A second problem is caused by the presence of calcium and magnesium salts in the water supply (hard water). These divalent cations cause aggregation of the micelles, which then deposit as a dirty scum.

In the reaction below, the sodium cation in soap is replaced by calcium to form calcium stearate. The white precipitate, also termed as soap scum could form deposits on surfaces and inside plumbing.

$$2\ C_{17}H_{35}COO^{-}Na^{+} + Ca^{2+} \rightarrow (C_{17}H_{35}COO)_2Ca + 2\ Na^{+}$$

Soap is still widely popular product as it is a low cost, readily available product used for personal hygiene and cleanliness. Use of soap doesn't lead to pollution. Soap is biodegradable as it can be broken down by microorganisms found in sewage.

Can Soap Really Kill the Coronavirus ?

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 21.1.1 *Soap and coronavirus.*

Water Softeners

Water softening is the removal of calcium, magnesium, and certain other metal cations in hard water. The resulting soft water requires less soap for the same cleaning effort, as soap is not wasted bonding with calcium ions. Soft water also extends the lifetime of plumbing by reducing or eliminating scale build-up in pipes and fittings. Water softening is usually achieved using lime softening or ion-exchange resins (see Figure 21.1.7) but is increasingly being accomplished using nanofiltration or reverse osmosis membranes.

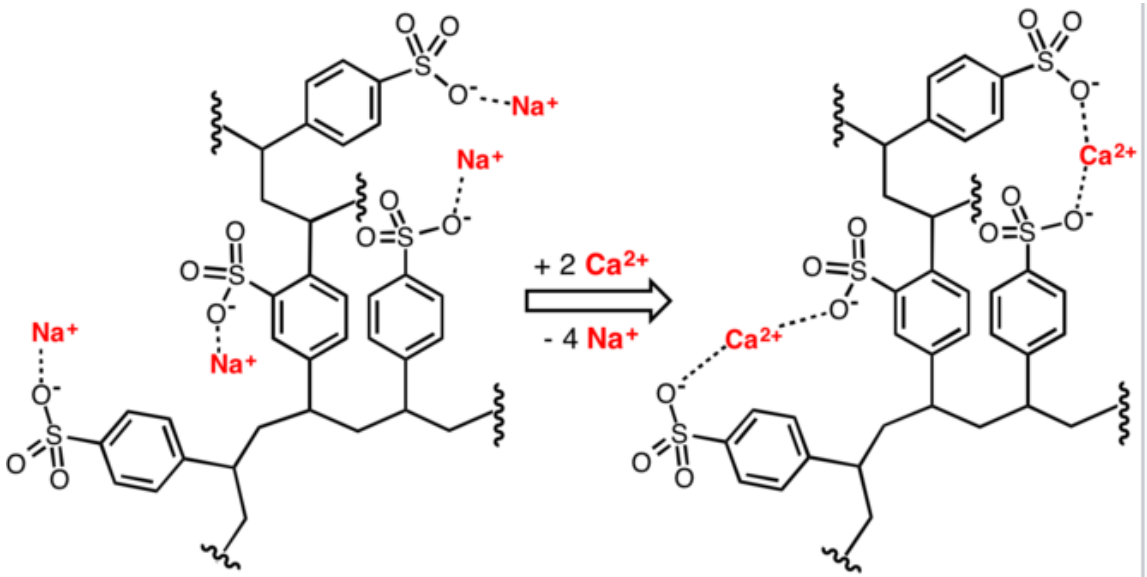


Figure 21.1.7 *Idealized image of water softening process involving replacement of calcium ions in water with sodium ions donated by a cation exchange resin*

How to soften hard water

Some wish to soften hard water to control its irritating, and in many cases damaging, effects. The diminished ability of soap to lather is not only annoying, but can also be potentially harmful economically. Businesses that depend on the foaming of soap, such as car washes and pet groomers, may wish to soften hard water to avoid excessive use of soap due to a decreased ability to lather. Likewise, it is often necessary to soften water that comes into contact with pipes to avoid the destructive and compromising build-up of deposits. Also, many people may find the calcifying effects that hard water has on faucets and other items unfavorable and choose to soften the water to prevent such mineral deposits from forming. Still others may dislike the sticky, dry feeling left by the precipitation of soap scum onto the skin. Whatever the reasons, there are many processes available to soften hard water.

Ion Exchange

One way to soften water is through a process called ion exchange. During ion exchange, the unwanted ions are "exchanged" for more acceptable ions. In many cases, it is desirable to replace the hard water ions, such as Ca^{2+} and Mg^{2+}, with more agreeable ions, like that of Na^{+}. To do this, the hard water is conducted through a zeolite or resin-containing column, which binds the unwanted ions to its surface and releases the more tolerable ions. In this process, the hard water ions become "fixed" ions because of their attachment to the resin material. These fixed ions displace the desirable ions (Na^{+}), now referred to as counterions, from the column, thus exchanging the ions in the water. This process is illustrated in Figure 21.1.8.

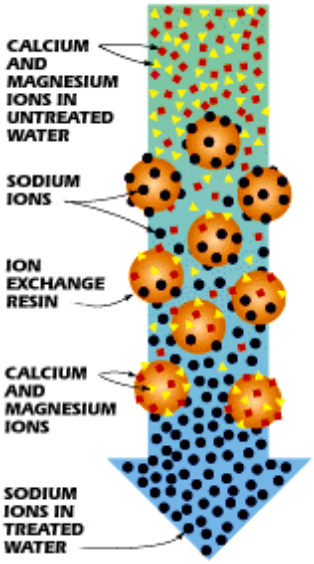


Figure 21.1.8 : Illustration of Ion Exchange.

Unfortunately, this process has the disadvantage of increasing the sodium content of drinking water, which could be potentially hazardous to the health of people with sodium-restricted diets.

Lime Softening

Another process is called lime softening. In this process, the compound calcium hydroxide, $Ca(OH)_2$, is added to the hard water. The calcium hydroxide, or "slaked lime," raises the pH of the water and causes the calcium and magnesium to precipitate into $CaCO_3$ and $Mg(OH)_2$. These precipitates can then be easily filtered out due to their insolubility in water, shown below by the small solubility constant of magnesium hydroxide (the solubility product constant for calcium carbonate is shown above). After precipitation and removal of the offending ions, acid is added to bring the pH of the water back to normal.

$$Mg(OH)_{2\ (s)} \rightleftharpoons Mg^{2+}_{(aq)} + 2OH^{-}_{(aq)} \tag{4a}$$

Chelation

Chelating agents can also be used to soften hard water. Polydentate ligands, such as the popular hexadentate ligand EDTA, bind the undesirable ions in hard water. These ligands are especially helpful in binding the magnesium and calcium cations, which as already mentioned are highly prevalent in hard water solutions. The chelating agent forms a very stable ring complex with the metal cations, which prevents them from interacting with any other substances that may be introduced to the solution, such as soap. In this way, chelators are able to diminish the negative effects associated with hard water. A simplified equation representing the chelation of the metal calcium cation (Ca^{2+}) with the hexadentate ligand EDTA is shown below. The large value of the formation constant (K_f) reflects the tendency of the reaction to proceed to completion in the forward direction.

$$Ca^{2+} + EDTA^{4-} \longrightarrow [Ca(EDTA)]^{2-} \tag{5a}$$

Reverse Osmosis

The final process, reverse osmosis, uses high pressures to force the water through a semipermeable membrane. This membrane is generally intended to be impermeable to anything other than water. The membrane serves to filter out the larger ions and molecules responsible for the water's hardness, resulting in softened water. During this process, the water is forced from an area with a high concentration of solute in the form of dissolved metal ions and similar compounds, to an area that is very low in the concentration of these substances. In other words, the water moves from a state of hardness to a softer composition as the ions causing the water's hardness are prevented passage through the membrane. Reverse Osmosis does have a disadvantage of wasting wastewater compared to other water treatment methods. This process is shown in Figure 21.1.9 below. Note that this figure describes the desalination of salt water. However, the process for softening hard water is the same.

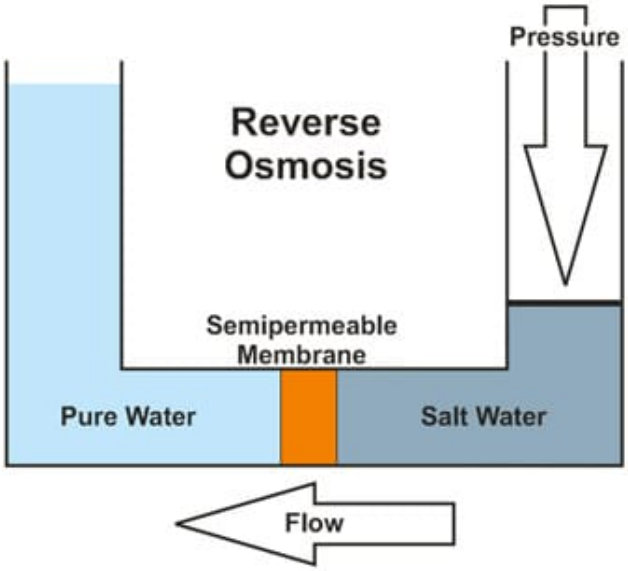


Figure 21.1.9: Depiction of Reverse Osmosis.

Making Hard Water Soft

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 21.1.2 *How to soften hard water.*

Summary

- Soap, as a cleaning agent, solubilizes particles and grime, which can then be easily removed from the article being cleaned.
- In hand washing, soap is an excellent surfactant, that destroys microorganisms by damaging their cellular membranes and denaturing their proteins.
- Soap is an inexpensive, readily available cleaning agent that is also's effectivenes is diminished biodegradable. However, it's effectiveness is diminished when used with hard water.

Contributors

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21.2: Synthetic Detergents

Learning Objectives

- Describe different types of detergents.
- List the key components of detergents and their functions.

A **detergent** is a surfactant or a mixture of surfactants with cleansing properties in dilute solutions (File:Diskflaskor.JPG(Figure 21.2.1)) . These substances are usually alkylbenzene sulfonates, a family of compounds that are similar to soap but are more soluble in hard water, because the polar sulfonate (of detergents) is less likely than the polar carboxylate (of soap) to bind to calcium and other ions found in hard water.

In domestic contexts, the term *detergent* by itself refers specifically to *laundry detergent* or *dish detergent*, as opposed to *hand soap* or other types of cleaning agents. Detergents are commonly available as powders or concentrated solutions. Detergents, like soaps, work because they are amphiphilic: partly hydrophilic (polar) and partly hydrophobic (non-polar). Their dual nature facilitates the mixture of hydrophobic compounds (like oil and grease) with water. Because air is not hydrophilic, detergents are also foaming agents to varying degrees.



Figure 21.2.1 Detergents. Source: Wikipedia

Detergents are classified into three broad groupings, depending on the electrical charge of the surfactants.

Anionic detergents

Typical anionic detergents are alkylbenzenesulfonates (ABS). The alkylbenzene portion of these anions is lipophilic and the sulfonate is hydrophilic. An estimated 6 billion kilograms of anionic detergents are produced annually for domestic markets. Two different varieties have been popularized, those with branched alkyl groups and those with linear alkyl groups (see Figure 21.2.2).

Branched Alkylbenzenesulfonates: Nonbiodegradable

Branched alkylbenzene sulfonates (BAS) were first introduced in the early 1930s and saw significant growth from the late 1940s onwards,[3] in early literature these synthetic detergents are often abbreviated as syndets.

Compared to traditional soaps BAS offered superior tolerance to hard water and better foaming.[5] However, the highly branched

tail made it difficult to biodegrade.[6] BAS was widely blamed for the formation of large expanses of stable foam in areas of wastewater discharge such as lakes, rivers and coastal areas (sea foams), as well as foaming problems encountered in sewage treatment[7] and contamination of drinking water.[8] As such BAS was phased out of most detergent products during the 1960s, being replaced with linear alkylbenzene sulfonates (LAS). It is still important in certain agrochemical and industrial applications, where rapid biodegradability is of reduced importance.

Linear Alkylbenzensulfonates: Biodegradable

Linear alkylbenzene sulfonates (LAS) are prepared industrially by the sulfonation of linear alkylbenzenes (LABs), which can themselves be prepared in several ways.[2] The term "linear" refers to the starting alkenes rather than the final product. The compound biodegrades far more quickly than BAS, making it the safer choice over time. It is biodegraded rapidly under aerobic conditions with a half-life of approximately 1–3 weeks. Under anaerobic conditions it degrades very slowly or not at all, causing it to exist in high concentrations in sewage sludge, but this is not thought to be a cause for concern as it will rapidly degrade once returned to an oxygenated environment.

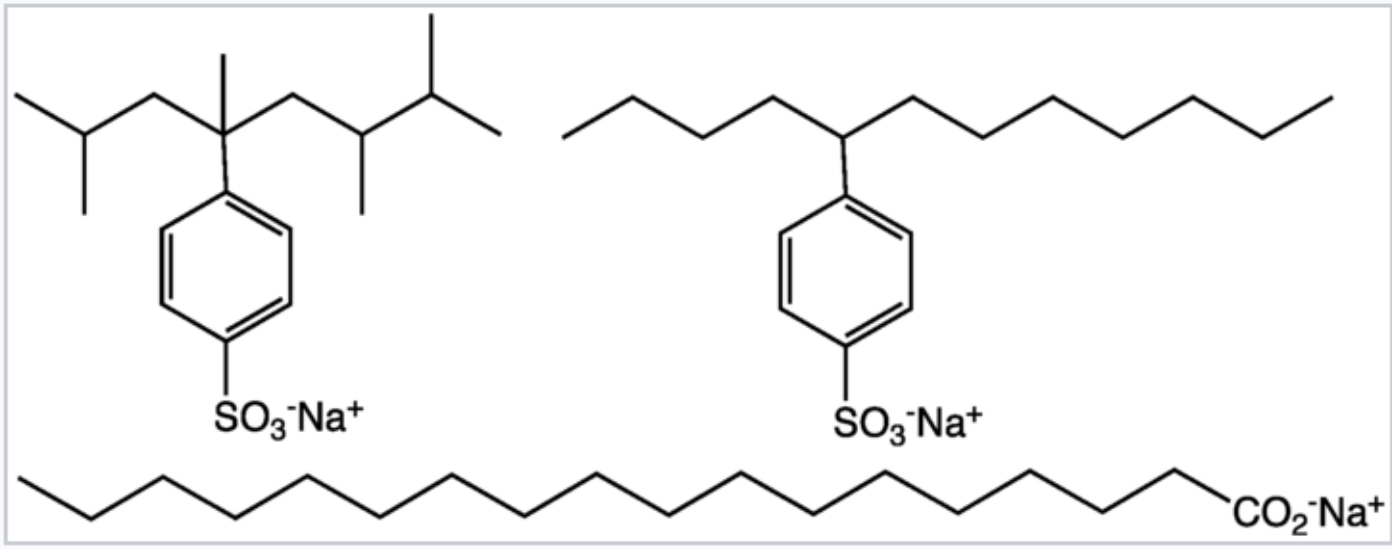


Figure 21.2.2 Three kinds of anionic detergetns: a branched sodium dodecylbenzenesulfonate, linear sodium dodecylbenzenesulfonate, and a soap. *Source: Wikipedia*

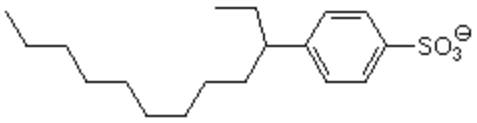
Cationic detergents

Cationic detergents are similar to the anionic ones, with a hydrophilic component, but, instead of the anionic sulfonate group, the cationic surfactants have quaternary ammonium as the polar end. The ammonium sulfate center is positively charged.[3]

Non-ionic and zwitter ionic detergents

Non-ionic detergents are characterized by their uncharged, hydrophilic headgroups. Typical non-ionic detergents are based on polyoxyethylene or a glycoside. Common examples of the former include Tween, Triton, and the Brij series. These materials are also known as ethoxylates or PEGylates and their metabolites, nonylphenol. Glycosides have a sugar as their uncharged hydrophilic headgroup. Examples include octyl thioglucoside and maltosides. HEGA and MEGA series detergents are similar, possessing a sugar alcohol as headgroup.

Zwitterionic detergents possess a net zero charge arising from the presence of equal numbers of +1 and –1 charged chemical groups. Examples include CHAPS. CHAPS is an abbreviation for 3-[(3-**ch**olamidopropyl)dimethyl**a**mmonio]-1-**p**ropane**s**ulfonate.



synthetic detergent

Laundry Detergent

Laundry detergent, or **washing powder**, is a type of detergent (cleaning agent) used for cleaning laundry. Laundry detergent is manufactured in powder and liquid form.

While powdered and liquid detergents hold roughly equal share of the worldwide laundry detergent market in terms of value, powdered detergents are sold twice as much compared to liquids in terms of volume.[1]



Figure 21.2.3 The two forms of laundry detergent: powder and liquid. *Source Wikipedia*

Components

Laundry detergents may contain builders (50% by weight, approximately), surfactants (15%), bleach (7%), enzymes (2%), soil antideposition agents, foam regulators, corrosion inhibitors, optical brighteners, dye transfer inhibitors, fragrances, dyes, fillers and formulation aids.[4]

Builders

Builders (also called chelating or sequestering agents) are water softeners. Hard water contains calcium, magnesium, and metallic cations (primarily, iron, copper, and manganese). These cations react with surfactant anions to form insoluble compounds (metallic or lime soaps) which precipitate onto fabrics and washing machines and which are difficult to remove. Builders remove the hard water ions through precipitation, chelation, or ion exchange. In addition, they help remove soil by dispersion. In most European regions, the water is hard. In North America, Brazil, and Japan, the water is comparatively soft.

The earliest builders were sodium carbonate (washing soda) and sodium silicate (waterglass). Since the 1930s, phosphates (sodium phosphates) and polyphosphates (sodium hexametaphosphate) were introduced, continuing with the introduction of phosphonates (HEDP, ATMP, EDTMP). These agents are now known to have serious environmental consequences leading to a drive towards more environmentally benign phosphorus-free agents, such as polycarboxylates (EDTA, NTA), citrates (trisodium citrate), silicates (sodium silicate), gluconic acid and polyacrylic acid; or ion exchange agents like zeolites.

Surfactants

Surfactants are responsible for most of the cleaning performance in laundry detergent. They provide this by absorption and emulsification of soil into the water and also by reducing the water's surface tension to improve wetting.

Laundry detergents contain mostly anionic and non-ionic surfactants. Cationic surfactants are normally incompatible with anionic detergents and have poor cleaning efficiency; they are employed only for certain special effects, as fabric softeners, antistatic agents, and biocides. Zwitterionic surfactants are rarely employed in laundry detergents mainly for cost reasons. Most detergents use a combination of various surfactants to balance their performance.

Bleaches

Despite the name, modern laundry bleaches do not include household bleach (sodium hypochlorite). Laundry bleaches are typically stable adducts of hydrogen peroxide, such as sodium perborate and sodium percarbonate, these are inactive as solids but will release hydrogen peroxide upon exposure to water. The main targets of bleaches are oxidisible organic stains, which are usually of vegetable origin (e.g. chlorophyll, anthocyanin dyes, tannins, humic acids, and carotenoid pigments). Hydrogen peroxide is insufficiently active as a bleach at temperature below 60°C, which traditionally made hot washes the norm. The development of bleach activators in the 1970s and 80s allowed for cooler washing temperatures to be effective. These compounds, such as tetraacetylethylenediamine (TAED), react with hydrogen peroxide to produce peracetic acid, which is an even more effective bleach, particularly at lower temperatures.

Enzymes

The use of enzymes for laundry was introduced in 1913 by Otto Rohm. The first preparation was a pancreatic extract obtained from slaughtered animals, which was unstable against alkali and bleach. Only in the latter part of the century with the availability of thermally robust bacterial enzymes did this technology become mainstream.

Enzymes are required to degrade stubborn stains composed of proteins (milk, cocoa, blood, egg yolk, grass), fats (chocolate, fats, oils), starch (flour and potato stains), and cellulose (damaged cotton fibrils, vegetable and fruit stains). Each type of stain requires a different type of enzyme: proteases (savinase) for proteins, lipases for greases, α-amylases for carbohydrates, and cellulases for cellulose.

Other ingredients

Many other ingredients are added depending on the expected circumstances of use. Such additives modify the foaming properties of the product by either stabilizing or counteracting foam. Other ingredients increase or decrease the viscosity of the solution, or solubilize other ingredients. Corrosion inhibitors counteract damage to washing equipment. "Dye transfer inhibitors" prevent dyes from one article from colouring other items. "Antiredeposition agents" such as carboxymethyl cellulose are used to prevent fine soil particles from reattaching to the product being cleaned.

A number of ingredients affect aesthetic properties of the item to be cleaned or the detergent itself before or during use. These agents include optical brighteners, fabric softeners, and colourants. A variety of perfumes are also components of modern detergents, provided that they are compatible with the other components and do not affect the colour of the cleaned item. The perfumes are typically a mixture of many compounds, common classes include terpene alcohols (citronellol, geraniol, linalool, nerol) and their esters (linalyl acetate), aromatic aldehydes (helional, hexyl cinnamaldehyde, lilial) and synthetic musks (galaxolide).

Dishwashing Detergents

Dishwashing liquid (or **washing-up liquid** in British English), also known as **dishwashing soap**, **dish detergent**, and **dish soap** is a detergent used to assist in dishwashing. It is usually a highly-foaming mixture of surfactants with low skin irritation, and is primarily used for hand washing of glasses, plates, cutlery, and cooking utensils in a sink or bowl. In addition to its primary use, dishwashing liquid also has various informal applications, such as for creating bubbles, clothes washing and cleaning oil-affected birds.

Hand dishwashing is generally performed in the absence of a dishwashing machine, when large "hard-to-clean" items are present,

or through preference. Some dishwashing liquids can harm household silver, fine glassware, anything with gold leaf, disposable plastics, and any objects made of brass, bronze, cast iron, pewter, tin, or wood, especially when combined with hot water and the action of a dishwasher. When dishwashing liquid is used on such objects it is intended that they be washed by hand.

Hand dishwashing detergents utilize surfactants to play the primary role in cleaning. The reduced surface tension of dishwashing water, and increasing solubility of modern surfactant mixtures, allows the water to run off the dishes in a dish rack very quickly. However, most people also rinse the dishes with pure water to make sure to get rid of any soap residue that could affect the taste of the food.

Dishwashing liquid can be a skin irritant and cause hand eczema. Those with "sensitive skin" are advised amongst other things to persuade someone else to do the washing up.

Dishwasher detergent is a detergent made for washing dishes in a dishwasher. Dishwasher detergent is different from dishwashing liquid made to wash dishes by hand.

When using a dishwasher, the user must select a special detergent for its use. All detergents are designed for use after the user scrapes leftover food from the dishes before washing. To function, the user places dishes in the dishwasher in such fashion that the surface of all dishes is open to the flow of water.

Most dishwasher detergents are incompatible for use with silver, brass, cast iron, bronze, aluminum, pewter, and goldleaf. They can also harm disposable plastic, anything wood, knives with hollow handles, and fine glassware.

Dishwashing detergents for dishwashers are manufactured and marketed variously as cartridges, gel, liquids, pacs, powder, and tablets. Any dishwashing liquid may contain bleach, enzymes, or rinsing aids. Some dishwashing detergents may be homemade, using ingredients such as borax, essential oil, eucalyptus oil and grated bar soap, among others.

Dishwashing detergents can be formulated to work under different circumstances. In some cases suitably formulated they can be used with cold water or sea water, although they will not generally work as well as those intended for, and used with, hot water.

Different kinds of dishwashing detergent contain different combinations of ingredients. Common ingredients include:

- **Phosphates**: Bind calcium and magnesium ions to prevent 'hard-water' type limescale deposits. They can cause ecological damage, and have been partially banned or phased out.
- **Oxygen-based bleaching agents** (older-style powders and liquids contain chlorine-based bleaching agents): Break up and bleach organic deposits.
- **Non-ionic surfactants**: Lower the surface tension of the water, emulsifies oil, lipid and fat food deposits, prevents droplet spotting on drying.
- **Alkaline salts**: These are a primary component in older and original-style dishwasher detergent powders[*citation needed*]. Highly alkaline salts attack and dissolve grease, but are extremely corrosive (fatal) if swallowed. Salts used may include metasilicates, alkali metal hydroxides, sodium carbonate etc.
- **Enzymes**: Break up protein-based food deposits, and possibly oil, lipid and fat deposits. The enzymes used are similar to the ones used in laundry.
- **Anti-corrosion agent(s)**: Often sodium silicate, this prevents corrosion of dishwasher components.[*citation needed*]

Dishwashing detergent may also contain:[*citation needed*]

- Anti-foaming agents:[*citation needed*] Foam interferes with the washing action. Foam may affect operation of the machine's water-level sensors and will leak past the door seals.
- Additives to slow down the removal of glaze & patterns from glazed ceramics
- Perfumes
- Anti-caking agents (in granular detergent)
- Starches (in tablet based detergents)
- Gelling agents (in liquid/gel based detergents)
- Sand (inexpensive powdered detergents)

Dishwasher detergents are generally strongly alkaline (basic).

Inexpensive powders may contain sand. Such detergents may harm the dishes and the dishwasher. Powdered detergents are

more likely to cause fading on china patterns.

Besides older style detergents for dishwashers, biodegradable detergents also exist for dishwashers. These detergents may be more environmentally friendly than conventional detergents.

Informal Uses

Reader's Digest notes its use as an ant killer, weed killer, to help spread water-borne fertilizer, and to wash human hair. *Good Housekeeping* says it can be used mixed with vinegar to attract and drown fruit flies. Dishwashing detergent has been used to clean mirrors as well as windows.

- Pling, an open source general purpose cleaner for glazed, plastic, chrome and inox bathroom and kitchen surfaces, published by Twibright Labs, uses dishwashing liquid as one of active ingredients.
- Dishwashing liquid can be mixed with water and additional ingredients such as glycerin and sugar to produce a bubble-blowing solution.
- Dishwashing liquid may be used for cleaning delicate clothing fabrics such as hosiery and lingerie.
- Dishwashing liquid is frequently recommended in a dilute solution to make decals and vinyl graphics easier to position when applying.
- In industry, dishwashing liquid is also used to inspect pressurized equipment for leaks, such as propane fittings. It is used to inspect pneumatic tires for flats, as well as for quality assurance during the installation process, and as a mounting bead lubricant.
- Dishwashing liquid has uses as an ingredient in making homemade garden pest deterrents. Oregon State University's Cooperative Extension Service notes the use of dishwashing liquid to get rid of spidermites. Dish soap has also been used to deter aphids. In some instances, the dish soap may be toxic to plant leaves and cause them to "burn". Use of soap or dish detergent to help spread pesticide on plants is noted by University of Georgia extension service, but not recommended.
- A solution of dishwashing liquid and water may be used to remove coffee, tea, olive oil, soda and fruit juice stains from fabrics. One dishwashing liquid brand has been used to remove stains from white or lightly-colored cloth napkins.
- Dishwashing liquid has been used to treat birds affected by oil spills. After the Exxon Valdez oil spill in 1989, the International Bird Rescue Research Center received hundreds of cases of dishwashing liquid that were used for this purpose. More dishwashing liquid was donated during the Deepwater Horizon oil spill to the International Bird Rescue Research Center and the Marine Mammal Center.

Figure 21.2.4 *An oiled Gannet being washed. Source Wikipedia*

Environmental concerns

Phosphates in detergent became an environmental concern in the 1950s and the subject of bans in later years.[8] Phosphates make laundry cleaner but also cause eutrophication, particularly with poor wastewater treatment.[9]

A recent academic study of fragranced laundry products found "more than 25 VOCs emitted from dryer vents, with the highest concentrations of acetaldehyde, acetone, and ethanol. Seven of these VOCs are classified as hazardous air pollutants (HAPs) and two as carcinogenic HAPs (acetaldehyde and benzene)".[10]

The EEC Directive 73/404/EEC stipulates an average biodegradability of at least 90% for all types of surfactants used in detergents. The phosphate content of detergents is regulated in many countries, e.g., Austria, Germany, Italy, The Netherlands, Norway, Sweden, Switzerland, United States, Canada, and Japan.

Summary

- Detergents are classified into anionic, cationic, and non-ionic detergents and zwitterionic detergents based on the electrical charge of the surfactants.
- Variations in detergent formulations are based on its end-use (i.e. laundry or for kitchenware).
- Phosphates make laundry cleaner but also cause eutrophication, particularly with poor wastewater treatment.[9]

ntributors and Attributions

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21.3: Laundry Auxiliaries- Softeners and Bleaches

Learning Objectives

- Describe a fabric softener and its use.
- Describe bleaches and their use.

A **fabric softener** (or **conditioner**) is a conditioner that is typically applied to laundry during the rinse cycle in a washing machine. In contrast to laundry detergents, fabric softeners may be regarded as a kind of after-treatment laundry aid.[1]

Machine washing puts great mechanical stress on textiles, particularly natural fibers such as cotton and wool. The fibers at the fabric surface are squashed and frayed, and this condition hardens while drying the laundry in air, giving the laundry a harsh feel. Adding a liquid fabric softener to the final rinse (rinse-cycle softener) results in laundry that feels softer.[2][1]

Fabric softeners coat the surface of a fabric with chemical compounds that are electrically charged, causing threads to "stand up" from the surface and thereby imparting a softer and fluffier texture. Cationic softeners, like those shown in Figure 21.3.1. bind by electrostatic attraction to the negatively charged groups on the surface of the fibers and neutralize their charge. The long aliphatic chains then line up towards the outside of the fiber, imparting lubricity.

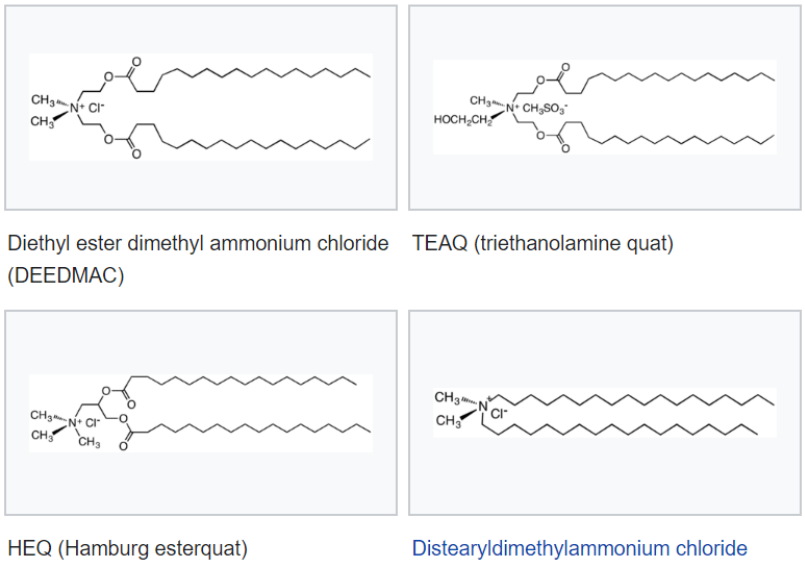


Figure 21.3.1 *Cationic surfactants in fabric softeners. Source: Wikipedia*

Fabric softeners impart antistatic properties to fabrics, and thus prevent the build-up of electrostatic charges on synthetic fibers, which in turn eliminates fabric cling during handling and wearing, crackling noises, and dust attraction. Also, fabric softeners make fabrics easier to iron and help reduce wrinkles in garments. In addition, they reduce drying times so that energy is saved when softened laundry is tumble-dried. Last but not least, they can also impart a pleasant fragrance to the laundry.[1]

Risks

As with soaps and detergents, fabric softeners may cause irritant dermatitis.[5] Manufacturers produce some fabric softeners without dyes and perfumes to reduce the risk of skin irritation. Fabric softener overuse may make clothes more flammable, due to the fat-based nature of most softeners. Some deaths have been attributed to this phenomenon,[6] and fabric softener makers recommend not using them on clothes labeled as flame-resistant.[*citation needed*]

Laundry Bleaches: Whiter Whites

Bleach is the generic name for any chemical product which is used industrially and domestically to clean, and to remove stains. It often refers, specifically, to a dilute solution of sodium hypochlorite, also called "liquid bleach".

Many bleaches have broad spectrum bactericidal properties, making them useful for disinfecting and sterilizing and are used in swimming pool sanitation to control bacteria, viruses, and algae and in many places where sterile conditions are required. They are also used in many industrial processes, notably in the bleaching of wood pulp. Bleaches also have other minor uses like removing mildew, killing weeds, and increasing the longevity of cut flowers.[1]

Bleaches work by reacting with many colored organic compounds, such as natural pigments, and turning them into colorless ones. While most bleaches are oxidizing agents (chemicals that can remove electrons from other molecules), some are reducing agents (that donate electrons).

Chlorine, a powerful oxidizer, is the active agent in many household bleaches. Since pure chlorine is a toxic corrosive gas, these products usually contain hypochlorite which releases chlorine when needed. "Bleaching powder" usually means a formulation containing calcium hypochlorite.

Oxidizing bleaching agents that do not contain chlorine are usually based on peroxides such as hydrogen peroxide, sodium percarbonate, and sodium perborate. These bleaches are called 'non-chlorine bleach,' 'oxygen bleach' or 'color-safe bleach.'[2]

Reducing bleaches have niche uses, such as sulfur dioxide used to bleach wool, either as gas or from solutions of sodium dithionite;[3] and sodium borohydride.

Bleaches generally react with many other organic substances besides the intended colored pigments, so they can weaken or damage natural materials like fibers, cloth, and leather, and intentionally applied dyes such as the indigo of denim. For the same reason, ingestion of the products, breathing of the fumes, or contact with skin or eyes can cause health damage.

Summary

- A fabric softener is an after-treatment laundry aid that imparts a softer and fluffier texture.
- Bleach is the generic name for any chemical product that is used industrially and domestically for cleaning and stain removal.

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21.4: All-Purpose and Special Purpose Cleaning Products

Learning Objective

- List various cleaners and their modes of action.

Cleaning agents or **hard-surface cleaners** are substances (usually liquids, powders, sprays, or granules) used to remove dirt, including dust, stains, bad smells, and clutter on surfaces. Purposes of cleaning agents include health, beauty, removing offensive odor, and avoiding the spread of dirt and contaminants to oneself and others. Some cleaning agents can kill bacteria (e.g. door handle bacteria, as well as bacteria on worktops and other metallic surfaces) and clean at the same time. Others, called degreasers, contain organic solvents to help dissolve oils and fats.

Acidic cleaning agents are mainly used for removal of inorganic deposits like scaling. The active ingredients are normally strong mineral acids and chelants. Often, surfactants and corrosion inhibitors are added to the acid.

Hydrochloric acid is a common mineral acid typically used for concrete. Vinegar can also be used to clean hard surfaces and remove calcium deposits that also helps to maintain our environment bacteria free. Sulphuric acid is used in acidic drain cleaners to unblock clogged pipes by dissolving greases, proteins, and even carbohydrate-containing substances such as toilet tissue.

Alkaline cleaning agents contain strong bases like sodium hydroxide or potassium hydroxide. Bleach (pH 12) and ammonia (pH 11) are common alkaline cleaning agents. Often, dispersants, to prevent redeposition of dissolved dirt, and chelants, to attack rust, are added to the alkaline agent.

Alkaline cleaners can dissolve fats (including grease), oils, and protein-based substances.

Neutral washing agents are pH-neutral and based on non-ionic surfactants that disperse different types.

Scouring agents are mixtures of the usual cleaning chemicals (surfactants, water softeners) as well as abrasive powders. The abrasive powder must be of a uniform particle size.

Particles are usually smaller than 0.05 mm. Pumice, calcium carbonate (limestone, chalk, dolomite), kaolinite, quartz, soapstone or talc are often used as abrasives, i.e. polishing agents.

Special bleaching powders contain compounds that release sodium hypochlorite, the classical household bleaching agent. These precursor agents include trichloroisocyanuric acid and mixtures of sodium hypochlorite ("chlorinated orthophosphate").

Examples of notable products include: Ajax, Bar Keepers Friend, Bon Ami, Comet, Vim, Zud, and others.

All-Purpose Cleaners

All-purpose cleansers (Figure 21.4.1) contain mixtures of anionic and nonionic surfactants, polymeric phosphates or other sequestering agents, solvents, hydrotropic substances, polymeric compounds, corrosion inhibitors, skin-protective agents, and sometimes perfumes and colorants.[7] Aversive agents, such as denatonium, are occasionally added to cleaning products to discourage animals and small children from consuming them.



Figure 21.4.1 *Fabuloso multipurpose cleaner and generic surface cleaners. Source: Wikipedia*

Some cleaners contain water-soluble organic solvents like glycol ethers and fatty alcohols, which ease the removal of oil, fat and paint. Disinfectant additives include quaternary ammonium compounds, phenol derivatives, terpene alcohols (pine oil), aldehydes, and aldehyde-amine condensation products.

All-purpose cleaners are usually concentrated solutions of surfactants and water softeners, which enhance the behavior of surfactant in hard water. Typical surfactants are alkylbenzenesulfonates, an anionic detergent, and modified fatty alcohols. A typical water softener is sodium triphosphate.

All-purpose cleansers are effective with most common kinds of dirt. Their dilute solutions are neutral or weakly alkaline, and are safe for use on most surfaces.

Special Purpose Cleaners

Traditional **oven cleaners** contain sodium hydroxide (lye), solvents, and other ingredients,[3][4][5] and work best when used in a slightly-warm (not hot) oven. If used in a self-cleaning oven, the lye will cause permanent damage to the oven.

New-style oven cleaners are based on ingredients other than lye. These products must be used in a cold oven. Most new-style oven cleaners can be used in self-cleaning ovens.

Oven cleaners are some of the most toxic household cleaning products available on the market.[6] Correct use of an oven cleaner may be reasonably safe, but incorrect use can have harmful effects.

One popular oven cleaner brand in the US is "Easy-Off", sold by Reckitt Benckiser. Popular choices in the UK include "Zep Oven Brite" and "Mr Muscle Oven Cleaner".

Toilet bowl cleaning agents often are aimed at removal of calcium carbonate deposits, which are attacked by acids. Powdered cleaners contain acids that come in the form of solid salts, such as sodium hydrogen sulfate. Liquid toilet bowl cleaners contain other acids, typically dilute hydrochloric, phosphoric, or formic acids. These convert the calcium carbonate into salts that are soluble in water or are easily rinsed away.

Chemical drain cleaners can be in solid or liquid form that are readily available through hardware stores, though some (primarily acidic ones) are intended for use by licensed plumbers.[1]Alkaline drain cleaners are available in either solid or liquid state while the acidic ones are usually in liquid form.



Figure 21.4.2 *Bottles of alkaline drain cleaners containing sodium hydroxide can dissolve greases and hair. Source: Wikipedia*

Metal cleaners are used for cleaning stainless steel sinks, faucets, metal trim, silverware, etc. These products contain abrasives (e.g., siliceous chalk, diatomaceous earth, alumina) with a particle size < 20 μm. Fatty alcohol or alkylphenol polyglycol ethers with 7-12 ethylene oxide (EO) units are used as surfactants.[7]

For ferrous metals, the cleaners contain chelating agents, abrasives, and surfactants. These agents include citric and phosphoric acids, which are nonaggressive. Surfactants are usually modified fatty alcohols. Silver cleaning is a specialty since silver is noble but tends to tarnish via formation of black silver sulfide, which is removable via silver-specific complexants such as thiourea.

Stainless steel, nickel, and chromium cleaners contain lactic, citric, or phosphoric acid. A solvent (mineral spirits) may be added.

Nonferrous metal cleaners contain ammonia, ammonium soaps (ammonium oleate, stearate) and chelating agents (ammonium citrate, oxalate).

For special type of precious metals especially those used for luxury watches and high-end jewelry, special type of cleaning agents are usually used to clean and protect them from the elements.

Glass cleaners. Light duty hard surface cleaners are not intended to handle heavy dirt and grease. Because these products are expected to clean without rinsing and result in a streak-free shine, they contain no salts. Typical window cleaning items consist of alcohols, either ethanol or isopropanol, and surfactants for dissolving grease. Other components include small amounts of ammonia as well as dyes and perfumes.

These are composed of organic,water-miscible solvent such as isopropyl alcohol and an alkaline detergent. Some glass cleaners also contain a fine, mild abrasive. Most glass cleaners are available as sprays or liquid. They are sprayed directly onto windows, mirrors and other glass surfaces or applied on with a soft cloth and rubbed off using a soft ,lint-free duster. A glass cloth ideal for the purpose and soft water to which some methylated spirit or vinegar is added which is an inexpensive glass cleaner.

Silverware can be freed of silver sulfide tarnish with thiourea, and either hydrochloric or sulfuric acid.

Building facade cleaners. For acid-resistant building facades, such as brick, acids are typically used. These include mixtures of phosphoric and hydrofluoric acids as well as surfactants. For acid-sensitive facades such as concrete, strongly alkaline cleaners are used such as sodium hydroxide and thickeners. Both types of cleaners require a rinsing and often special care since the solutions are aggressive toward skin.

Drain Cleaners: Danger and Usage Considerations

Danger arises from chemical drain cleaners' potential to injure eyes, lungs, and skin; and damage to clothing and household materials such as wood, paint, aluminum, and fiberglass. Chemical drain cleaners should be used only according to the manufacturer's instructions, as other use may cause injury.[7] Strongly corrosive and acid drain cleaners are among the most hazardous household products available to the public. Chemical drain cleaners can cause strong reactions—sometimes

explosively—with other chemicals that may have been used previously, which can result in serious injury to anyone in the vicinity.[8] In one such incident, a five-year-old boy was left scarred for life after an acidic drain cleaner leaked through his bedroom ceiling as he slept.[9]

Strong Alkali Drain cleaners are equally capable of causing rapid, severe burns, as seen in the cases of a woman doused with concentrated lye in an attack. A small girl was also permanently disfigured by a common lye drain opener.,[10][11] Moreover, because the acidic or basic drain cleaners themselves are washed down the drain, this contributes to pollution in the water supply. The heat generation can also soften plastic PVC pipes, and the pressure buildup by gas generation can cause older pipes to burst. Commercial chemical based solutions can cause corrosion and other damage to your pipes and sewer lines[12]

Oftentimes, individuals may unknowingly mix two different types of drain cleaners, which can even lead to deadly results. For example, consider the mixing of an acidic and basic drain cleaner:

Sulfuric Acid + Sodium Hydroxide → sodium sulfate (a salt) + water

$H_2SO_4 + 2\ NaOH \rightarrow Na_2SO_4 + 2H_2O$

The neutralization reaction of the acid and base may seem harmless, but in reality this reaction is extremely exothermic and can cause pipes to violently explode. Consider another example of mixing, this time between an acid drain cleaner and bleach:

Hydrochloric acid + bleach → water + table salt + chlorine gas

$2HCl + NaClO \rightarrow H_2O + NaCl + Cl_2$

This reaction generates chlorine gas, which is toxic to the lungs.

Green Cleaners

Green cleaning refers to using cleaning methods and products with environmentally friendly ingredients and procedures which are designed to preserve human health and environmental quality.[1] Green cleaning techniques and products avoid the use of products which contain toxic chemicals, some of which emit volatile organic compounds causing respiratory, dermatological and other conditions.[2] Green cleaning can also describe the way residential and industrial cleaning products are manufactured, packaged and distributed. If the manufacturing process is environmentally friendly and the products are biodegradable, then the term "*green*" or "*eco-friendly*" may apply.

Common household ingredients that are safe to use on its own or in combination for a variety of cleaning applications include baking soda, soap, alcohol, cornstarch, lemon juice, white vinegar, citrus solvent, washing soda (SAL soda or sodium carbonate), oxygen bleach, vegetable oil, and hydrogen peroxide.

WEB LINK

The links below provide information on safe ingredients for homemade substitutions and homemade cleaning products.

https://learn.eartheasy.com/guides/non-toxic-home-cleaning/#homecleaning

Summary

- All-purpose cleansers are effective with most common kinds of dirt and are formulated to contain mixtures of surfactants, sequestering agents, solvents, hydrotropic substances, polymeric compounds, corrosion inhibitors, skin-protective agents, and sometimes perfumes and colorants.
- Special purpose cleaners are formulated with specific chemicals to effectively remove dirt, grime or stain from a particular surface (e.g. glass cleaner, metal cleaner, etc.) or appliance (e.g. oven cleaner).

- Green cleaners are gaining popularity among environmentalists who are interested in using cleaners that are made of biodegradable and eco-friendly ingredients.

Contributors

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21.5: Solvents, Paints, and Waxes

Learning Objective

- List the properties and uses of solvents, paints, and, waxes.

Solvents

A **solvent** is a substance that dissolves a solute, resulting in a solution. A solvent is usually a liquid but can also be a solid, a gas, or a supercritical fluid. The quantity of solute that can dissolve in a specific volume of solvent varies with temperature. Common uses for organic solvents are in dry cleaning (e.g. tetrachloroethylene), as paint thinners (e.g. toluene, turpentine), as nail polish removers and glue solvents (acetone, methyl acetate, ethyl acetate), in spot removers (e.g. hexane, petrol ether), in detergents (citrus terpenes) and in perfumes (ethanol). Water is a solvent for polar molecules and the most common solvent used by living things; all the ions and proteins in a cell are dissolved in water within a cell. Solvents find various applications in chemical, pharmaceutical, oil, and gas industries, including in chemical syntheses and purification processes.

Most organic solvents are flammable or highly flammable, depending on their volatility. Exceptions are some chlorinated solvents like dichloromethane and chloroform. Mixtures of solvent vapors and air can explode. Solvent vapors are heavier than air; they will sink to the bottom and can travel large distances nearly undiluted. Solvent vapors can also be found in supposedly empty drums and cans, posing a flash fire hazard; hence empty containers of volatile solvents should be stored open and upside down.

Paints

Paint is any pigmented liquid, liquefiable, or solid mastic composition that, after application to a substrate in a thin layer, converts to a solid film. It is most commonly used to protect, color, or provide texture to objects.

Paint was one of the earliest inventions of humanity. Some cave paintings drawn with red or yellow ochre, hematite, manganese oxide, and charcoal may have been made by early *Homo sapiens* as long as 40,000 years ago.[3] Paint may be even older. In 2003 and 2004, South African archeologists reported finds in Blombos Cave of a 100,000-year-old human-made ochre-based mixture that could have been used like paint.[4][5] Further excavation in the same cave resulted in the 2011 report of a complete toolkit for grinding pigments and making a primitive paint-like substance.[5][6]

By the proper onset of the Industrial Revolution, in the mid-18th century, paint was being ground in steam-powered mills, and an alternative to lead-based pigments had been found in a white derivative of zinc oxide. Interior house painting increasingly became the norm as the 19th century progressed, both for decorative reasons and because the paint was effective in preventing the walls rotting from damp. Linseed oil was also increasingly used as an inexpensive binder.

In 1866, Sherwin-Williams Figure $21.5.1$ in the United States opened as a large paint-maker and invented a paint that could be used from the tin without preparation.

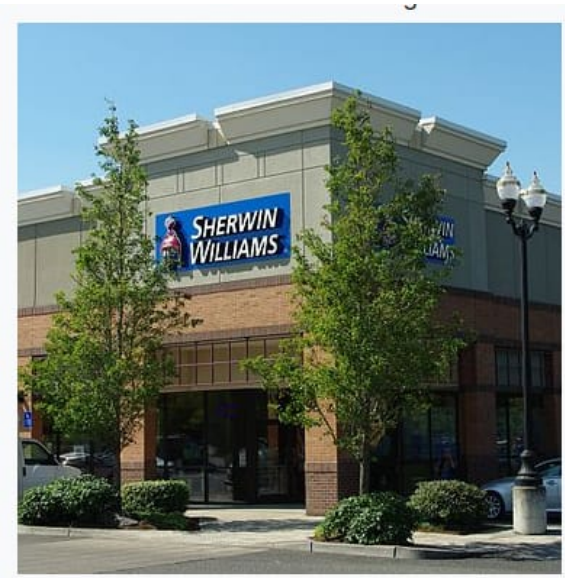


Figure 21.5.1 Sherwin Williams company store in Hillsboro, Oregon

The **binder** is the film-forming component of paint.[10] It is the only component that is always present among all the various types of formulations. Many binders are too thick to be applied and must be thinned. The type of thinner, if present, varies with the binder. The binder imparts properties such as gloss, durability, flexibility, and toughness.[11] Binders include synthetic or natural resins such as alkyds, acrylics, vinyl-acrylics, vinyl acetate/ethylene (VAE), polyurethanes, polyesters, melamine resins, epoxy, silanes or siloxanes or oils.

The main purposes of the **diluent** are to dissolve the polymer and adjust the viscosity of the paint. It is volatile and does not become part of the paint film. It also controls flow and application properties, and in some cases can affect the stability of the paint while in liquid state. Its main function is as the carrier for the non volatile components. To spread heavier oils (for example, linseed) as in oil-based interior house paint, a thinner oil is required. These volatile substances impart their properties temporarily—once the solvent has evaporated, the remaining paint is fixed to the surface. Some paints have no diluent. Water is the main diluent for water-borne paints, even the co-solvent types.

Solvent-borne, also called oil-based, paints can have various combinations of organic solvents as the diluent, including aliphatics, aromatics, alcohols, ketones and white spirit. Specific examples are organic solvents such as petroleum distillate, esters, glycol ethers, and the like. Sometimes volatile low-molecular weight synthetic resins also serve as diluents.

Pigments are granular solids incorporated in the paint to contribute color. **Dyes** are colorants that dissolve in the paint. **Fillers** are granular solids incorporated to impart toughness, texture, give the paint special properties,[16] or to reduce the cost of the paint. During production, the size of such particles can be measured with a Hegman gauge. Rather than using only solid particles, some paints contain dyes instead of or in combination with pigments.

Pigments can be classified as either natural or synthetic. Natural pigments include various clays, calcium carbonate, mica, silicas, and talcs. Synthetics would include engineered molecules, calcined clays, blanc fixe, precipitated calcium carbonate, and synthetic pyrogenic silicas.

Some pigments are toxic, such as the lead pigments that are used in lead paint. Paint manufacturers began replacing white lead pigments with titanium white (titanium dioxide), before lead was banned in paint for residential use in 1978 by the US Consumer Product Safety Commission. The titanium dioxide used in most paints today is often coated with silica/alumina/zirconium for various reasons, such as better exterior durability, or better hiding performance (opacity) promoted by more optimal spacing within the paint film.[17]

Waxes

Waxes are organic compounds, hydrocarbons that characteristically consist of long aliphatic alkyl chains, although aromatic compounds may also be present. Natural waxes may contain unsaturated bonds and include various functional groups such as

fatty acids, primary and secondary alcohols, ketones, aldehydes and fatty acid esters. **Synthetic waxes** (e.g. polyethylene and polypropylene waxes) often consist of homologous series of long-chain aliphatic hydrocarbons (alkanes or paraffins) that lack functional groups.[1]

The best known animal wax is **beeswax** used in constructing the honeycombs of honeybees, but other insects secrete waxes. A major component of the beeswax is myricyl palmitate which is an ester of triacontanol and palmitic acid. Its melting point is 62-65 °C. **Spermaceti** occurs in large amounts in the head oil of the sperm whale. One of its main constituents is cetyl palmitate, another ester of a fatty acid and a fatty alcohol. **Lanolin** is a wax obtained from wool, consisting of esters of sterols.[1]

Plants secrete waxes into and on the surface of their cuticles as a way to control evaporation, wettability and hydration.[3] The epicuticular waxes of plants are mixtures of substituted long-chain aliphatic hydrocarbons, containing alkanes, alkyl esters, fatty acids, primary and secondary alcohols, diols, ketones and aldehydes.[2] From the commercial perspective, the most important plant wax is **carnauba wax**, a hard wax obtained from the Brazilian palm *Copernicia prunifera*. Containing the ester myricyl cerotate, it has many applications, such as confectionery and other food coatings, car and furniture polish, floss coating, and surfboard wax. Other more specialized vegetable waxes include **jojoba oil**, **candelilla wax** and **ouricury wax**.

Paraffin wax (or **petroleum wax**) is a soft colorless solid derived from petroleum, coal or shale oil that consists of a mixture of hydrocarbon molecules containing between twenty and forty carbon atoms.Waxes are mainly consumed industrially as components of complex formulations, often for coatings.The main use of polyethylene and polypropylene waxes is in the formulation of colourants for plastics. Waxes confer matting effects and wear resistance to paints. Polyethylene waxes are incorporated into inks in the form of dispersions to decrease friction. They are employed as release agents, find use as slip agents in furniture, and confer corrosion resistance.



Figure 21.5.2 Paraffin candle.

Waxes such as paraffin wax or beeswax, and hard fats such as tallow are used to make candles (Figure 21.5.2). used for lighting and decoration. Waxes are used as finishes and coatings for wood products.[10] Beeswax is frequently used as a lubricant on drawer slides where wood to wood contact occurs. Waxes are used to make wax paper, impregnating and coating paper and card to waterproof it or make it resistant to staining, or to modify its surface properties. Waxes are also used in shoe polishes, wood polishes, and automotive polishes, as mold release agents in mold making, as a coating for many cheeses, and to waterproof leather and fabric. Wax has been used since antiquity as a temporary, removable model in lost-wax casting of gold, silver and other materials.

Wax with colorful pigments added has been used as a medium in encaustic painting, and is used today in the manufacture of crayons, china markers and colored pencils. Carbon paper, used for making duplicate typewritten documents was coated with carbon black suspended in wax, typically montan wax, but has largely been superseded by photocopiers and computer printers. In another context, lipstick and mascara are blends of various fats and waxes colored with pigments, and both beeswax and lanolin are used in other cosmetics. Ski wax is used in skiing and snowboarding. Also, the sports of surfing and skateboarding often use wax to enhance the performance.

Some waxes are considered food-safe and are used to coat wooden cutting boards and other items that come into contact with food. Beeswax or coloured synthetic wax is used to decorate Easter eggs in Romania, Ukraine, Poland, Lithuania and the Czech Republic. Paraffin wax is used in making chocolate covered sweets.

Summary

- A solvent is a liquid, solid, a gas, or a supercritical fluid that dissolves a solute to form a solution. Solvents are found in various personal and household items, and also used in chemical, pharmaceutical, oil, and gas industries, including in chemical syntheses and purification processes.
- Paint is any pigmented liquid, liquefiable, or solid mastic composition that, after application to a substrate in a thin layer, converts to a solid film. It is most commonly used to protect, color, or provide texture to objects.
- Natural and synthetic waxes are used for lighting, for surface coating and polishing, for waterproofing leather and fabric. Waxes are also key ingredients in cosmetics and personal care products.

Contributors and Attributions

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21.6: Cosmetics - Personal Care Chemicals

Learning Objectives

- List the main ingredients in different personal care products and their functions.
- Describe the steps in formation of temporary and permanent waves.

In the United States, the Food and Drug Administration (FDA), which regulates cosmetics, defines cosmetics as products "intended to be applied to the human body for cleansing, beautifying, promoting attractiveness, or altering the appearance without affecting the body's structure or functions". This broad definition includes any material intended for use as an ingredient of a cosmetic product, with the FDA specifically excluding pure soap from this category.



Figure 21.6.1 Assorted cosmetics and tools.

Cosmetics (Figure 21.6.1) have been in use for thousands of years. Egyptian men and women used makeup to enhance their appearance. They were very fond of eyeliner and eye-shadows in dark colors including blue, red, and black. Ancient Sumerian men and women were possibly the first to invent and wear lipstick, about 5,000 years ago. They crushed gemstones and used them to decorate their faces, mainly on the lips and around the eyes.

According to one source, early major developments include:

- Kohl used by ancient Egypt as a protectant of the eye (Figure 21.6.2).
- Castor oil used by ancient Egypt as a protective balm.
- Skin creams made of beeswax, olive oil, and rose water, described by Romans.
- Vaseline and lanolin in the nineteenth century.

Although modern makeup has been traditionally used mainly by women, an increasing number of men are using cosmetics usually associated with women to enhance or cover their own facial features such as blemishes and dark circles, as well the use of eyeshadow, mascara and lipstick by some. Cosmetics brands have increasingly also targeted men in the sale of cosmetics, with some products targeted specifically at men.



Figure 21.6.2 Nefertiti Bust showing the use of eye liner made of kohl.

The Skin

The cutaneous membrane is the technical term for our skin. The skin's primary role is to help protect the rest of the body's tissues and organs from physical damage such as abrasions, chemical damage such as detergents, and biological damage from microorganisms. For example, while the skin harbors many permanent and transient bacteria, these bacteria are unable to enter the body when healthy, intact skin is present.

Our skin is made of three general layers (Figure 21.6.3). In order from most superficial to deepest they are the epidermis, dermis, and subcutaneous tissue (hypodermis).

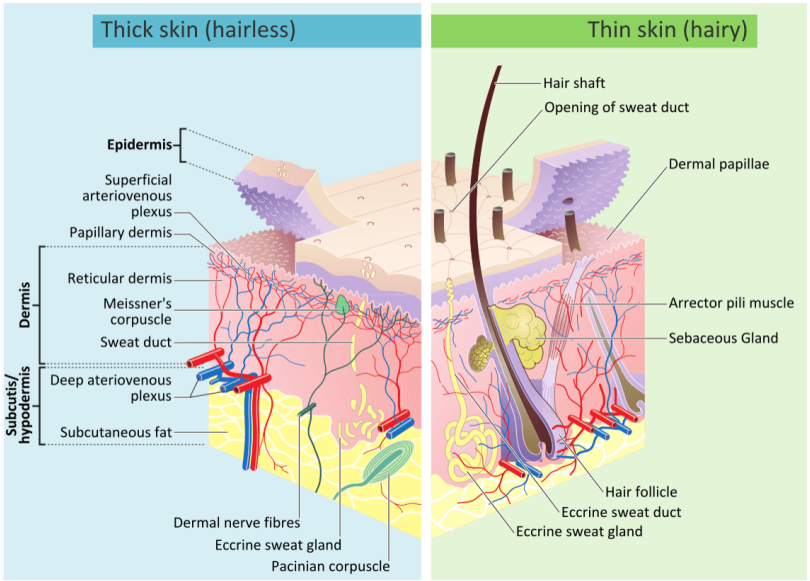


Figure 21.6.3 Skin layers, of both the hairy and hairless skin.

There are several different types of cells in the **epidermis**. All of the cells are necessary for the important functions of the epidermis.

- The epidermis consists mainly of stacks of keratin-producing epithelial cells called keratinocytes. These cells make up at least 90 percent of the epidermis. Near the top of the epidermis, these cells are also called squamous cells.
- Another 8 percent of epidermal cells are melanocytes. These cells produce the pigment melanin that protects the dermis

from UV light.
- About 1 percent of epidermal cells are Langerhans cells. These are immune system cells that detect and fight pathogens entering the skin.
- Less than 1 percent of epidermal cells are Merkel cells, which respond to light touch and connect to nerve endings in the dermis.

The epidermis has several crucial functions in the body. These functions include protection, water retention, and vitamin D synthesis. The epidermis provides protection to underlying tissues from physical damage, pathogens, and UV light.

Skin Creams and Lotions

A **lotion** is a low-viscosity topical preparation intended for application to the skin. By contrast, creams and gels have higher viscosity, typically due to lower water content. Lotions are applied to external skin with bare hands, a brush, a clean cloth, or cotton wool.

While a lotion may be used as a medicine delivery system, many lotions, especially **hand lotions** and **body lotions** are meant instead to simply smooth, moisturize, soften and perhaps perfume the skin.

Most cosmetic lotions are moisturizing lotions, although other forms, such as tanning lotion, also exist.

Cosmetic lotions may be marketed as anti-aging lotions, which can also be classified as a cosmetic in many cases, and may contain fragrances. The Food and Drug Administration voiced concern about lotions not classified as drugs that advertise anti-aging or anti-wrinkle properties.

Most lotions are oil-in-water emulsions using a substance such as cetearyl alcohol to keep the emulsion together, but water-in-oil lotions are also formulated.

A **cream** is a preparation usually for application to the skin. Creams for application to mucous membranes such as those of the rectum or vagina are also used. Creams may be considered pharmaceutical products as even cosmetic creams are based on techniques developed by pharmacy and unmedicated creams are highly used in a variety of skin conditions (dermatoses). The use of the finger tip unit concept may be helpful in guiding how much topical cream is required to cover different areas.

Creams are semi-solid emulsions of oil and water. They are divided into two types: oil-in-water (O/W) creams which are composed of small droplets of oil dispersed in a continuous water phase, and water-in-oil (W/O) creams which are composed of small droplets of water dispersed in a continuous oily phase. Oil-in-water creams are more comfortable and cosmetically acceptable as they are less greasy and more easily washed off using water. Water-in-oil creams are more difficult to handle but many drugs which are incorporated into creams are hydrophobic and will be released more readily from a water-in-oil cream than an oil-in-water cream. Water-in-oil creams are also more moisturizing as they provide an oily barrier which reduces water loss from the stratum corneum, the outermost layer of the skin.

Ointment is a semisolid dosage form it is used for topical application to the medication

Water, oil, emulsifier, and thickening agent are four main ingredients of cold creams and lotions.

Moisturizer or **moisturiser** is a cosmetic preparation used for protecting, moisturizing, and lubricating the skin. These functions are normally performed by sebum produced by healthy skin.

Moisturizers modify the rate of water loss, with active ingredients of moisturizers falling into one of two categories: occlusives and humectants

Occlusives form a coating on the surface of the skin, keeping moisture from escaping.

Humectants absorb water. They can absorb this water from the air and moisturize the skin when the humidity is greater than 70%, but more commonly they draw water from the dermis into the epidermis, making skin dryer. A study published in Skin Research and Technology in 2001 found no link between humectants and moisturizing effect. When used in practical applications, they are almost always combined with occlusives.

Moisturizers often contain water, which acts as a temporary hydration agent and as a way for the absorption of some components and evaporation of the moisturizer.

There are many different types of moisturizers. Petrolatum is one of the most effective moisturizers, although it can be unpopular due to its oily consistency. Other popular moisturizers are cetyl alcohol, cetearyl alcohol, cocoa butter, isopropyl myristate, isopropyl palmitate, lanolin, liquid paraffin, polyethylene glycols, shea butter, silicone oils, stearic acid, stearyl alcohol and castor oil, as well as other oils.

Moisturizers may also be available as lotions, creams, ointments, bath oils, or soap substitutes.

Mineral oils and waxes are insensitive to oxidation or rancidity. For this reason, they have essentially replaced vegetable oils in emollients and topical medication.

Moisturizer cosmetics may additionally contain antioxidants, ceramides, emulsifiers, fragrances, penetration enhancers, preservatives, and solvents. Some products are marketed as having anti-wrinkle and skin enhancement effects. Many plant and animal extracts have been claimed to impart skin benefits, with little scientific evidence.

Shaving Creams

Shaving cream or **shave cream** is a category of cosmetics used for shaving preparation. The purpose of shaving cream is to soften the hair by providing lubrication.

Different types of shaving creams include aerosol shaving cream (also known as shaving foam), latherless shaving cream (also called brushless shaving cream and non-aerosol shaving cream), and lather shaving cream or lathering shaving cream. The term shaving cream can also refer to the lather produced with a shaving brush from shaving soap or a lather shaving cream.

Shaving creams commonly consist of an emulsion of oils, soaps or surfactants (e.g. triethanolamine steatrate), and water. In addition to soap, lather shaving creams include a humectant for softer consistency and keeping the lather moisturised. Brushless shaving creams, on the other hand, don't contain soap and so don't produce lather. They are an oil-in-water mixture to which humectants, wetting agents, and other ingredients are added. Aerosol shaving creams are basically lather shaving cream in liquid form with propellants, vegetable waxes, and various oils added.

Does Shaving Cream Do Anything?

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 21.6.1 *What is shaving cream?*

Sunscreen and Sunblock

UVB radiation in sunlight allows the skin to produce vitamin D. This vitamin prevents bone disorders like rickets and osteoporosis (brittle bone disease). The American Academy of Dermatology suggests vitamin D be obtained through foods or nutritional supplements. Excessive exposure to UV can be damaging and the pigment **melanin**, deposited in cells at the base of the epidermis, helps to protect the underlying layers of the skin from this damage. Melanin also colors the skin and variations in the amount of melanin produces colors from pale yellow to black. The darker the skin tone, the more melanin one has, and the less likely skin cancer will occur.

Excess exposure to the sun can cause sunburn. This is common in humans, but light skinned animals like cats and pigs can also be sunburned, especially on the ears. Skin cancer can also result from excessive exposure to the sun. As holes in the ozone layer increase exposure to the sun's UV rays, so too does the rate of skin cancer in humans and animals.

Sunscreens and sunblocks are designed to protect skin from ultraviolet rays. *Sunblocks* contain inorganic ingredients like zinc oxide or titanium dioxide. These chemicals act as UV filters by reflecting the sun's UV rays. Sunblocks can have grainy textures due to the inorganic components. The thick nature of a sunblock can make it difficult to spread evenly on the skin. *Sunscreens*

contain organic compounds like oxybenzone, avobenzone, homosalate, and octinoxate (Figure 21.6.4). By absorbing ultraviolet rays, these compounds decompose and give off heat. Sunscreens apply smoother than sunblocks. Often, manufacturers will combine sunscreen and sunblock ingredients to make their products.

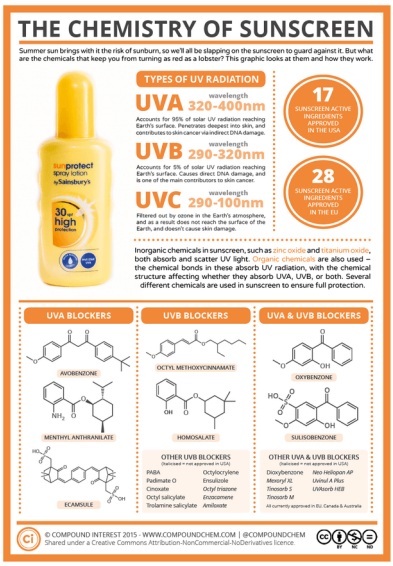


Figure 21.6.4 Chemistry of Sunscreen.

Sun protection factor (SPF) measures a product's protection from UVB rays. SPF does not quantify protection from UVA radiation. The American Academy of Dermatology recommends you select a sunscreen or sunblock with a minimum SPF factor of 30. This SPF value means a lotion can filter out 97% of UVB rays. Moving to a SPF of 50 will only filter out 1 more percentage of UVB rays. Increasing a SPF factor past 30 really does very little in shielding skin from UVB radiation.

Products that protect skin from UVA must be labeled as being a broad spectrum. Sunblocks provide UVA and UVB protection, but sunscreens can vary on what they can screen. Every two hours, sunscreens/sunblocks should be reapplied to the skin. Sweating and swimming can remove sunscreen/sunblock products. No sun products are waterproof, but some are labeled as being water-resistant. Consumers are encouraged to reapply these products every two hours as well.

Sunscreen Label

Figure 21.6.5 *Sunscreen label. Source: Badger: Healthy Body Care*

Is Sunscreen Safe?

Check the link below on FAQs regarding sunscreen.

https://www.aad.org/public/everyday-care/sun-protection/sunscreen/understand-sunscreen-labels

Lipsticks and Lip Balms

Lipstick, lip gloss, lip liner, lip plumper, lip balm, lip stain, lip conditioner, lip primer, lip boosters, and lip butters: Lipsticks are intended to add color and texture to the lips and often come in a wide range of colors, as well as finishes such as matte, satin, gloss and lustre.

Lipstick contains wax, oils, antioxidants, and emollients. Wax provides the structure to the solid lipstick. Lipsticks may be made from several waxes such as beeswax, ozokerite and candelilla wax. Because of its high melting point, carnauba wax is a key ingredient in terms of strengthening the lipstick. Various oils and fats are used in lipsticks, such as olive oil, mineral oil, cocoa butter, lanolin, and petrolatum.

Lipsticks get their colors from a variety of pigments and lake dyes including, but not limited to bromo acid, D&C Red No. 21, Calcium Lake such as D&C Red 7 and D&C Red 34, and D&C Orange No. 17. Pink lipsticks are made by mixing white titanium dioxide and red shades. Both organic and inorganic pigments are employed.

Lip stains have a water or gel base and may contain alcohol to help the product stay on leaving a matte look. They temporarily saturate the lips with a dye. Usually designed to be waterproof, the product may come with an applicator brush, directly through the applicator, rollerball, or could be applied with a finger. Lip glosses are intended to add shine to the lips and may add a tint of color, as well as being scented or flavored. Lip balms are most often used to moisturize, tint, and protect the lips. Some brands contain sunscreen. Using a priming lip product such as lip balm or chapstick can prevent chapped lips.

Eye Make-up

- **Mascara** is a cosmetic commonly used to enhance the eyelashes. It may darken, thicken, lengthen, and/or define the eyelashes. Normally in one of three forms—liquid, powder, or cream—the modern mascara product has various formulas; however, most contain the same basic components of pigments, oils, waxes, and preservatives. The most common form of mascara is a liquid in a tube.
- **Eye shadow** (or **eyeshadow**) is a cosmetic applied primarily to the eyelids to make the wearer's eyes stand out or look more attractive. Eye shadow can also be applied under eyes or to brow bones.

  Eye shadow can add depth and dimension to one's eyes, complement one's eye color, make one's eyes appear larger, or simply draw attention to the eyes. Eye shadow comes in many different colors and textures. It is usually made from a powder but can also be found in liquid, pencil, cream or mousse form. Just like other trends, eyeshadow looks also have trends.

  Eye shadows typically consist of four types of ingredients: base fillers, binders, slip and preservatives. In order to make eye shadow, there must be a balance between the fillers and binders.

  Base fillers are usually minerals such as mica, talc or kaolin clay, which add bulk and texture to eye shadow. They make up about 30% of eye shadow powders and 25% of cream eye shadows. Mica absorbs moisture, gives the eye shadow shine and luster, and makes it opaque. Mica powders, iron oxides and clays can give color pigments to eye shadows.

  Binders help eye shadow adhere and stay attached to skin. Eye shadows can have dry or liquid binders. Zinc and magnesium, which are both white powders, are commonly used as dry binders. Zinc also adds color and can be used to increase the thickness of the eyeshadow. Silicone, paraffin wax, mineral oil or vegetable oils may be used as liquid binders.

  Slip allows eye shadow to glide across the skin smoothly. Products may use silica or nylon, which are fine, colorless powders. Other types of slip include dimethicone, boron nitride or bismuth oxychloride.

  Preservatives help products stay bacteria free and extend their lifespan. Common preservatives in eye shadow are glycol and tocopherol.



Figure 21.6.6 Eyes with heavy gold eye shadow. Source: Wikipedia

Eye liner or **eyeliner** is a cosmetic used to define the eyes. It is applied around the contours of the eye(s) to create a variety of aesthetic effects. It can come in the form of a pencil, a gel, or a liquid and can be found in almost any color. Traditional wax-based

eye liners are made from about 20 components. About 50% by weight are waxes (e.g., Japan wax, fats, or related soft materials that easily glide on to the skin. Stearyl heptanoate is found in most cosmetic eyeliner. Typical pigments include black iron oxides, as well as smaller amounts of titanium dioxide and Prussian blue.

Eyebrow shaders, and pencils are often used to define the eyebrow or make it appear fuller. These can create an outline for the brows or mimic hairs where there are sparse areas. Brow gels are also used in creating a thicker brow; they allow for the hairs to be more textured, which gives the appearance of thicker, fuller brows. Lastly, brow powders or even eye shadows are used for those who want a fuller and more natural look, by placing the brow powder or eye shadow (closest to the natural hair color) in areas where there is less hair.

Deodorants and Antiperspirants

A **deodorant** is a substance applied to the body to prevent or mask body odor due to bacterial breakdown of perspiration in the armpits, groin, and feet, and in some cases vaginal secretions. A subclass of deodorants, called **antiperspirants**, prevents sweating itself, typically by blocking sweat glands. Antiperspirants are used on a wider range of body parts, at any place where sweat would be inconvenient or unsafe, since unwanted sweating can interfere with comfort, vision, and grip (due to slipping). Other types of deodorant allow sweating but prevent bacterial action on sweat, since human sweat only has a noticeable smell when it is decomposed by bacteria.

In the United States, the Food and Drug Administration classifies and regulates most deodorants as cosmetics but classifies antiperspirants as over-the-counter drugs.

In the United States, deodorants are classified and regulated as cosmetics by the U.S. Food and Drug Administration (FDA) and are designed to eliminate odor. Deodorants are often alcohol based. Alcohol initially stimulates sweating but may also temporarily kill bacteria. Other active ingredients in deodorants include sodium stearate, sodium chloride, and stearyl alcohol. Deodorants can be formulated with other, more persistent antimicrobials such as triclosan that slow bacterial growth or with metal chelant compounds such as EDTA. Deodorants may contain perfume fragrances or natural essential oils intended to mask the odor of perspiration. In the past, deodorants included chemicals such as zinc oxide, acids, ammonium chloride, sodium bicarbonate, and formaldehyde, but some of these ingredients were messy, irritating to the skin, or even carcinogenic.

Over-the-counter products, often labeled as "natural deodorant crystal", contain the chemical rock crystals potassium alum or ammonium alum, which prevents bacterial action on sweat. These have gained popularity as an alternative health product, in spite of concerns about possible risks related to aluminum (see below – all alum salts contain aluminum in the form of aluminum sulphate salts) and contact dermatitis.

In the United States, deodorants combined with antiperspirant agents are classified as drugs by the FDA. Antiperspirants attempt to stop or significantly reduce perspiration and thus reduce the moist climate in which bacteria thrive. Aluminium chloride, aluminium chlorohydrate, and aluminium-zirconium compounds, most notably aluminium zirconium tetrachlorohydrex gly and aluminium zirconium trichlorohydrex gly, are frequently used in antiperspirants. Aluminium chlorohydrate and aluminium-zirconium tetrachlorohydrate gly are the most frequent active ingredients in commercial antiperspirants. Aluminium-based complexes react with the electrolytes in the sweat to form a gel plug in the duct of the sweat gland. The plugs prevent the gland from excreting liquid and are removed over time by the natural sloughing of the skin. The metal salts work in another way to prevent sweat from reaching the surface of the skin: the aluminium salts interact with the keratin fibrils in the sweat ducts and form a physical plug that prevents sweat from reaching the skin's surface. Aluminium salts also have a slight astringent effect on the pores; causing them to contract, further preventing sweat from reaching the surface of the skin. The blockage of a large number of sweat glands reduces the amount of sweat produced in the underarms, though this may vary from person to person. Methenamine (Figure 21.6.7) in the form of cream or spray is effective in the treatment of excessive sweating and attendant odor. Antiperspirants are usually best applied before bed.

Figure 21.6.7 *Methenamine-based antiperspirant for treatment of excessive sweating.*

Toothpaste: Soap with Grit and Flavor

Toothpaste (Figure 21.6.8) is a paste or gel dentifrice used with a toothbrush to clean and maintain the aesthetics and health of teeth. Toothpaste is used to promote oral hygiene: it is an abrasive that aids in removing dental plaque and food from the teeth, assists in suppressing halitosis, and delivers active ingredients (most commonly fluoride) to help prevent tooth decay (dental caries) and gum disease (gingivitis). Salt and sodium bicarbonate (baking soda) are among materials that can be substituted for

commercial toothpaste. Large amounts of swallowed toothpaste can be toxic.



Figure 21.6.8 A variety of brands of toothpaste.

In addition to 20%–42% water, toothpastes are derived from a variety of components, the three main ones being abrasives, fluoride, and detergents.

Abrasives constitute at least 50% of a typical toothpaste. These insoluble particles are designed to help remove plaque from the teeth. The removal of plaque and calculus prevents the accumulation of tartar and is widely claimed to help minimize cavities and periodontal disease, although the clinical significance of this benefit is debated. Representative abrasives include particles of aluminum hydroxide ($Al(OH)_3$), calcium carbonate ($CaCO_3$), various calcium hydrogen phosphates, various silicas and zeolites, and hydroxyapatite ($Ca_5(PO_4)_3OH$).

Abrasives, like the dental polishing agents used in dentists' offices, also cause a small amount of enamel erosion which is termed "polishing" action. Some brands contain powdered white mica, which acts as a mild abrasive, and also adds a cosmetically pleasing glittery shimmer to the paste. The polishing of teeth removes stains from tooth surfaces, but has not been shown to improve dental health over and above the effects of the removal of plaque and calculus.

The abrasive effect of toothpaste is indicated by its RDA value. Too high RDA values are deleterious. Some dentists recommend toothpaste with an RDA value no higher than 50 for daily use.

Fluoride in various forms is the most popular active ingredient in toothpaste to prevent cavities. Fluoride is present in small amounts in plants, animals, and some natural water sources. The additional fluoride in toothpaste has beneficial effects on the formation of dental enamel and bones. Sodium fluoride (NaF) is the most common source of fluoride, but stannous fluoride (SnF_2), olaflur (an organic salt of fluoride), and sodium monofluorophosphate (Na_2PO_3F) are also used. Stannous fluoride has been shown to be more effective than sodium fluoride in reducing the incidence of dental caries and controlling gingivitis, but causes somewhat more surface stains.

Much of the toothpaste sold in the United States has 1,000 to 1,100 parts per million fluoride. In European countries, such as the UK or Greece, the fluoride content is often higher; a NaF content of 0.312% w/w (1,450 ppm fluoride) is common. All of these concentrations are likely to prevent tooth decay, according to a 2019 Cochrane review. Concentrations below 1,000 ppm are not likely to be preventive, and the preventive effect increases with concentration. Clinical trials support the use of high fluoride dentifrices, as it was found to reduce the amount of plaque accumulated, decrease the number of mutans streptococci and lactobacilli and possibly promote calcium fluoride deposits to a higher degree than after the use of traditional fluoride containing dentifrices. However, these effects must be balanced with the increased risk of harm at higher concentrations.

Many, although not all, toothpastes contain sodium lauryl sulfate (SLS) or related **surfactants (detergents)**. SLS is found in many other personal care products as well, such as shampoo, and is mainly a foaming agent, which enables uniform distribution of toothpaste, improving its cleansing power.

Other Components in toothpaste formulations include:

- Antibacterial agents. Triclosan or zinc chloride prevent gingivitis and, according to the American Dental Association, helps reduce tartar and bad breath.
- Flavorants. Toothpaste comes in a variety of colors and flavors intended to encourage use of the product. The three most common flavorants are peppermint, spearmint, and wintergreen.
- Reminalizers. Hydroxyapatite nanocrystals and a variety of calcium phosphates are included in formulations for remineralization, i.e. the reformation of enamel.

Agents are added to suppress the tendency of toothpaste to dry into a powder. Included are various sugar alcohols, such as glycerol, sorbitol, or xylitol, or related derivatives, such as 1,2-propylene glycol and polyethyleneglycol

Strontium chloride or potassium nitrate is included in some toothpastes to reduce sensitivity. Two systemic meta-analysis reviews reported that arginine, and calcium sodium phosphosilicate - CSPS containing toothpastes are also effective in alleviating dentinal hypersensitivity respectively. Another randomized clinical trial found superior effects when both formulas were combined together.

Sodium polyphosphate is added to minimize the formation of tartar. Other example to components in toothpastes is the Biotene, which has proved its efficiency in relieving the symptoms of dry mouth in people who suffer from xerostomia according to the results of two randomized clinical trials.

Chlorohexidine mouthwash has been popular for its positive effect on controlling plaque and gingivitis, however, a systemic review studied the effects of chlorohexidine toothpastes and found insufficient evidence to support its use, tooth surface discoloration was observed as a side effect upon using it, which is considered a negative side effect that can affect patients' compliance.

Sodium hydroxide, also known as lye or caustic soda, is listed as an inactive ingredient in some toothpaste, for example Colgate Total.

Some studies have demonstrated that toothpastes with xylitol as an ingredient are more effective at preventing dental caries in permanent teeth of children than toothpastes containing fluoride alone.

Perfumes, Colognes, and Aftershaves

Perfume (Figure 21.6.9) is a mixture of fragrant essential oils or aroma compounds, fixatives and solvents, used to give the human body, animals, food, objects, and living-spaces an agreeable scent. Perfume types reflect the concentration of aromatic compounds in a solvent, which in fine fragrance is typically ethanol or a mix of water and ethanol. Various sources differ considerably in the definitions of perfume types. The intensity and longevity of a perfume is based on the concentration, intensity, and longevity of the aromatic compounds, or perfume oils, used. Specific terms are used to describe a fragrance's approximate concentration by the percent of perfume oil in the volume of the final product. The most widespread terms are:

- **parfum** or **extrait**, in English known as perfume extract, pure perfume, or simply perfume: 15–40% aromatic compounds (IFRA: typically ~20%);
- **esprit de parfum** (ESdP): 15–30% aromatic compounds, a seldom used strength concentration in between EdP and perfume;
- **eau de parfum** (EdP) or **parfum de toilette** (PdT) (The strength usually sold as "perfume"): 10–20% aromatic compounds (typically ~15%); sometimes called "eau de perfume" or "millésime"; parfum de toilette is a less common term, most popular in the 1980s, that is generally analogous to eau de parfum;
- **eau de toilette** (EdT): 5–15% aromatic compounds (typically ~10%); This is the staple for most masculine perfumes.
- **eau de Cologne** (EdC): often simply called cologne: 3–8% aromatic compounds (typically ~5%);
- **eau fraiche**: products sold as "splashes", "mists", "veils" and other imprecise terms. Generally these products contain 3% or less aromatic compounds and are diluted with water rather than oil or alcohol.



Figure 21.6.9 A bottle of perfume by Yves Saint Laurent

Perfume is described in a musical metaphor as having three sets of *notes*, making the harmonious scent *accord*. The notes unfold over time, with the immediate impression of the top note leading to the deeper middle notes, and the base notes gradually appearing as the final stage. These notes are created carefully with knowledge of the evaporation process of the perfume.

- **Top notes**: Also called the ***head notes***. The scents that are perceived immediately on application of a perfume. Top notes consist of small, light molecules that evaporate quickly. They form a person's initial impression of a perfume and thus are very important in the selling of a perfume. Examples of top notes include mint, lavender and coriander.
- **Middle notes**: Also referred to as ***heart notes***. The scent of a perfume that emerges just prior to the dissipation of the top note. The middle note compounds form the "*heart*" or main body of a perfume and act to mask the often unpleasant initial impression of base notes, which become more pleasant with time. Examples of middle notes include seawater, sandalwood and jasmine.
- **Base notes**: The scent of a perfume that appears close to the departure of the middle notes. The base and middle notes together are the main theme of a perfume. Base notes bring depth and solidity to a perfume. Compounds of this class of scents are typically rich and "deep" and are usually not perceived until 30 minutes after application. Examples of base notes include tobacco, amber and musk.

The scents in the top and middle notes are influenced by the base notes; conversely, the scents of the base notes will be altered by the types of fragrance materials used as middle notes. Manufacturers who publish perfume notes typically do so with the fragrance components presented as a *fragrance pyramid*, using imaginative and abstract terms for the components listed.

Aftershave is a product applied to skin after shaving. Traditionally it is an alcohol based liquid (splash), but it can be a lotion, gel, or even a paste.

It often contains an antiseptic agent such as denatured alcohol, stearate citrate or witch hazel to prevent infection of cuts, as well as to act as an astringent to reduce skin irritation. Menthol is used in some varieties as well to numb irritated skin.

An alcohol-based aftershave usually causes an immediate stinging sensation after applying it post-shave, with effects sometimes lasting several minutes, but most commonly only for seconds. For this reason, a market consisting of highly differentiated products has been created—some using alcohols, some not.

Aftershave balms are frequently recommended for winter use as they tend to be alcohol free and lotion-like, moisturizing the skin.

Some aftershaves use fragrance or essential oil to enhance scent. Moisturizers—natural and artificial, are often touted as able to soften the skin.

Aftershave is sometimes mistakenly referred to as Eau de Cologne due to the very similar nature of the two products. Some aftershave manufacturers encourage using their fragranced aftershave as if it were cologne, in order to increase sales by encouraging consumers to use it in a more versatile manner, rather than just after a shaving session. Some aftershaves were

inspired by a cologne.

Early aftershaves included witch-hazel and bay rum, and have been documented in shaving guides. Both still are sold as aftershaves.

Hairy Chemistry

Hair keratin consists of many protein alpha-helices (Figure 21.6.10). Three alpha-helices are interwoven into a left-handed coil called a protofibril. Eleven protofibrils are bonded and coiled together to make a microfibril. Hundreds of these microfibrils are cemented into an irregular bundle called a macrofibril. These in turn are mixed with dead and living cells to make a complete strand of hair.

The alpha-helices are extensively cross-linked with disulfide bonds from cysteine. These bonds enable keratin to have a somewhat elastic nature. If the alpha -helices stretch unevenly past each other, the disulfide cross-links return them to the original position when the tension is released.

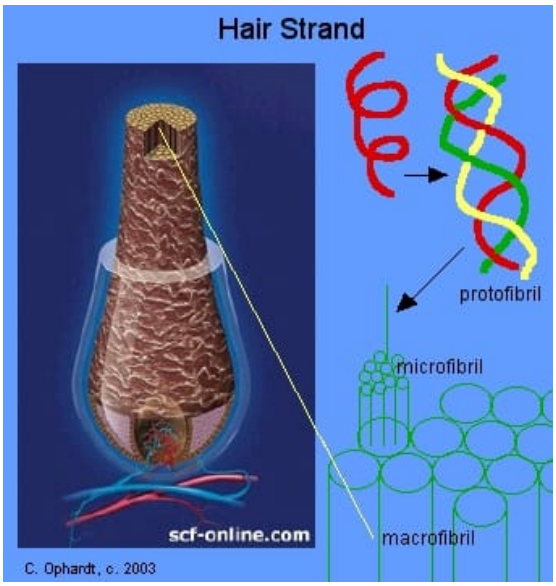


Figure 21.6.10 Protein alpha-helices in a hair strand.

Shampoo

Shampoo (/ʃæmˈpuː/) is a hair care product, typically in the form of a viscous liquid, that is used for cleaning hair. Less commonly, shampoo is available in bar form, like a bar of soap. Shampoo is used by applying it to wet hair, massaging the product into the scalp, and then rinsing it out. Some users may follow a shampooing with the use of hair conditioner.

The typical reason of using shampoo is to remove the unwanted build-up of sebum in the hair without stripping out so much as to make hair unmanageable. Shampoo is generally made by combining a surfactant, most often sodium lauryl sulfate or sodium laureth sulfate, with a co-surfactant, most often cocamidopropyl betaine in water. The sulphate ingredient acts as a surfactant, essentially heavy duty soap that makes it easier to trap oil and grease.

Specialty shampoos are marketed to people with dandruff, color-treated hair, gluten or wheat allergies, an interest in using an organic product, and infants and young children ("baby shampoo" is less irritating). There are also shampoos intended for animals that may contain insecticides or other medications to treat skin conditions or parasite infestations such as fleas.

Shampoo is generally made by combining a surfactant, most often sodium lauryl sulfate or sodium laureth sulfate, with a co-surfactant, most often cocamidopropyl betaine in water to form a thick, viscous liquid. Other essential ingredients include salt (sodium chloride), which is used to adjust the viscosity, a preservative and fragrance. Other ingredients are generally included in shampoo formulations to maximize the following qualities:

- pleasing foam
- ease of rinsing
- minimal skin and eye irritation
- thick or creamy feeling
- pleasant fragrance
- low toxicity
- good biodegradability
- slight acidity (pH less than 7)
- no damage to hair
- repair of damage already done to hair

Many shampoos are pearlescent. This effect is achieved by the addition of tiny flakes of suitable materials, e.g. glycol distearate, chemically derived from stearic acid, which may have either animal or vegetable origins. Glycol distearate is a wax. Many shampoos also include silicone to provide conditioning benefits.

How Does Shampoo Work?

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 21.6.2 *Shampoo applied to wet hair.*

Hair Coloring

Hair color is the pigmentation of hair follicles due to two types of melanin: eumelanin and pheomelanin. Generally, if more eumelanin is present, the color of the hair is darker; if less eumelanin is present, the hair is lighter. Levels of melanin can vary over time causing a person's hair color to change, and it is possible to have hair follicles of more than one color on the same person. Particular hair colors are often associated with ethnic groups, while gray or white hair is associated with age.

Hair coloring, or **hair dyeing**, is the practice of changing the hair color. The main reasons for this are cosmetic: to cover gray or white hair, to change to a color regarded as more fashionable or desirable, or to restore the original hair color after it has been discolored by hairdressing processes or sun bleaching.

Hair coloring can be done professionally by a hairdresser or independently at home. Today, hair coloring is very popular, with 75% of women and 18% of men living in Copenhagen having reported using hair dye (according to a study by the University of Copenhagen). At-home coloring in the United States reached $1.9 billion in 2011 and was expected to rise to $2.2 billion by 2016.

Hair color can be changed by a chemical process. Hair coloring is classed as "permanent" or "semi-permanent".

Permanent hair color means that the hair's structure has been chemically altered until it is eventually cut away. This does not mean that the synthetic color will remain permanently. During the process, the natural color is removed, one or more shades, and synthetic color has been put in its place. All pigments wash out of the cuticle. Natural color stays in much longer and artificial will fade the fastest (depending on the color molecules and the form of the dye pigments).

Permanent hair coloring requires three components: (1) 1,4-diaminobenzene (historically) or 2,5-diaminotoluene (currently), (2) a coupling agent, and (3) an oxidant. The process is typically performed under basic conditions. The mechanism of oxidation dyes involves three steps: 1) Oxidation of 1,4-diaminobenzene derivative to the quinone state. 2) Reaction of this diimine with a coupler compound (more detail below). 3) Oxidation of the resulting compound to give the final dye.

Figure 21.6.11 *Shown here are three red couplers (A, B, C), two yellow-green couplers (D, E) and a blue coupler (F). Couplers are chemical compounds that define the color of the hair dye.*

Steps in Permanent Hair Coloring

The first step shows the oxidation of p-phenylenediamine to the quinonediimine ($C_6H_4(NH)_2$):

Quinodiimine.png

The second step involves the attack of this quinonediimine on the coupler.

Quinodiimine+Coupler.png

In the third and final step, the product from the quinonediimine-coupler reaction oxidizes to the final hair dye.

QuinodiimineCouplerOx.png

It was once believed that the dye forms in the above reaction bonds to hair permanently. It was later shown that the main reason that this reaction imparts a permanent color on hair by producing larger dye molecules, which is locked inside the hair.

Semi-permanent color washes out over a period of time—typically four to six weeks, so root regrowth is less noticeable. The final color of each strand is affected by its original color and porosity, so there will be subtle variations in color across the head—more natural and less harsh than a permanent dye. However, this means that gray and white hair will not dye to the same color as the rest of the head (in fact, some white hair will not absorb the color at all). A few gray and white hairs will blend in sufficiently not to be noticeable, but as they become more widespread, there will come a point where a semi-permanent alone will not be enough. The move to 100% permanent color can be delayed by using a semi-permanent as a base color, with permanent highlights.

Semi-permanent hair color cannot lighten hair. Hair can only be lightened using chemical lighteners, such as bleach. Bleaching is always permanent because it removes the natural pigment.

"Rinses" are a form of temporary hair color, usually applied to hair during a shampoo and washed out again the next time the hair is wash.

Plant based dyes include henna, indigo and anthocyanin pigments extracted form blackcurrant skin waste.

How Does Hair Dye Work?

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 $21.6.3$ *Applying hair dye.*

Permanent and Temporary Waving

Temporary Wave. When the hair gets wet, water molecules intrude into the keratin strands. The sheer numbers of water molecules are able to disrupt some of the hydrogen bonds which also help to keep the alpha-helices aligned. The helices are able to slip past each other and will retain a new shape in the hair drying process as new hydrogen bonds are formed. The hair strands are able for a short time to maintain the new curl in the hair.

A **permanent hairstyle**, commonly called a **perm** or "**permanent**" (sometimes called a "perm" to distinguish it from a "straight perm"), is a hairstyle consisting of styles set into the hair. The hairstyle may last a number of months, hence the name.

Perms may be applied using thermal or chemical means. In the latter method, chemicals are applied to the hair, which is then wrapped around forms to produce hairstyles. The same process is used for chemical straightening or relaxing, with the hair being flattened instead of curled during the chemical reaction.

The formation of disulfide bonds has a direct application in producing curls in hair by the permanent wave process. Disulfide bonds Figure $21.6.12$ are formed by oxidation of the sulfhydryl groups on cysteine. Different protein chains or loops within a single

chain are held together by the strong covalent disulfide bonds. The alpha-helices in the hair strands are bonded by disulfide links.

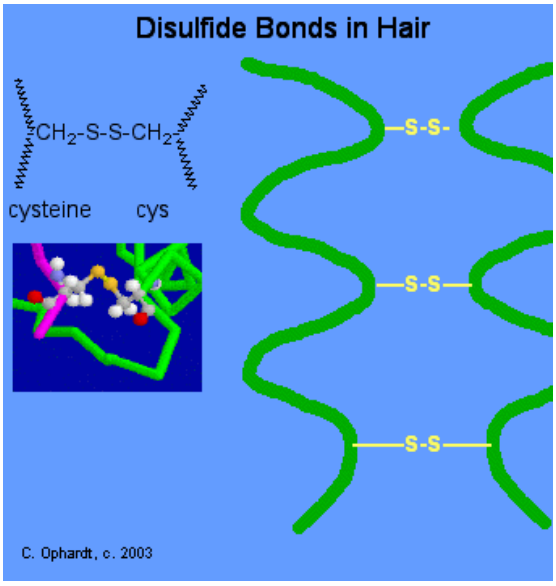


Figure 21.6.12 Disulfide bonds in hair.

In the permanent wave process, a basic reducing substance (usually ammonium thioglycolate) is first added to reduce and rupture some of the disulfide cross-links, see Figure 21.6.13 below.

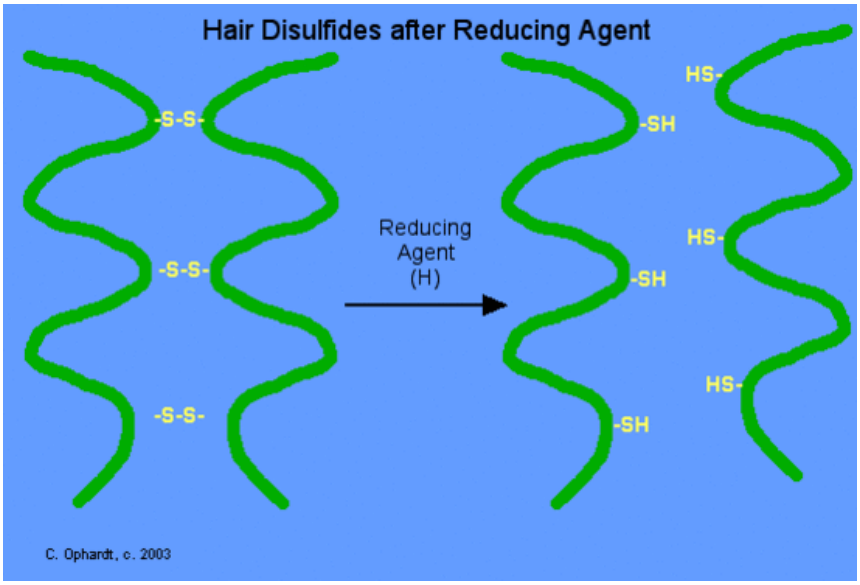


Figure 21.6.13 Addition of a reducing agent to disrupt the disulfide bonds.

The hair is put on rollers or curlers. Since the alpha-helices are no longer tightly cross-linked to each other, the alpha-helices can shift positions in relation to each other. An oxidizing agent, usually a dilute solution of hydrogen peroxide, (also called the neutralizer) is added to reform the disulfide bonds in their new positions (Figure 21.6.14). The permanent will hold these new disulfide bond positions until the hair grows out, since new hair growth is of course not treated.

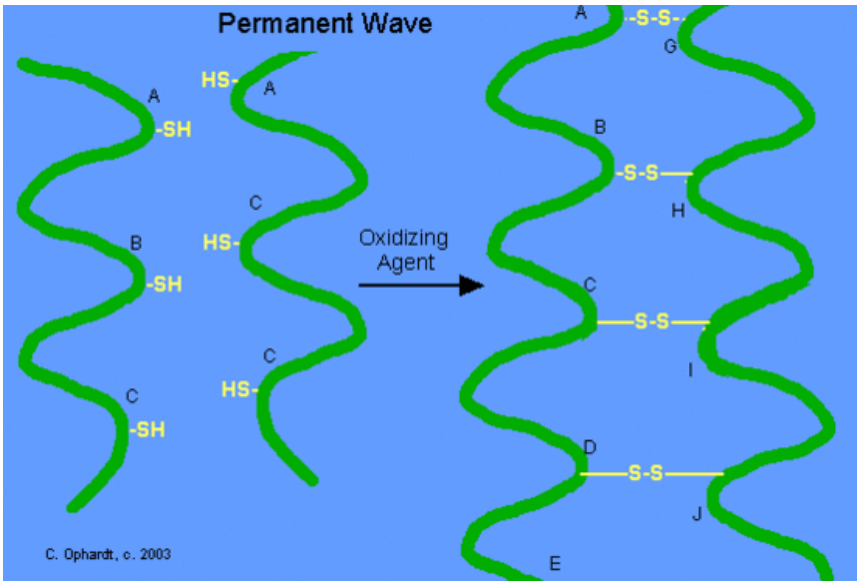


Figure 21.6.14 Addition of a oxidizing agent to reform disulfide bonds.

Hair spray

Hair spray is a common household aqueous solution which is used to stiffen hair into a certain style. It was first developed and manufactured in 1948 by Chase Products, based in Broadview, Illinois. Weaker than hair gel or hair wax, it is sprayed directly onto the hair to hold styles for long periods of time. It sprays evenly over the hair using a pump or aerosol spray nozzle. The product may leave hair feeling 'crunchy' unless brushed out.

The active ingredients in hair spray are called polymers, which keep the hair stiff and firm without snapping. Solvents, which make up most of the content of the hairspray, are responsible for carrying these polymers in a solution.

Originally, the solvent found in hair spray was a chlorofluorocarbon (CFC). CFCs are nontoxic, nonflammable, and make almost ideal aerosol propellants. However, when research concluded that CFCs cause destruction of stratospheric ozone, they were replaced with other solvents, such as alcohols and hydrocarbons.

Hair sprays consist of the following components: concentrate, plasticizers, luster agents, and fragrances, as well as propellants.

One of the polymers used in hair spray is polyvinylpyrrolidone (Figure 21.6.15) , which is water-soluble. The non-water-soluble polymer polydimethylsiloxane is added to make the hold last a bit longer. Some less common polymers found in hair spray include copolymers with vinyl acetate and copolymers with maleic anhydride.

Figure 21.6.15 Polyvinylpyrrolidone *is a common component of hair spray that confers stiffness to hair.*

Some hair sprays use natural polymers and solvents like vegetable gums dissolved in alcohol. One popular ingredient in natural hair sprays is gum arabic, which is made from the sap of various species of the acacia tree. Gum tragacanth is another herbal gum that is used to stiffen calico and crepe, as well as hair.

Hair Removers

Depilation is the removal of the part of the hair above the surface of the skin. The most common form of depilation is shaving or trimming. Another option is the use of chemical depilatories, which work by breaking the disulfide bonds that link the protein chains that give hair its strength.

A **chemical depilatory** is a cosmetic preparation used to remove hair from the skin. Common active ingredients are salts of thioglycolic acid and thiolactic acids. These compounds break the disulfide bonds in keratin and also hydrolyze the hair so that it is easily removed. Formerly, sulfides such as strontium sulfide were used, but due to their unpleasant odor, they have been replaced by thiols.

The main chemical reaction effected by the thioglycolate is:

2 $HSCH_2CO_2H$ (thioglycolic acid) + R-S-S-R (cystine) → HO_2CCH_2-S-S-CH_2CO_2H (dithiodiglycolic acid) + 2 RSH (cysteine)

Chemical depilatories contain 5–6% calcium thioglycolate in a cream base (to avoid runoff). Calcium hydroxide or strontium hydroxide maintain a pH of about 12. Hair destruction requires about 10 minutes. Depilation is followed by careful rinsing with water, and various conditioners are applied to restore the skin's pH to normal. Depilation does not destroy the dermal papilla, and the hair grows back.

Chemical depilatories are available in gel, cream, lotion, aerosol, roll-on, and powder forms. Common brands include Nair, Magic Shave and Veet.

Depilatory ointments, or plasters, were known to Greek and Roman authors as *psilothrum*. In Jewish lore, King Solomon is said to have discovered a chemical depilatory made from a mixture of lime and water and orpiment (arsenic trisulfide).

Hair Restorers

Treatments for the various forms of hair loss have only moderate success. Three medications have evidence to support their use in male pattern hair loss: finasteride, dutasteride and minoxidil. They typically work better to prevent further hair loss than to regrow lost hair.

They may be used together when hair loss is progressive or further regrowth is desired after 12 months. Other medications include ketoconazole, and in female androgenic alopecia spironolactone and flutamide. Combinations of finasteride, minoxidil and ketoconazole are more effective than individual use.

Minoxidil is applied topically, is widely used for the treatment of hair loss. It may be effective in helping promote hair growth in both men and women with androgenic alopecia. About 40% of men experience hair regrowth after 3–6 months. It is the only topical product that is FDA approved in America for androgenic hair loss. However, increased hair loss has been reported.

Finasteride is used to treat male pattern hair loss. Treatment provides about 30% improvement in hair loss after six months of treatment, and effectiveness only persists as long as the drug is taken. There is no good evidence for its use in women. It may cause gynecomastia, erectile dysfunction and depression.

Dutasteride is used off label for male pattern hair loss.

There is tentative support for **spironolactopne** in women. Due to its feminising side effects and risk of infertility it is not often used by men. It can also cause low blood pressure, high blood potassium, and abnormal heart rhythms. Also, women who are pregnant or trying to become pregnant generally cannot use the medication as it is a teratogen, and can cause ambiguous genitalia in newborn children.

There is tentative evidence for **flutamide** in women; however, it is associated with relatively high rates of liver problems. Like spironolactone, it is typically only used by women.

Ketoconazole shampoo in conjunction with an oral 5α-reductase inhibitor such as finasteride or dutasteride has been used off label to treat androgenic alopecia.

Summary

- Various personal care products contain ingredients to protect the skin, protect the hair, promote hygiene, for aesthetic purposes etc.
- Temporary and permanent waves are formed due to the disruption and reformation of disulfide bonds in hair strands.

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- Libretext: Human Biology (Wakim and Grewal)
- Libretext: Supplemental Module (Biological Chemistry)
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22: POISONS

22.1: Natural Poisons and Food Poisoning
22.2: Poisons and How They Act
22.3: More Chemistry of the Nervous System
22.4: The Lethal Dose
22.5: The Liver as a Detox Facility
22.6: Carcinogens and Teratogens
22.7: Hazardous Wastes

What is Toxicology?

Toxicology is traditionally defined as "the science of poisons." Over time, our understanding of how various agents can cause harm to humans and other organisms has increased, resulting in a more descriptive definition of toxicology as "the *study of the adverse effects of chemical, physical, or biological agents on living organisms and the ecosystem, including the prevention and amelioration of such adverse effects.*"

These adverse effects can take many forms, ranging from immediate death to subtle changes not appreciated until months or years later. They may occur at various levels within the body, such as an organ, a type of cell, or a specific biochemical. Our understanding of how toxic agents damage the body has progressed along with medical knowledge. We now know that various observable changes in anatomic or bodily functions actually result from previously unrecognized changes in specific biochemicals in the body.

A poison is any substance that is harmful to your body. You might swallow it, inhale it, inject it, or absorb it through your skin. Any substance can be poisonous if too much is taken. Poisons can include

- Prescription or over-the-counter medicines taken in doses that are too high
- Overdoses of illegal drugs
- Carbon monoxide from gas appliances
- Household products, such as laundry powder or furniture polish
- Pesticides
- Indoor or outdoor plants
- Metals such as lead and mercury

The effects of poisoning range from short-term illness to brain damage, coma, and death. To prevent poisoning it is important to use and store products exactly as their labels say. Keep dangerous products where children can't get to them. Treatment for poisoning depends on the type of poison.

Sources

National Institute of Health (NIH) US National Library of Medicine

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22.1: Natural Poisons and Food Poisoning

Learning Objectives

- List different plant and animal poisons and their properties.
- List various causes of food poisoning.

In biology, **poisons** are substances that cause death, injury or harm to organs, usually by chemical reactions or other activity on the molecular scales, when an organism absorbs a sufficient quantity. The fields of medicine (particularly veterinary) and zoology often distinguish a poison from a toxin, and from a venom. Toxins are poisons produced by organisms in nature, and venoms are toxins injected by a bite or sting (this is exclusive to animals). The difference between venom and other poisons is the delivery method.

The **history of poison** stretches from before 4500 BCE to the present day. Poisons have been used for many purposes across the span of human existence, most commonly as weapons, anti-venoms, and medicines. Poison has allowed much progress in branches, toxicology, and technology, among other sciences.

Over the centuries, the variety of harmful uses of poisons continued to increase. The means for curing these poisons also advanced in parallel. In the modern world, intentional poisoning is less common than the Middle Ages. Rather, the more common concern is the risk of accidental poisoning from everyday substances and products.

Constructive uses for poisons have increased considerably in the modern world. Poisons are now used as pesticides, disinfectants, cleaning solutions, and preservatives. Nonetheless, poison continues to be used as a hunting tool in remote parts of developing countries, including Africa, South America, and Asia.

Poisonous Plants

Poisonous plants are plants that produce toxins that deter herbivores from consuming them. Plants cannot move to escape their predators, so they must have other means of protecting themselves from herbivorous animals. Some plants have physical defenses such as thorns, spines and prickles, but by far the most common type of protection is chemical. Over millennia, through the process of natural selection, plants have evolved the means to produce a vast and complicated array of chemical compounds in order to deter herbivores. Tannin, for example, is a defensive compound that emerged relatively early in the evolutionary history of plants, while more complex molecules such as polyacetylenes are found in younger groups of plants such as the Asterales. Many of the known plant defense compounds primarily defend against consumption by insects, though other animals, including humans, that consume such plants may also experience negative effects, ranging from mild discomfort to death. Several poisonous plants, the specific toxins and the poisonous effects are listed below.

Poison ivy (Figure 22.1.1) - The poison Urushiol is an oily mixture of organic compounds with allergic properties. Symptoms of a reaction include itching, redness, swelling, and blisters. It is important to note that the blisters are not contagious.



Figure 22.1.1 Poison Ivy.

Western water hemlock (Figure 22.1.2) - The toxin, cicutoxin and oenanthotoxin, are conjugated polyacetylenes. These unsaturated alcohols have a strong carrot-like odor and are noncompetitive antagonists for the gamma-aminocutyric acid (GABA) neural transmitter in the central nervous system. GABA role is to inhibit neuron excitability; essentially it has a relaxing function. Blocking this results in convulsing and grand mal seizures and eventually death can occur.



Figure 22.1.2 Western water hemlock.

Autumn skullcap - The toxin amatoxin in the form of γ-amanitin, β-amanitin, and α-amanitin causes severe abdominal pain, vomiting, and diarrhea may last for six-nine hours. The toxins affect the liver, results in gastrointestinal bleeding, coma, kidney failure, or even death, within seven days of consumption

Henbane - The toxins in this plant are atropine and scopolamine, found in leaves. Apoatropine and cuscohygrine are the main alkaloids of the root. The main alkaloid in seeds is hyoscyamine, little hyoscine and little atropine. the plant is toxic to cattle, wild animals, fish, and birds. Pigs are immune. In humans, it could cause hallucinations, dilated pupils, restlessness, fast heart, seizure, vomiting, high blood pressure, and ataxia. Initial effects last for 3-4 hours, after effects last up to three days.

Oak - Tannic acid, binds and precipitates proteins. Cattle, sheep, horses and goats are most affected while pigs are immune. In humans, Tannic acid poisoning could cause anorexia, depression, constipation, diarrhea, blood in urine. Signs typically occur around 3-7 days after consumption, with

The links below are an extensive, if incomplete, list of plants containing one or more poisonous parts that pose a serious risk of illness, injury, or death to humans or domestic animals. There is significant overlap between plants considered poisonous and those with psychotropic properties, some of which are toxic enough to present serious health risks at recreational doses. There is a distinction between plants that are poisonous because they naturally produce dangerous phytochemicals, and those that may become dangerous for other reasons, including but not limited to infection by bacterial, viral, or fungal parasites; the uptake of toxic compounds through contaminated soil or groundwater; and/or the ordinary processes of decay after the plant has died; this list deals exclusively with plants that produce phytochemicals. Many plants, such as peanuts, produce compounds that are only dangerous to people who have developed an allergic reaction to them, and with a few exceptions, those plants are not included here (see list of allergens instead). Despite the wide variety of plants considered poisonous, human fatalities caused by poisonous plants – especially resulting from accidental ingestion – are rare in the developed world.

WEB LINK

A more extensive list of poisonous plants can be found on the link below.

https://en.Wikipedia.org/wiki/List_o...isonous_plants

Poisonous Animals

Several deadly poisons are from snakes and spiders. Several poisonous animals, the specific toxins and the poisonous effects are listed below.

Timber rattlesnake - There are 4 types of toxin. Type A : A neurotoxin known as canebrake. Type B : A hemorrhagic and proteolytic toxin. Type A + B: Intergrade between snakes with Type A and Type B. Type C : relatively weak. The toxins could cause myokymia, defibrination syndrome, numbness, lightheadedness, weakness, vomiting, blurred vision, sweating, salivating. It can be treated with CroFab Antivenom.

Eastern coral snake (Figure 22.1.3).- Phospholipase A2 and three-finger toxins (abbreviated as 3FTx). 3FTx proteins are neurotoxins, attacking nerve tissue. Phospholipase A2 can cause inflammation and pain at the site of the bite, though this is uncommon. The toxins could also cause slurred speech, double vision, muscle paralysis, and can lead to cardiac arrest if left untreated.



Figure 22.1.3 *The eastern coral snake*

Cotton mouth snake - Cotton mouth toxins mainly consist of three protein families: phospholipase A2 (PLA2), metalloproteases (SVMP), and serine proteases (SVSP). PLA2s are responsible for inflammation and pain, while SVMPs are responsible for hemorrhage and SVSPs affect the coagulation of blood. The poison could lead to low blood pressure, weakness, change in skin color at site of bite, trouble breathing, nausea, increase in heart rate.

Black widow spider (Figure 22.1.4) - Latrotoxins are the main component of the venom, but other compounds such as

polypeptides, adenosine, and guanosine are active as well. Only the bite of the female is dangerous to humans, as their venom glands are very large. The toxin can cause pain and sweating at the site of the bite, muscle cramps, headache, nausea, vomiting, weakness. Typically only localized pain is felt, but in some cases the pain can spread. Symptoms typically last from 3-7 days after the bite takes place.

Brown recluse spider - Brown recluse venom possesses potentially deadly hemotoxins and cytotoxins that affect the red blood cells and their ability to clot. It is a mixture of enzymes such as collagenase, protease, and phospholipase. Symptoms include redness, fever, weakness, pain and nausea. In around 10% of victims necrosis can occur at the site of the bite, and in even fewer cases hemolysis (bursting of red blood cells) can occur.



Figure 22.1.4 *Western black widow.*

Other Poisonous Animals

The list below is a partial list of animals that are poisonous to humans (and other animals), or put another way, their flesh is toxic if consumed, or in some cases touched:

Birds: Pitohui, Blue-capped ifrit, Little shrikethrush, Spur-winged goose[1] (diet-dependent), and Common quail (diet-dependent)

Snakes: Rhabdophis keelback snakes and Garter snake (diet-dependent, when feeding on Pacific newts)[2]

Frogs and toads: American toad, Asiatic toad, Cane toad, Colorado River toad, Common toad, Corroboree frog, European green toad, Fowler's toad, Mantella, and poison dart frog (Figure 22.1.5).



Figure 22.1.5 *Poison dart frogs are well known for their brightly colored skin, which serves as a warning to predators of their toxicity.*

Salamanders: Pacific newts

Fish: Tetraodontidae (Blowfish, Pufferfish), Greenland shark, and Barracuda (age and diet dependent)

Cephalophods: Blue-ringed octopus and Pfeffer's flamboyant cuttlefish

Insects: Blister beetle, Birdwings, Milkweed butterfly, Battus (butterfly), Diamphidia, and Monarch (butterfly)

Food Poisoning

Foodborne illness (also **foodborne disease** and colloquially referred to as **food poisoning**)[1] is any illness resulting from the spoilage of contaminated food, pathogenic bacteria, viruses, or parasites that contaminate food,[2] as well as toxins such as poisonous mushrooms and various species of beans that have not been boiled for at least 10 minutes.

Many different disease-causing germs (Figure 22.1.6 below) can contaminate foods, so there are many different foodborne infections. The US CDC estimates that each year 48 million people get sick from a foodborne illness, 128,000 are hospitalized, and 3,000 die. Researchers have identified more than 250 foodborne diseases. Most of them are infections, caused by a variety of bacteria, viruses, and parasites. Harmful toxins and chemicals also can contaminate foods and cause foodborne illness.

Although anyone can get a foodborne illness, some people are more likely to develop one. Those groups include Pregnant women, Young children, Older adults, People with immune systems weakened from medical conditions, such as diabetes, liver disease, kidney disease, organ transplants, HIV/AIDS, or from receiving chemotherapy or radiation treatment. Most people with a foodborne illness get better without medical treatment, but people with severe symptoms should see their doctor.

Food Poisoning Symptoms

Common symptoms of foodborne diseases are nausea, vomiting, stomach cramps, and diarrhea. However, symptoms may differ among the different types of foodborne diseases. Symptoms can sometimes be severe and some foodborne illnesses can even be life-threatening. Most people have only mild illnesses, lasting a few hours to several days. However, some people need to be hospitalized, and some illnesses result in long-term health problems or even death. Infections transmitted by food can result in chronic arthritis, brain and nerve damage, and hemolytic uremic syndrome (HUS), which causes kidney failure.

Food poisoning symptoms may range from mild to severe and may differ depending on the germ you swallowed (see Table 22.1.1 below). After you consume a contaminated food or drink, it may take hours or days before you develop symptoms. See your doctor or healthcare provider if you have symptoms that are severe, including:

- High fever (temperature over 101.5°F, measured orally)
- Blood in stools
- Frequent vomiting that prevents keeping liquids down (which can lead to dehydration)
- Signs of dehydration, including a marked decrease in urination, a very dry mouth and throat, or feeling dizzy when standing up.
- Diarrhea that lasts more than 3 days

The top five germs that cause illnesses from food eaten in the United States are *Norovirus, Salmonella, Clostridium perfringens, Campylobacter, and Staphylococcus aureus (Staph).*

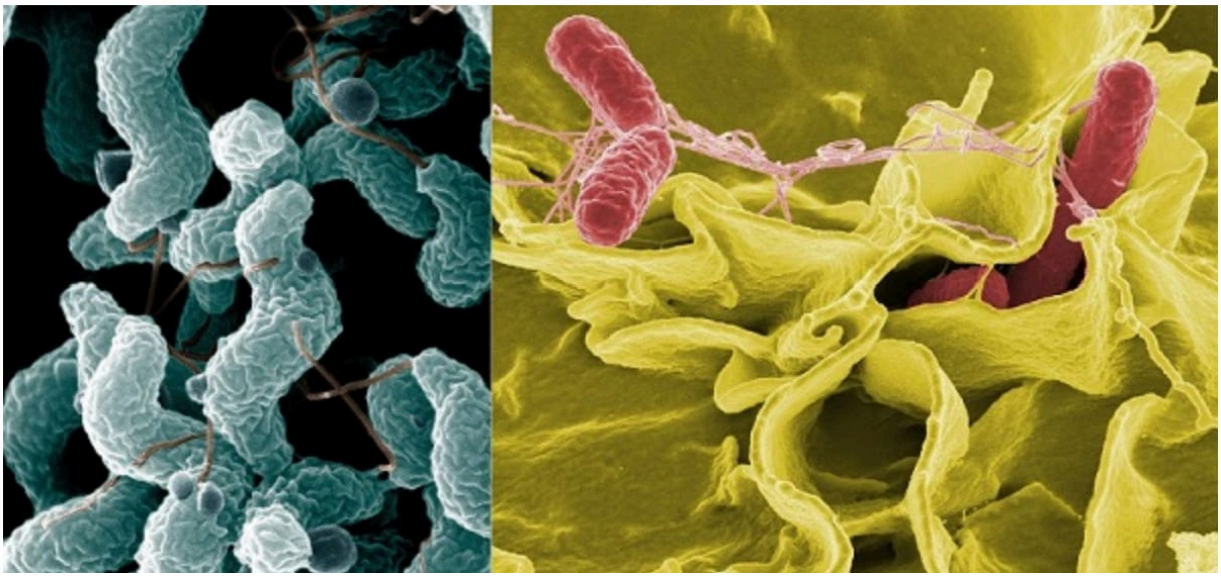


Figure 22.1.6 Campylobacter (left) , a bacteria that is a major cause of food poisoning and Salmonella (right). Images used with permission (Public Domain; De Wood, Pooley, USDA (left) and Rocky Mountain Laboratories, NIAID, NIH).

Some other germs don't cause as many illnesses, but when they do, the **illnesses are more likely to lead to hospitalizatio**n. Those germs include *Clostridium botulinum* (botulism), *Listeria, Escherichia coli (E. coli), and Vibrio.*

Table 22.1.1 Symptoms and Sources of 10 Foodborne Germs

Germ and Typical Time for Symptoms to Appear	Typical Signs and Symptoms	Common Food Sources
Campylobacter 2 – 5 days	Diarrhea (often bloody), stomach cramps/pain, fever	Raw or undercooked poultry, raw (unpasteurized) milk, and contaminated water
Clostridium botulinum 18 – 36 hours	Double or blurred vision, drooping eyelids, slurred speech. Difficulty swallowing, breathing and dry mouth. Muscle weakness and paralysis. Symptoms start in the head and move down as severity increases	Improperly canned or fermented foods, usually homemade. Prison-made illicit alcohol.
Clostridium perfringens 6 – 24 hours	Diarrhea, stomach cramps. Vomiting and fever are uncommon. Usually begins suddenly and lasts for less than 24 hours	Beef or poultry, especially large roasts; gravies; dried or precooked foods
Cyclospora 1 week	Watery diarrhea, loss of appetite and weight loss. Stomach cramps/pain, bloating, increased gas, nausea, and fatigue.	Raw fruits or vegetables, and herbs
Escherichia coli 3 – 4 days	Severe stomach cramps, diarrhea (often bloody), and vomiting. Around 5-10% of people diagnosed with this infection develop a life-threatening complication.	Raw or undercooked ground beef, raw (unpasteurized) milk and juice, raw vegetables (such as lettuce), and raw sprouts, contaminated water
Listeria 1 – 4 weeks	Pregnant women typically experience fever and other flu-like symptoms, such as fatigue and muscle aches. Infections during pregnancy can lead to serious illness or even death in newborns. Other people (most often older adults): headache, stiff neck, confusion, loss of balance and convulsions in addition to fever and muscle aches.	Raw (unpasteurized) milk, soft cheeses made with raw milk, raw sprouts, melons, hot dogs, pâtés, lunch meats, and cold cuts, smoked seafood

Germ and Typical Time for Symptoms to Appear	Typical Signs and Symptoms	Common Food Sources
Norovirus 12 – 48 hours	Diarrhea, nausea/stomach pain, vomiting	Infected person, contaminated food like leafy greens, fresh fruits, shellfish (such as oysters), or water, or by touching contaminated surfaces
Salmonella 12 – 72 hours	Diarrhea, fever, stomach cramps, vomiting	Eggs, raw or undercooked poultry or meat, unpasteurized milk or juice, cheese, raw fruits and vegetables
Staphylococcus aureus (Staph) 30 minutes – 6 hours	Diarrhea, nausea, stomach cramps, vomiting	Foods that are handled by people and not cooked (sliced meat, puddings, pastries, and sandwiches). Raw (unpasteurized) milk and cheese made from it.
Vibrio 1 – 4 days	Watery diarrhea, nausea. stomach cramps, vomiting, fever, chills	Raw or undercooked shellfish, particularly oysters

The Top 5 Strangest Posions That Can Kill You

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 22.1.1 *Strange poisons.*

Summary

- Various plants produce toxins that could be lethal or cause allergic reactions in herbivores. A few examples of poisonous plants include poison ivy, western water hemlock, autumn skullcap, henbane, oak, etc.
- Several deadly poisons come from snakes and spiders. Various birds, fishes, frogs, insects, etc. are deadly when consumed or touched due to their toxic flesh.
- The top five germs that cause illnesses from food eaten in the United States are *Norovirus, Salmonella, Clostridium perfringens, Campylobacter, and Staphylococcus aureus (Staph).*

Contributors

- Wikipedia
- Scioly.org
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22.2: Poisons and How They Act

Learning Objective

- Describe the modes of action and treatments for different poisons.

Corrosive Substances

A **corrosive substance** is one that will damage or destroy other substances with which it comes into contact by means of a chemical reaction. Corrosives are different from ***poisons*** in that corrosives are immediately dangerous to the tissues they contact, whereas poisons may have systemic toxic effects that require time to become evident. Colloquially, corrosives may be called *poisons* but the concepts are technically distinct. However, there is nothing which precludes a corrosive from being a poison; there are substances that are both corrosives and poisons.

There are several household products that contain chemical substances which are considered highly reactive and thus are very dangerous upon ingestion or skin contact. Chemical poisoning with corrosive agents occurs by ingestion of: acids (hydrochloric, nitric, sulfuric, perchloric, chloric), alkalis (sodium and potassium, soaps, detergents), heavy metal salts (sublimate), strong oxidizing agents, formalin, iodine tincture and many other chemical substances. Strong acids or bases, readily decomposes proteins and lipids through amide and ester hydrolysis upon contact with living tissues, such as skin and flesh.

Oxidizing Agents as Poisons

Household cleaning products with strong oxidizing agents like **sodium hypochlorite** (NaOCl) and **hydrogen peroxide** (H_2O_2) are dangerous when ingested. Generally speaking, the ingestion of bleaches (Figure 22.2.2) will cause damage to the esophagus and stomach, possibly leading to death. On contact with the skin or eyes, it causes irritation, drying, and potentially burns. Inhalation of bleach fumes can damage the lungs. Personal protective equipment should always be used when using bleach. Bleach should never be mixed with vinegar or other acids as this will create highly toxic chlorine gas and can cause severe burns internally and externally. Mixing bleach with ammonia similarly produces toxic chloramine gas, which can burn the lungs. Mixing bleach with hydrogen peroxide results in an exothermic chemical reaction that releases oxygen, and may cause the contents to splatter and cause skin and eye injury. Heating bleach and boiling it may produce chlorates, a strong oxidizer which may lead to a fire or explosion.



Figure 22.2.1 Clorox bleach. Source: Wikipedia.

Ozone. For the last few decades, scientists studied the effects of acute and chronic ozone exposure on human health. Hundreds of studies suggest that ozone is harmful to people at levels currently found in urban areas. Ozone has been shown to affect the

respiratory, cardiovascular and central nervous system. Early death and problems in reproductive health and development are also shown to be associated with ozone exposure.

Acute ozone exposure ranges from hours to a few days. Because ozone is gas, it directly affects the lungs and the entire respiratory system. Inhaled ozone causes inflammation and acute -but reversible- changes in lung function, as well as airway hyperresponsiveness. These changes lead to shortness of breath, wheezing, and coughing which may exacerbate lung diseases, like asthma or chronic obstructive pulmonary disease (COPD) resulting in the need to receive medical treatment. Acute and chronic exposure to ozone has been shown to cause an increased risk of respiratory infections, due to the following mechanism.

Multiple studies have been conducted to determine the mechanism behind ozone's harmful effects, particularly in the lungs. These studies have shown that exposure to ozone causes changes in the immune response within the lung tissue, resulting in disruption of both the innate and adaptive immune response, as well as altering the protective function of lung epithelial cells. It is thought that these changes in immune response and the related inflammatory response are factors that likely contribute to the increased risk of lung infections, and worsening or triggering of asthma and reactive airways after exposure to ground-level ozone pollution.

Inhaling ozone not only affects the immune system and lungs, but it may also affect the heart as well. Ozone causes short-term autonomic imbalance leading to changes in heart rate and reduction in heart rate variability; and high levels exposure for as little as one-hour results in a supraventricular arrhythmia in the elderly, both increase the risk of premature death and stroke. Ozone may also lead to vasoconstriction resulting in increased systemic arterial pressure contributing to increased risk of cardiac morbidity and mortality in patients with pre-existing cardiac diseases.

Metabolic Poisons

Carbon monoxide and cyanide are chemical substances that interfere with the normal bodily functions i.e. during the delivery of oxygen to bodily tissues and cellular respiration.

Carbon Monoxide Poisoning

Carbon monoxide poisoning typically occurs from breathing in carbon monoxide (CO) at excessive levels. Symptoms (Figure 22.2.2) are often described as "flu-like" and commonly include headache, dizziness, weakness, vomiting, chest pain, and confusion. Large exposures can result in loss of consciousness, arrhythmias, seizures, or death. The classically described "cherry red skin" rarely occurs. Long-term complications may include chronic fatigue, trouble with memory, and movement problems.

CO is a colorless and odorless gas which is initially non-irritating. It is produced during incomplete burning of organic matter. This can occur from motor vehicles, heaters, or cooking equipment that run on carbon-based fuels. Carbon monoxide primarily causes adverse effects by combining with hemoglobin to form carboxyhemoglobin (HbCO) preventing the blood from carrying oxygen and expelling carbon dioxide as carbaminohemoglobin. Additionally, many other hemoproteins such as myoglobin, Cytochrome P450, and mitochondrial cytochrome oxidase are affected, along with other metallic and non-metallic cellular targets.

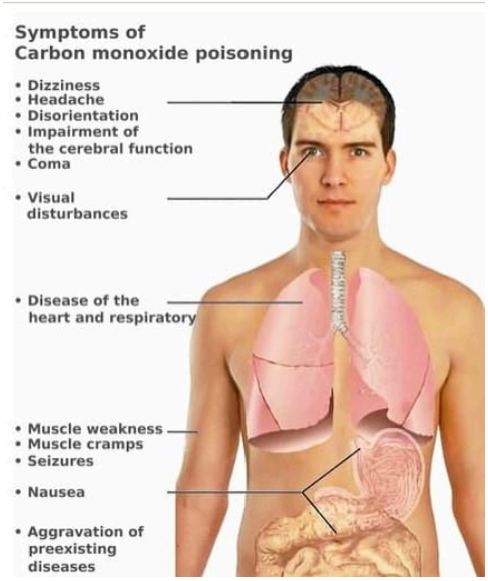


Figure 22.2.2 CO toxicity symptoms. Source: Wikipedia.

Initial treatment for carbon monoxide poisoning is to immediately remove the person from the exposure without endangering further people. Those who are unconscious may require CPR on site. Administering oxygen via non-rebreather mask shortens the half-life of carbon monoxide from 320 minutes, when breathing normal air, to only 80 minutes. Oxygen hastens the dissociation of carbon monoxide from carboxyhemoglobin, thus turning it back into hemoglobin. Due to the possible severe effects in the baby, pregnant women are treated with oxygen for longer periods of time than non-pregnant people.

Cyanide Poisoning

Cyanide poisoning is poisoning that results from exposure to a number of forms of cyanide. Early symptoms include headache, dizziness, fast heart rate, shortness of breath, and vomiting. This may then be followed by seizures, slow heart rate, low blood pressure, loss of consciousness, and cardiac arrest. Onset of symptoms is usually within a few minutes. If a person survives, there may be long-term neurological problems.

Toxic cyanide-containing compounds include hydrogen cyanide gas and a number of cyanide salts. Poisoning is relatively common following breathing in smoke from a house fire. Other potential routes of exposure include workplaces involved in metal polishing, certain insecticides, and the medication nitroprusside. Liquid forms of cyanide can be absorbed through the skin. Cyanide ions interfere with cellular respiration, resulting in the body's tissues being unable to use oxygen.

In addition to its uses as a pesticide and insecticide, cyanide is contained in tobacco smoke and smoke from building fires, and is present in many seeds or kernels such as those of almonds, apricots, apples, oranges, and in foods including cassava (also known as tapioca, yuca or manioc), and bamboo shoots. Vitamin B12, in the form of hydroxocobalamin (also spelled hydroxycobalamin), may reduce the negative effects of chronic exposure, and a deficiency can lead to negative health effects following exposure. Flaxseed also contains cyanogenic glycosides.

Cyanide is a potent cytochrome *c* oxidase (COX, a.k.a Complex IV) inhibitor. As such, cyanide poisoning is a form of histotoxic hypoxia, because it interferes with an essential step in aerobic metabolism called oxidative phosphorylation.

The United States standard cyanide antidote kit first uses a small inhaled dose of amyl nitrite, followed by intravenous sodium nitrite, followed by intravenous sodium thiosulfate. Hydroxocobalamin is newly approved in the US and is available in Cyanokit antidote kits. Sulfanegen TEA, which could be delivered to the body through an intra-muscular (IM) injection, detoxifies cyanide and converts the cyanide into thiocyanate, a less toxic substance. Alternative methods of treating cyanide intoxication are used in other countries.

Arsenic Poisoning

Arsenic poisoning is a medical condition that occurs due to elevated levels of arsenic in the body. If arsenic poisoning occurs over a brief period of time, symptoms may include vomiting, abdominal pain, encephalopathy, and watery diarrhea that contains

blood. Long-term exposure can result in thickening of the skin, darker skin, abdominal pain, diarrhea, heart disease, numbness, and cancer.

The most common reason for long-term exposure is contaminated drinking water. Groundwater most often becomes contaminated naturally; however, contamination may also occur from mining or agriculture. It may also be found in the soil and air. Recommended levels in water are less than 10–50 µg/L (10–50 parts per billion). Other routes of exposure include toxic waste sites and traditional medicines. Most cases of poisoning are accidental. Arsenic acts by changing the functioning of around 200 enzymes. Diagnosis is by testing the urine, blood, or hair.

Prevention is by using water that does not contain high levels of arsenic. This may be achieved by the use of special filters or using rainwater. There is not good evidence to support specific treatments for long-term poisoning. For acute poisonings treating dehydration is important. Dimercaptosuccinic acid (DMSA) or dimercaptopropane sulfonate (DMPS) may be used while dimercaprol (BAL) is not recommended. Hemodialysis may also be used.

WEBLINK

More Information on arsenic can be found on the link below

https://www.niehs.nih.gov/health/topics/agents/arsenic/index.cfm

Heavy Metal Poisoning

Lead poisoning, also known as **plumbism** and **saturnism**, is a type of metal poisoning caused by lead in the body. The brain is the most sensitive. Symptoms may include abdominal pain, constipation, headaches, irritability, memory problems, infertility, and tingling in the hands and feet. It causes almost 10% of intellectual disability of otherwise unknown cause and can result in behavioral problems. Some of the effects are permanent. In severe cases, anemia, seizures, coma, or death may occur.

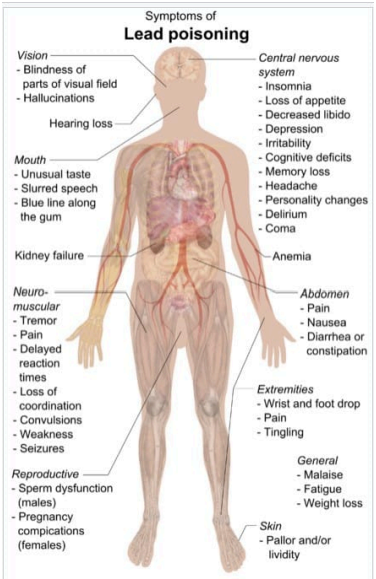


Figure 22.2.3. Symptoms of lead poisoning. SOurce: Wikipedia.

Exposure to lead can occur by contaminated air, water, dust, food, or consumer products. Children are at greater risk as they are more likely to put objects in their mouth such as those that contain lead paint and absorb a greater proportion of the lead that they eat. Exposure at work is a common cause of lead poisoning in adults with certain occupations at particular risk. Diagnosis is typically by measurement of the blood lead level. The Centers for Disease Control (US) has set the upper limit for blood lead for adults at 10 µg/dl (10 µg/100 g) and for children at 5 µg/dl. Elevated lead may also be detected by changes in red blood cells or dense lines in the bones of children as seen on X-ray.

Lead has no known physiologically relevant role in the body, and its harmful effects are myriad. Lead and other heavy metals create

reactive radicals which damage cell structures including DNA and cell membranes. Lead also interferes with DNA transcription, enzymes that help in the synthesis of vitamin D, and enzymes that maintain the integrity of the cell membrane. Anemia may result when the cell membranes of red blood cells become more fragile as the result of damage to their membranes. Lead interferes with metabolism of bones and teeth and alters the permeability of blood vessels and collagen synthesis. Lead may also be harmful to the developing immune system, causing production of excessive inflammatory proteins; this mechanism may mean that lead exposure is a risk factor for asthma in children. Lead exposure has also been associated with a decrease in activity of immune cells such as polymorphonuclear leukocytes. Lead also interferes with the normal metabolism of calcium in cells and causes it to build up within them.

Lead poisoning is preventable. This includes individual efforts such as removing lead-containing items from the home, workplace efforts such as improved ventilation and monitoring, state laws that ban the use of and national policies such as laws that ban lead in products such as paint, gasoline, ammunition, wheel weights, and fishing weights reduce allowable levels in water or soil, and provide for cleanup of contaminated soil. Workers' education could be helpful as well. The major treatments are removal of the source of lead and the use of medications that bind lead so it can be eliminated from the body, known as chelation therapy. Chelation therapy in children is recommended when blood levels are greater than 40–45 µg/dl. Medications used include dimercaprol, edetate calcium disodium, and succimer.

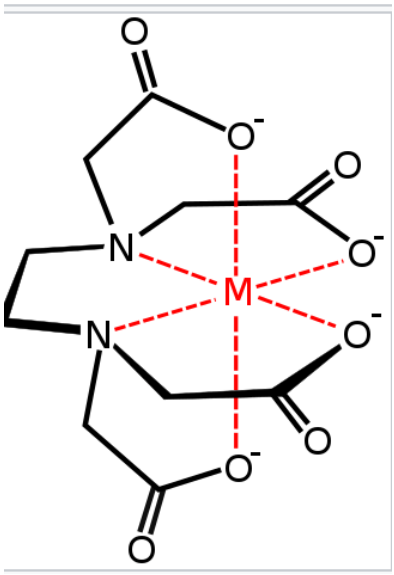


Figure 22.2.4 EDTA, a chelating agent, binds a heavy metal, sequestering it.

WEBLINKS

Links to various lead and mercury related topics can be found below

https://medlineplus.gov/leadpoisoning.html

https://medlineplus.gov/mercury.html

Mercury poisoning is a type of metal poisoning due to exposure to mercury. Symptoms depend upon the type, dose, method, and duration of exposure. They may include muscle weakness, poor coordination, numbness in the hands and feet, skin rashes, anxiety, memory problems, trouble speaking, trouble hearing, or trouble seeing. High-level exposure to methylmercury is known as Minamata disease. Methylmercury exposure in children may result in acrodynia (pink disease) in which the skin becomes pink and peels. Long-term complications may include kidney problems and decreased intelligence. The effects of long-term low-dose exposure to methylmercury are unclear.

Forms of mercury exposure include metal, vapor, salt, and organic compound. Most exposure is from eating fish, amalgam based dental fillings, or exposure at work. In fish, those higher up in the food chain generally have higher levels of mercury. Less commonly, poisoning may occur as a method of attempted suicide. Human activities that release mercury into the environment include the burning of coal and mining of gold. Tests of the blood, urine, and hair for mercury are available but do not relate well to the amount in the body.

The primary mechanism of mercury toxicity involves its irreversible inhibition of selenoenzymes, such as thioredoxin reductase. High mercury exposures deplete the amount of cellular selenium available for the biosynthesis of thioredoxin reductase and other selenoenzymes that prevent and reverse oxidative damage, which, if the depletion is severe and long lasting, results in brain cell dysfunctions that can ultimately cause death.

Prevention includes eating a diet low in mercury, removing mercury from medical and other devices, proper disposal of mercury, and not mining further mercury. In those with acute poisoning from inorganic mercury salts, chelation with either dimercaptosuccinic acid (DMSA) or dimercaptopropane sulfonate (DMPS) appears to improve outcomes if given within a few hours of exposure. Chelation for those with long-term exposure is of unclear benefit.

Cadmium poisoning. Cadmium is a naturally occurring toxic metal with common exposure in industrial workplaces, plant soils, and from smoking. Due to its low permissible exposure in humans, overexposure may occur even in situations where trace quantities of cadmium are found. Cadmium is used extensively in electroplating, although the nature of the operation does not generally lead to overexposure. Cadmium is also found in some industrial paints and may represent a hazard when sprayed. Operations involving removal of cadmium paints by scraping or blasting may pose a significant hazard. The primary use of cadmium is in the manufacturing of NiCd rechargeable batteries. The primary source for cadmium is as a byproduct of refining zinc metal. Exposures to cadmium are addressed in specific standards for the general industry, shipyard employment, the construction industry, and the agricultural industry.

Acute exposure to cadmium fumes may cause flu-like symptoms including chills, fever, and muscle ache sometimes referred to as "the cadmium blues." Symptoms may resolve after a week if there is no respiratory damage. More severe exposures can cause tracheo-bronchitis, pneumonitis, and pulmonary edema. Symptoms of inflammation may start hours after the exposure and include cough, dryness and irritation of the nose and throat, headache, dizziness, weakness, fever, chills, and chest pain.

Inhaling cadmium-laden dust quickly leads to respiratory tract and kidney problems which can be fatal (often from kidney failure). Ingestion of any significant amount of cadmium causes immediate poisoning and damage to the liver, bones, and the kidneys. Compounds containing cadmium are also carcinogenic.

Summary

- Corrosive poisons are chemicals (that can be found in many household products) that are considered highly reactive and thus are very dangerous upon ingestion or skin contact.
- Metabolic poisons such as carbon monoxide and cyanide interfere with the bodily functions.
- Human exposure to lead, mercury, and cadmium have affected the nervous system, respiratory system, brain, and other various organs.

Contributors

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- Robert J. Lancashire (University of West Indies-Mona)

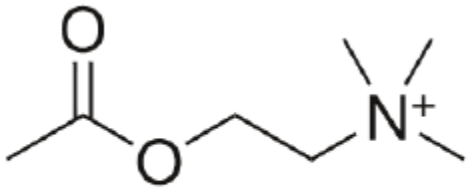
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22.3: More Chemistry of the Nervous System

Learning Objectives

- Describe the overall mechanism of neurotransmission.
- Describe how various nerve agents interrupt the neurotransmission process.

Acetylcholine is an organic chemical that functions in the brain and body of many types of animals, including humans, as a neurotransmitter—a chemical released by nerve cells to send signals to other cells. Its name is derived from its chemical structure: it is an ester of acetic acid and choline. Parts in the body that use or are affected by acetylcholine are referred to as cholinergic. Substances that interfere with acetylcholine activity are called anticholinergics.



Acetylcholine: The chemical structure of acetylcholine is depicted.

Acetylcholine is the neurotransmitter used at the neuromuscular junction—in other words, it is the chemical that motor neurons of the nervous system release in order to activate muscles. This property means that drugs that affect cholinergic systems can have very dangerous effects ranging from paralysis to convulsions. Acetylcholine is also used as a neurotransmitter in the autonomic nervous system, both as an internal transmitter for the sympathetic nervous system and as the final product released by the parasympathetic nervous system.

In the brain, acetylcholine functions as a neurotransmitter and as a neuromodulator. The brain contains a number of cholinergic areas, each with distinct functions. They play an important role in arousal, attention, memory and motivation.

Mechanism of Action

When a normally functioning motor nerve is stimulated, it releases the neurotransmitter acetylcholine, which transmits the impulse to a muscle or organ.

1. During neurotransmission (Figure $22.3.1$), ACh is released from the presynaptic neuron into the synaptic cleft and binds to ACh receptors on the post-synaptic membrane, relaying the signal from the nerve.

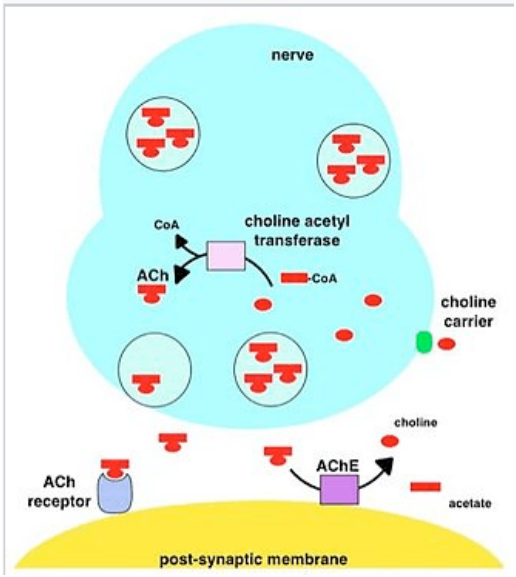


Figure 22.3.1 Different steps during neurotransmission.

2. AChE, also located on the post-synaptic membrane, terminates the signal transmission by hydrolyzing ACh (Figure 22.3.2). Source: Wikipedia.

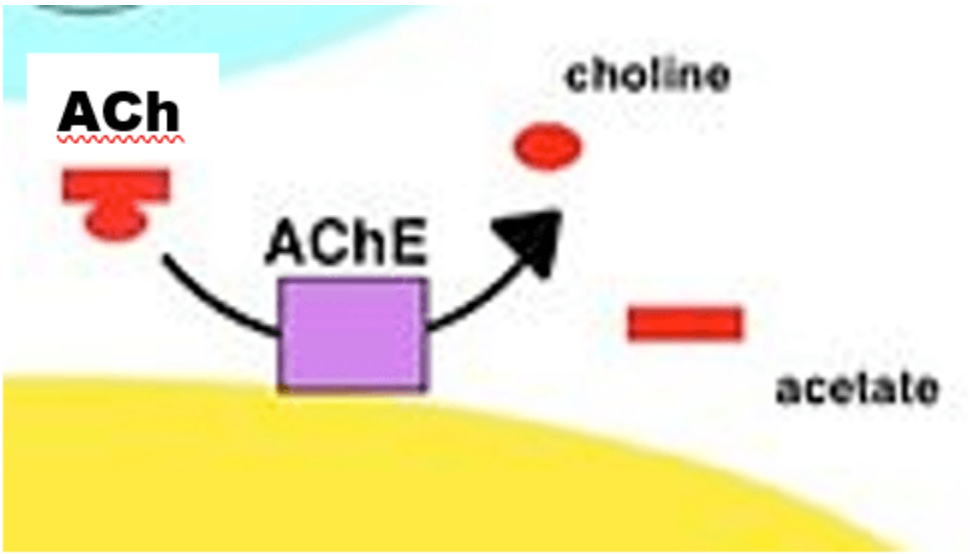


Figure 22.3.2 Acetylcholinesterase (AChe) breaks down acetylcholine (ACh) to choline and acetate (acetic acid). Source: Wikipedia.

3. The liberated choline is taken up again by the pre-synaptic neuron and ACh is synthesized by combining with acetyl-CoA through the action of choline acetyltransferase.[19][20]

Nerve Poisons and the Acetylcholine Cycle

Botulinum toxin (**Botox**) is a neurotoxic protein produced by the bacterium *Clostridium botulinum* and related species.[1] It prevents the release of the neurotransmitter acetylcholine from axon endings at the neuromuscular junction and thus causes flaccid paralysis.[2]The toxin causes the disease botulism. The toxin is also used commercially for medical and cosmetic purposes.

Foodborne botulism can be transmitted through food that has not been heated correctly prior to being canned, or food from a can that has not been cooked correctly. Most infant botulism cases cannot be prevented because the bacteria that cause this disease are in soil and dust. The bacteria can also be found inside homes on floors, carpet, and countertops, even after cleaning.

Honey can contain the bacteria that cause infant botulism, so children less than 12 months old should not be fed honey.

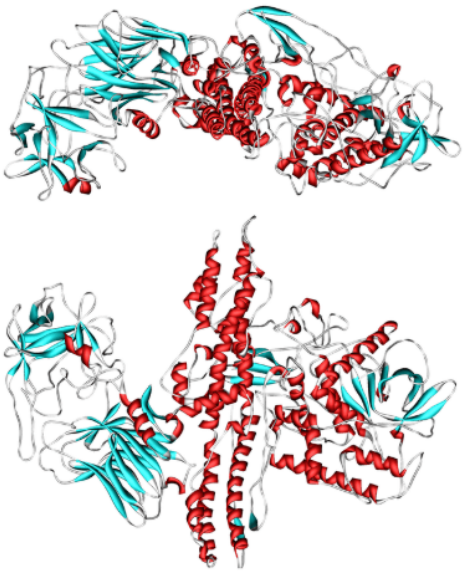
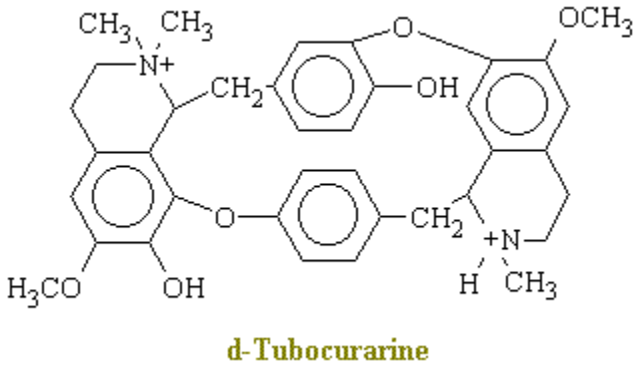


Figure 22.3.3 *Structure of Botulinum toxin.*

Curare is a generic term for various South American arrow poisons. The main active ingredient in curare is d-tubocurarine (Figure 22.3.4), which has the chemical structure shown below.



d-Tubocurarine

Figure 22.3.4 *Structure of d-tubocurarine.*

In brief, d-tubocurarine, blocks competitively the transmitter action of acetylcholine. When the drug is applied directly to the end-plate of a single isolated muscle fiber under microscopic control, the muscle cell becomes insensitive to motor-nerve impulses and to direct applied acetylcholine; however, the end -plate region and the remainder of the muscle fiber membrane retain their normal sensitivity to the application of potassium ions, and the muscle fiber still responds to direct electrical stimulation. Because acetylcholine release into the neuromuscular junction muscle is what initiates contraction, curare causes muscle relaxation and paralysis.

Nerve agents, sometimes also called **nerve gases**, are a class of organic chemicals that disrupt the mechanisms by which nerves transfer messages to organs. The disruption is caused by the blocking of acetylcholinesterase (AChE), an enzyme that catalyzes the breakdown of acetylcholine, a neurotransmitter. Nerve agents are acetylcholinesterase inhibitors used as poison.

Poisoning by a nerve agent leads to constriction of pupils, profuse salivation, convulsions, and involuntary urination and defecation, with the first symptoms appearing in seconds after exposure. Death by asphyxiation or cardiac arrest may follow in minutes due to the loss of the body's control over respiratory and other muscles. Some nerve agents are readily vaporized or aerosolized, and the primary portal of entry into the body is the respiratory system. Nerve agents can also be absorbed through the skin, requiring that those likely to be subjected to such agents wear a full body suit in addition to a respirator.

Nerve agents are generally colorless to amber-colored, tasteless liquids that may evaporate to a gas. Agents Sarin and VX are

odorless; Tabun has a slightly fruity odor and Soman has a slight camphor odor.

Organophosphorous Compounds as Insecticides and Weapons of War

This first class of nerve agents, the G-series, was accidentally discovered in Germany on December 23, 1936, by a research team headed by Gerhard Schrader working for IG Farben. Since 1934, Schrader had been working in a laboratory in Leverkusen to develop new types of insecticides for IG Farben. While working toward his goal of improved insecticide, Schrader experimented with numerous compounds, eventually leading to the preparation of tabun (GA).

In experiments, tabun was extremely potent against insects: as little as 5 ppm of tabun killed all the leaf lice he used in his initial experiment. In January 1937, Schrader observed the effects of nerve agents on human beings first-hand when a drop of tabun spilled onto a lab bench. Within minutes he and his laboratory assistant began to experience miosis (constriction of the pupils of the eyes), dizziness and severe shortness of breath. It took them three weeks to recover fully. The G-series naming system was created by the United States when it uncovered the German activities, labeling (Figure 22.3.5.

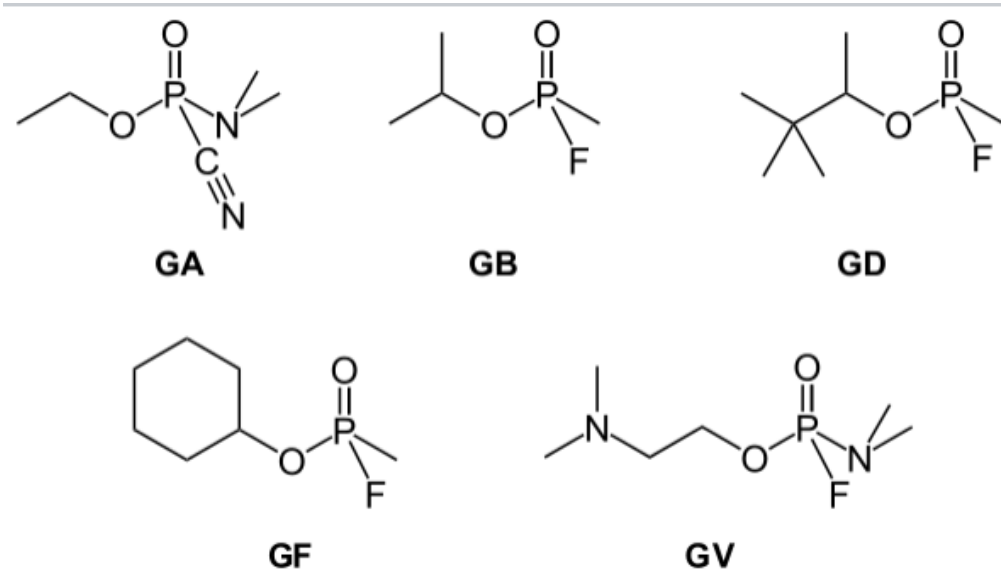


Figure 22.3.5 The G-series of nerve agents. Tabun as GA (German Agent A), sarin as GB and soman as GD. Ethyl sarin was tagged GE and cyclosarin as GF. *Source: Wikipedia.*

In 1935 the Nazi government had passed a decree that required all inventions of possible military significance to be reported to the Ministry of War, so in May 1937 Schrader sent a sample of tabun to the chemical warfare (CW) section of the Army Weapons Office in Berlin-Spandau. Schrader was summoned to the Wehrmacht chemical lab in Berlin to give a demonstration, after which Schrader's patent application and all related research was classified as secret. Colonel Rüdiger, head of the CW section, ordered the construction of new laboratories for the further investigation of tabun and other organophosphate compounds and Schrader soon moved to a new laboratory at Wuppertal-Elberfeld in the Ruhr valley to continue his research in secret throughout World War II. The compound was initially codenamed Le-100 and later Trilon-83.

Sarin was discovered by Schrader and his team in 1938 and named in honor of its discoverers: **S**chrader, **A**mbros, Gerhard **R**itter, and von der L**in**de.[26] It was codenamed T-144 or Trilon-46. It was found to be more than ten times as potent as tabun.

Soman was discovered by Richard Kuhn in 1944 as he worked with the existing compounds; the name is derived from either the Greek 'to sleep' or the Latin 'to bludgeon'. It was codenamed T-300.

Cyclosarin was also discovered during WWII but the details were lost and it was rediscovered in 1949.

Some **insecticides**, including carbamates and organophosphates such as dichlorvos, malathion and parathion, are nerve agents (Figure 22.3.6). The metabolism of insects is sufficiently different from mammals that these compounds have little effect on humans and other mammals at proper doses, but there is considerable concern

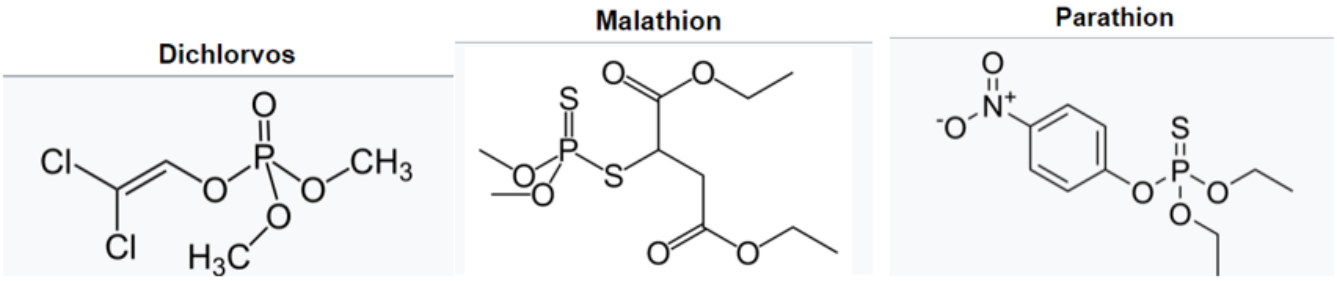


Figure 22.3.6 Organophosphate insecticides. Source: Wikipedia

about the long-term exposure to these chemicals by farm workers and animals alike. At high enough doses, acute toxicity and death can occur through the same mechanism as other nerve agents. Some insecticides such as demeton, dimefox and paraoxon are sufficiently toxic to humans that they have been withdrawn from agricultural use, and were at one stage investigated for potential military applications. Paraoxon was allegedly used as an assassination weapon by the apartheid South African government as part of Project Coast. Organophosphate pesticide poisoning is a major cause of disability in many developing countries and is often the preferred method of suicide.[24]

Treatment

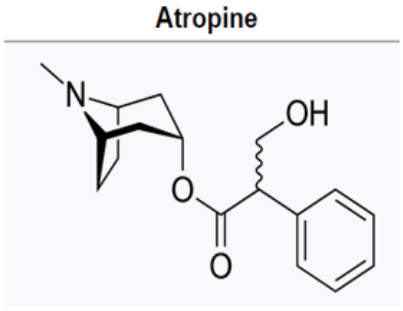
Standard treatment for nerve agent poisoning is a combination of an anticholinergic to manage the symptoms, and an oxime as an antidote. Anticholinergics treat the symptoms by reducing the effects of acetylcholine, while oximes displaces phosphate molecules from the active site of the cholinesterase enzymes, allowing the breakdown of acetylcholine. Military personnel are issued the combination in an autoinjector (e.g. ATNAA), for ease of use in stressful conditions.

Atropine (Figure 22.3.7 is the standard anticholinergic drug used to manage the symptoms of nerve agent poisoning. It acts as an antagonist to muscarinic acetylcholine receptors, blocking the effects of excess acetylcholine. Some synthetic anticholinergics, such as biperiden, may counteract the central symptoms of nerve agent poisoning more effectively than atropine, since they pass the blood–brain barrier better than atropine. While these drugs will save the life of a person affected by nerve agents, that person may be incapacitated briefly or for an extended period, depending on the extent of exposure. The endpoint of atropine administration is the clearing of bronchial secretions.

Pralidoxime chloride (also known as *2-PAMCl*) is the standard oxime used to treat nerve agent poisoning. Rather than counteracting the initial effects of the nerve agent on the nervous system as does atropine, pralidoxime chloride reactivates the poisoned enzyme (acetylcholinesterase) by scavenging the phosphoryl group attached on the functional hydroxyl group of the enzyme, counteracting the nerve agent itself. Revival of acetylcholinesterase with pralidoxime chloride works more effectively on nicotinic receptors while blocking acetylcholine receptors with atropine is more effective on muscarinic receptors.

Anticonvulsants, such as diazepam, may be administered to manage seizures, improving long term prognosis and reducing risk of brain damage. This is not usually self-administered as its use is for actively seizing patients.

a.



b.



Figure 22.3.7 a. Atrophine molecule and b. an ampoule containing atropine injection 1mL/0.5mg.

Summary

- Upon stimulation, a normally functioning motor nerve releases the neurotransmitter acetylcholine, which transmits the impulse to a muscle or organ.
- Nerve poisons (i.e. carbamates and organophosphorus compounds) disrupt the nervous system by inhibiting the function of the enzyme acetylcholinesterase. Acetylcholine thus builds up and continues to act so that any nerve impulses are continually transmitted and muscle contractions do not stop.
- The botulin toxin and curare interfere with nerve impulses (by preventing the release of acetylcholine) and causes flaccid (sagging) paralysis of muscles.
- Atropine (Figure 22.3.7 is the standard anticholinergic drug used to manage the symptoms of nerve agent poisoning.

Contributors and Attributions

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22.4: The Lethal Dose

Learning Objectives

- Describe the LD_{50} value and its limitations.
- Know the LD_{50} value of various substances.

The LD_{50} is a standardized measure for expressing and comparing the toxicity of chemicals. The LD_{50} is the dose that kills half (50%) of the animals tested (LD = "lethal dose"). The animals are usually rats or mice, although rabbits, guinea pigs, hamsters, and so on are sometimes used. In all these tests, the dose must be calculated relative to the size of the animal. The most common units are milligrams of chemical per kilogram of test animal (mg/kg or ppm). (Table 22.4.1) provides examples of LD_{50} values for various substances.

As a measure of toxicity, lethal dose is somewhat unreliable and results may vary greatly between testing facilities due to factors such as the genetic characteristics of the sample population, animal species tested, environmental factors and mode of administration.

There can be wide variability between species as well; what is relatively safe for rats may very well be extremely toxic for humans (*cf.* paracetamol toxicity), and vice versa. For example, chocolate, comparatively harmless to humans, is known to be toxic to many animals. When used to test venom from venomous creatures, such as snakes, LD_{50} results may be misleading due to the physiological differences between mice, rats, and humans. Many venomous snakes are specialized predators of mice, and their venom may be adapted specifically to incapacitate mice; and mongooses may be exceptionally resistant. While most mammals have a very similar physiology, LD_{50} results may or may not have equal bearing upon every mammal species, including humans.

Table 22.4.1: LD_{50} Values of Various Substances. Source: Wikipedia

Substance	Animal Route	LD_{50} (mg/kg)
Water	rat, oral	90,000
Sucrose (table sugar)	rat, oral	29,700
Glucose (blood sugar)	rat, oral	25,800
Monosodium glutamate (MSG)	rat, oral	16,600
Cadmium sulfide	rat, oral	7,080
Ethanol (grain alcohol)	rat, oral	7,060
Methanol	human, oral	810
Sodium chloride (table salt)	rat, oral	3,000
Metallic arsenic	rat, oral	763
Arsenic trisulfide	rat, oral	185-6400
Sodium cyanide	rat, oral	6.4
Hydrogen cyanide	mouse, oral	3.7
Ibuprofen	rat, oral	636
Aspirin	rat, oral	200
Caffeine	rat, oral	192
Cocaine	mouse, oral	96
Nicotine	rat, oral	50

Substance	Animal Route	LD_{50} (mg/kg)
Heroin (diamorphine)	mouse, intravenous	21.8
Methamphetamine	rat, intraperitoneal	57
Mercury(II) chloride	rat, oral	1
Strychnine	human, oral	1-2
Sarin	mouse, subcutaneous injection	172 microgram/kg
Ricin (from castor oil plant)	rat, oral	20-30
Botulinum toxin (Botox)	human, oral injection, inhalation	1 ng/kg

(Table 22.4.2) gives the LD50 values of some insecticides. In each case, the chemical was fed to laboratory rats. Note that the lower the LD50, the more toxic the chemical. Even adjusting for the test animal's weight, the LD50 for one species is often quite different from that for another. Thus any LD50 value gives only a rough estimate of the risk to humans. The way in which the chemical is administered also has a marked effect on LD50 values. The chemical may be fed, injected, applied to the animal's skin, etc., and each method usually generates a different LD50.

Table 22.4.2: LD_{50} Values of Pesticides.

Chemical	Category	Oral LD_{50} in Rats (mg/kg)
Aldicarb ("Temik")	Carbamate	1
Carbaryl ("Sevin")	Carbamate	307
DDT	Chlorinated hydrocarbon	87
Dieldrin	Chlorinated hydrocarbon	40
Diflubenzuron ("Dimilin")	Chitin inhibitor	10,000
Malathion	Organophosphate	885
Methoprene	JH mimic	34,600
Methoxychlor	Chlorinated hydrocarbon	5,000
Parathion	Organophosphate	3
Piperonyl butoxide	Synergist	7,500
Pyrethrin	Plant extract	200
Rotenone	Plant extract	60

Summary

- The LD50 is the dose that kills half (50%) of the animals tested (LD = "lethal dose"). It is a standardized measure for expressing and comparing the toxicity of chemicals.
- LD50 values are given for common drugs (e.g. ibuprofen and aspirin), common household ingredients including water, table sugar (sucrose), salt (sodium chloride), insecticides (e.g. DDT and pyrethrin), and harmful drugs (e.g. cocaine and heroin).

Contributors and Attributions

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22.5: The Liver as a Detox Facility

Learning Objective

- Describe the different mechanisms of drug detoxification in the liver.

The human liver is thought to be responsible for up to 500 separate functions, usually in combination with other systems and organs. The liver breaks down or modifies toxic substance, such as alcohol and most medicial products, in a process called drug metabolism. This sometimes results in toxication, when the metabolite is more toxic than its precursor.

Alcohol Metabolism

Giving the liver enough time to fully metabolize the ingested alcohol is the only effective way to avoid alcohol toxicity. Drinking coffee or taking a shower will not help. The legal limit for intoxication is a BAC of 0.08. Taking into account the rate at which the liver metabolizes alcohol after drinking stops, and the alcohol excretion rate, it takes at least five hours for a legally intoxicated person to achieve sobriety.

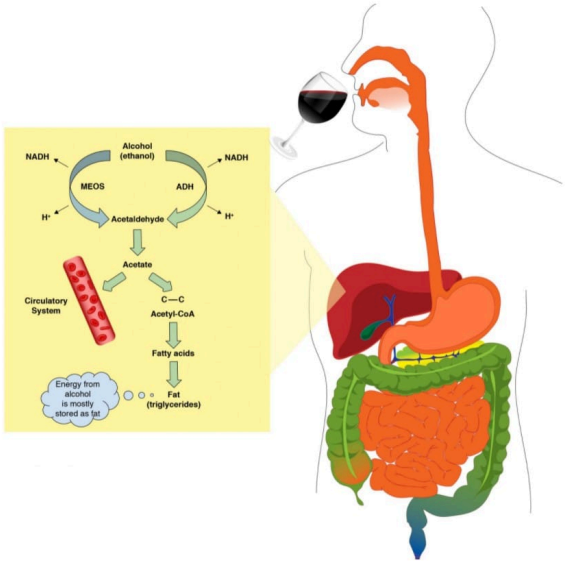


Figure 22.5.1: Alcohol Metabolism Summary.

The liver metabolizes up to 85% – 98% of the circulatory ethanol. The liver uses two metabolic processes to get rid of this circulatory ethanol as quickly and safely as possible.

1. Alcohol dehydrogenase system
2. Microsomal ethanol oxidizing system (MEOS)

Alcohol Dehydrogenase System

About 80 to 90% of the total hepatic ethanol uptake is processed via the alcohol dehydrogenase system.The degradation of ethanol begins in the liver. The enzyme that catalyzes this reaction is called alcohol dehydrogenase. The products from this reaction are acetaldehyde, NADH (a reduced coenzyme that carries electrons from one reaction to another) and H+ ion. Acetaldehyde is very toxic to the liver and the body's cells. The moment acetaldehyde is produced; it must be degraded to protect the liver cells. The enzyme that will carry this type of degradation reaction is acetaldehyde dehydrogenase (ALDH). Acetaldehyde dehydrogenase converts acetaldehyde into acetate, a non-toxic molecule.

Microsomal Ethanol Oxidizing System (MEOS)

In a moderate drinker, about 10 to 20% of the total liver ethanol uptake is processed via the microsomal ethanol oxidizing system (MEOS). During periods of heavy drinking, the MEOS system will metabolize most of the excess ethanol ingested. Heavy drinking stimulates the human body to include the MEOS system enzymes to clear ethanol faster from the body.

The MEOS system is also located in the liver. Similar to the Alcohol dehydrogenase system, acetaldehyde dehydrogenase will immediately convert acetaldehyde into acetate, a non-toxic molecule. Other products from this reaction are NADH and H+ ion.

Fate of Acetate

The acetate produced (from the alcohol dehydrogenase system and microsomal ethanol oxidizing system) is either released into circulation or retained inside the liver cells. In the liver cells, acetate is converted to acetyl CoA where it is used to produce other molecules like CO2 or used in the synthesis of fatty acids and cholesterol.

Nicotine and Ammonia

In humans, **nicotine i**s extensively metabolized in the liver into various metabolites. About 70-80% of nicotine is broken down to cotinine, the predominant metabolite. Other primary metabolites include nicotine *N*'-oxide, nornicotine, nicotine isomethonium ion, 2-hydroxynicotine and nicotine glucuronide. Under some conditions, other substances may be formed such as myosmine.

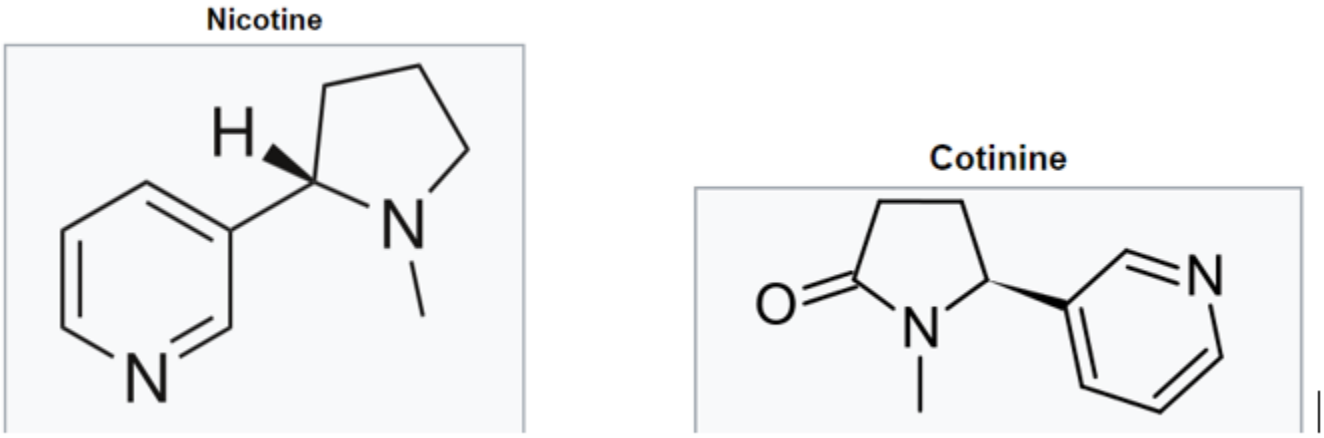


Figure 22.5.1 Nicotine and cotinine.

The liver converts ammonia into urea as part of the ornithine cycle or the urea cycle, and the urea is excreted in the urine.

Summary

- The liver is involved in the breakdown or modification of various substances in a process called drug metabolism, but the metabolites are not directly removed from the body.
- Ethanol is broken down through a series of steps (involving various liver enzymes) to carbon dioxide and water.
- Ethanol therapy is the traditional treatment for methanol and ethylene glycol poisoning.
- Nicotine is extensively metabolized in the liver into a variety of breakdown products whereas toxic ammonia is converted to non toxic urea.

Contributors and Attributions

- Wikipedia

- Benowitz, N. L., Hujjanen, J., Peyton III, J. Nicotine Chemistry, Metabolism, Kinetics, and Biomarkers. Hand Exp Pharmacol. 2009. (192): 29-60.
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22.6: Carcinogens and Teratogens

Learning Objectives

- Explain the process of cancer development.
- List the factors that may increase and lower the risk of cancer.
- Define teratogens and describe the birth defects that result from them.

A **carcinogen** is any agent that directly increases the incidence of cancer. Most, but not all carcinogens are mutagens. Carcinogens that do not directly damage DNA include substances that accelerate cell division, thereby leaving less opportunity for cell to repair induced mutations, or errors in replication. Carcinogens that act as mutagens may be biological, physical, or chemical in nature, although the term is most often used in relation to chemical substances.

Defining Cancer

Cancer is actually a group of more than 100 diseases, all of which involve abnormal cell growth with the potential to invade or spread to other parts of the body. In general terms, cancer occurs when the cell cycle is no longer regulated due to DNA damage. The number of potential underlying causes of this DNA damage is great, so there are many different risk factors for cancer. Any cells that become cancerous divide more quickly than normal cells. They may form a mass of abnormal cells called a tumor. The rapidly dividing cells take up nutrients and space, damaging the normal cells around them. If the cancer cells spread to other parts of the body, they invade and damage other tissues and organs. They may eventually lead to death.

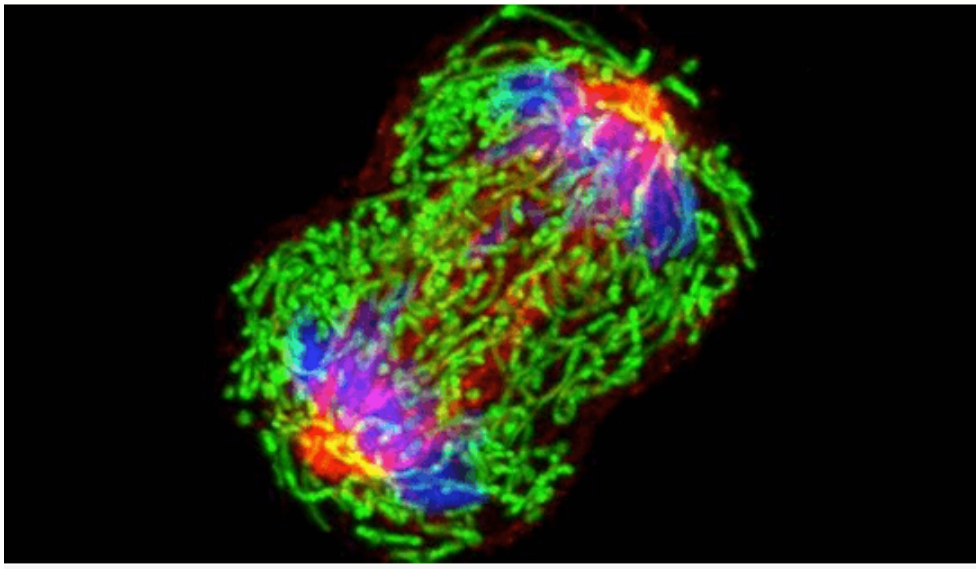


Figure 22.6.1 A dividing breast cancer cell. Source: National Cancer Institute/Univ. of Pittsburgh Cancer Institute

By far, the most common of the 100-plus types of human cancer is basal cell carcinoma, the type of skin cancer Bernie Sanders had removed in 2016. Basal cell carcinoma makes up 40 percent of all new cancers each year in the United States. Other common types of cancer include lung, colorectal, prostate (in males), and breast (in females) cancers. These cancers are not as common as skin cancer, but they cause the majority of cancer deaths.

How Cancer Develops

Carcinogenesis, also called **oncogenesis** or **tumorigenesis,** is the formation of a cancer, whereby normal cells are transformed into cancer cells. The transformation of a normal cell into a cancer cell is a multi-step process that involves initiation, promotion, progression and finally malignancy (see Figure 22.6.2). This process takes years and starts with a single cell in which the right

genes are mutated so the cell does not appropriately die and begins to proliferate abnormally. Then, additional mutations occur that select for more rapidly growing cells within this population leading to a tumor with rapid growth and malignancy. By the time the cells are cancerous, proto-oncogenes have been activated and tumor suppressor genes inactivated. Even within the same tumor type, like colon cancer, the specific genes mutated can vary from person to person making cancer a unique disease for each individual.

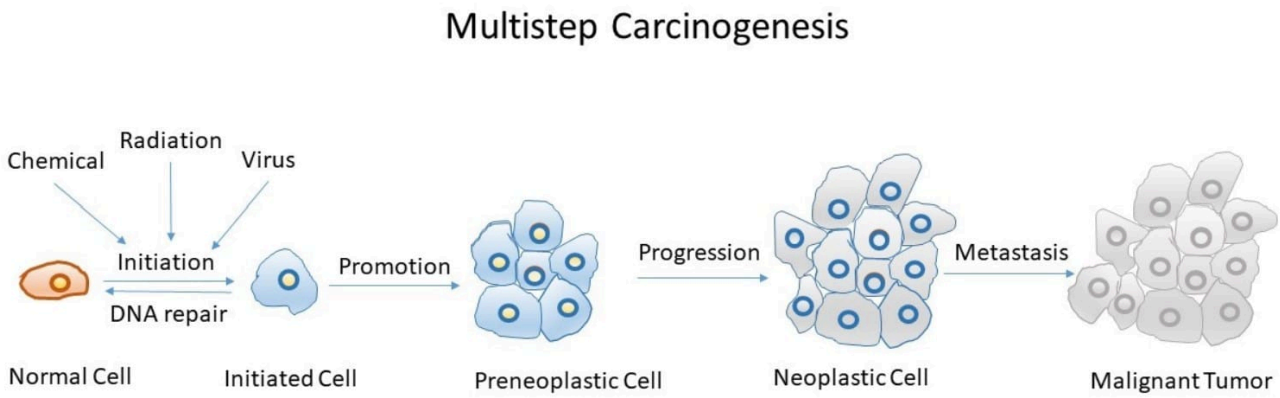


Figure 22.6.2: Multistep process involved in carcinogenesis that transforms a normal cell into a malignant tumor.

How Cancer Spreads

Once a normal cell transforms into a cancer cell and starts dividing out of control, cancer cells can spread from the original site (called the primary tumor) to other tissues. This can occur in three different ways. One way is local spread, in which aggressively dividing cancer cells directly invade nearby tissues. Another way involves the lymphatic system. Cancer cells can spread to regional lymph nodes through lymph vessels that pass by the primary tumor.

The third way cancer cells can spread is through the blood to distant sites. This is called metastasis, and the new cancers that form are called **metastases.** Although the blood can carry cancer cells to tissues everywhere in the body, cancer cells generally grow only in certain sites (Figure 22.6.3). Different types of cancers tend to metastasize to particular organs. The most common places for metastases to occur are the brain, lungs, bones, and liver. Almost all cancers can metastasize, especially during the late stages of the disease. Cancer that has metastasized generally has the worst prognosis and is associated with most cancer deaths.

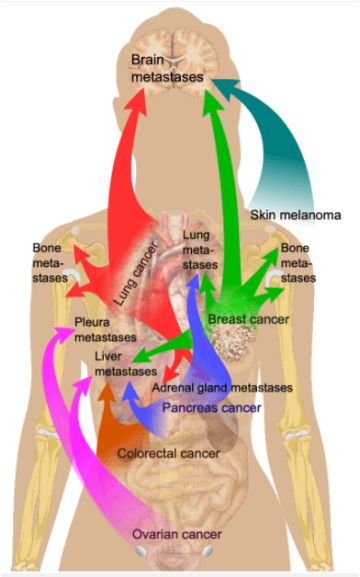


Figure 22.6.3: Cancer cells that originate in one organ may metastasize by traveling in the blood to distant sites (metastases). Metastasized lung cancer grows in the brain, bone, and adrenal gland. Metastasized pancreas cancer grows in the liver and lungs. Metastasized breast cancer can grow in the bone, brain, and liver. Metastasized Colon and Ovarian cancer grow in the liver.

Chemical Carcinogens

Chemical carcinogens (Table 22.6.1) can be either natural or synthetic compounds that, based on animal feeding trials or **epidemiological** (i.e. human population) studies, increase the incidence of cancer. The definition of a chemical as a carcinogen is problematic for several reasons. Some chemicals become carcinogenic only after they are metabolized into another compound in the body; not all species or individuals may metabolize chemicals in the same way. Also, the carcinogenic properties of a compound are usually dependent on its dose. It can be difficult to define a relevant dose for both lab animals and humans. Nevertheless, when a correlation between cancer incidence and chemical exposure is observed, it is usually possible to find ways to reduce exposure to that chemical.

Table 22.6.1: Some Classes of Chemical Carcinogens.

Class	Examples and/or Sources
PAHs (polycyclic aromatic hydrocarbons)	benzo[a]pyrene and several other components of the smoke of cigarettes, wood, and fossil fuels
Aromatic amines	compounds formed in food when meat (including fish, poultry) are cooked at high temperature
Nitrosamines and nitrosamides	found in tobacco and in some smoked meat and fish
Azo dyes	various dyes and pigments used in textiles, leather, paints.
Carbamates	ethyl carbamate (urethane) found in some distilled beverages and fermented foods
Halogenated compounds	e.g. pentachlorophenol used in some wood preservatives and pesticides.
Inorganic compounds	asbestos; may induce chronic inflammation and reactive oxygen species
Miscellaneous compounds	e.g. alkylating agents, phenolics

WEB LINK

A detailed list of occupational carcinogens can be found on the link below

https://bio.libretexts.org/Bookshelves/Human_Biology/Book:_Human_Biology_(Wakim_and_Grewal)/21:_Disease/21.7:_Cancer

The carcinogens implicated as the main causative agents of the four most common cancers worldwide are given in the table below. These four cancers are lung, breast, colon, and stomach cancers. Together they account for about 41% of worldwide cancer incidence and 42% of cancer deaths.

Table 22.6.2: Major Carcinogens Implicated In The Four Most Common Cancers Worldwide.

Type of Cancer	Carcinogen
Lung Cancer	Tobacco smoke
Breast Cancer	Estrogen
Colon Cancer	Tobacco smoke and bile acids: deoxycholic acid (DCA) or lithocholic acid (LCA)
Stomach Cancer	Heliobacter pylori

WEB LINK

Note: A more detailed description for each major carcinogen listed in Table 22.6.2 can be found on the link below

https://en.Wikipedia.org/wiki/Carcin...cers_worldwide

Anticarcinogens

Dietary fiber and calorie restriction are two anti-carcinogen or anti-promoters that decrease the risk of tumor formation. Dietary fiber is both and is inversely associated with cancer, particularly colon cancer. So the more fiber you eat, the less risk you have of developing colon cancer. One mechanism by which fiber acts is hastening bile acid excretion. Fiber also increases the rate of passage of materials through the colon resulting in decreased production and exposure of the colon to cancer-causing agents, ie dilutes the concentration of carcinogens.

Animal studies have shown that restricting caloric intake by 30% reduces tumor growth and increases life span. The mechanism is not known but may be due to less oxidation thus damage to DNA.

Antioxidants can help block the action of initiators or promoters if their mode of action is to damage DNA by oxidation. Vitamin A, C, E, beta-carotene, and selenium are antioxidant nutrients. Some work locally, like vitamin E in the colon, while other work more globally like selenium and vitamin C. Vitamin A appears to work by keeping cells differentiated which slows the growth rate.

Other compounds in food, particularly fruits and vegetables, have been shown to slow tumor formation. Cruciferous vegetables (eg broccoli, cauliflower, cabbage, and Brussel sprouts to name a few) are rich in nutrients, fiber, glucosinolates which are sulfur-containing chemicals, indoles, and isothiocyanates. Animal studies have found these substances inhibit the development of cancer in several organs in rats and mice (Hecht SS. Inhibition of carcinogenesis by isothiocyanates. *Drug Metabolism Reviews* 2000;32(3-4):395-411; Murillo G, Mehta RG. Cruciferous vegetables and cancer prevention. *Nutrition and Cancer* 2001;41(1-2):17-28). Indoles and isothiocyanates help protect cells from DNA damage; help inactivate carcinogens; have antiviral and antibacterial effects; have anti-inflammatory effects; induce cell death (apoptosis); and inhibit tumor blood vessel formation (angiogenesis) and tumor cell migration (needed for metastasis) (National Cancer Institute, Cruciferous Vegetables and Cancer Prevention, 2012, https://www.cancer.gov/about-cancer/...les-fact-sheet). Studies in humans, however, have shown mixed results.

Test for Carcinogens

In genetics, a **mutagen** is a physical or chemical agent that permanently changes genetic material, usually DNA, in an organism and thus increases the frequency of mutations above the natural background level. As many mutations can cause cancer, such mutagens are therefore carcinogens, although not all necessarily are. Many different systems for detecting mutagen have been developed. Animal systems may more accurately reflect the metabolism of human, however, they are expensive and time-consuming (may take around three years to complete), they are therefore not used as a first screen for mutagenicity or carcinogenicity.

The **Ames test** is a widely employed method that uses bacteria to test whether a given chemical can cause mutations in the

DNA of the test organism. More formally, it is a biological assay to assess the mutagenic potential of chemical compounds. A positive test indicates that the chemical is mutagenic and therefore may act as a carcinogen, because cancer is often linked to mutation. The test serves as a quick and convenient assay to estimate the carcinogenic potential of a compound because standard carcinogen assays on mice and rats are time-consuming (taking two to three years to complete) and expensive. However, false-positives and false-negatives are known. Other tests, similar to the Ames tests have also been developed using yeast and other bacteria.

Drosophila, plants, and cell cultures have been used in various test assays for mutagenecity of chemicals.

In **animal test systems,** rodents are usually used in animal test. The chemicals under test are usually administered in the food and in the drinking water, but sometimes by dermal application, by gavage, or by inhalation, and carried out over the major part of the life span for rodents. **Transgenic mouse assay** using a mouse strain infected with a viral shuttle vector is another method for testing mutagens. Animals are first treated with suspected mutagen, the mouse DNA is then isolated and the phage segment recovered and used to infect *E. coli*.

Did You Know?

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 22.6.1 *Risk factors for cancer.*

WEB LINKS - American Cancer Society and NIH:MedlinePlus & National Cancer Institute

Risk factors for Cancer

https://www.cancer.gov/about-cancer/causes-prevention/patient-prevention-overview-pdq#_199

Common Cancer Myths and Misconceptions

https://www.cancer.gov/about-cancer/causes-prevention/risk/myths

List of Probable Carcinogens

https://www.cancer.org/cancer/cancer-causes/general-info/known-and-probable-human-carcinogens.html?sitearea=who

Cancer Prevention: Take Charge of Your Lifestyle

https://medlineplus.gov/ency/patientinstructions/000825.htm

Cruciferous Vegetables and Cancer Prevention

https://www.cancer.gov/about-cancer/causes-prevention/risk/diet/cruciferous-vegetables-fact-sheet

Birth Defects:Teratogens

A teratogen is a compound that permanently deforms the function or structure of a developing embryo or fetus in utero. In general, the degree of teratogenicity depends on:

- The potency of the drug as a mutagen.
- The susceptibility of the fetus to teratogenesis.

- The dose of the teratogen.
- The duration of teratogen exposure.
- The time of exposure.
- The degree of transfer from maternal to fetal circulation.

The global average of all live births complicated by malformation is 6% (Environmental Health Perspectives, (NIH), October 2009). The majority of these complications are due to unknown factors. The vast majority of recognized etiologies are genetic, with only 10% being attributed to environmental etiologies such as maternal health, infection, and toxicants. In general, the central nervous and skeletal systems are the most affected.

Thalidomide (a sedative previously marketed in Europe to prevent morning sickness) see Figure 22.6.4is a classic teratogen that caused limb defects in babies born to women who took this drug in the 1960s (see Figure 22.6.5). Thalidomide was first marketed in 1957 in West Germany, where it was available over the counter.[5][6] When first released, thalidomide was promoted for anxiety, trouble sleeping, "tension", and morning sickness.[6][7] While initially deemed to be safe in pregnancy, concerns regarding birth defects were noted in 1961 and the medication was removed from the market in Europe that year.[6][5] The total number of people affected by use during pregnancy is estimated at 10,000, of which about 40% died around the time of birth.[6][3] Those who survived had limb, eye, urinary tract, and heart problems.[5]

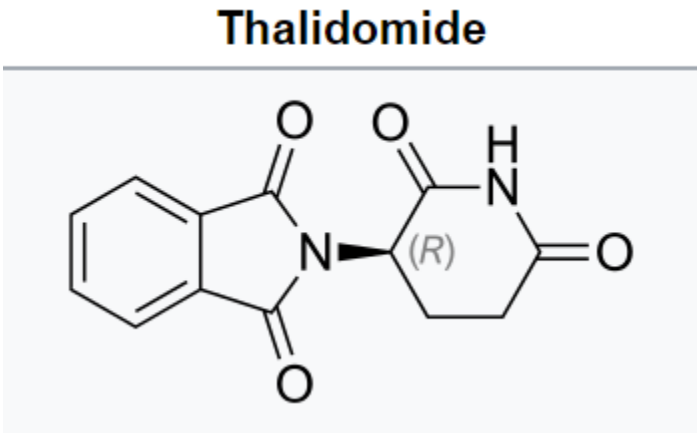


Figure 22.6.4. Chemical structure of Thalidomide.

Its initial entry into the US market was prevented by Frances Kelsey at the FDA.[7] The birth defects of thalidomide led to the development of greater drug regulation and monitoring in many countries. in 2006 the U.S. Food and Drug Administration granted accelerated approval for thalidomide in combination with dexamethasone for the treatment of newly diagnosed multiple myeloma patients.



Figure 22.6.5. *Thalidomide effects: A photograph of the limbs ofbaby born to a mother who took thalidomide while pregnant.*

Women may encounter a number of other teratogens. **Smoking** is most likely to cause growth retardation, but has also been implicated in the prelabor rupture of the membranes, preterm labor, abruption of the placenta, spontaneous abortion, perinatal morbidity and mortality, and sudden infant death syndrome. Smoking may exert its effects through competitive binding of carbon monoxide with hemoglobin and/or through the various other components found in cigarettes that cause adverse biological effects.

Alcohol use in pregnancy may result in fetal alcohol syndrome (FAS) see Figure 22.6.6, which occurs in approximately 1% of all births. Children with FAS present with a flattened and thin upper lip, small palpebral fissures, epicanthal folds, flattened nasal bridge, and a short nose. They may also exhibit microcephaly, mental retardation, and have learning disabilities. It is not clear if there is any safe amount of alcohol consumption in pregnancy.

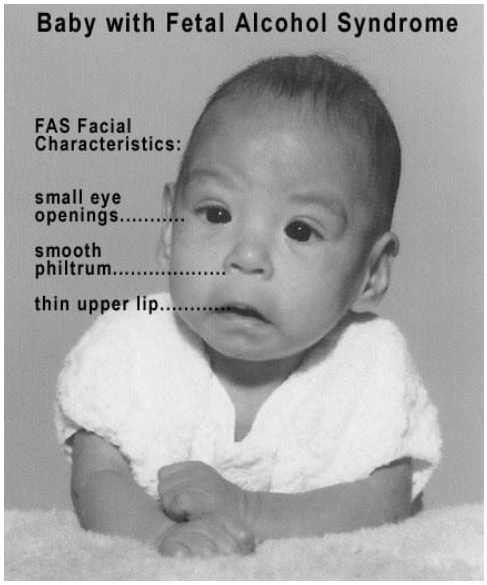


Figure 22.6.6. Fetal alcohol syndrome: Alcohol is a teratogen. When consumed in pregnancy, it can result in mothers giving birth to children with fetal alcohol syndrome. The facial characteristics highlighted in the photograph are small eye opening, smooth philtrum, and a thin upper lip.

Cocaine generally produces growth restriction, preterm delivery, microcephaly, spontaneous abortion, placental abruption, limb anomalies, and central nervous system abnormalities. Cocaine appear to exert a number of its effects through peripheral vasoconstriction that leads to fetal hypoxia.

Women with indications for **warfarin** therapy should either abstain from pregnancy or switch to low molecular weight heparins. Warfarin typically produces mental retardation, growth restriction, nasal hypoplasia, and opthalmic abnormalities.

Angiotensin converting enzyme (ACE) inhibitors will cause fetal renal failure and oligohydramnios that lead to pulmonary hypoplasia and limb contracture. Fetal cranial bone abnormalities are also common.

Isotretinoin (Accutane), used to treat acne, may cause cardiac, oral, otological, thymic, and central nervous system abnormalities. In one quarter of cases, it causes mental retardation.

Other teratogenic substance classes and conditions include

- Various prescription drugs and nutrient deficiencies (e.g., insufficient folic acid).
- Chemical compounds such as methyl iodide (used in pesticides) and bisphenol A (used in plastics) are suspected teratogens.

Summary

- A carcinogen is any agent that directly increases the incidence of cancer.
- Cancer is caused by changes to the DNA which could be inherited or acquired.
- Various tests have been developed to test for carcinogens.
- The American Cancer Society provides an extensive list of probable chemical carcinogens including those found in processed foods and beverages, various household products, pesticides etc.
- The effects of a teratogen on the fetus depend on several factors: the potency of the teratogen, the susceptibility of the fetus to the teratogen, the dose and duration of teratogen exposure, the degree of transfer from maternal to fetal circulation, and when during development the exposure occurs.
- Approximately 10% of congenital malformations are attributed to environmental factors, and 20% are due to genetic or hereditary factors. The rest have unknown causes or are due to a mix of different factors.
- Cigarette components, alcohol, cocaine, warfarin, ACE inhibitors, and Accutane are all teratogens that affect fetal development.

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22.7: Hazardous Wastes

Learning Objectives

- List the different types of hazardous wastes based on their classification.
- Describe the handling of hazardous waste.

Hazardous waste is waste that has substantial or potential threats to public health or the environment. Hazardous wastes may be found in different physical states such as gaseous, liquids, or solids. A hazardous waste is a special type of waste because it cannot be disposed of by common means like other by-products of our everyday lives. Depending on the physical state of the waste, treatment and solidification processes might be required.

Statutory Definition of Hazardous Waste

A discussion of the definition of hazardous waste should begin with Congress' original statutory definition of the term. RCRA (Resource Recovery and Conservation Act) §1004(5) defines hazardous waste as: A solid waste, or combination of solid waste, which because of its quantity, concentration, or physical, chemical, or infectious characteristics may (a) cause, or significantly contribute to, an increase in mortality or an increase in serious irreversible, or incapacitating reversible, illness; or (b) pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, transported, or disposed of, or otherwise managed.

Listed, Characteristic, and Mixed Wastes

Listed hazardous wastes (see Table 22.7.1) are materials specifically listed as hazardous wastes which are from non-specific sources, specific sources, or discarded chemical products. Title 40 of the Code of Federal Regulations (CFR) in section 261 provides four lists (the F, K, P and U lists) of hazardous materials.

Table 22.7.1 List Hazardous Wastes. Source US EPA.

List Type	Section	Description of Waste
F List	40 CFR section 261.31	Wastes from common manufacturing and industrial processes • Spent solvent wastes, • Electroplating and other metal finishing wastes, • Dioxin-bearing wastes, • Chlorinated aliphatic hydrocarbons production, • Wood preserving wastes, • Petroleum refinery wastewater treatment sludges, and • Multisource leachate.

K List	40 CFR section 261.32	Source specific wastes from 13 various industries and manufacturers namely: • Wood preservation, • Organic chemicals manufacturing, • Pesticides manufacturing, • Petroleum refining, • Veterinary pharmaceuticals manufacturing, • Inorganic pigment manufacturing, • Inorganic chemicals manufacturing, • Explosives manufacturing, • Iron and steel production, • Primary aluminum production, • Secondary lead processing, • Ink formulation, and • Coking (processing of coal to produce coke).
P List	40 CFR section 261.33	Acute hazardous wastes from discarded commercial chemical products. • The chemical in the waste must be unused; and • The chemical in the waste must be in the form of a commercial chemical product.
U List	40 CFR section 261.33	Hazardous wastes from discarded commercial chemical products • The chemical in the waste must be unused; and • The chemical in the waste must be in the form of a commercial chemical product.

- **Characteristic hazardous wastes** are materials that are dangerous because it is toxic, corrosive, flammable, or reactive. Detailed information provided by the US Environmental Agency (US EPA) is summarized in Table 22.7.2.

Table 22.7.2 Characteristic Hazardous Wastes. Source US EPA.

Waste Characteristic	EPA Waste Code	Section	Description of Waste
Ignitability	D001	40 CFR section 261.21	Liquids with flash points below 60 °C (e.g. used solvents and waste oils), non-liquids that cause fire through specific conditions, ignitable compressed gases and oxidizers
Corrosivity	D002	40 CFR section 261.22	Aqueous wastes with a pH of less than or equal to 2 (acids), a pH greater than or equal to 12.5 (bases) or based on the liquids ability to corrode steel. Example: battery acid
Reactivity	D003	40 CFR section 261.23	Wastes that are unstable under normal conditions, may react with water, may give off toxic gases and may be capable of detonation or explosion under normal conditions or when heated. Examples: lithium–sulfur batteries and explosives.
Toxicity	D004 through D043	40 CFR section 261.24	Wastes that are harmful when ingested or absorbed. Toxic waste can be reactive, ignitable, and corrosive. Examples: old batteries, pesticides, paint, and car oil

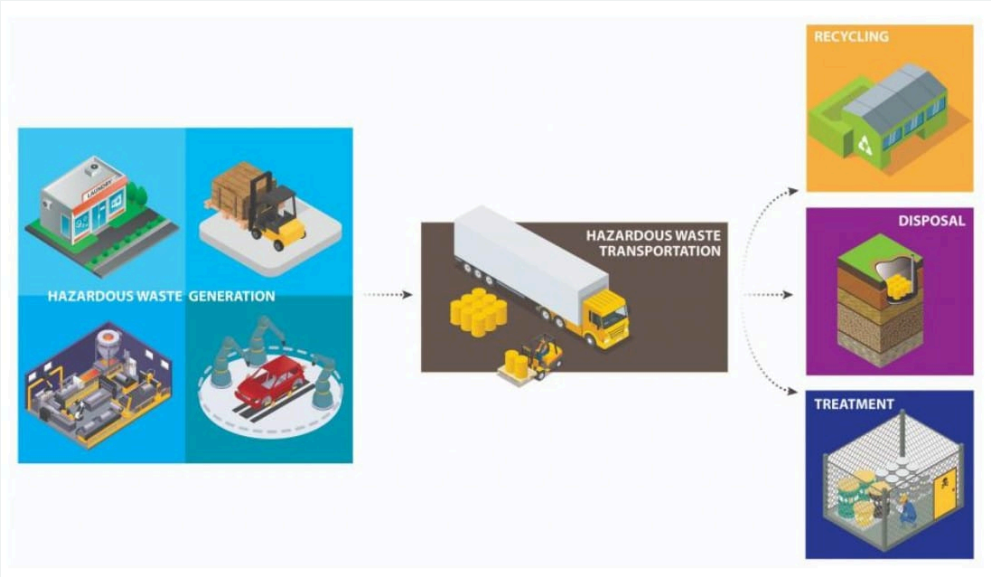
Mixed wastes is the term for hazardous wastes that also contain radioactive material and is regulated under the EPAs Resource Conservation and Recovery Act (RCRA) and the Department of Energy's Atomic Energy Act.

EPA's Cradle-to-Grave Hazardous Waste Management Program

https://www.epa.gov/hw/learn-basics-...ous-waste#hwid

In the mid-twentieth century, solid waste management issues rose to new heights of public concern in many areas of the United States because of increasing solid waste generation, shrinking disposal capacity, rising disposal costs, and public opposition to the siting of new disposal facilities. These solid waste management challenges continue today, as many communities are struggling to develop cost-effective, environmentally protective solutions. The growing amount of waste generated has made it increasingly important for solid waste management officials to develop strategies to manage wastes safely and cost effectively.

RCRA set up a framework for the proper management of hazardous waste . From this authority, EPA established a comprehensive regulatory program to ensure that hazardous waste is managed safely from "cradle to grave" meaning from the time it is created, while it is transported, treated, and stored, and until it is disposed:



Hazardous Waste Generation

Under RCRA, hazardous waste generators are the first link in the hazardous waste management system. All generators must determine if their waste is hazardous and must oversee the ultimate fate of the waste. Furthermore, generators must ensure and fully document that the hazardous waste that they produce is properly identified, managed, and treated prior to recycling or disposal. The degree of regulation that applies to each generator depends on the amount of waste that a generator produces.

Hazardous Waste Transportation

After generators produce a hazardous waste, transporters may move the waste to a facility that can recycle, treat, store or dispose of the waste. Since such transporters are moving regulated wastes on public roads, highways, rails and waterways, United States Department of Transportation hazardous materials regulations, as well as EPA's hazardous waste regulations, apply.

Hazardous Waste Recycling, Treatment, Storage and Disposal

To the extent possible, EPA tried to develop hazardous waste regulations that balance the conservation of resources, while ensuring the protection of human health and environment. Many hazardous wastes can be recycled safely and effectively, while other wastes will be treated and disposed of in landfills or incinerators.

Recycling hazardous waste has a variety of benefits including reducing the consumption of raw materials and the volume of waste materials that must be treated and disposed. However, improper storage of those materials might cause spills, leaks, fires, and contamination of soil and drinking water. To encourage hazardous waste recycling while protecting health and the environment, EPA developed regulations to ensure recycling would be performed in a safe manner.

Treatment Storage and Disposal Facilities (TSDFs) provide temporary storage and final treatment or disposal for hazardous wastes. Since they manage large volumes of waste and conduct activities that may present a higher degree of risk, TSDFs are stringently regulated. The TSDF requirements establish generic facility management standards, specific provisions governing hazardous waste management units and additional precautions designed to protect soil, ground water and air resources.

Comprehensive information on the final steps in EPA's hazardous waste management program is available online, including Web pages and resources related to:

- Hazardous waste recycling,
- Regulations that apply to treatment, storage and disposal facilities, and
- Descriptions of land disposal restrictions.

Summary

- Hazardous waste is defined as solid waste, or combination of solid waste, which because of its quantity, concentration, or physical, chemical, or infectious characteristics may (a) cause, or significantly contribute to, an increase in mortality or an increase in serious irreversible, or incapacitating reversible, illness; or (b) pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, transported, or disposed of, or otherwise managed.
- Listed wastes are wastes from common manufacturing and industrial processes, specific industries and can be generated from discarded commercial products.
- Characteristic wastes are wastes that exhibit any one or more of the following characteristic properties: ignitability, corrosivity, reactivity or toxicity.
- A waste that has a hazardous component and a radioactive component is called a **mixed waste** and is regulated under both the Resource Conservation and Recovery Act (RCRA) and the Atomic Energy Act.
- The Environmental Protection Agency (EPA) has developed a hazardous waste management program to ensure proper handling of hazardous waste from recycling, treatment, storage, and disposal.

Contributors and Attributions

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INDEX

A

acids
7.1: Acids and Bases - Experimental Definitions

addition polymer
10.3: Addition Polymerization - One + One + One + ... Gives One!

allergies
18.2: Cold and Allergy Medicines

B

bases
7.1: Acids and Bases - Experimental Definitions

C

carboxylic acids
9.8: Carboxylic Acids and Esters

carcinogens
22.6: Carcinogens and Teratogens

cardiovascular disease
18.6: Drugs for the Heart

Chemotherapy
18.4: Chemicals Against Cancer

colds
18.2: Cold and Allergy Medicines

corrosion
8.4: Corrosion and Explosion

E

esters
9.8: Carboxylic Acids and Esters

explosion
8.4: Corrosion and Explosion

F

functional group
9.5: The Functional Group

H

histamine
18.2: Cold and Allergy Medicines

hormones
18.5: Hormones - The Regulators

hypertension
18.6: Drugs for the Heart

I

ionizing power
11.6: Penetrating Power of Radiation

N

neurotransmitters
18.7: Drugs and the Mind

nuclear equations
11.2: Nuclear Equations

P

penetration power
11.6: Penetrating Power of Radiation

polymerization
10.1: Polymerization - Making Big Ones Out of Little Ones

Psychoactive Drugs
18.7: Drugs and the Mind

S

Sulfonamides
18.3: Drugs and Infectious Diseases

T

teratogens
22.6: Carcinogens and Teratogens

V

vulcanization
10.4: Rubber and Other Elastomers

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GLOSSARY

S

Sample Word 1 | Sample Definition 1

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- 7.2: Acids and Bases - *CC BY-NC-SA 4.0*
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- 7.4: Strong and Weak Acids and Bases - *CC BY-NC-SA 4.0*
- 7.5: Neutralization - *CC BY-NC-SA 4.0*
- 7.6: The pH Scale - *CC BY-NC-SA 4.0*
- 7.7: Buffers and Conjugate Acid-Base Pairs - *CC BY-NC-SA 4.0*
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- 8.1: Oxidation and Reduction - Four Views - *CC BY-NC-SA 4.0*
- 8.2: Oxidizing and Reducing Agents - *CC BY-NC-SA 4.0*
- 8.3: Electrochemistry- Cells and Batteries - *CC BY-NC-SA 4.0*
- 8.4: Corrosion and Explosion - *CC BY-NC-SA 4.0*
- 8.5: Oxygen - An Abundant and Essential Oxidizing Agent - *CC BY-SA 4.0*
- 8.6: Some Common Reducing Agents - *CC BY-NC-SA 4.0*
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- 9.4: Halogenated Hydrocarbons- Many Uses, Some Hazards - *CC BY-NC-SA 4.0*
- 9.5: The Functional Group - *CC BY-NC-SA 4.0*
- 9.6: Alcohols, Phenols, and Ethers - *CC BY-NC-SA 4.0*
- 9.7: Aldehydes and Ketones - *CC BY-NC-SA 4.0*
- 9.8: Carboxylic Acids and Esters - *Unknown License*
- 9.9: Nitrogen-Containing Compounds- Amines and Amides - *CC BY-NC-SA 4.0*

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- 10.1: Polymerization - Making Big Ones Out of Little Ones - *CC BY-SA 4.0*
- 10.2: Polyethylene - From the Battle of Britain to Bread Bags - *CC BY-SA 4.0*
- 10.3: Addition Polymerization - One + One + One + ... Gives One! - *CC BY-NC-SA 4.0*
- 10.4: Rubber and Other Elastomers - *CC BY-SA 4.0*
- 10.5: Condensation Polymers - *CC BY-NC-SA 4.0*
- 10.6: Properties of Polymers - *CC BY-NC-SA 4.0*
- 10.7: Plastics and the Environment - *CC BY-NC-SA 4.0*

◦ 11: Nuclear Chemistry - *CC BY-NC-SA 4.0*
- 11.1: Natural Radioactivity - *CC BY-NC-SA 4.0*
- 11.2: Nuclear Equations - *CC BY-NC-SA 4.0*
- 11.3: Half-Life and Radioisotopic Dating - *CC BY-NC-SA 4.0*
- 11.4: Artificial Transmutation - *CC BY-NC-SA 4.0*
- 11.5: Uses of Radioisotopes - *CC BY-NC-SA 4.0*
- 11.6: Penetrating Power of Radiation - *CK-12 License*
- 11.7: Energy from the Nucleus - *CC BY-NC-SA 4.0*
- 11.8: Nuclear Bombs - *CC BY-NC-SA 4.0*
- 11.9: Uses and Consequences of Nuclear Energy - *CC BY-NC-SA 4.0*

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- 12.1: Spaceship Earth- Structure and Composition - *CC BY-NC-SA 4.0*
- 12.2: Silicates and the Shapes of Things - *CC BY-NC-SA 4.0*
- 12.3: Metals and Ores - *CC BY-NC-SA 4.0*
- 12.4: Earth's Dwindling Resources - *CC BY-NC-*

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  - 13.1: Earth's Atmosphere- Divisions and Composition - CC BY-NC-SA 4.0
  - 13.2: Chemistry of the Atmosphere - CC BY-NC-SA 4.0
  - 13.3: Outdoor Air Pollution - CC BY-NC-SA 4.0
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  - 13.5: Photochemical Smog- Making Haze While the Sun Shines - CC BY-NC-SA 4.0
  - 13.6: Acid Rain- Air Pollution Water Pollution - CC BY-NC-SA 4.0
  - 13.7: Indoor Air Pollution - CC BY-NC-SA 4.0
  - 13.8: Stratospheric Ozone- Earth's Vital Shield - CC BY-NC-SA 4.0
  - 13.9: Carbon Dioxide and Climate Change - CC BY-NC-SA 4.0
  - 13.10: Who Pollutes? Who Pays? - CC BY-NC-SA 4.0
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  - 14.1: Water - Some Unique Properties - Unknown License
  - 14.2: Water in Nature - CC BY-NC-SA 4.0
  - 14.3: Chemical and Biological Contamination - CC BY-NC-SA 4.0
  - 14.4: Groundwater Contamination to Tainted Tap Water - CC BY-NC-SA 4.0
  - 14.5: Water Who Uses It and How Much? - CC BY-NC-SA 4.0
  - 14.6: Making Water Fit to Drink - CC BY-NC-SA 4.0
  - 14.7: 14.7?- Making Water Fit to Drink - CC BY-NC-SA 4.0
  - 14.8: Wastewater and Sewage Treatment - CC BY-NC-SA 4.0
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  - 15.1: Our Sun, a Giant Nuclear Power Plant - CC BY-NC-SA 4.0
  - 15.2: Energy and Chemical Reactions - CC BY-NC-SA 4.0
  - 15.3: Reaction Rates - CC BY-NC-SA 4.0
  - 15.4: The Laws of Thermodynamics - CC BY-NC-SA 4.0
  - 15.5: Power- People, Horses, and Fossils - CC BY-NC-SA 4.0
  - 15.6: Coal - The Carbon Rock of Ages - CC BY-NC-SA 4.0
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  - 15.8: Convenient Energy - CC BY-NC-SA 4.0
  - 15.9: Nuclear Energy - CC BY-NC-SA 4.0
  - 15.10: Renewable Energy Sources - CC BY-NC-SA 4.0
- 16: Biochemistry - CC BY-NC-SA 4.0
  - 16.1: Energy and the Living Cell - CC BY-NC-SA 4.0
  - 16.2: Carbohydrates- A Storehouse of Energy - CC BY-NC-SA 4.0
  - 16.3: Fats and Other Lipids - CC BY-NC-SA 4.0
  - 16.4: Proteins- Polymers of Amino Acids - CC BY-NC-SA 4.0
  - 16.5: Structure and Function of Proteins - CC BY-NC-SA 4.0
  - 16.6: Nucleic Acids- Parts, Structure, and Function - CC BY-NC-SA 4.0
  - 16.7: The Human Genome - CC BY-NC-SA 4.0
  - 16.8: RNA Protein Synthesis and the Genetic Code - CC BY-NC-SA 4.0
- 17: Food - CC BY-NC-SA 4.0
  - 17.1: Carbohydrates in the Diet - CC BY-NC-SA 4.0
  - 17.2: Fats and Cholesterol - CC BY-NC-SA 4.0
  - 17.3: Proteins- Muscle and Much More - CC BY-NC-SA 4.0
  - 17.4: Minerals, Vitamins, and Other Essentials - CC BY-NC-SA 4.0
  - 17.5: Starvation, Fasting, and Malnutrition - CC BY-NC-SA 4.0
  - 17.6: Flavorings- Spicy and Sweet - CC BY-NC-SA 4.0
  - 17.7: Other Food Additives- Beneficial or Dangerous - CC BY-NC-SA 4.0
  - 17.8: Problems with our Food - CC BY-NC-SA 4.0
- 18: Drugs - CC BY-NC-SA 4.0
  - 18.1: Pain Relievers- From Aspirin to Oxycodone - CC BY-NC-SA 4.0
  - 18.2: Cold and Allergy Medicines - CC BY-SA 4.0
  - 18.3: Drugs and Infectious Diseases - CC BY-NC-SA 4.0
  - 18.4: Chemicals Against Cancer - CC BY-NC-SA 4.0
  - 18.5: Hormones - The Regulators - CC BY-NC-SA 4.0
  - 18.6: Drugs for the Heart - CC BY-NC-SA 4.0
  - 18.7: Drugs and the Mind - CC BY-NC-SA 4.0
  - 18.8: Drugs and Society - CC BY-NC-SA 4.0
- 19: Fitness and Health - CC BY-NC-SA 4.0
  - 19.1: Calories - Quantity and Quality - CC BY-NC-SA 4.0
  - 19.2: Vitamins, Minerals, Fluids, and Electrolytes - CC BY-NC-SA 4.0
  - 19.3: Weight Loss - Diets and Exercise - CC BY-NC-SA 4.0
  - 19.4: Measuring Fitness - CC BY-NC-SA 4.0
  - 19.5: Some Muscular Chemistry - CC BY-NC-SA 4.0
  - 19.6: Drugs, Athletic Performance, and the Brain - CC BY-NC-SA 4.0
- 20: Chemistry Down on the Farm - CC BY-NC-SA 4.0
  - 20.1: Farming and Chemicals- Fertilizers - CC BY-NC-SA 4.0
  - 20.2: The War against Pests - CC BY-NC-SA 4.0
  - 20.3: Herbicides and Defoliants - CC BY-NC-SA 4.0

- 20.4: Sustainable Agriculture - *CC BY-NC-SA 4.0*
- 21: Household Chemicals - *CC BY-NC-SA 4.0*
  - 21.1: Cleaning with Soap - *CC BY-NC-SA 4.0*
  - 21.2: Synthetic Detergents - *CC BY-NC-SA 4.0*
  - 21.3: Laundry Auxiliaries- Softeners and Bleaches - *CC BY-NC-SA 4.0*
  - 21.4: All-Purpose and Special Purpose Cleaning Products - *CC BY-NC-SA 4.0*
  - 21.5: Solvents, Paints, and Waxes - *CC BY-NC-SA 4.0*
  - 21.6: Cosmetics - Personal Care Chemicals - *CC BY-NC-SA 4.0*
- 22: Poisons - *CC BY-NC-SA 4.0*
  - 22.1: Natural Poisons and Food Poisoning - *CC BY-NC-SA 4.0*
  - 22.2: Poisons and How They Act - *CC BY-NC-SA 4.0*
  - 22.3: More Chemistry of the Nervous System - *CC BY-NC-SA 4.0*
  - 22.4: The Lethal Dose - *CC BY-NC-SA 4.0*
  - 22.5: The Liver as a Detox Facility - *CC BY-NC-SA 4.0*
  - 22.6: Carcinogens and Teratogens - *CC BY-NC-SA 4.0*
  - 22.7: Hazardous Wastes - *CC BY-NC-SA 4.0*
- Back Matter - *Undeclared*
  - Index - *Undeclared*
  - Glossary - *Undeclared*
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    - TitlePage - *Undeclared*
    - InfoPage - *Undeclared*
    - Table of Contents - *Undeclared*
    - Licensing - *Undeclared*
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    - 1.2: Science- Reproducible, Testable, Tentative, Predictive, and Explanatory - *CC BY-NC-SA 4.0*
    - 1.3: Solving Society's Problems - Scientific Research - *CC BY-NC-SA 4.0*
    - 1.4: Chemistry - A Study of Matter and Its Changes - *CC BY-NC-SA 4.0*
    - 1.5: Classification of Matter - *CC BY-NC-SA 4.0*
    - 1.6: The Measurement of Matter - *CC BY-NC-SA 4.0*
    - 1.7: Density - *CC BY-NC-SA 4.0*
    - 1.8: Energy - Heat and Temperature - *CK-12 License*
  - 2: Atoms - *CC BY-NC-SA 4.0*
    - 2.1: Atoms - Ideas from the Ancient Greeks - *CC BY-NC 4.0*
    - 2.2: Scientific Laws - Conservation of Mass and Definite Proportions - *CC BY-NC-SA 4.0*
    - 2.3: John Dalton and the Atomic Theory of Matter - *CC BY-NC-SA 4.0*
    - 2.4: The Mole and Molar Mass - *CC BY-NC 4.0*
    - 2.5: Mendeleev and Periodic Table - *CC BY-NC-SA 4.0*
    - 2.6: Atoms and Molecules- Real and Relevant - *CC BY-NC-SA 4.0*
  - 3: Atomic Structure - *CC BY-NC-SA 4.0*
    - 3.1: Electricity and the Atom - *CC BY-NC-SA 4.0*
    - 3.2: Serendipity in Science - X-Rays and Radioactivity - *CC BY-NC-SA 4.0*
    - 3.3: Three Types of Radioactivity - *CC BY-NC-SA 4.0*
    - 3.4: Rutherford's Experiment- The Nuclear Model of the Atom - *CC BY-NC-SA 4.0*
    - 3.5: The Atomic Nucleus - *CC BY-NC-SA 4.0*
    - 3.6: Electron Arrangement- The Bohr Model (Orbits) - *CC BY-NC-SA 4.0*
    - 3.7: Electron Arrangement- The Quantum Model - *CC BY-NC-SA 4.0*
    - 3.8: Electron Configurations and the Periodic Table - *CC BY-NC-SA 4.0*
  - 4: Chemical Bonds - *CC BY-NC-SA 4.0*
    - 4.1: The Art of Deduction- Stable Electron Configurations - *CC BY-NC-SA 4.0*
    - 4.2: Lewis (Electron-Dot) Symbols - *CC BY-NC-SA 4.0*
    - 4.3: The Reaction of Sodium with Chlorine - *CC BY-NC-SA 4.0*
    - 4.4: Using Lewis Symbols for Ionic Compounds - *CC BY-NC-SA 4.0*
    - 4.5: Formulas and Names of Binary Ionic Compounds - *CC BY-NC-SA 4.0*
    - 4.6: Covalent Bonds- Shared Electron Pairs - *CC BY-NC-SA 4.0*

- 4.7: Unequal Sharing- Polar Covalent Bonds - *CC BY-NC-SA 4.0*
- 4.8: Polyatomic Molecules- Water, Ammonia, and Methane - *CC BY-NC-SA 4.0*
- 4.9: Polyatomic Ions - *CC BY-NC-SA 4.0*
- 4.10: Rules for Writing Lewis Formulas - *CC BY-NC-SA 4.0*
- 4.11: Molecular Shapes- The VSEPR Theory - *CC BY-NC-SA 4.0*
- 4.12: Shapes and Properties- Polar and Nonpolar Molecules - *CC BY-NC-SA 4.0*

◦ 5: Chemical Accounting - *CC BY-NC-SA 4.0*
- 5.1: Chemical Sentences- Equations - *CC BY-NC-SA 4.0*
- 5.2: Volume Relationships in Chemical Equations - *Unknown License*
- 5.3: Avogadro's Number and the Mole - *CC BY-NC-SA 4.0*
- 5.4: Molar Mass- Mole-to-Mass and Mass-to-Mole Conversions - *CC BY-NC-SA 4.0*
- 5.5: Solutions - *CC BY-NC-SA 4.0*
- 5.6: Section 6- - *CC BY-NC-SA 4.0*

◦ 6: Gases, Liquids, Solids, ... and Intermolecular Forces - *CC BY-NC-SA 4.0*
- 6.1: Solids, Liquids, and Gases - *CC BY-NC-SA 4.0*
- 6.2: Comparing Ionic and Molecular Substances - *CC BY-NC-SA 4.0*
- 6.3: Forces between Molecules - *CC BY-NC-SA 4.0*
- 6.4: Forces in Solutions - *CC BY-NC-SA 4.0*
- 6.5: Gases- The Kinetic-Molecular Theory - *CC BY-NC-SA 4.0*
- 6.6: The Simple Gas Laws - *CC BY-NC-SA 4.0*
- 6.7: The Ideal Gas Law - *CC BY-NC-SA 4.0*

◦ 7: Acids and Bases - *CC BY-NC-SA 4.0*
- 7.1: Acids and Bases - Experimental Definitions - *CC BY-NC 4.0*
- 7.2: Acids and Bases - *CC BY-NC-SA 4.0*
- 7.3: Acidic and Basic Anhydrides - *CC BY-SA 4.0*
- 7.4: Strong and Weak Acids and Bases - *CC BY-NC-SA 4.0*
- 7.5: Neutralization - *CC BY-NC-SA 4.0*
- 7.6: The pH Scale - *CC BY-NC-SA 4.0*
- 7.7: Buffers and Conjugate Acid-Base Pairs - *CC BY-NC-SA 4.0*
- 7.8: Acids and Bases in Industry and in Daily Life - *CC BY-NC-SA 4.0*

◦ 8: Oxidation and Reduction - *CC BY-NC-SA 4.0*
- 8.1: Oxidation and Reduction - Four Views - *CC BY-NC-SA 4.0*
- 8.2: Oxidizing and Reducing Agents - *CC BY-NC-SA 4.0*
- 8.3: Electrochemistry- Cells and Batteries - *CC BY-NC-SA 4.0*
- 8.4: Corrosion and Explosion - *CC BY-NC-SA 4.0*
- 8.5: Oxygen - An Abundant and Essential Oxidizing Agent - *CC BY-SA 4.0*
- 8.6: Some Common Reducing Agents - *CC BY-NC-SA 4.0*
- 8.7: Oxidation, Reduction, and Living Things - *CC BY-NC-SA 4.0*

◦ 9: Organic Chemistry - *CC BY-NC-SA 4.0*
- 9.1: Prelude to Organic Chemistry - *CC BY-NC-SA 4.0*
- 9.2: Aliphatic Hydrocarbons - *CC BY-NC-SA 4.0*
- 9.3: Aromatic Compounds- Benzene and Its Relatives - *CC BY-NC-SA 4.0*
- 9.4: Halogenated Hydrocarbons- Many Uses, Some Hazards - *CC BY-NC-SA 4.0*
- 9.5: The Functional Group - *CC BY-NC-SA 4.0*
- 9.6: Alcohols, Phenols, and Ethers - *CC BY-NC-SA 4.0*
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- 9.9: Nitrogen-Containing Compounds- Amines and Amides - *CC BY-NC-SA 4.0*

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- 10.1: Polymerization - Making Big Ones Out of Little Ones - *CC BY-SA 4.0*
- 10.2: Polyethylene - From the Battle of Britain to Bread Bags - *CC BY-SA 4.0*
- 10.3: Addition Polymerization - One + One + One + ... Gives One! - *CC BY-NC-SA 4.0*
- 10.4: Rubber and Other Elastomers - *CC BY-SA 4.0*
- 10.5: Condensation Polymers - *CC BY-NC-SA 4.0*
- 10.6: Properties of Polymers - *CC BY-NC-SA 4.0*
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- 11.1: Natural Radioactivity - *CC BY-NC-SA 4.0*
- 11.2: Nuclear Equations - *CC BY-NC-SA 4.0*
- 11.3: Half-Life and Radioisotopic Dating - *CC BY-NC-SA 4.0*
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- 11.5: Uses of Radioisotopes - *CC BY-NC-SA 4.0*
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- 11.7: Energy from the Nucleus - *CC BY-NC-SA 4.0*
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- 12.1: Spaceship Earth- Structure and Composition - *CC BY-NC-SA 4.0*
- 12.2: Silicates and the Shapes of Things - *CC BY-NC-SA 4.0*
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  - 13.1: Earth's Atmosphere- Divisions and Composition - CC BY-NC-SA 4.0
  - 13.2: Chemistry of the Atmosphere - CC BY-NC-SA 4.0
  - 13.3: Outdoor Air Pollution - CC BY-NC-SA 4.0
  - 13.4: Automobile Emissions - CC BY-NC-SA 4.0
  - 13.5: Photochemical Smog- Making Haze While the Sun Shines - CC BY-NC-SA 4.0
  - 13.6: Acid Rain- Air Pollution Water Pollution - CC BY-NC-SA 4.0
  - 13.7: Indoor Air Pollution - CC BY-NC-SA 4.0
  - 13.8: Stratospheric Ozone- Earth's Vital Shield - CC BY-NC-SA 4.0
  - 13.9: Carbon Dioxide and Climate Change - CC BY-NC-SA 4.0
  - 13.10: Who Pollutes? Who Pays? - CC BY-NC-SA 4.0
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  - 14.1: Water - Some Unique Properties - Unknown License
  - 14.2: Water in Nature - CC BY-NC-SA 4.0
  - 14.3: Chemical and Biological Contamination - CC BY-NC-SA 4.0
  - 14.4: Groundwater Contamination to Tainted Tap Water - CC BY-NC-SA 4.0
  - 14.5: Water Who Uses It and How Much? - CC BY-NC-SA 4.0
  - 14.6: Making Water Fit to Drink - CC BY-NC-SA 4.0
  - 14.7: 14.7?- Making Water Fit to Drink - CC BY-NC-SA 4.0
  - 14.8: Wastewater and Sewage Treatment - CC BY-NC-SA 4.0
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  - 15.1: Our Sun, a Giant Nuclear Power Plant - CC BY-NC-SA 4.0
  - 15.2: Energy and Chemical Reactions - CC BY-NC-SA 4.0
  - 15.3: Reaction Rates - CC BY-NC-SA 4.0
  - 15.4: The Laws of Thermodynamics - CC BY-NC-SA 4.0
  - 15.5: Power- People, Horses, and Fossils - CC BY-NC-SA 4.0
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  - 15.8: Convenient Energy - CC BY-NC-SA 4.0
  - 15.9: Nuclear Energy - CC BY-NC-SA 4.0
  - 15.10: Renewable Energy Sources - CC BY-NC-SA 4.0
- 16: Biochemistry - CC BY-NC-SA 4.0
  - 16.1: Energy and the Living Cell - CC BY-NC-SA 4.0
  - 16.2: Carbohydrates- A Storehouse of Energy - CC BY-NC-SA 4.0
  - 16.3: Fats and Other Lipids - CC BY-NC-SA 4.0
  - 16.4: Proteins- Polymers of Amino Acids - CC BY-NC-SA 4.0
  - 16.5: Structure and Function of Proteins - CC BY-NC-SA 4.0
  - 16.6: Nucleic Acids- Parts, Structure, and Function - CC BY-NC-SA 4.0
  - 16.7: The Human Genome - CC BY-NC-SA 4.0
  - 16.8: RNA Protein Synthesis and the Genetic Code - CC BY-NC-SA 4.0
- 17: Food - CC BY-NC-SA 4.0
  - 17.1: Carbohydrates in the Diet - CC BY-NC-SA 4.0
  - 17.2: Fats and Cholesterol - CC BY-NC-SA 4.0
  - 17.3: Proteins- Muscle and Much More - CC BY-NC-SA 4.0
  - 17.4: Minerals, Vitamins, and Other Essentials - CC BY-NC-SA 4.0
  - 17.5: Starvation, Fasting, and Malnutrition - CC BY-NC-SA 4.0
  - 17.6: Flavorings- Spicy and Sweet - CC BY-NC-SA 4.0
  - 17.7: Other Food Additives- Beneficial or Dangerous - CC BY-NC-SA 4.0
  - 17.8: Problems with our Food - CC BY-NC-SA 4.0
- 18: Drugs - CC BY-NC-SA 4.0
  - 18.1: Pain Relievers- From Aspirin to Oxycodone - CC BY-NC-SA 4.0
  - 18.2: Cold and Allergy Medicines - CC BY-SA 4.0
  - 18.3: Drugs and Infectious Diseases - CC BY-NC-SA 4.0
  - 18.4: Chemicals Against Cancer - CC BY-NC-SA 4.0
  - 18.5: Hormones - The Regulators - CC BY-NC-SA 4.0
  - 18.6: Drugs for the Heart - CC BY-NC-SA 4.0
  - 18.7: Drugs and the Mind - CC BY-NC-SA 4.0
  - 18.8: Drugs and Society - CC BY-NC-SA 4.0
- 19: Fitness and Health - CC BY-NC-SA 4.0
  - 19.1: Calories - Quantity and Quality - CC BY-NC-SA 4.0
  - 19.2: Vitamins, Minerals, Fluids, and Electrolytes - CC BY-NC-SA 4.0
  - 19.3: Weight Loss - Diets and Exercise - CC BY-NC-SA 4.0
  - 19.4: Measuring Fitness - CC BY-NC-SA 4.0
  - 19.5: Some Muscular Chemistry - CC BY-NC-SA 4.0
  - 19.6: Drugs, Athletic Performance, and the Brain - CC BY-NC-SA 4.0
- 20: Chemistry Down on the Farm - CC BY-NC-SA 4.0
  - 20.1: Farming and Chemicals- Fertilizers - CC BY-NC-SA 4.0
  - 20.2: The War against Pests - CC BY-NC-SA 4.0
  - 20.3: Herbicides and Defoliants - CC BY-NC-SA 4.0

        - 20.4: Sustainable Agriculture - *CC BY-NC-SA 4.0*
    - 21: Household Chemicals - *CC BY-NC-SA 4.0*
        - 21.1: Cleaning with Soap - *CC BY-NC-SA 4.0*
        - 21.2: Synthetic Detergents - *CC BY-NC-SA 4.0*
        - 21.3: Laundry Auxiliaries- Softeners and Bleaches - *CC BY-NC-SA 4.0*
        - 21.4: All-Purpose and Special Purpose Cleaning Products - *CC BY-NC-SA 4.0*
        - 21.5: Solvents, Paints, and Waxes - *CC BY-NC-SA 4.0*
        - 21.6: Cosmetics - Personal Care Chemicals - *CC BY-NC-SA 4.0*
    - 22: Poisons - *CC BY-NC-SA 4.0*
        - 22.1: Natural Poisons and Food Poisoning - *CC BY-NC-SA 4.0*
        - 22.2: Poisons and How They Act - *CC BY-NC-SA 4.0*
        - 22.3: More Chemistry of the Nervous System - *CC BY-NC-SA 4.0*
        - 22.4: The Lethal Dose - *CC BY-NC-SA 4.0*
        - 22.5: The Liver as a Detox Facility - *CC BY-NC-SA 4.0*
        - 22.6: Carcinogens and Teratogens - *CC BY-NC-SA 4.0*
        - 22.7: Hazardous Wastes - *CC BY-NC-SA 4.0*
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        - Index - *Undeclared*
        - Glossary - *Undeclared*
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