CHEM 10: INTRODUCTION TO CHEMISTRY



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This text was compiled on 01/11/2026

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Licensing

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CHAPTER OVERVIEW

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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.

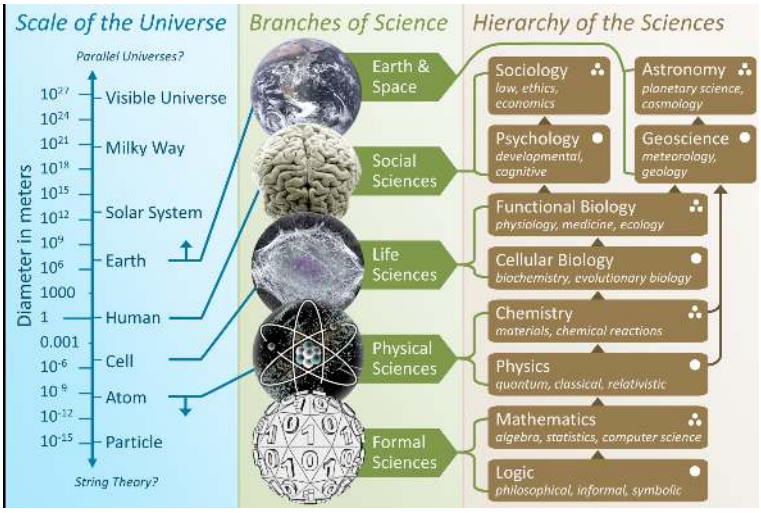


Figure 1.1.1: The scale of the universe mapped to the branches of science. (Source: Wikipedia)

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.

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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.



***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**).

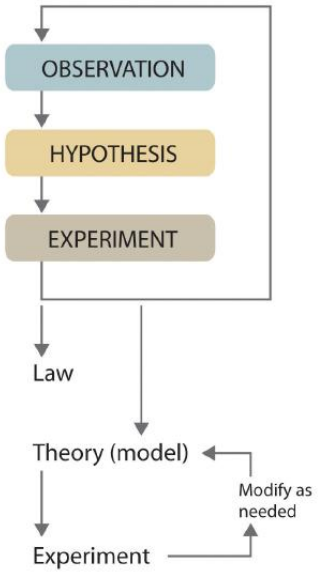


Figure 1.2.1 *The steps in the scientific method.*

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:

experiment

Answer 2:

law

Answer 3:

theory

Answer 4:

hypothesis

Answer 5:

observation

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.

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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.

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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 ^{o}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 1.4.1*A*

Which of the following is a physical property of matter?

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

Answer

3.

Exercise 1.4.1*B*

Which of the following is a chemical property?

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

Answer

1.

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, CH_4, and two molecules of oxygen, O_2; on the right are two molecules of water, H_2O, and one molecule of carbon dioxide, 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: $\mathrm{Fe + O_2 \rightarrow Fe_2O_3}$
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:
physical change

Answer 2:
chemical change

Answer 3:
physical change

Answer 4:
chemical change

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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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°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.



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

If we heat liquid mercury to its boiling point of **357°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
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.

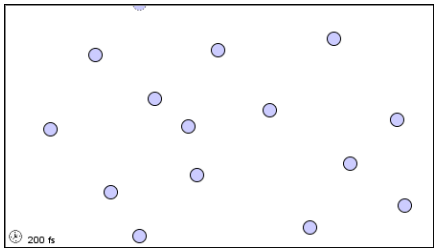
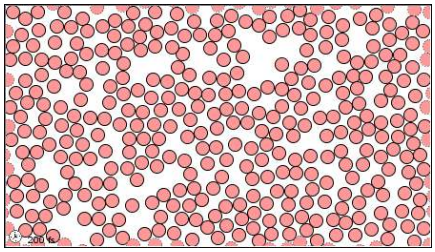
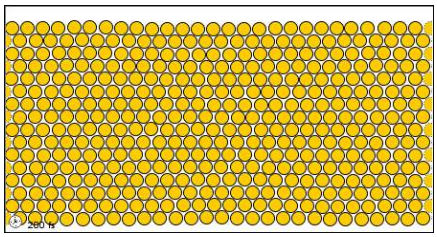
Images		
The gaseous state	*The liquid state*	*The solid state*
		

***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:

solid

Answer b:

gas

Answer c:

solid

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.

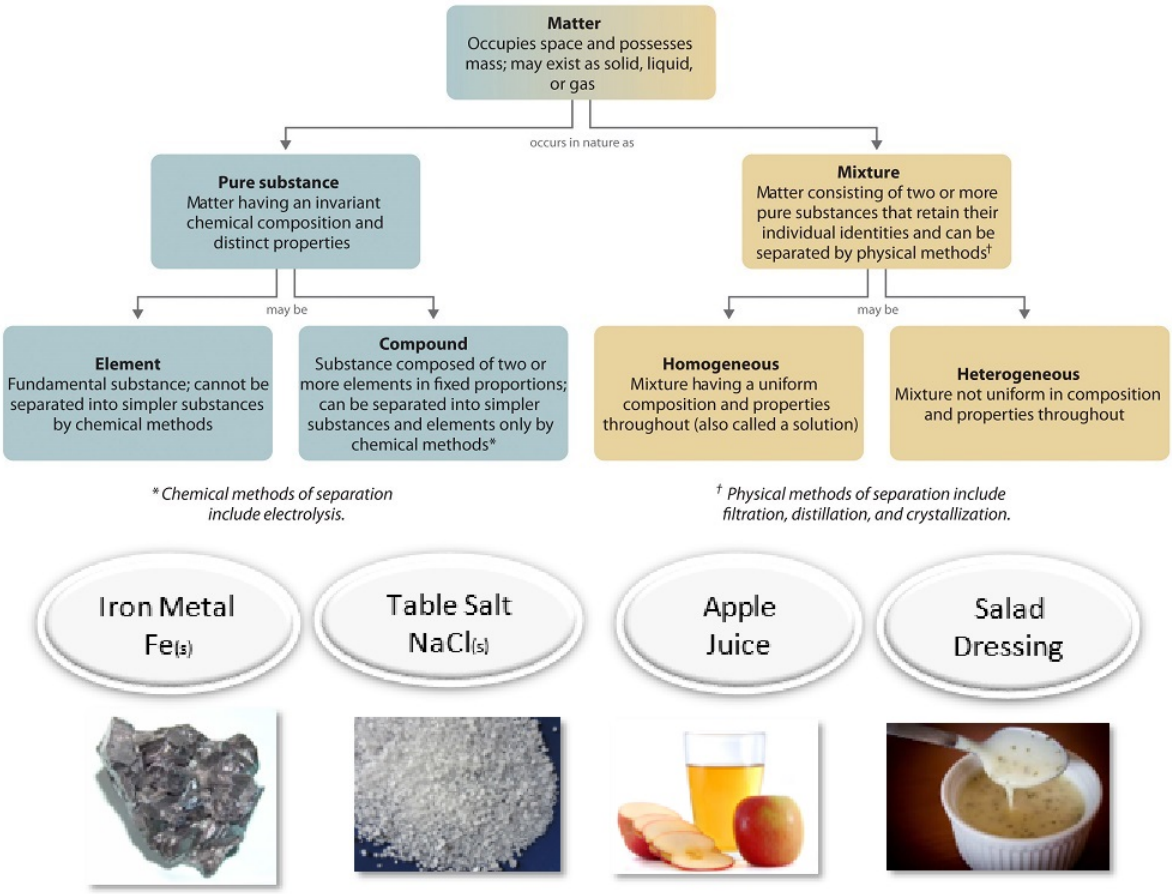


Figure **1.5.3**: Relationships between the types of matter and the methods used to separate mixtures.

Atoms, Elements, and Compounds



***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:
homogeneous mixture (solution)

Answer b:
element

Answer c:
heterogeneous mixture

Answer d:
compound

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:

a homogeneous mixture (solution)

Answer b:

element

Answer c:

heterogeneous mixture.

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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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

6.7×10^{10}

Answer b

1.689×10^{3}

Answer c

1.26×10^{1}

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

6.567×10^{-6}

Answer b

0.0622

Answer c

0.0000000099

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 μεγας, 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 (**Gm**) = 10^9 **m**
mega	**M**	1,000,000	1 megameter (**Mm**) = 10^6 **m**
kilo	**k**	1,000	1 kilometer (**km**) = 1,000 **m**
hecto	**h**	100	1 hectometer (**hm**) = 100 **m**
deka	**da**	10	1 dekameter (**dam**) = 10 **m**
		1	1 meter (**m**)
deci	**d**	1/10	1 decimeter (**dm**) = 0.1 **m**
centi	**c**	1/100	1 centimeter (**cm**) = 0.01 **m**
milli	**m**	1/1,000	1 millimeter (**mm**) = 0.001 **m**
micro	**μ**	1/1,000,000	1 micrometer (**μm**) = 10^{-6} **m**
nano	**n**	1/1,000,000,000	1 nanometer (**nm**) = 10^{-9} **m**
pico	**p**	1/1,000,000,000,000	1 picometer (**pm**) = 10^{-12} **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 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 kg**, this is easier than saying it weighs **6500 g** or **0.65 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:

km

Answer b:

mg

Answer c:

ns

Answer d:

cL

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 L** of liquid water at **4°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 $1000\ \text{g}$ in $1\ \text{kg}$. A milligram is 1/1000th of a gram, so there are $1000\ \text{mg}$ in $1\ \text{g}$.

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 (μm).

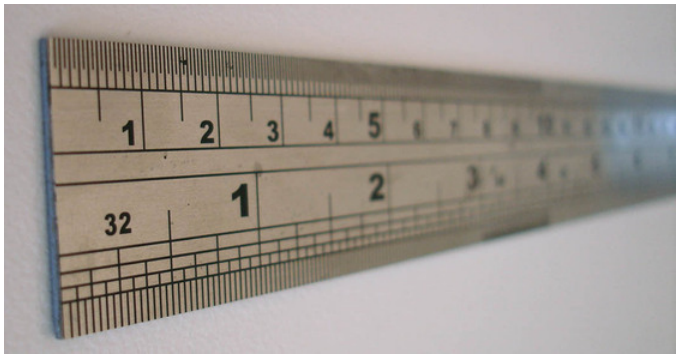


Figure **1.6.3**: Metric and English measuring devices. (CC BY-SA 4.0; Ejay)

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 $1\ \text{m}$ 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 $10\ \text{cm}$ ($1\ \text{dm}$) on each side. A liter is thus equal to both $1000\ \text{cm}^3$ ($10\ \text{cm} \times 10\ \text{cm} \times 10\ \text{cm}$) and to $1\ \text{dm}^3$.

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

A smaller unit of volume that is commonly used is the milliliter (mL). A milliliter is the volume of a cube that measures $1\ \text{cm}$ on each side. Therefore, a milliliter is equal to a cubic centimeter (cm^3).

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

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



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

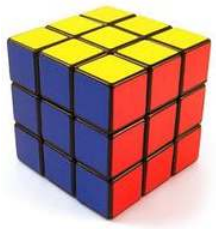


Figure 1.6.5 This Rubik's cube is 5.7 cm on each side and has a volume of 185.2 cm^3 or 185.2 mL.

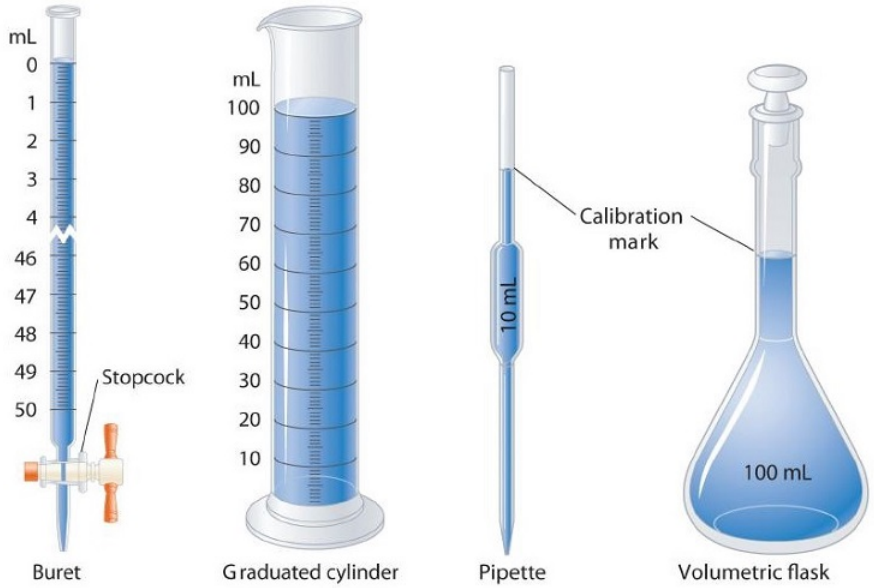


Figure 1.6.6: Buret & graduated cylinder: graduated glassware is used to deliver variable volumes of liquid. Pipette & volumetric flask: volumetric glassware is used to deliver (pipette) or contain (volumetric flask) a single volume accurately when filled to the mark. (CC BY-SA-NC; anonymous).

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
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.

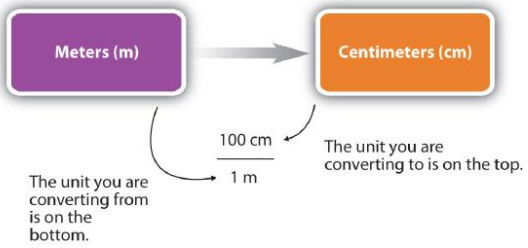
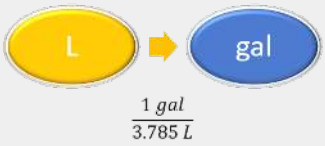
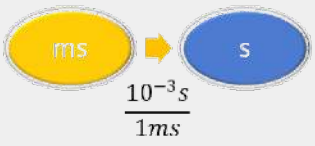


Figure 1.6.7: A Concept Map for Conversions. This is how you construct a conversion factor to convert from one unit to another.

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	Example 1.6.3
Steps for Problem Solving	The average volume of blood in an adult male is 4.7 L. What is this volume in gallons?	A hummingbird can flap its wings once in 18 ms. How many seconds are in 18 ms?
Identify the "given" information and what the problem is asking you to "find."	Given: 4.7 L Find: gal	Given: 18 ms Find: s
List other known quantities.	$1\,L = 3.785 gal$	$1\,ms = 10^{-3} s$
Prepare a concept map and use the proper conversion factor.	 $\frac{1\ gal}{3.785\ L}$	 $\frac{10^{-3} s}{1 ms}$
Cancel units and calculate.	$4.7 \cancel{L} \times \frac{1\ \text{gal}}{3.785\ \cancel{L}} = 1.2\ \text{gal}$	$18\ \cancel{\text{ms}} \times \frac{10^{-3}\ \text{s}}{1\ \cancel{\text{ms}}} = 0.018\ \text{s}$ or $18\ \cancel{\text{ms}} \times \frac{1\ \text{s}}{1{,}000\ \cancel{\text{ms}}} = 0.018\ \text{s}$
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 should be 1/1000 the given amount in ms.

? 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:

$1.01000x10^{-4} s$

Answer b:

$3.208x10^{4} g$

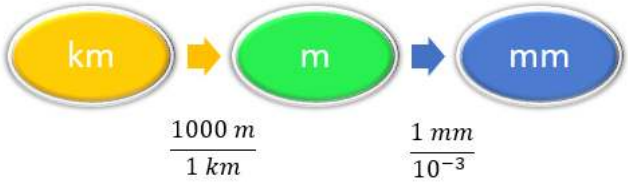
Answer c:

$1.53x10^{2} g$

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

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

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

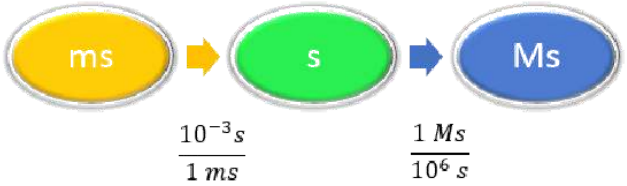
> *In each step, the previous unit is canceled and the next unit in the sequence is produced; each successive unit cancels out, until only the unit needed in the answer is left.*

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.	$1ms = 10^{-3}s$ $1Ms = 10^{6}s$
Prepare a concept map.	 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
Prepare a concept map.	 Convert day to hour to minute to second: use conversion factors 24 hours per day, 60 minutes per hour, and 60 seconds per minute
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:

$4.3007x10^{-14}kg$

Answer b:

83.75 ft

Answer c:

19 km

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

-
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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

$0.274\,kg/L$

Answer b

$1.049\ g/mL$

Summary

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

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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 $32°F$ and the boiling point as $212°F$. 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 $0°C$ and $100°C$, 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 $0\ K$, also known as absolute zero, being the point where all molecular motion ceases. The freezing point of water on the Kelvin scale is $273.15\ K$, while the boiling point is $373.15\ K$. 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.

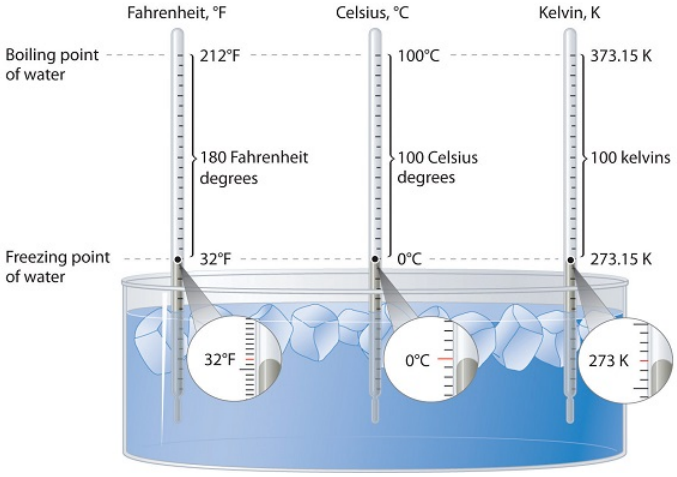


Figure 1.8.1: A Comparison of the Fahrenheit, Celsius, and Kelvin Temperature Scales. Because the difference between the freezing point of water and the boiling point of water is 100° on both the Celsius and Kelvin scales, the size of a degree Celsius (°C) and a kelvin (K) are precisely the same. In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

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

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

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

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)

5527 °C, 9980 °F

Answer (b)

2807 °C, 5084 °F

Answer (c)

-195.8 °C, -320.4 °F

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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CHAPTER OVERVIEW

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

Thumbnail: Spinning Buckminsterfullerene (C_{60}). (CC BY-SA 3.0; unported; Sponk).

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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.

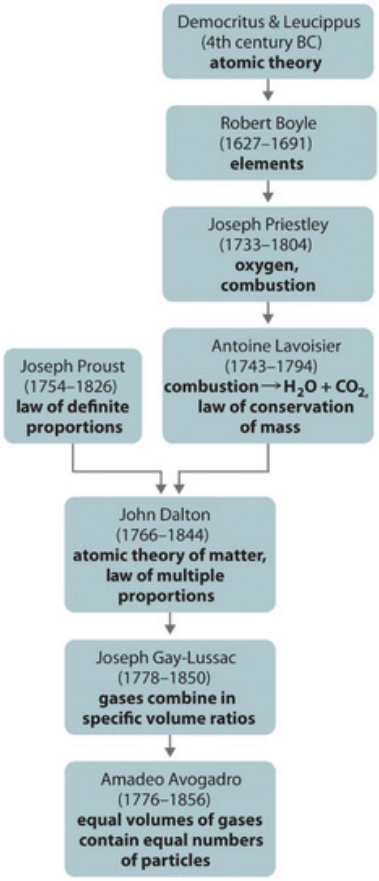


Figure **2.2.1**: A summary of the historical development of the concept of the atom.

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.

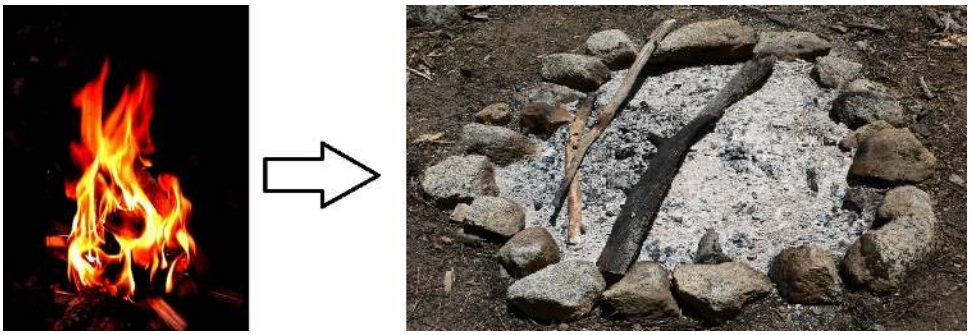


Figure **2.2.2**: Burning is a chemical process. The flames are caused as a result of a fuel undergoing combustion (burning). Images used with permission (CC BY-SA 2.5; Einar Helland Berger for fire and for ash).

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.

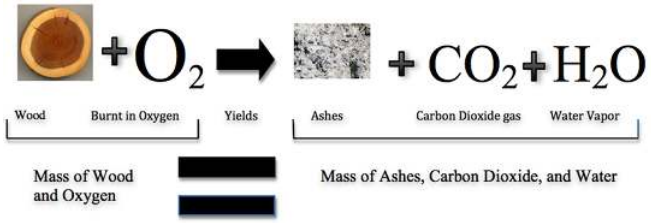


Figure **2.2.3**: Image of the wood courtesy of Ehamberg and Stannered on Wikimedia Commons, available under Creative Commons Attribution 2.5 Generic license. Image of ashes courtesy of Walter Siegmund. Image as a whole constructed by Jessica Thornton (UCD).

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.



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

276.4 g of potassium carbonate

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.

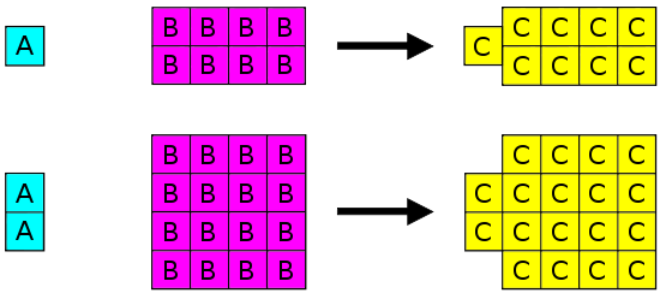


Figure 2.2.4: If 1 gram of A reacts with 8 grams of B, then by the Law of Definite Proportions, 2 grams of A must react with 16 grams of B. If 1 gram of A reacts with 8 grams of B, then by the Law of Conservation of Mass, they must produce 9 grams of C. Similarly, when 2 grams of A react with 16 grams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



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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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).

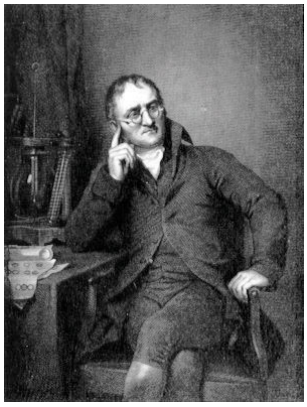


Figure **2.3.1**: John Dalton was an English scientist who enunciated the modern atomic theory.

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.

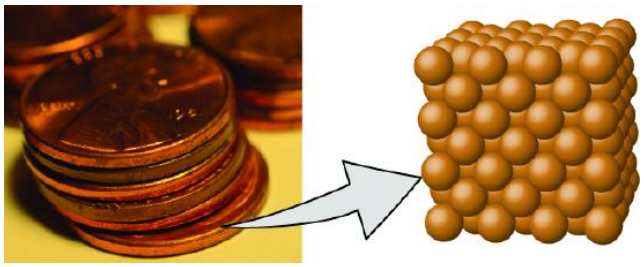


Figure **2.3.2**: A pre-1982 copper penny (left) contains approximately 3×10^{22} copper atoms (several dozen are represented as brown spheres at the right), each of which has the same chemical properties. (Credit: modification of work by “slgckgc”/Flickr.)

- 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.

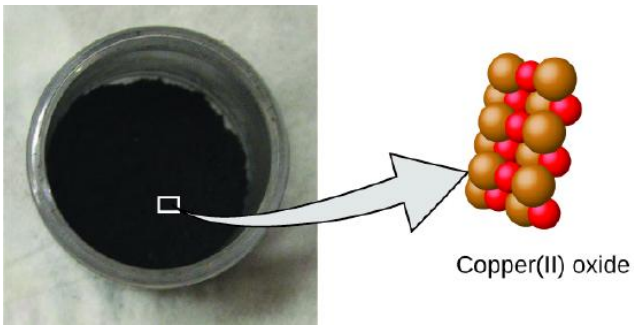


Figure **2.3.3**: Copper(II) oxide, a powdery, black compound, results from the combination of two types of atoms—copper (brown spheres) and oxygen (red spheres)—in a 1:1 ratio. (Credit: modification of work by “Chemicalinterest”/Wikimedia Commons.)

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.

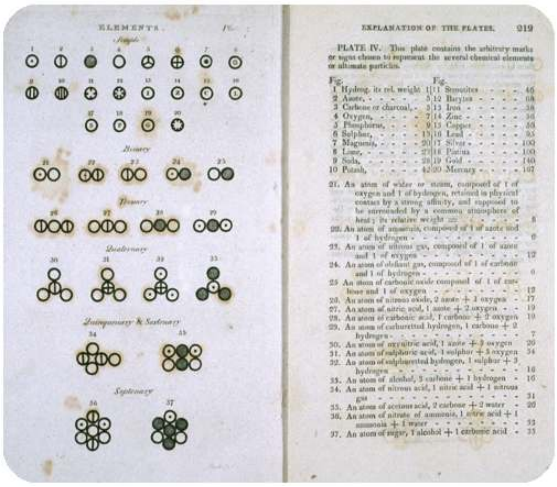


Figure **2.3.5** Dalton's symbols from his text "A New System of Chemical Philosophy."

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

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.

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.

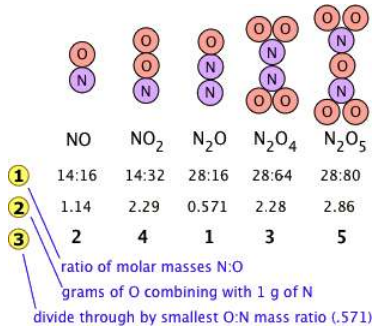


Figure **2.3.6**: Law of Multiple Proportions applied to nitrogen oxides (NO_x) compounds. (CC-BY; Stephen Lower.)

- 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 $(1 \times 14) : (2 \times 16) = 14:32$. (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.*



***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

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.

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.



***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.

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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 H_2, N_2, O_2, F_2, Cl_2, Br_2, and I_2. The representative particle for these elements is the molecule. Likewise, all molecular compounds such as H_2O and CO_2 exist as molecules, and so the molecule is their representative particle. For ionic compounds such as NaCl and $Ca(NO_3)_2$, the representative particle is the formula unit. A mole of any substance contains Avogadro's number (6.02×10^{23}) 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 atoms is 4.72×10^{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
Prepare a concept map and use the proper conversion factor.	# C atoms → mol C $\frac{1\ mol\ C}{6.022 \times 10^{23} C\ atoms}$
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 greater than 1 mole. Since Avogadro's number is a measured quantity with three significant figures, the result of the calculation is 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 ($\mathbf{CaCl_2}$). 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 $\mathbf{CaCl_2}$ 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 ($CaCl_2$).

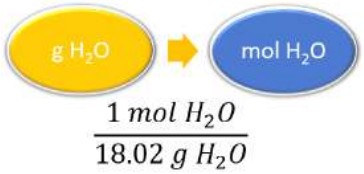
Steps for Problem Solving	Calculate the mass of 3.00 moles of calcium chloride ($CaCl_2$).
Identify the "given" information and what the problem is asking you to "find."	Given: 3.00 moles of $CaCl_2$ Find: g $CaCl_2$
List other known quantities.	1 ml $CaCl_2$ = 110.98 g $CaCl_2$
Prepare a concept map and use the proper conversion factor.	mol $CaCl_2$ → g $CaCl_2$ $\frac{110.98\ g\ CaCl_2}{1\ mol\ CaCl_2}$
Cancel units and calculate.	$3.00\ \cancel{mol\ CaCl_2} \times \frac{110.98\ g\ CaCl_2}{1\ \cancel{mol\ CaCl_2}} = 333\ g\ CaCl_2$
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.	$1\ mol\ H_2O = 18.02\ g\ H_2O$
Prepare a concept map and use the proper conversion factor.	 $\frac{1\ mol\ H_2O}{18.02\ g\ H_2O}$
Cancel units and calculate.	$108\ \cancel{g\ H_2O} \times \frac{1\ mol\ H_2O}{18.02\ \cancel{g\ H_2O}} = 5.99\ mol\ H_2O$
Think about your result.	

? Exercise 2.4.1: Nitrogen Gas

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

Answer:

210 g

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.

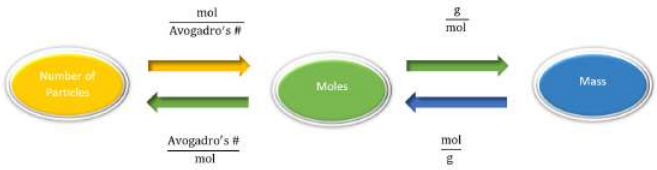


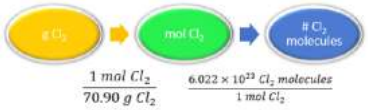
Figure 2.4.4: Conversion from number of particles to mass, or from mass to number of particles, requires two steps. To convert from number of particles to moles, use mol/Avogrado's #, and to convert from moles to mass, use g/mol.

✓ Example 2.4.4: Chlorine

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

Solution

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

Steps for Problem Solving	How many molecules is 20.0 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.	$20.0\ \cancel{g\ Cl_2} \times \frac{1\ \cancel{mol\ Cl_2}}{70.90\ \cancel{g\ Cl_2}} \times \frac{6.02 \times 10^{23}\ molecules\ Cl_2}{1\ \cancel{mol\ Cl_2}} = 1.70 \times 10^{23}\ molecules\ Cl_2$
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:

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

Summary

- A mole of any substance contains Avogadro's number (6.02×10^{23}) 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

-
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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.

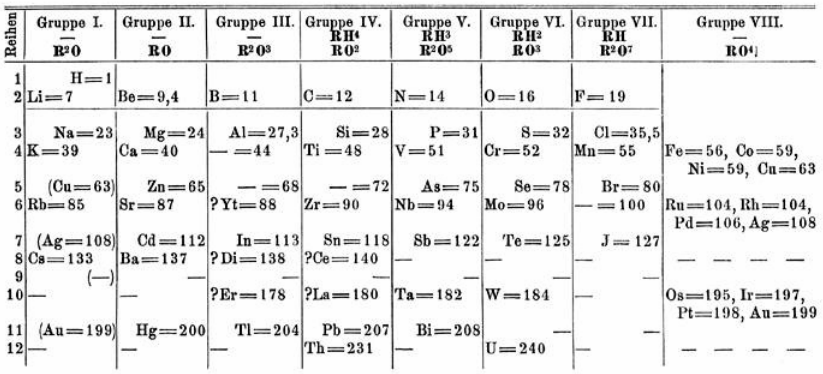
By the mid-19th century, the atomic masses of many of the elements had been determined. Scientists like John Newlands and Alexandre-Emile Béguyer de Chancourtois formed their own versions of periodic tables. The English chemist John Newlands (1838–1898), who hypothesized that the chemistry of the elements 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. $\frac{}{R^2O}$	Gruppe II. $\frac{}{RO}$	Gruppe III. $\frac{}{R^2O^3}$	Gruppe IV. $\frac{RH^4}{RO^2}$	Gruppe V. $\frac{RH^3}{R^2O^5}$	Gruppe VI. $\frac{RH^2}{RO^3}$	Gruppe VII. $\frac{RH}{R^2O^7}$	Gruppe VIII. $\frac{}{RO^4}$
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.



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
	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.

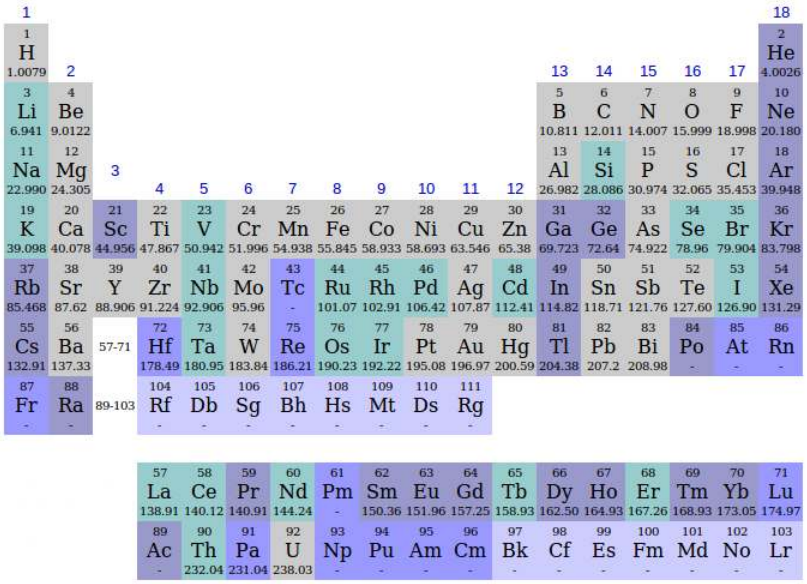


Figure **2.5.2** *Periodic table showing when each element was discovered*

- 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.

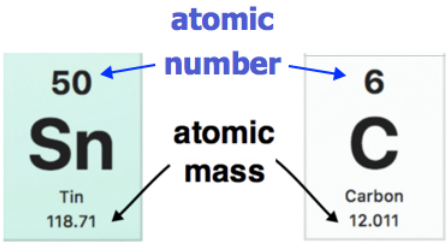


Figure **2.5.3**: Key information of an element indicated on entries of the Periodic Table. (public Domain; Pubchem)

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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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.

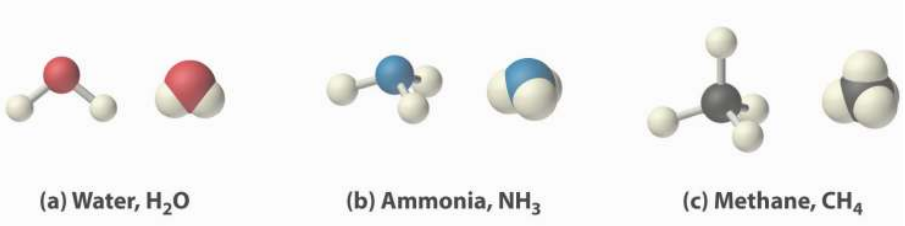
A **molecule** is an electrically neutral group of two or more atoms held together by chemical bonds. Molecules are distinguished from ions by their lack of electrical charge. However, in quantum physics, organic chemistry, and biochemistry, the term *molecule* is often used less strictly—as it is also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



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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CHAPTER OVERVIEW

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

Thumbnail: Electron shell diagram for Sodium, the 19th element in the periodic table of elements. (CC BY-SA; 2.5; Pumbaa).

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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.

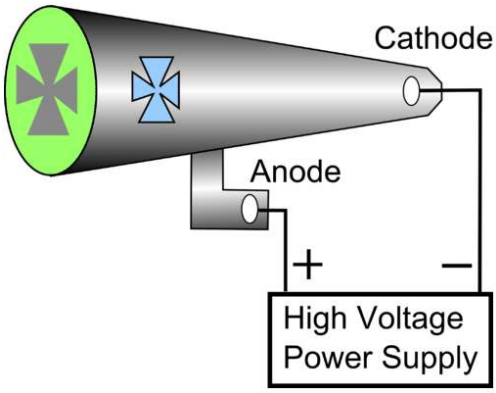


Picture of cathode ray tube monitor

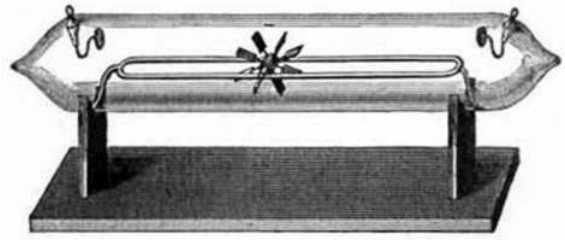
The first cathode ray tube prototype was developed by Heinrich Geissler, a German glassblower and physicist. He used a mercury pump to create a vacuum in a tube. Geissler explored a number of techniques to remove air from the tube and to prevent leaks, as well as ways to get good connections of the wires 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.

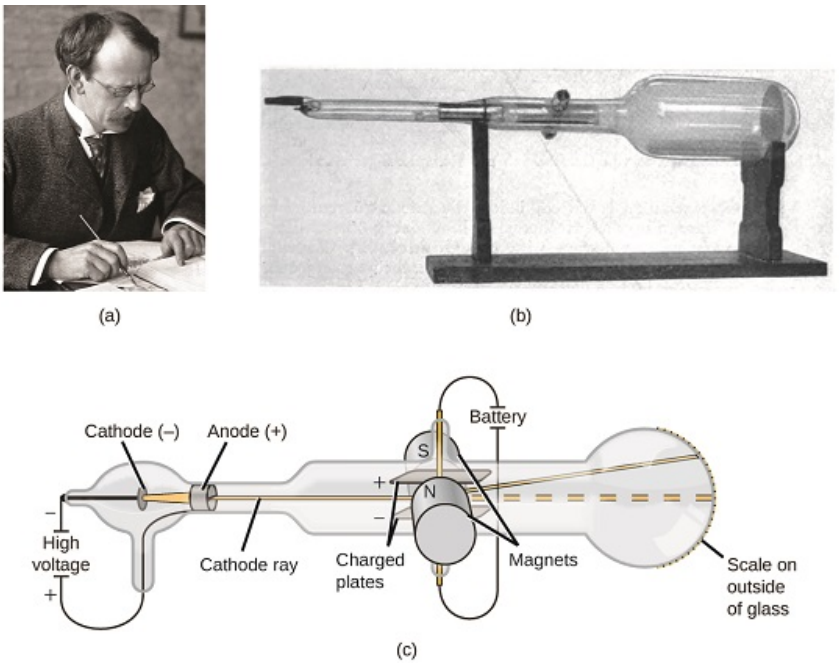


Figure **3.1.1** (a) J. J. Thomson produced a visible beam in a cathode ray tube. (b) This is an early cathode ray tube, invented in 1897 by Ferdinand Braun. (c) In the cathode ray, the beam (shown in yellow) comes from the cathode and is accelerated past the anode toward a fluorescent scale at the end 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).

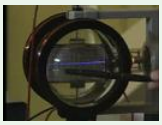
Cathode ray tube



***Video* 3.1.1** *A cathode ray tube.*

Thomson's experiment

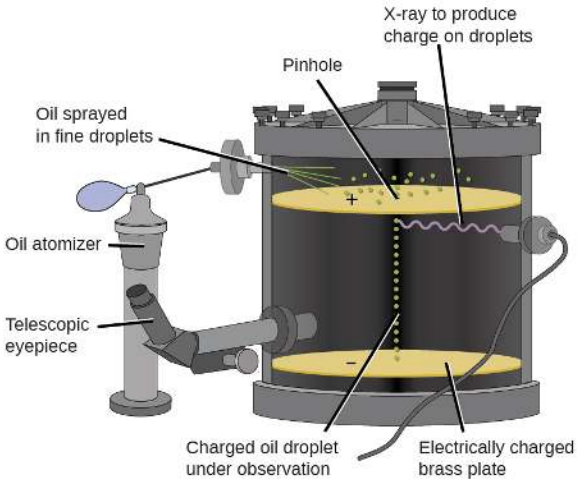




from Davidson College demonstrating Thompson's e/m experiment. You can also use an applet from the ysics Flash to simulate the experiment and here is another applet, from Kings Center for Visual Exploration in Alberta (KCVE) with a detailed explanation

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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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 electron 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.

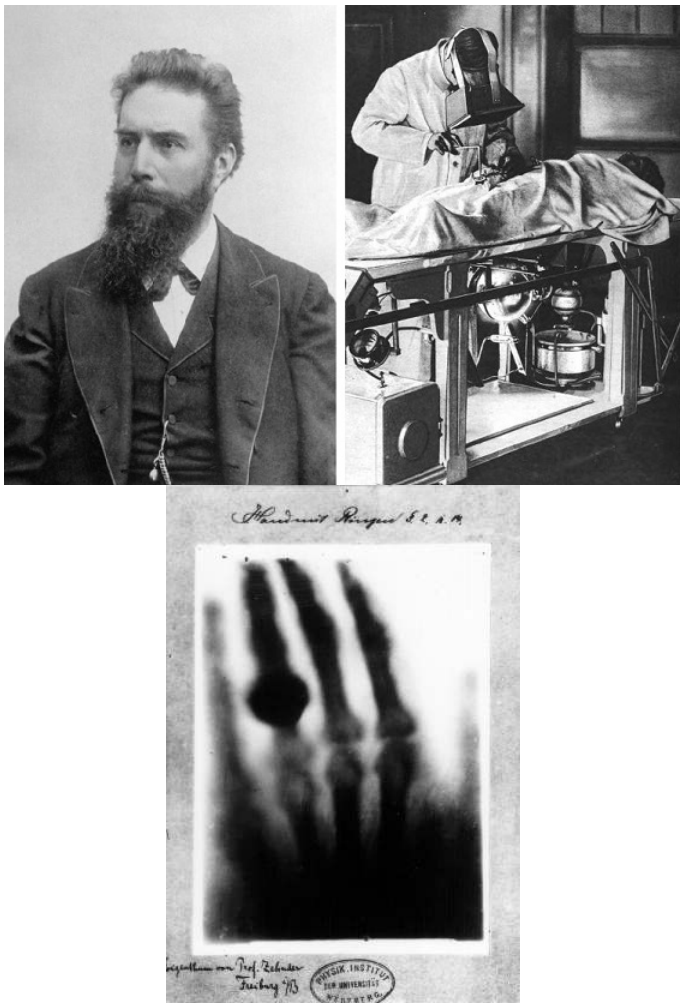


Figure 3.2.1

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 …"

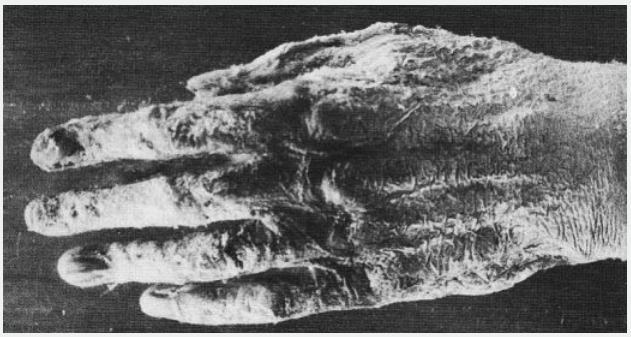


Figure **3.2.3**: Radiation poisoning due to over exposure of x-rays.

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

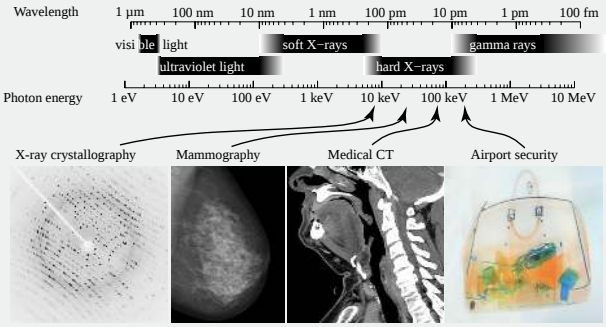


Figure **3.2.4**: X-rays are part of the electromagnetic spectrum, with wavelengths shorter than visible light.

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 g** of a previously unknown element, radium, in the form of the compound radium chloride. This radium was many times more radioactive than uranium.

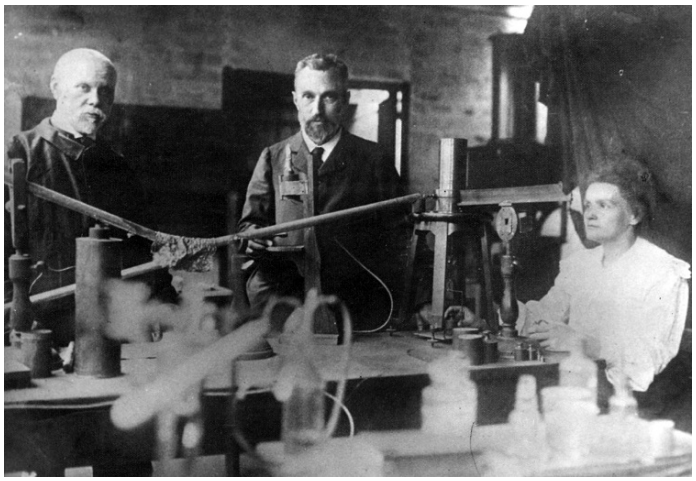


Figure **3.2.6**: Marie (left) and Pierre Curie (middle) with Henri Becquerel (right) shared the 1903 Nobel Prize

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.



Video**3.2.2**: 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

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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.

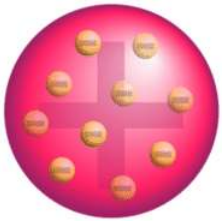


Figure **3.4.1** The "plum pudding" model.

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.

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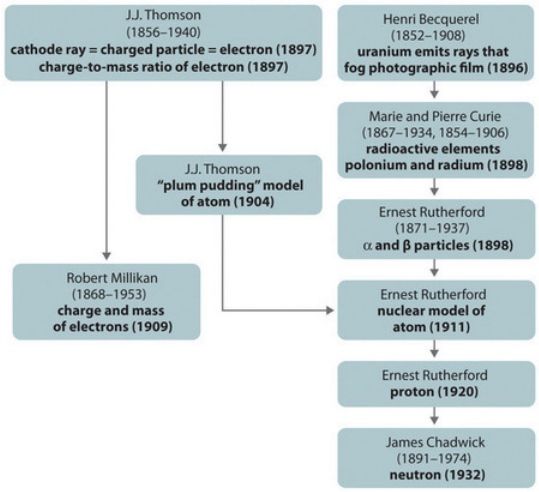
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3.5: The Atomic Nucleus

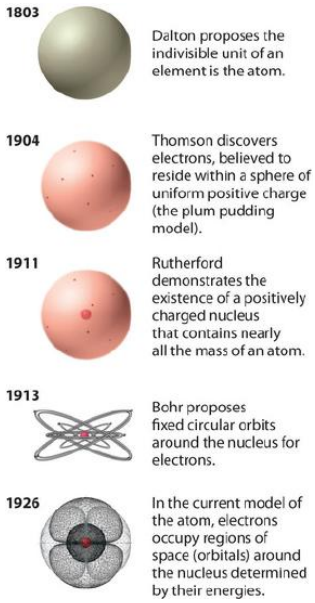
Learning Objectives

- 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.

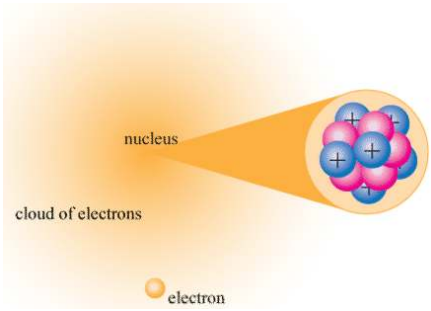


Figure **3.5.3** The nuclear atom

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

$1\ \text{amu} = 1.6605 \times 10^{-24}\ \text{g} = 1.6605 \times 10^{-27}\ \text{kg}$

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
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

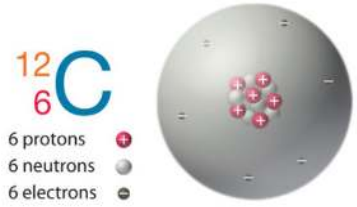
The **mass number** (A) of an atom is the total number of protons and neutrons in its nucleus. The mass of the atom is a unit called the atomic mass unit (**amu**). One atomic mass unit is the mass of a proton, or about 1.67×10^{-27} kilograms, which is an extremely small mass. A neutron has just a tiny 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 amu** for the protons + **2 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

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

$\textbf{(number of neutrons)} = \mathbf{2}$

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

$\textbf{mass number} = \mathbf{2 + 2 = 4}$

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.

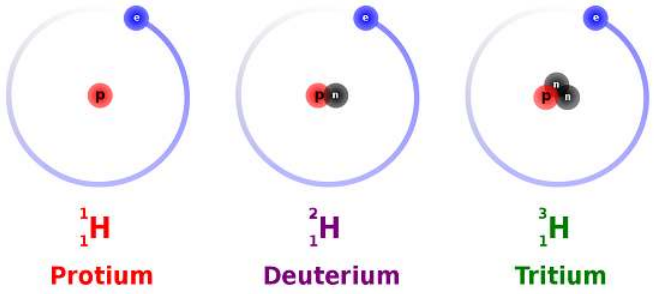


Figure **3.5.4**: The three most stable isotopes of hydrogen: protium (A = 1), deuterium (A = 2), and tritium (A = 3). (CC SA-BY 3.0; Balajijagadesh).

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

? 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

Atomic number = 50, mass number = 118

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

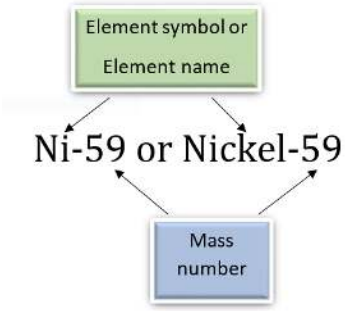
The following nuclear symbols are for a nickel nucleus with 31 neutrons and a uranium nucleus with 146 neutrons.

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

$^{238}_{92}U$

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 $^{40}_{19}K$?

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:

27 protons, 27 electrons, 33 neutrons

Answer b:

11 protons, 11 electrons, 13 neutrons

Answer c:

20 protons, 20 electrons, 25 neutrons

Answer d:

38 protons, 38 electrons, 52 neutrons

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

-
- 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: 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)

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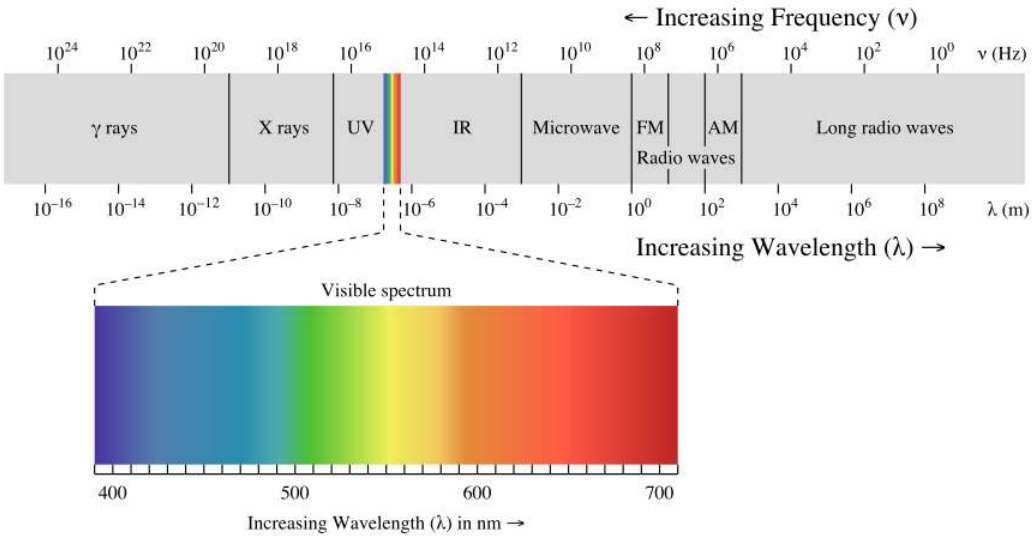
3.6: Electron Arrangement- The Bohr Model (Orbits)

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.

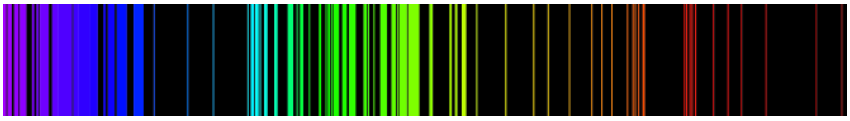


Figure **3.6.4** Atomic Emission Spectrum of Iron.

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.

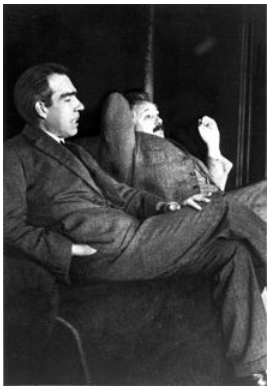
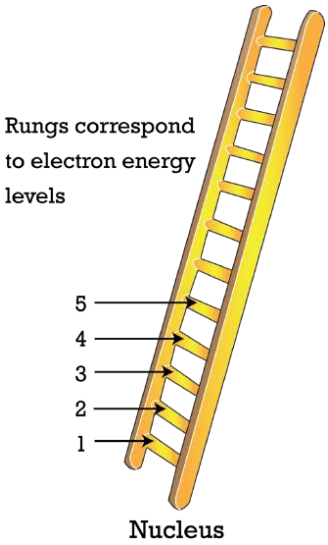


Figure* 3.6.5*: *Niels Bohr with Albert Einstein at Paul Ehrenfest's home in Leiden (December 1925).*



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.*

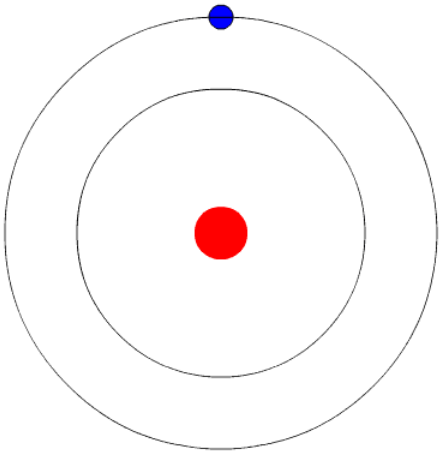


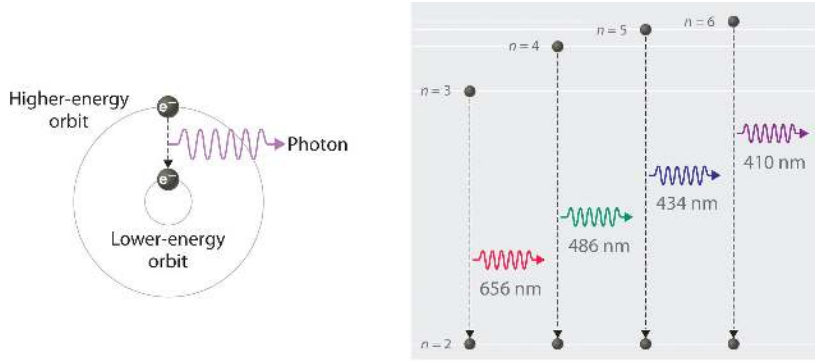
Figure **3.6.7** In Bohr's Model of the atom, electrons absorb energy to move to a higher level and release energy to move to lower levels. (CC BY-SA 3.0; Kurzon).

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).



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.

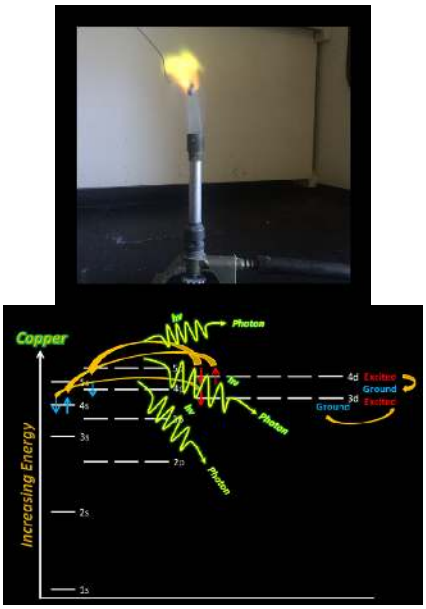


Figure 3.6.9 *(left): Copper is heated and as the electrons fall back, certain color of light is emitted. (right): Submicroscopic view of the electron movement, as electrons fall.*

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.

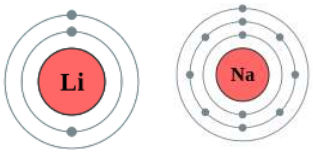


***Figure* 3.6.10** *A shell diagram of lithium (left) and Sodium (right)*

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



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

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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.

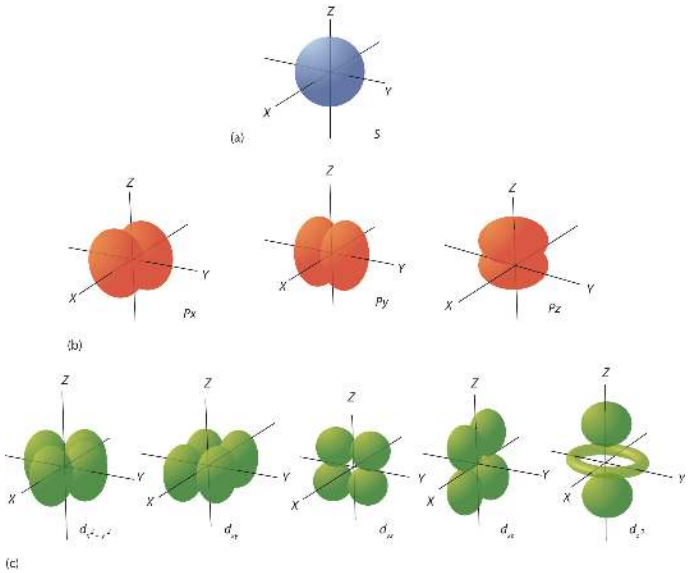


Figure **3.7.2**: Electron Orbitals. (a) The lone *s* orbital is spherical in distribution. (b) The three *p* orbitals are shaped like dumbbells, and each one points in a different direction. (c) The five *d* orbitals are rosette in shape, except for the *orbital, which is a "dumbbell + torus" combination.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

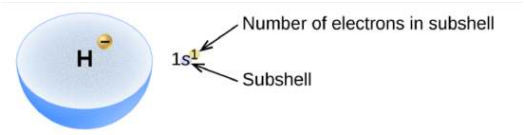
Table **3.7.1** Electron Arrangement Within Energy Levels

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
	3p	3 (3px 3py 3pz)	6
	3d	5 (refer to Figure **3.7.2***c*)	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	$1s^2 2s^2 2p^1$
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.

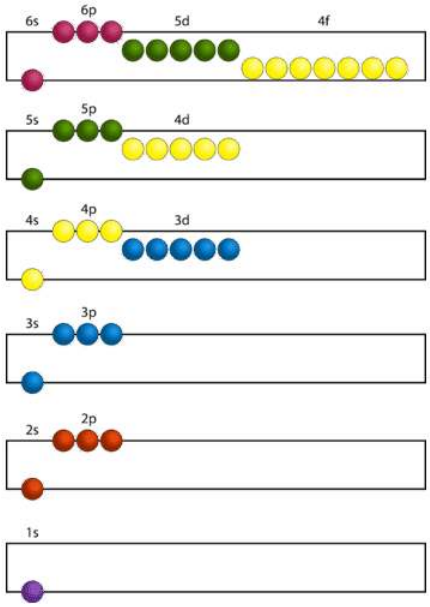


Figure **3.7.4**: Electrons are added to atomic orbitals in order from low energy (bottom of the graph) to high (top of the graph) according to the Aufbau principle. Principle energy levels are color coded, while sublevels are grouped together and each circle represents an orbital capable of holding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

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

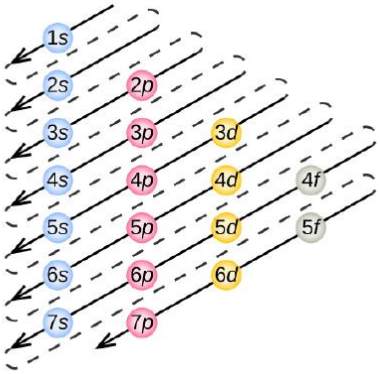


Figure **3.7.5** *The arrow leads through each subshell in the appropriate filling order for electron configurations. This chart is straightforward to construct. Simply make a column for all the s orbitals with each n shell on a separate row. Repeat for p, d, and f. Be sure to only include orbitals allowed 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 1*s* sublevel. **This gives $1s^2$**. Now all of the orbitals in the red $n = 1$ block are filled.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Remember, 4*s* comes before 3*d*!

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

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

Answer Na

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

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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- TextMap: Beginning Chemistry (Ball et al.)

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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**.

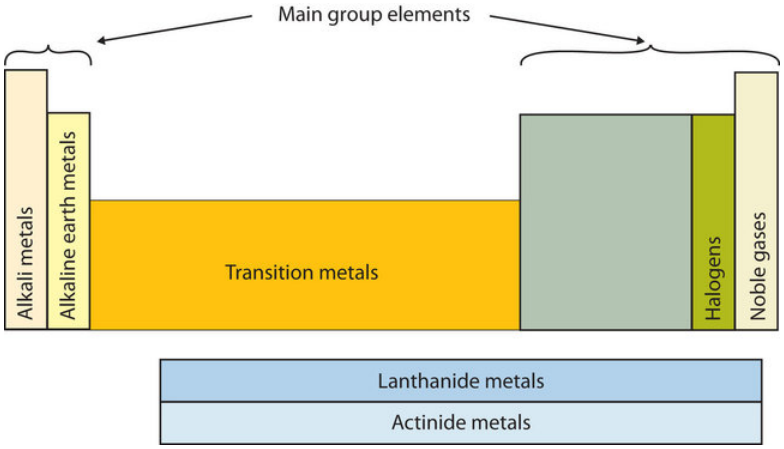


Figure **3.8.1**: Special names for sections of the periodic table.

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



***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:

Fluorine is a halogen (Group 17)

Answer b:

Calcium is a alkaline earth metal (Group 2)

Answer c:

Krypton is a noble gas (Group 18)

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.

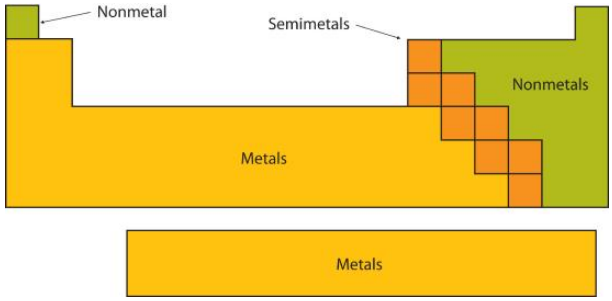


Figure **3.8.2**: Types of Elements. Elements are either metals, nonmetals, or metalloids (or semi metals). Each group is located in a different part of the periodic table.

✔ 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

Indium is a metal.

✔ 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:

Fluorine is a nonmetal.

Answer b:

Uranium is a metal (and a inner transition metal too)

Answer c:

Copper is a metal (and a transition metal too)

Alkali Metals



***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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1. Petrucci, Ralph H., William S. Harwood, F. G. Herring, and Jeffrey D. Madura. General Chemistry: Principles and Modern Applications. 9th ed. Upper Saddle River: Pearson Education, Inc., 2007.
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3. Petrucci, Ralph H., Carey Bissonnette, F. G. Herring, and Jeffrey D. Madura. General Chemistry: Principles and Modern Applications. Custom Edition for CHEM 2. Pearson Learning Solutions, 2010.

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CHAPTER OVERVIEW

4: Nuclear Chemistry

4.1: Natural Radioactivity
4.2: Nuclear Equations
4.3: Half-Life and Radioisotopic Dating
4.4: Artificial Transmutation
4.5: Uses of Radioisotopes
4.6: Penetrating Power of Radiation
4.7: Energy from the Nucleus
4.8: Nuclear Bombs
4.9: Uses and Consequences of Nuclear Energy

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4.1: 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* 4.1.1** *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 **4.1.1**).

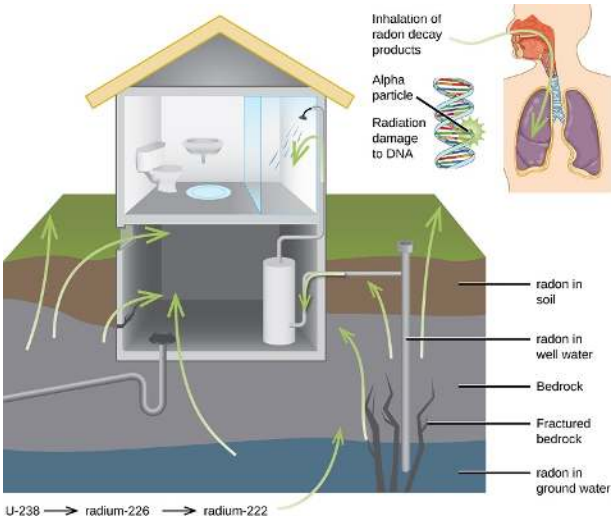


Figure **4.1.1**: Radon-222 seeps into houses and other buildings from rocks that contain uranium-238, a radon emitter. The radon enters through cracks in concrete foundations and basement floors, stone or porous cinderblock foundations, and openings for water and gas pipes.

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 **4.1.2**). 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.

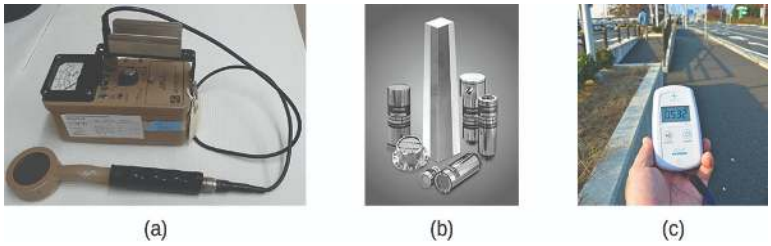


Figure **4.1.2**: Devices such as (a) Geiger counters, (b) scintillators, and (c) dosimeters can be used to measure radiation. (credit c: modification of work by "osaMu"/Wikimedia commons).

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 **4.1.3**).

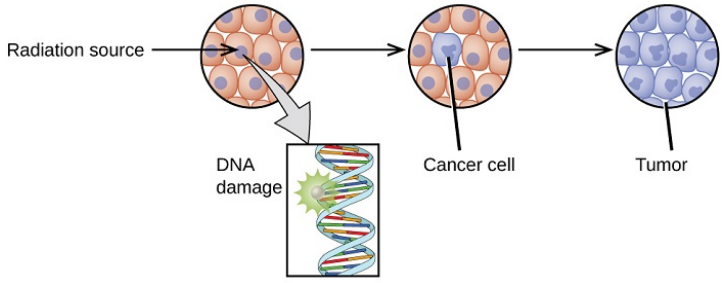


Figure **4.1.3**: Radiation can harm biological systems by damaging the DNA of cells. If this damage is not properly repaired, the cells may divide in an uncontrolled manner and cause cancer.

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 **4.1.4**).

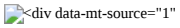


Figure **4.1.4**: Lower frequency, lower-energy electromagnetic radiation is nonionizing, and higher frequency, higher-energy electromagnetic radiation is ionizing.

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:

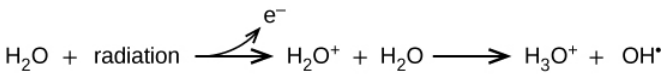


Figure **4.1.5**.

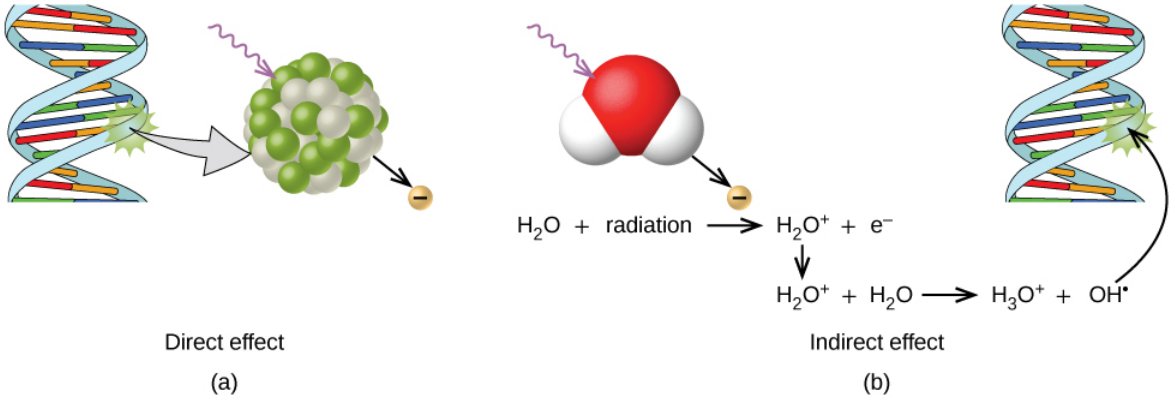


Figure **4.1.5**: Ionizing radiation can (a) directly damage a biomolecule by ionizing it or breaking its bonds, or (b) create an H_2O^+ ion, which reacts with H_2O to form a hydroxyl radical, which in turn reacts with the biomolecule, causing damage indirectly.

The effects of radiation depend on the type, energy, and location of the radiation source, and the length of exposure. As shown in Figure **4.1.6**, 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).

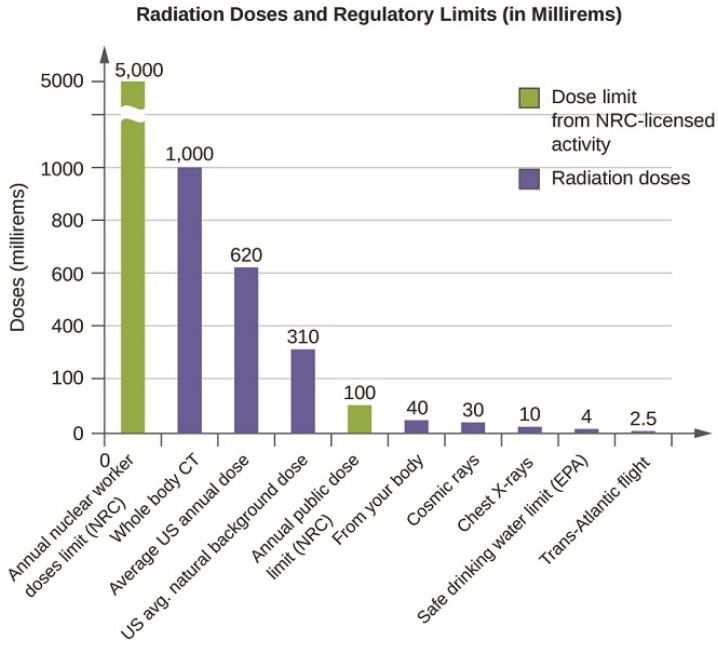


Figure **4.1.6** The total annual radiation exposure for a person in the US is about 620 mrem. The various sources and their relative amounts are shown in this bar graph. (source: U.S. Nuclear Regulatory Commission).

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 **4.1.2**.

Table **4.1.2** 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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4.2: 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 **4.2.1**.

Table **4.2.1** 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 **4.2.1** 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:

$$^{238}_{92}\text{U} \rightarrow {}^{234}_{90}\text{Th} + {}^{4}_{2}\alpha^{+}$$

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.

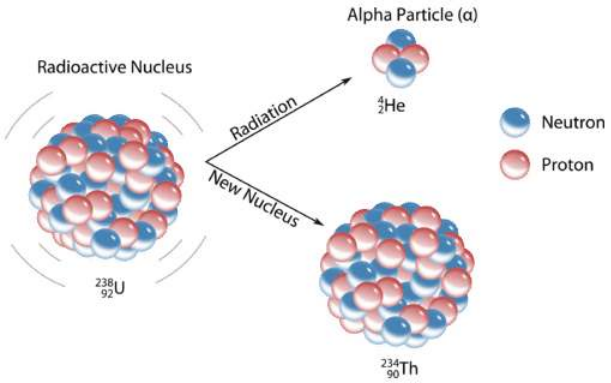


Figure 4.2.1 *Emission of an alpha particle from the nucleus.*

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,

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

is the parent isotope, and

$$^{234}_{90}\text{Th}$$

is the daughter isotope. When one element changes into another in this manner, it undergoes **radioactive decay**.

Example 4.2.1

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

$$^{222}_{86}\text{Rn}$$

We represent the alpha particle as

$$^{4}_{2}\text{He}$$

Use subtraction (222 − 4 = 218 and 86 − 2 = 84) to identify the daughter isotope as polonium:

$$^{222}_{86}\text{Rn} \rightarrow {}^{4}_{2}\text{He} + {}^{218}_{84}\text{Th}$$

Exercise 4.2.1

Write the nuclear equation that represents radioactive decay of polonium-208 by alpha particle emission and identify the daughter isotope.

Answer

$$^{208}_{80}\text{Po} \rightarrow {}^{4}_{2}\text{He} + {}^{204}_{82}\text{Pb}$$

$$^{204}_{82}\text{Pb}$$

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.

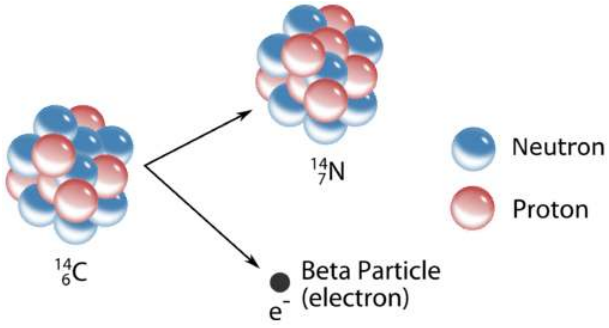


Figure 4.2.2 *Beta emission.*

A typical beta decay process involves carbon-14, often used in radioactive dating techniques. The reaction forms nitrogen-14 and an electron:

$$^{14}_{6}\text{C} \rightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}\text{e}$$

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 4.2.2

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 $^{4}_{2}\text{He}$

while one of the products is $^{0}_{-1}\text{e}$

So that the mass and atomic numbers have the same value on both sides, the mass number of the daughter isotope must be 12, and its atomic number must be 6. The element having an atomic number of 6 is carbon. Thus the complete nuclear equation is as follows:

$$^{12}_{5}\text{B} \rightarrow {}^{12}_{6}\text{C} + {}^{0}_{-1}\text{e} + \gamma$$

The daughter isotope is carbon-12.

? Exercise 4.2.2

Write the nuclear equation that represents the radioactive decay of rubidium-87 by beta particle emission and identify the daughter isotope.

Answer

$$^{87}_{37}\text{Rb} \rightarrow \ ^{87}_{38}\text{Sr} + ^{0}_{-1}\text{e}$$

$$^{87}_{38}\text{Sr}$$

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:

$$^{238}_{92}\text{U} \rightarrow \underset{\substack{\text{excited}\\ \text{nuclear}\\ \text{state}}}{^{234}_{90}\text{Th}^{*}} + ^{4}_{2}\alpha \xrightarrow{\text{relaxation}} ^{234}_{90}\text{Th} + ^{0}_{0}\gamma \tag{4.2.1}$$

If we disregard the decay event that created the excited nucleus, then

$$^{234}_{88}\text{Th}^{*} \rightarrow \ ^{234}_{88}\text{Th} + ^{0}_{0}\gamma \tag{4.2.2}$$

or more generally,

$$^{A}_{Z}\text{X}^{*} \rightarrow \ ^{A}_{Z}\text{X} + ^{0}_{0}\gamma \tag{4.2.3}$$

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:

$$^{11}_{6}\text{C} \rightarrow \ ^{11}_{5}\text{B} + \ ^{0}_{+1}\beta$$

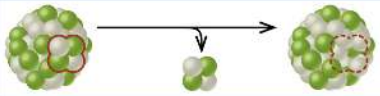
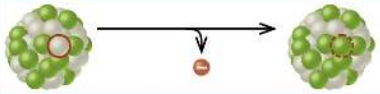
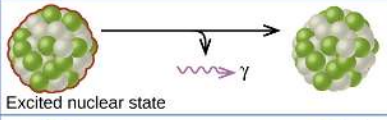
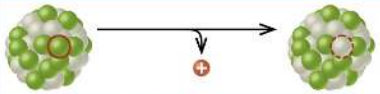
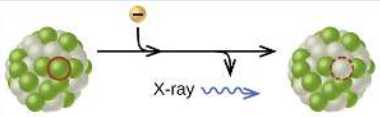
Electron Capture

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.

$$^{106}_{47}\text{Ag} + \ ^{0}_{-1}\text{e} \rightarrow \ ^{106}_{46}\text{Pd}$$

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 **4.2.2** Different Types of Decay and Changes in Atomic and Mass Numbers.

Type	Nuclear equation	Representation	Change in mass/atomic numbers
Alpha decay	${}^{A}_{Z}X \rightarrow {}^{4}_{2}He + {}^{A-4}_{Z-2}Y$		A: decrease by 4 Z: decrease by 2
Beta decay	${}^{A}_{Z}X \rightarrow {}^{0}_{-1}e + {}^{A}_{Z+1}Y$		A: unchanged Z: increase by 1
Gamma decay	${}^{A}_{Z}X \rightarrow {}^{0}_{0}\gamma + {}^{A}_{Z}Y$		A: unchanged Z: unchanged
Positron emission	${}^{A}_{Z}X \rightarrow {}^{0}_{+1}e + {}^{A}_{Y-1}Y$		A: unchanged Z: decrease by 1
Electron capture	${}^{A}_{Z}X + {}^{0}_{-1}e \rightarrow {}^{A}_{Y-1}Y$		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:

$$^{212}_{84}\text{Po} \longrightarrow {}^{208}_{82}\text{Pb} + {}^{4}_{2}\text{He}$$

- 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:

$$^{14}_{7}\text{N} + {}^{4}_{2}\alpha \longrightarrow {}^{17}_{8}\text{O} + {}^{1}_{1}\text{H}$$

- 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:

$$^{9}_{4}\text{Be} + {}^{4}_{2}\text{He} \longrightarrow {}^{12}_{6}\text{C} + {}^{1}_{0}\text{n}$$

- 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, $^{2}_{1}\text{H}$), by Emilio Segre and Carlo Perrier in 1937:

$$^{2}_{1}\text{H} + {}^{97}_{42}\text{Mo} \longrightarrow 2{}^{1}_{0}\text{n} + {}^{97}_{43}\text{Tc}$$

- 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:

$$^{235}_{92}\text{U} + {}^{1}_{0}\text{n} \longrightarrow {}^{87}_{35}\text{Br} + {}^{146}_{57}\text{La} + 3{}^{1}_{0}\text{n}$$

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.

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4.3: 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 **4.3.1**). 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.

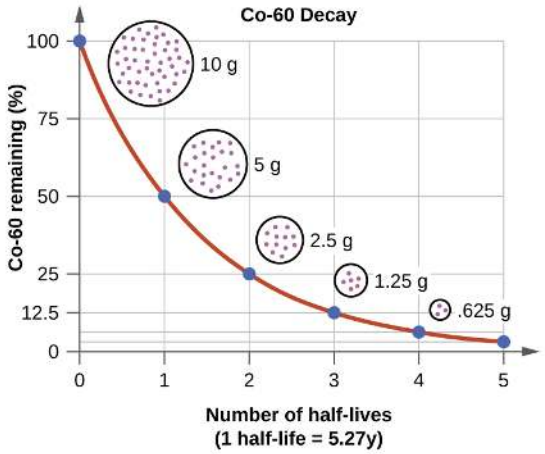


Figure **4.3.1** For cobalt-60, which has a half-life of 5.27 years, 50% remains after 5.27 years (one half-life), 25% remains after 10.54 years (two half-lives), 12.5% remains after 15.81 years (three half-lives), and so on.

We can determine the amount of a radioactive isotope remaining after a given number half-lives by using the following expression:

$$\textit{amount remaining} = \textit{initial amount} \times \left(\frac{1}{2}\right)^{n}$$

where *n* is the number of half-lives. This expression works even if the number of half-lives is not a whole number.

Example 4.3.1:

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:

$$\textit{amount remaining} = 5.00g \times \left(\frac{1}{2}\right)^{4}$$
$$\textit{amount remaining} = 5.00g \times \left(\frac{1}{16}\right)$$
$$\textit{amount remaining} = 0.313g$$

Less than one-third of a gram of fluorine-20 remains.

Exercise 4.3.1

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

0.0375 g

Example 4.3.2

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 g** of our original **60 g** sample would remain the radioactive isotope **Np**-240.

Exercise 4.3.2

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 $^{209}_{83}\mathrm{Bi}$ is 1.9×10^{19} years; $^{239}_{94}\mathrm{Ra}$ is 24,000 years; $^{222}_{86}\mathrm{Rn}$ 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 **4.3.1**: 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 **4.3.2**). In all three series, the end-product is a stable isotope of lead.

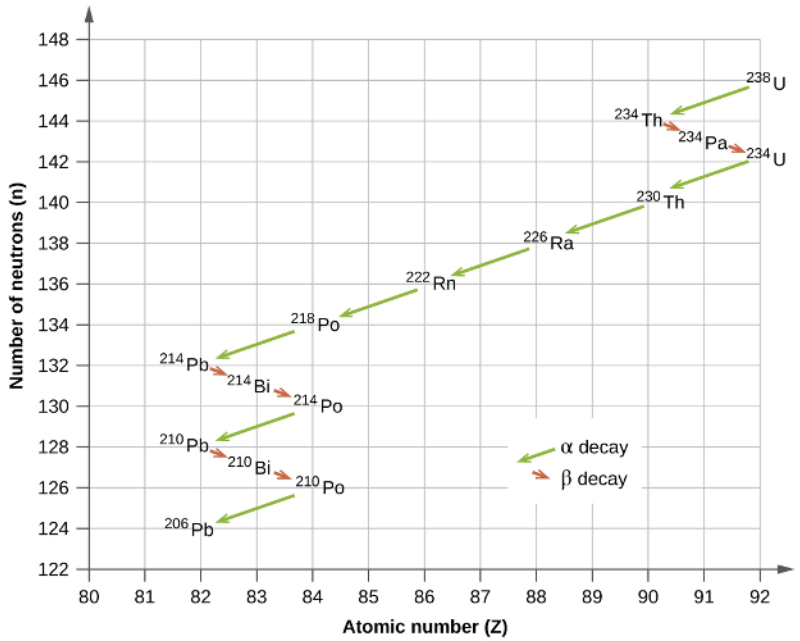


Figure **4.3.2** Uranium-238 undergoes a radioactive decay series consisting of 14 separate steps before producing stable lead-206. This series consists of eight α decays and six β decays.

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 $^{14}_{6}\text{C}$ being 5730 years, if the $^{14}_{6}\text{C}:\ ^{12}_{6}\text{C}$ 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.

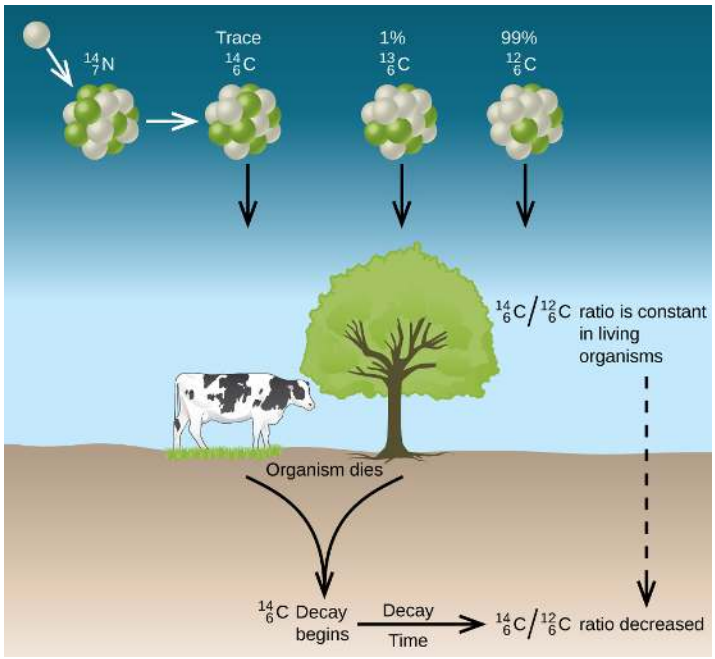


Figure **4.3.3**: Along with stable carbon-12, radioactive carbon-14 is taken in by plants and animals, and remains at a constant level within them while they are alive. After death, the C-14 decays and the C-14:C-12 ratio in the remains decreases. Comparing this ratio to the C-14:C-12 ratio in living 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 4.3.3

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.

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



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.

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:

$$\textit{amount remaining} = \textit{initial amount} \times \left(\frac{1}{2}\right)^n$$

  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

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4.4: 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 **4.4.1**). 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 **4.4.1**: 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:

$$^{238}_{92}\text{U} + ^{1}_{0}\text{n} \longrightarrow ^{239}_{92}\text{U} \tag{4.4.1}$$

$$^{239}_{92}\text{U} \longrightarrow ^{239}_{93}\text{Np} + ^{0}_{-1}\text{e} \quad t_{\frac{1}{2}} \quad \text{half-life} = 23.5\ \text{min} \tag{4.4.2}$$

$$^{239}_{93}\text{Np} \longrightarrow ^{239}_{94}\text{Pu} + ^{0}_{-1}\text{e} \quad t_{\frac{1}{2}} \quad \text{half-life} = 2.36\ \text{days} \tag{4.4.3}$$

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:

$$^{238}_{92}\text{U} + ^{1}_{0}\text{n} \longrightarrow ^{239}_{92}\text{U} \xrightarrow{\beta^-} ^{239}_{93}\text{Np} \xrightarrow{\beta^-} ^{239}_{94}\text{Pu}$$

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 **4.4.1**.

Table **4.4.1** Preparation of Some of the Transuranium Elements

Name	Symbol	Atomic Number	Reaction
americium	Am	95	$^{239}_{94}\text{Pu} + ^{1}_{0}\text{n} \longrightarrow ^{240}_{95}\text{Am} + ^{0}_{-1}\text{e}$
curium	Cm	96	$^{239}_{94}\text{Pu} + ^{4}_{2}\text{He} \longrightarrow ^{242}_{96}\text{Cm} + ^{1}_{0}\text{n}$
californium	Cf	98	$^{242}_{96}\text{Cm} + ^{4}_{2}\text{He} \longrightarrow ^{245}_{98}\text{Cf} + ^{1}_{0}\text{n}$
einsteinium	Es	99	$^{238}_{92}\text{U} + 15\,^{1}_{0}\text{n} \longrightarrow ^{253}_{99}\text{Es} + 7\,^{0}_{-1}\text{e}$
mendelevium	Md	101	$^{253}_{99}\text{Es} + ^{4}_{2}\text{He} \longrightarrow ^{256}_{101}\text{Md} + ^{1}_{0}\text{n}$
nobelium	No	102	$^{246}_{96}\text{Cm} + ^{12}_{6}\text{C} \longrightarrow ^{254}_{102}\text{No} + 4\,^{1}_{0}\text{n}$
rutherfordium	Rf	104	$^{249}_{98}\text{Cf} + ^{12}_{6}\text{C} \longrightarrow ^{257}_{104}\text{Rf} + 4\,^{1}_{0}\text{n}$
seaborgium	Sg	106	$^{206}_{82}\text{Pb} + ^{54}_{24}\text{Cr} \longrightarrow ^{257}_{106}\text{Sg} + 3\,^{1}_{0}\text{n}$ $^{249}_{98}\text{Cf} + ^{18}_{8}\text{O} \longrightarrow ^{263}_{106}\text{Sg} + 4\,^{1}_{0}\text{n}$
meitnerium	Mt	107	$^{209}_{83}\text{Bi} + ^{58}_{26}\text{Fe} \longrightarrow ^{266}_{109}\text{Mt} + ^{1}_{0}\text{n}$

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.

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4.5: 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:

$$6\,CO_2(g) + 6\,H_2O(l) \longrightarrow C_6H_{12}O_6(s) + 6\,O_2(g),$$

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 $^{14}_{6}C$. 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 **4.5.1** The preservation of strawberries with Ionizing Radiation.

In the fall of 2001, anthrax laced letters *(*Figure **4.5.2**) 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 **4.5.2** 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 **4.5.3**). 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.

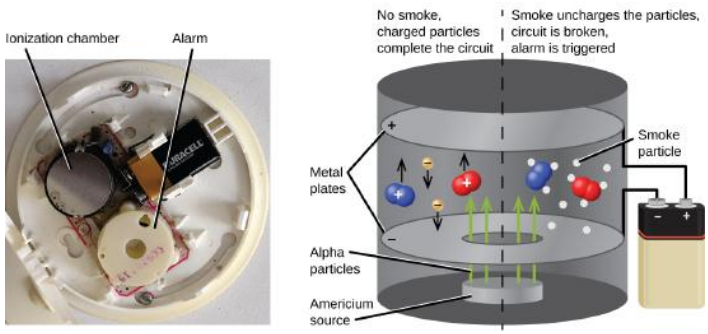


Figure **4.5.3** Inside a smoke detector, Am-241 emits α particles that ionize the air, creating a small electric current. During a fire, smoke particles impede the flow of ions, reducing the current and triggering an alarm. (credit a: modification of work by "Muffet"/Wikimedia Commons)

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 **4.5.4**). 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.

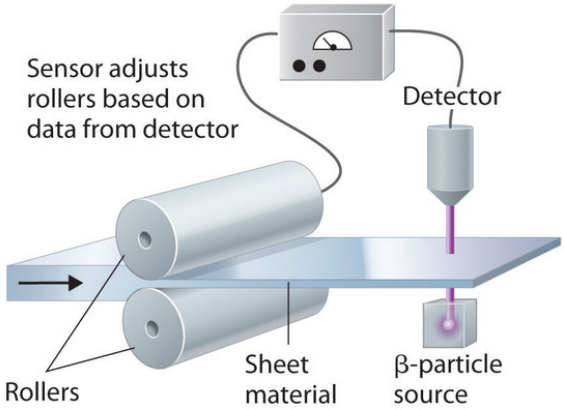


Figure **4.5.4** Using radiation to control the thickness of a material. Because the amount of radiation absorbed by a material is proportional to its thickness, radiation can be used to control the thickness of plastic film, tin foil, or paper. As shown, a beta emitter is placed on one side of the material 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



***Video* 4.5.1** *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

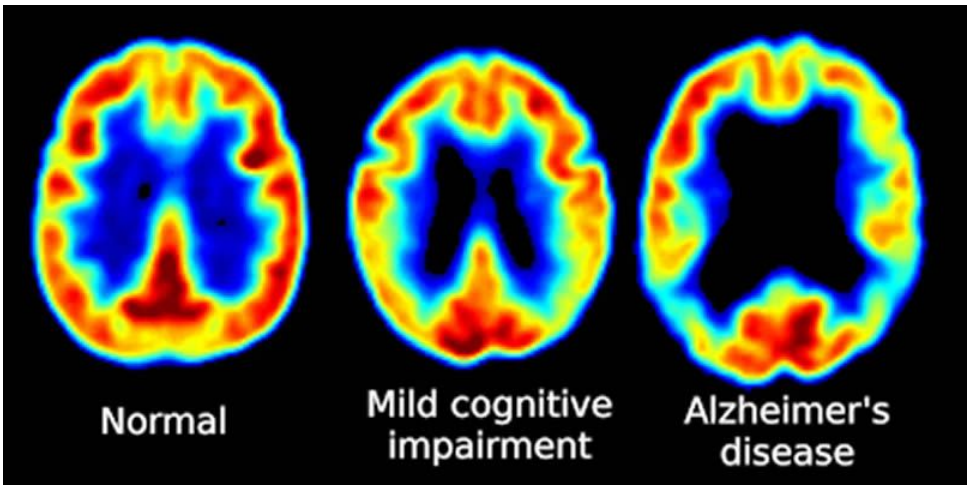


Figure **4.5.5** Mild cognitive impairment (MCI) is a state between normal ageing and dementia, where someone's mind is functioning less well than would be expected for their age. This image is for illustrative purposes only. (Public Domain; Center For Functional Imaging, Lawrence Berkeley National Laboratory. Alzheimer's Disease Neuroimaging Initiative (ADNI).

PET Scanning, is used to image the physiological aspects of the body rather than the anatomy (Figures **4.5.5** and **4.5.6**). 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.

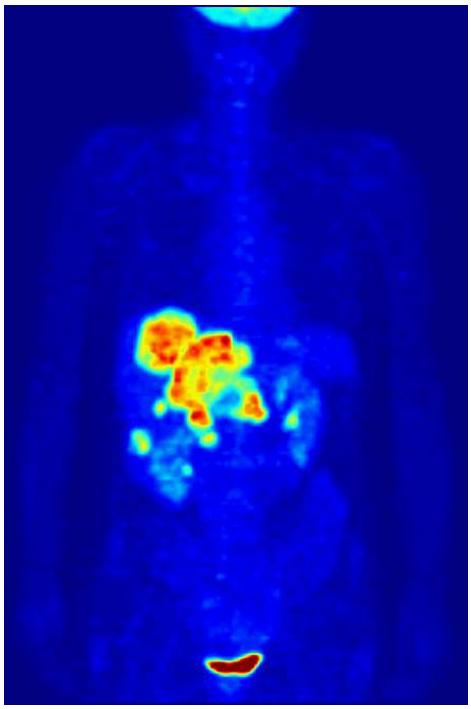


Figure 4.5.6 A whole body analysis by a PET scan. (Public Domain; Jens Maus, http://jens-maus.de/)

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 ($^{99}_{43}Tc$), thallium-201 ($^{201}_{81}Tl$), iodine-131 ($^{131}_{53}I$), and sodium-24 ($^{24}_{11}Na$). 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 4.5.7) 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 4.5.7 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 "Blue0ctane"/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 **4.5.1**. 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 **4.5.1** 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

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 4.5.8 *(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



***Video* 4.5.2** *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.



***Video*4.5.3** *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.

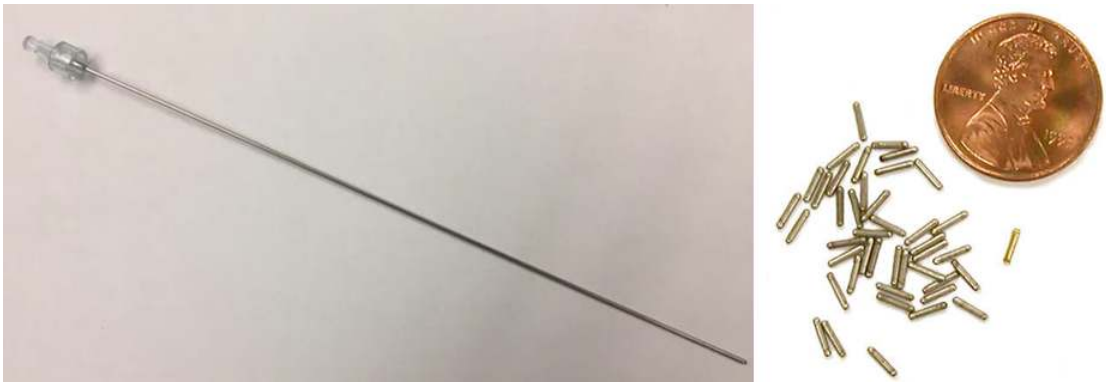


Figure **4.5.9** The picture on the left shows a brachytherapy rod. This device would be connected to a gamma source and connected inside a human body. The second images shows radioactive pellets or seeds that can be surgically implanted near a tumor. Note how small the pellets are when compared to an 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 **4.5.2** list commonly used radionuclides for brachtherapy.

Table **4.5.2** 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 **4.5.10**) and phenergan can help with nausea. Special mouthwashes have been formulated to reduce dry mouth and cavities.

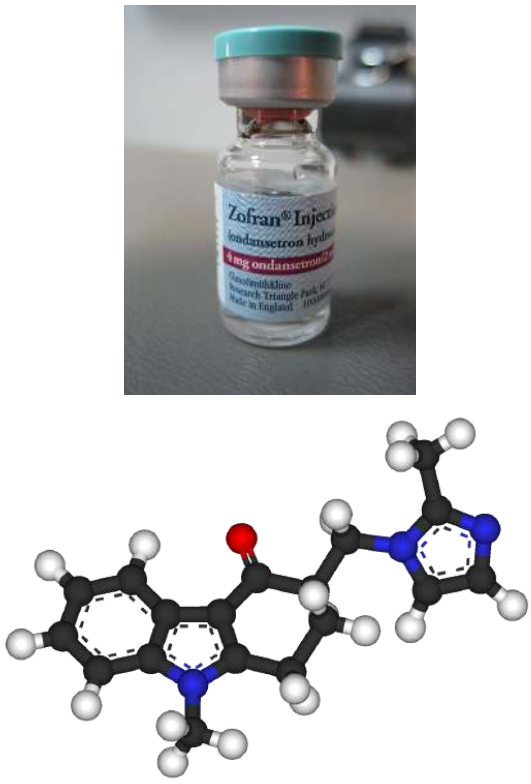


Figure **4.5.10**(left) *Zofran is a medication used to prevent nausea and vomiting caused by cancer chemotherapy, radiation therapy, or surgery. (right) A vial of Zofran 4 mg containing ondansetron for intravenous injection. This medicine is a controlled substance and is used for nausea. Images used 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.

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4.6: 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.

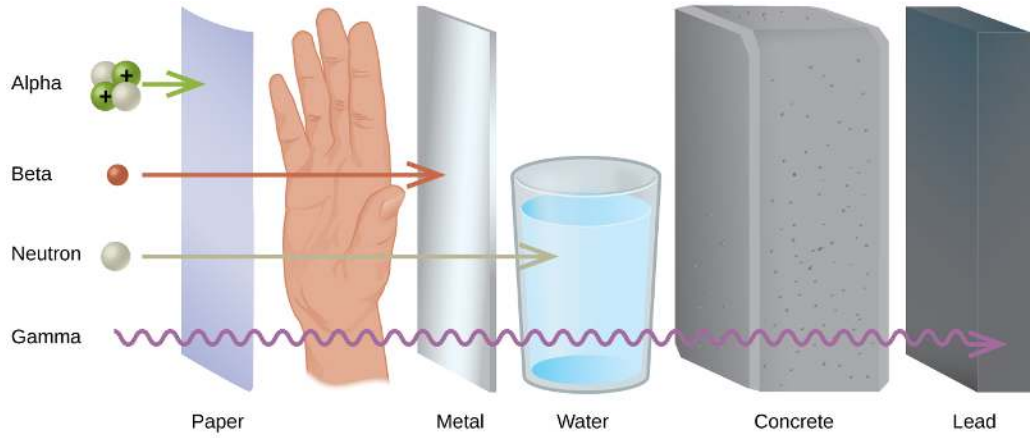


Figure **4.6.1**: The ability of different types of radiation to pass through material is shown. From least to most penetrating, they are alpha < beta < neutron < gamma. (CC BY-SA 4.0; OpenStax).

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 **4.6.1**.

Table **4.6.1** 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	1/2000amu	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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4.7: 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 4.7.1 illustrates the difference between nuclear fission and nuclear fusion.

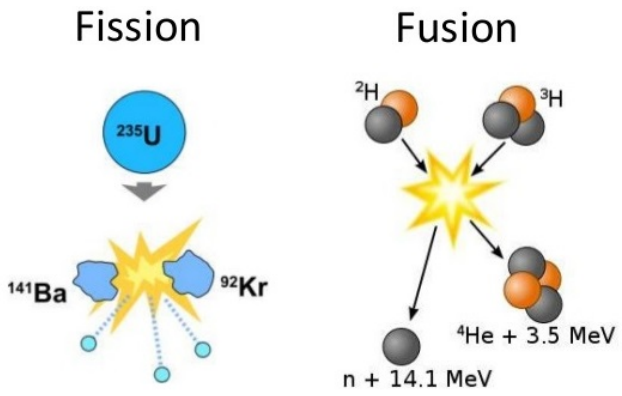


Figure 4.7.1 Nuclear fission occurs with one large nuclear is split into two or more smaller nuclei (left) . Nuclear fusion happens when two small nuclei combine to make a larger nucleus (right) .

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:

$$^{235}_{235.0439}\text{U} \rightarrow ^{139}_{138.9088}\text{Ba} + ^{94}_{93.9343}\text{Kr} + ^{2^1}_{2\times1.0087}\text{n}$$

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.

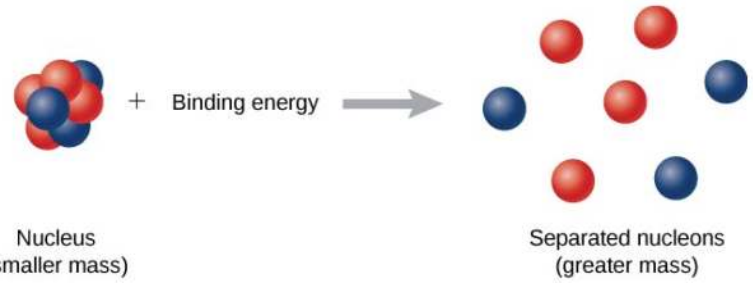


Figure **4.7.2** *The binding energy is the energy required to break a nucleus into its constituent protons and neutrons. A system of separated nucleons has a greater mass than a system of bound nucleons.*

As shown in figure **4.7.2**, 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

$$E_b = (\Delta m)c^2. \tag{4.7.1}$$

In nuclear physics, one of the most important experimental quantities is the *binding energy per nucleon (BEN)*, which is defined by

$$BEN = \frac{E_b}{A} \tag{4.7.2}$$

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 **4.7.3** 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-.

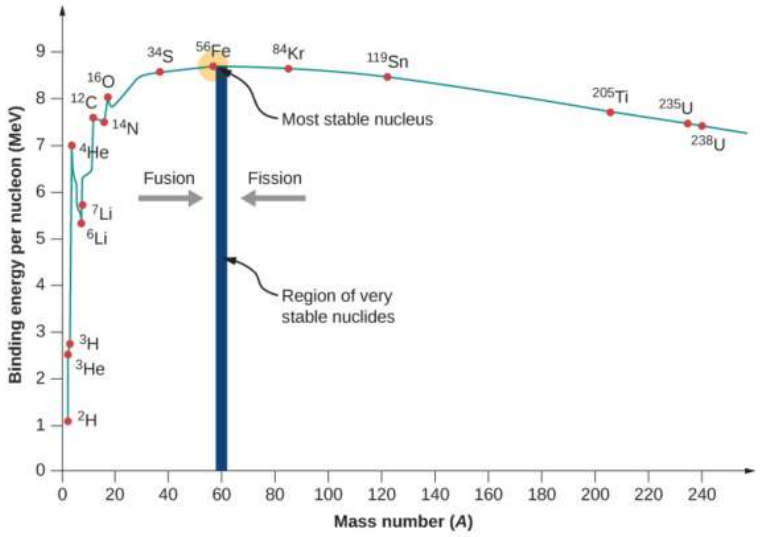


Figure **4.7.3** In this graph of binding energy per nucleon for stable nuclei, the BEN is greatest for nuclei with a mass near ^{56}Fe. Therefore, fusion of nuclei with mass numbers much less than that of Fe, and fission of nuclei with mass numbers greater than that of Fe, are exothermic processes. (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 **4.7.3** 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 **4.7.4**) and her nephew Otto Robert Frisch. Frisch named the process "fission" by analogy with biological fission of living cells.

Figure **4.7.4** *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 **4.7.5**.

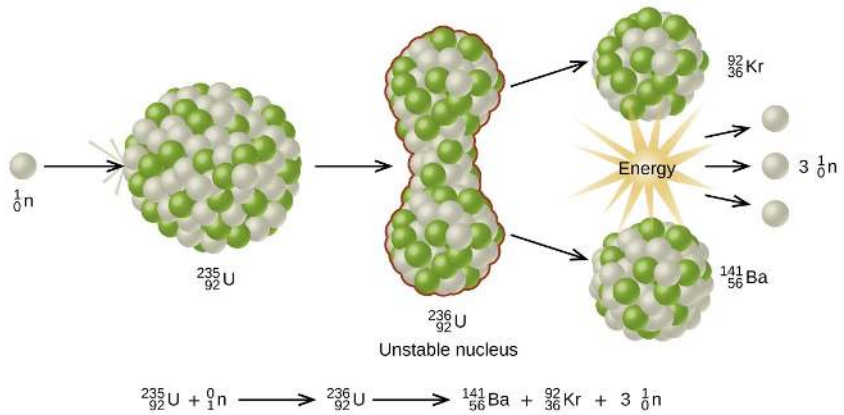


Figure **4.7.5** When a slow neutron hits a fissionable U-235 nucleus, it is absorbed and forms an unstable U-236 nucleus. The U-236 nucleus then rapidly breaks apart into two smaller nuclei (in this case, Ba-141 and Kr-92) along with several neutrons (usually two or three), and releases a very large 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 **4.7.6**). On the other hand, if too many neutrons escape the bulk material without interacting with a nucleus, then no chain reaction will occur.

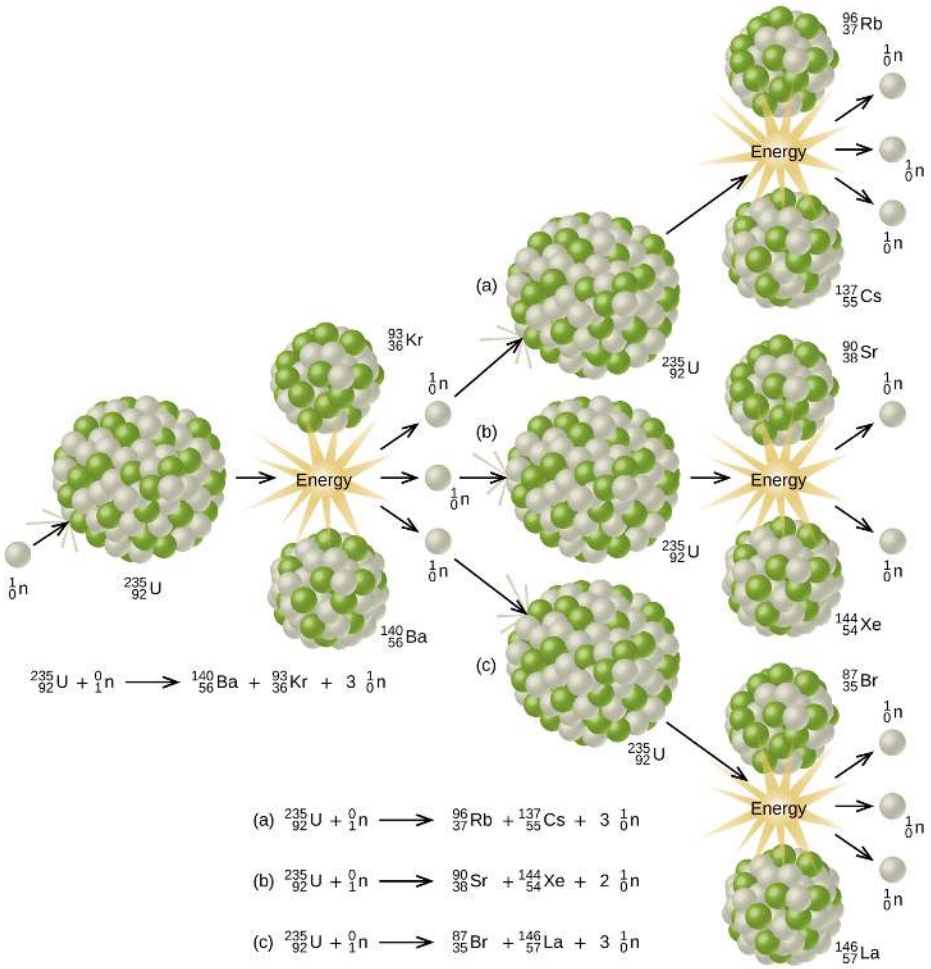


Figure **4.7.6** The fission of a large nucleus, such as U-235, produces two or three neutrons, each of which is capable of causing fission of another nucleus by the reactions shown. If this process continues, a nuclear chain reaction occurs.

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 **4.7.7**).

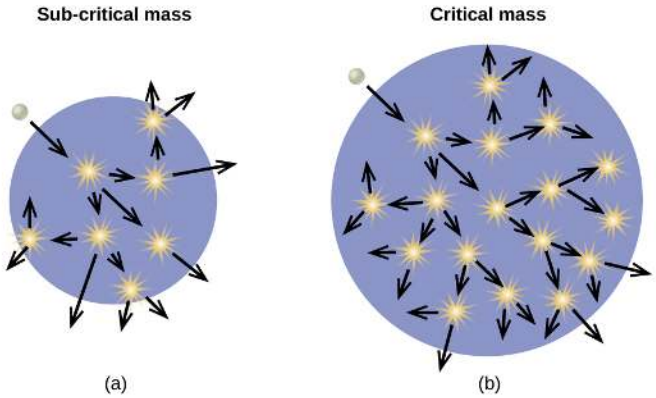


Figure **4.7.7** (a) In a subcritical mass, the fissile material is too small and allows too many neutrons to escape the material, so a chain reaction does not occur. (b) In a critical mass, a large enough number of neutrons in the fissile material induce fission to create a chain reaction.

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 **4.7.8**).

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).

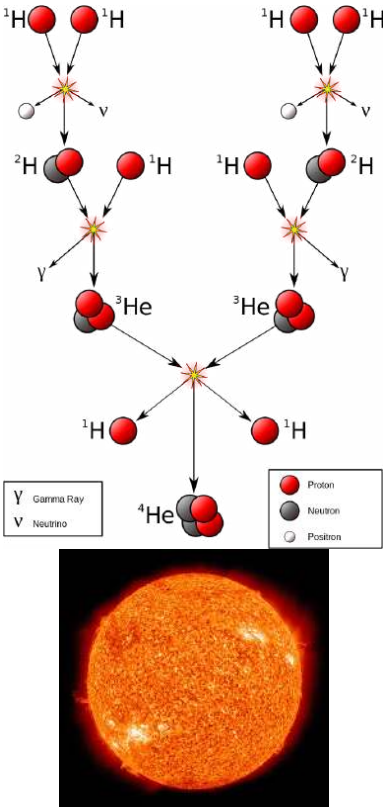


Figure **4.7.8** Nuclear fusion producing helium (left). The Sun is a main-sequence star, and thus generates its energy by nuclear fusion of hydrogen nuclei into helium (right).

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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4.8: 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.

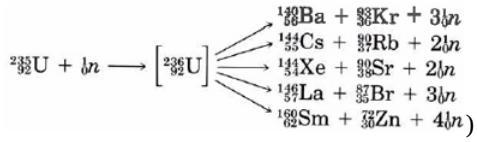
The first atomic bomb was dropped on Hiroshima on August 6, 1945 by the Enola Gay. The bomb destroyed the city, killing almost 100,000 people. The city of Hiroshima was essentially leveled. Following this attack, on August 9, 1945 another atomic bomb was dropped on Nagasaki. The same effects were felt 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 **4.8.1** (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.



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 $^{235}\mathrm{U}$ from the more abundant $^{238}\mathrm{U}$. Most of this work was performed at the at . This was done by preparing the gaseous compound $\mathrm{UF_6}$ 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 $^{235}\mathrm{U}$ 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 $^{238}\mathrm{U}$:

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{239}_{94}\mathrm{Pu} + 2\,{}^{0}_{-1}\beta$$

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 $\mathrm{mol^{-1}}$) as $^{235}\mathrm{U}$.

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 $\mathrm{mol^{-1}}$ 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



Video **4.8.1** *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 **4.8.2**). 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.

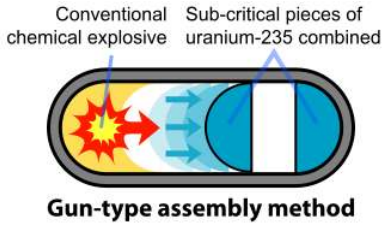


Figure **4.8.2**: Little Boy: Gun-Type Device. (Public Domain).

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.

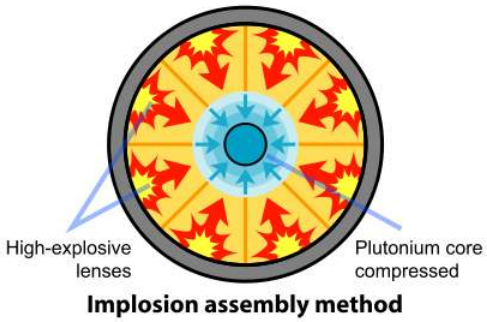


Figure 4.8.3: Fat Man: Implosion-type bomb. (Public Domain).

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 4.8.3). 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 4.8.1

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.



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 4.8.4).

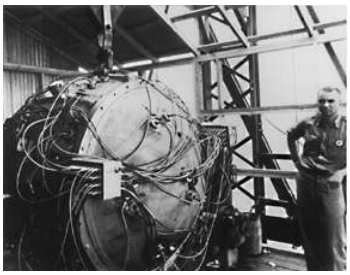


Figure 4.8.4: The Gadget at the Trinity Test Site, 1945. Courtesy of the U.S. Department of Defense

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 4.8.5).



Figure 4.8.5: 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 4.8.6). 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.

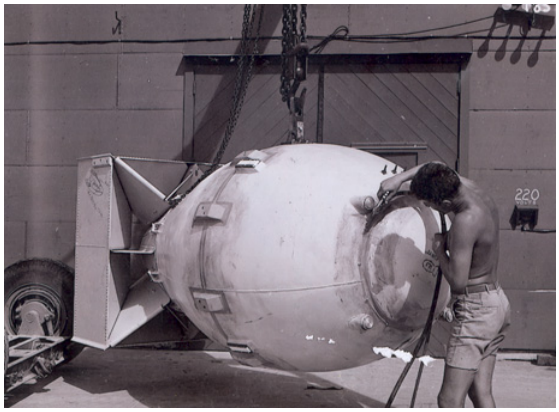


Figure 4.8.6: *Fat Man – One of many Pu-239 nuclear weapons constructed during WWII. Courtesy of the U.S. Department of Defense*

Example 4.8.2

Start the video below at the 23:20 mark and stop it at the 29-minute setting. Then, answer the questions below:



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.

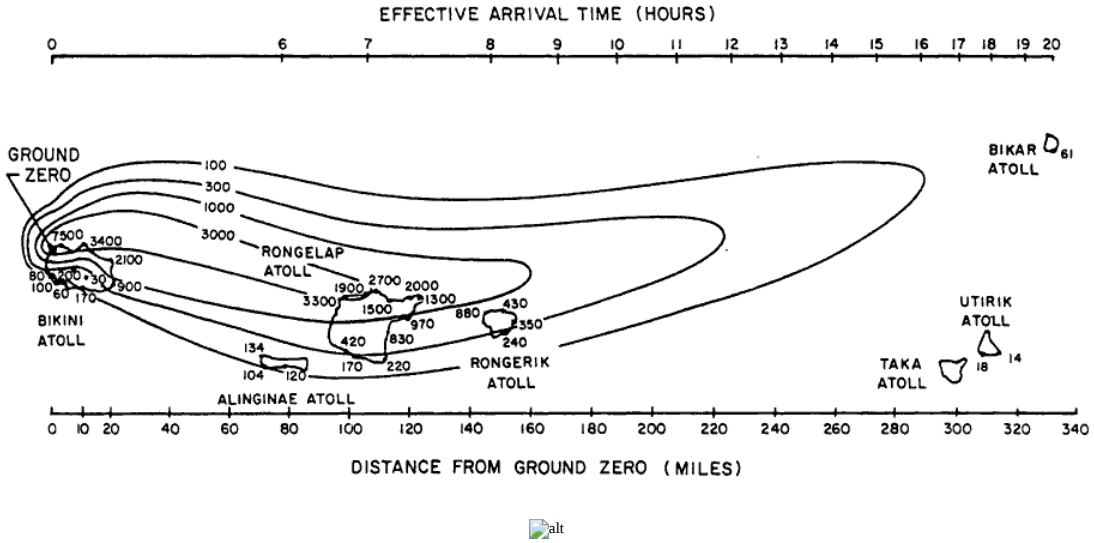


Figure 4.8.2: The 450 km (280 mi) fallout plume from 15 Mt shot Castle Bravo, 1954. (Pubic Domain; United States Department of Energy via Wikipedia)

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:



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).

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4.9: 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 4.9.1). 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 4.9.1) 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.

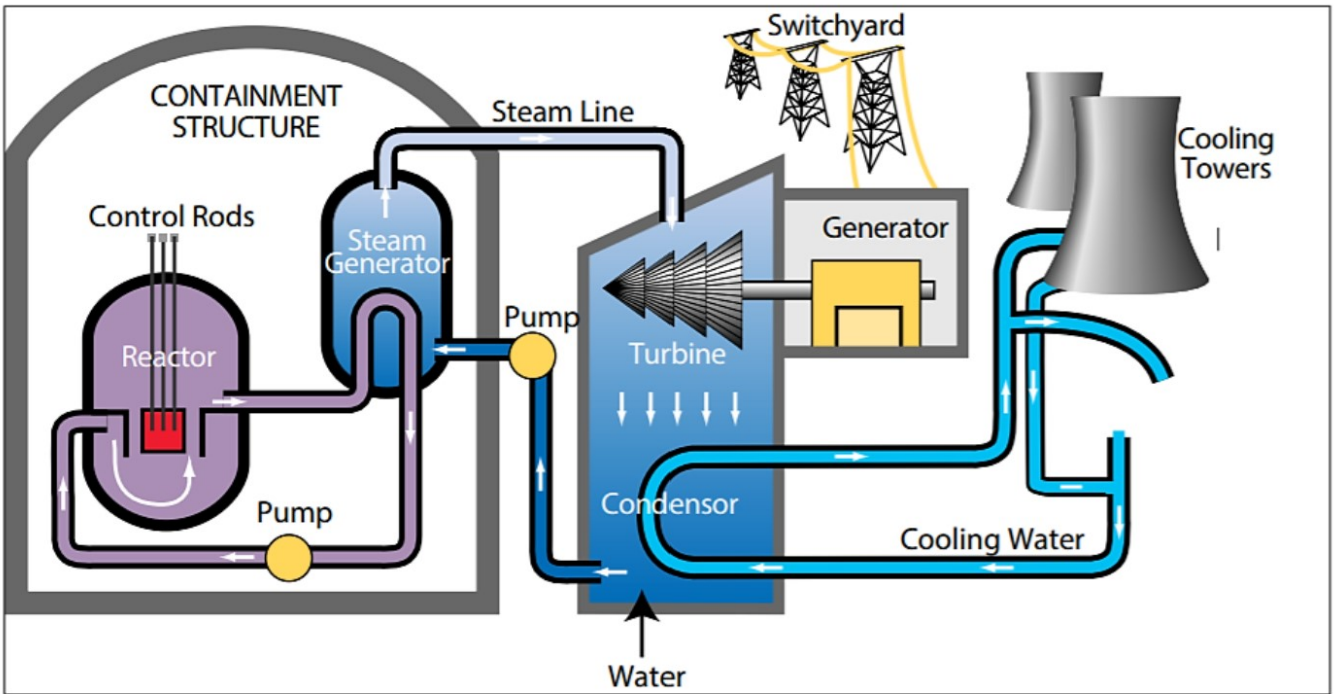


Figure 4.9.1: *A schematic diagram of a pressurized water reactor (PWR), the most common type of nuclear reactor. Diagram from Tennessee Valley Authority (public domain). www.tva.com*

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 **4.9.2** *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 **4.9.3**) 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.



Figure **4.9.3** (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



***Video* 4.9.1** *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.

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CHAPTER OVERVIEW

5: Chemical Bonds

5.1: The Art of Deduction- Stable Electron Configurations
5.2: Lewis (Electron-Dot) Symbols
5.3: The Reaction of Sodium with Chlorine
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5.8: Polyatomic Molecules- Water, Ammonia, and Methane
5.9: Polyatomic Ions
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5.11: Molecular Shapes- The VSEPR Theory
5.12: Shapes and Properties- Polar and Nonpolar Molecules

Thumbnail: Non-polar covalent bonds in methane (CH_4). The Lewis structure shows electrons shared between C and H atoms. (CC BY-sa 2.5; via).

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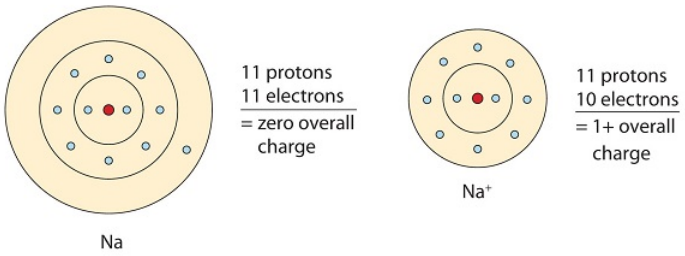
5.1: The Art of Deduction- Stable Electron Configurations

Learning Objective

- Define the octet rule.

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

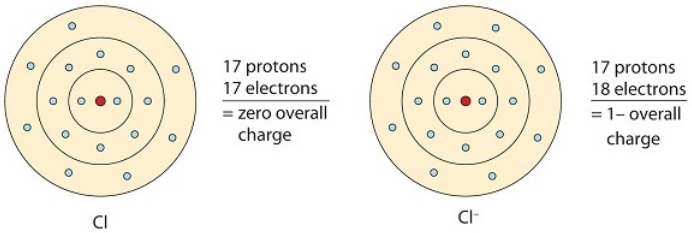
Referring to the octet rule, atoms attempt to get a noble gas electron configuration, which is eight valence electrons in most cases. Metals have few electrons in their outer-most orbitals. By losing those electrons, these metals can achieve noble gas configuration and satisfy the octet rule. Sodium has one valence electron, so giving it up would result in the same electron configuration as **neon**. Due to the loss of an 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 a completely filled valence shell and the electron configuration of a noble gas.

Contributor

Organic Chemistry Supplemental_Modules_(Organic_Chemistry)/Fundamentals/Ionic_and_Covalent_Bonds

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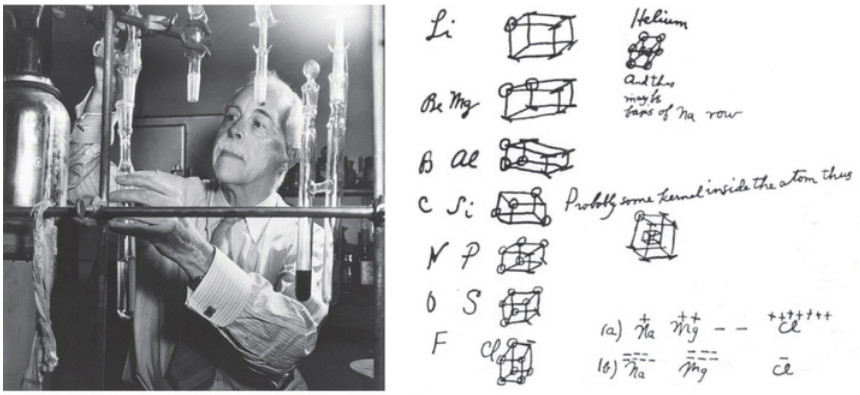
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5.2: Lewis (Electron-Dot) Symbols

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.



(a) (b)

Figure 5.2.1 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

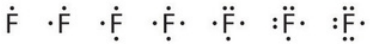
- convenient representation of valence electrons
- allows scientists to keep track of valence electrons during bond formation
- consists of the atomic symbol for the element plus a dot for each **valence** electron

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 5.2.1.

Table **5.2.1** Lewis Dot Symbols of the Main Group Elements

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

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 3*s* electrons:

$$\dot{Al}:$$

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

$$\cdot\ddot{Se}:$$

? Exercise 5.2.1

What is the Lewis electron dot diagram for each element?

a. phosphorus
b. argon

Answer a

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

Answer b

$$:\ddot{Ar}:$$

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.

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5.3: 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 **5.3.1**). 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 **5.3.1** (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 **5.3.2**). 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 **5.3.3**). 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* 5.3.2** *NaCl crystals. (Public Domain; NASA).*

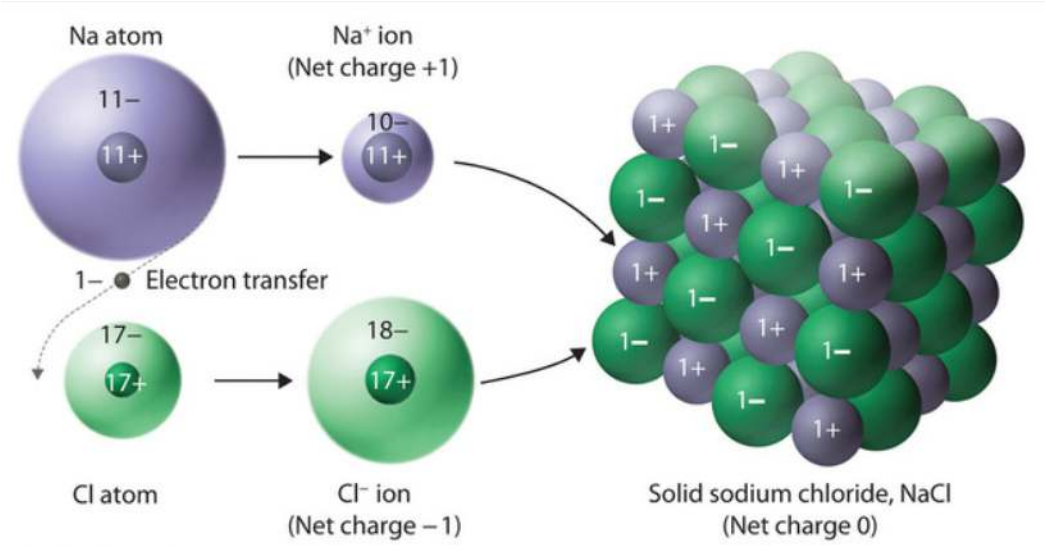
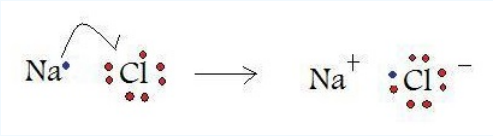


Figure **5.3.3** The formation of sodium chloride from the attraction of sodium and chloride ions.

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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5.4: 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 5.4.1). 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.

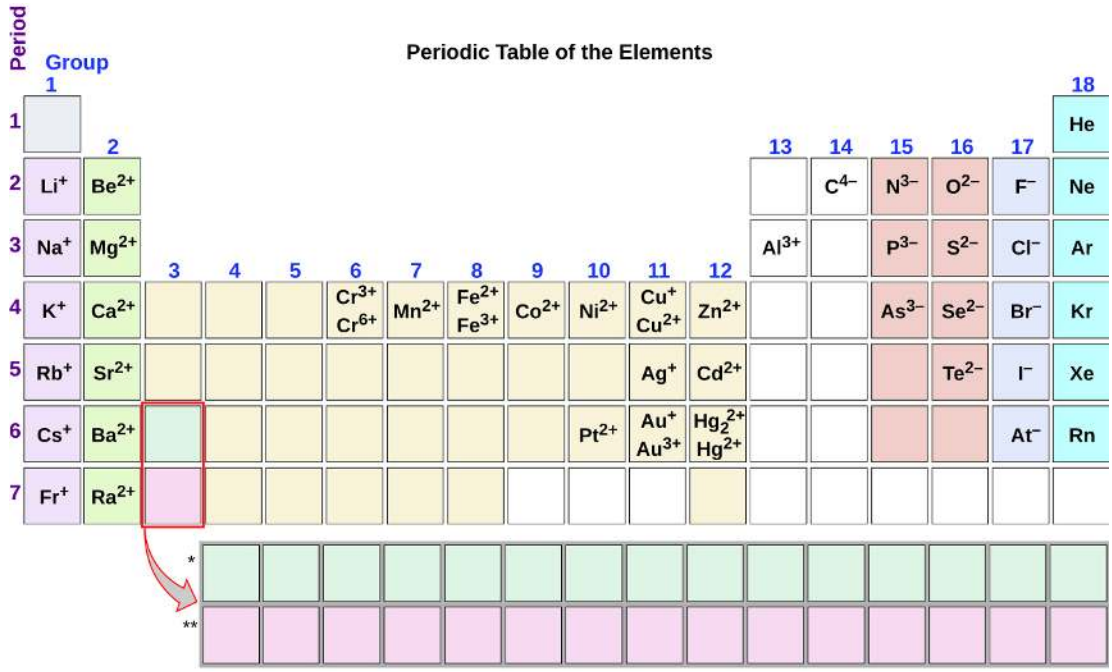


Figure 5.4.1: Some elements exhibit a regular pattern of ionic charge when they form ions.

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:

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

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

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:

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

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:

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

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:



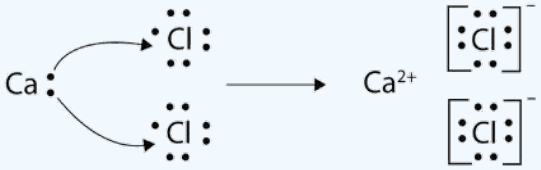
These three ions attract each other to give an overall neutral-charged ionic compound, which we write as Na_2O. The need for the number of electrons lost being equal to the number of electrons gained explains why ionic compounds have the ratio of cations to anions that they do. This is required by the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

Example 5.4.1: 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:

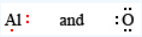


The oppositely charged ions attract each other to make $CaCl_2$.

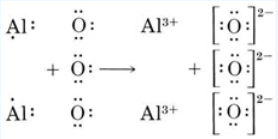
Example 5.4.2: Ionic Formula

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

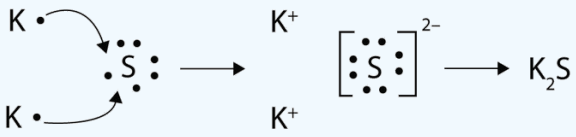


The resultant oxide consists of aluminum ions, Al^{3+}, and oxide ions, O^{2-}, in the ratio of 2:3. The formula is Al_2O_3.

Exercise 5.4.1

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

Answer:



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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5.5: 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 5.5.1), 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 5.5.1: 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
		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 **5.5.1** lists the elements that use the common system, along with their respective cation names.

Table **5.5.2**: 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 **5.5.2** lists the names of some common monatomic ions.

✔ Example 5.5.1

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 5.5.1

Name each ion.

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

Answer a:
iron(II) ion

Answer b:
iron(III) ion

Answer c:
barium ion

Example 5.5.2

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 5.5.2

Write the formula for each ion.

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

Answer a:

F^-

Answer b:

Sn^{2+}

Answer c:

K^+

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 5.5.1 for the compound $BaCl_2$. The word *ion* is dropped from both parts.

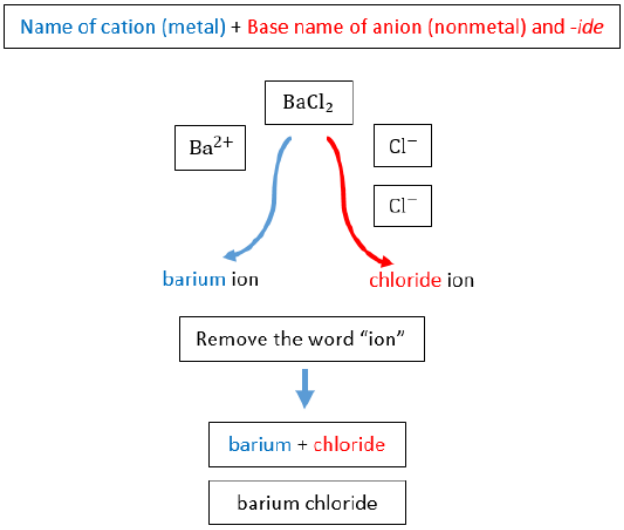


Figure 5.5.1 *Naming* $BaCl_2$

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 5.5.3: 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 5.5.3

Name each ionic compound.

a. AgI
b. MgO
c. Ca_3P_2

Answer a:

silver iodide

Answer b:

magnesium oxide

Answer c:

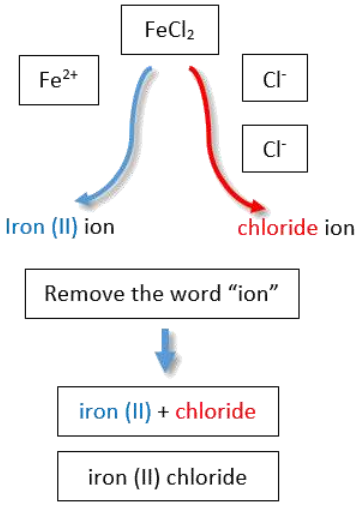
calcium phosphide

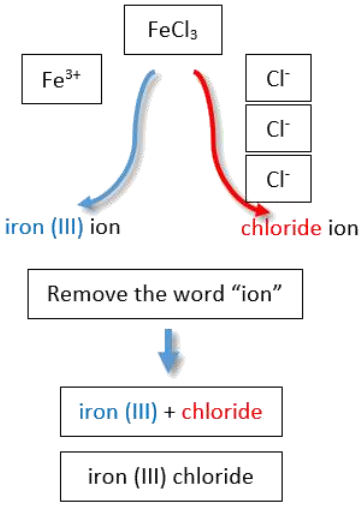
Naming Binary Ionic Compounds with a Metal That Forms More Than One Type of Cation

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 5.5.2).

Figure 5.5.2 Naming the $FeCl_2$ and $FeCl_3$ compounds in the modern/stock system.

Name of cation (metal) + (Roman Numeral in parenthesis) + Base name of anion (nonmetal) and *-ide*



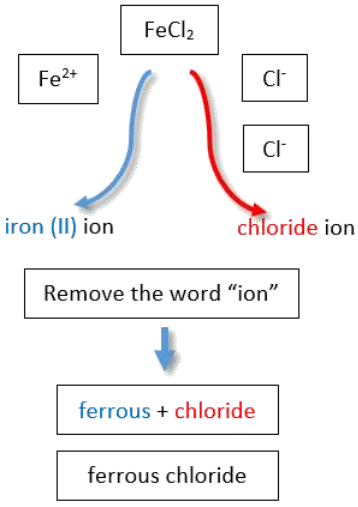


If we were to use the stems and suffixes of the common system, the names would be ferrous chloride and ferric chloride, respectively (Figure 5.5.3) .

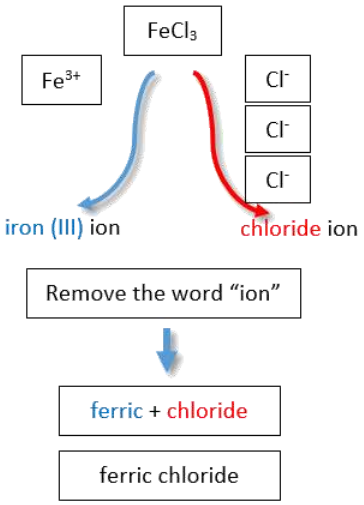
Figure 5.5.3 Naming the $FeCl_2$ and $FeCl_3$ compounds in the old/common System.

"Old" base name of cation (metal) and *-ic or -ous* + Base name of anion (nonmetal) and *-ide*

-ous (for ions with lower charge)



-ic (for ions with higher charge)



Example 5.5.4:

Name each ionic compound.

a. Co_2O_3

b. FeCl2

Solution

Example **5.5.4**: Explanation of the names of ionic compounds

	Ionic Compound	Explanation	Answer
d	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
d	FeCl2	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 5.5.4

Name each ionic compound.

a. $AuCl_3$
b. PbO_2
c. CuO

Answer a:
gold(III) chloride

Answer b:
lead(IV) oxide

Answer c:
copper(II) oxide

Figure **5.5.4** is a synopsis of how to name simple ionic compounds.

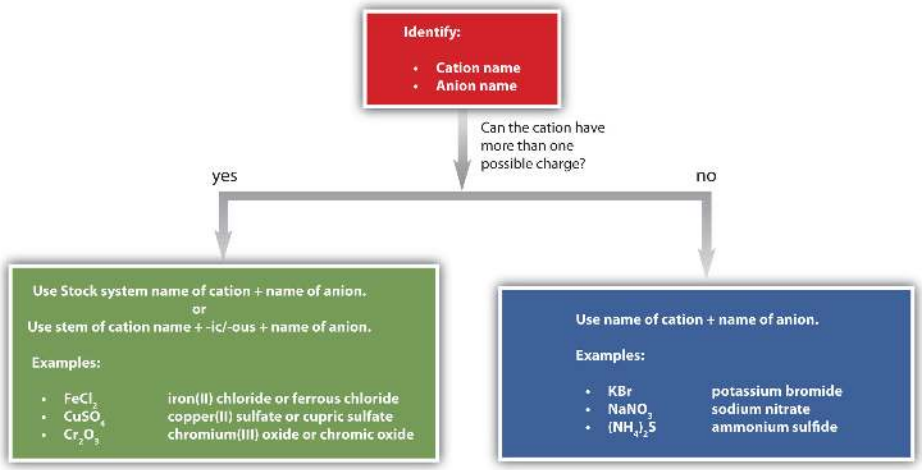


Figure 5.5.4: A Guide to Naming Simple Ionic Compounds.

? Exercise 5.5.5

Name each ionic compound.

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

Answer a:

zinc bromide

Answer b:

aluminum oxide

Answer c:

gold(III) fluoride or auric fluoride

Answer d:

silver fluoride

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 5.5.5: Aluminum Nitride and Lithium Oxide

Write the formula for aluminum nitride and lithium oxide.

Solution

Example 5.5.5: 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.	Al^{3+} N^{3-}	Li^{+} O^{2-}
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 5.5.6: The Crisscross Method for lead (IV) oxide

Write the formula for lead (IV) oxide.

Solution

Example 5.5.6: 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.	Pb^{4+} O^{2-}
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 5.5.6

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:

CaO

Answer b:

CuS

Answer c:

Cu_2S

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

Example 5.5.7: Sulfur Compound

Write the formula for sodium combined with sulfur.

Solution

Example **5.5.7**: 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.	$Na^+ \quad S^{2-}$
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 5.5.7

Write the formula for each ionic compound.

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

Answer a:
NaBr

Answer b:
LiCl

Answer c:
MgO

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 5.5.8

Identify each compound as ionic or not ionic.

a. Na_2O
b. PCl_3
c. OF_2

Solution

Example **5.5.8**: 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 5.5.8

Identify each compound as ionic or not ionic.

a. N_2O
b. $FeCl_3$

Answer a:

not ionic

Answer b:

ionic

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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5.6: 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**.

The Octet Rule

The number of bonds an atom can form can often be predicted from the number of electrons needed to reach an octet (eight valence electrons); this is especially true of the nonmetals of the second period of the periodic table (C, N, O, and F).

For example, each atom of group 7A has seven electrons in its outermost shell, requiring one more electron to reach an octet. This electron can be gained by forming one covalent bond. When forming halogen molecules (F_2, Cl_2, Br_2, I_2, and At_2) form bonds like those in the chlorine molecule: one single bond between atoms and three lone pairs of electrons per atom. This allows each halogen atom to have a noble gas electron configuration. The tendency of main group atoms to form enough bonds to obtain eight valence electrons is known as the octet rule.

Writing Lewis Structures with the Octet Rule

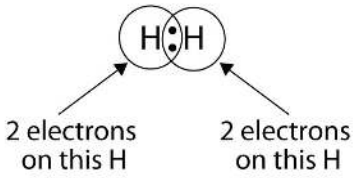
Chemists frequently use Lewis diagrams to represent covalent bonding in molecular substances. For example, the Lewis diagrams of two separate hydrogen atoms are as follows:



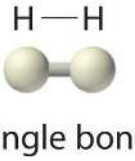
The Lewis diagram of two hydrogen atoms sharing electrons looks like this:



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:



Single bond

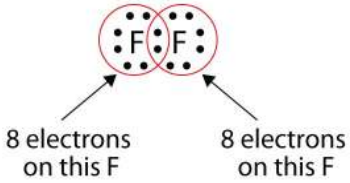
Because two atoms are sharing one pair of electrons, this covalent bond is called a **single bond**. As another example, consider fluorine. F atoms have seven electrons in their valence shell:



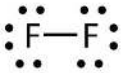
These two atoms can do the same thing that the H atoms did; they share their unpaired electrons to make a covalent bond.



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:

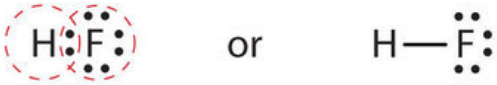


There are two different types of electrons in the fluorine diatomic molecule. The **bonding electron pair** makes the covalent bond. Each F atom has three other pairs of electrons that do not participate in the bonding; they are called **lone pair electrons**. Each F atom has one bonding pair and three 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 5.6.1:

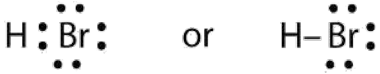
Use Lewis electron dot diagrams to illustrate the covalent bond formation in HBr.

Solution

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



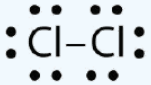
The two atoms can share their unpaired electron:



Exercise 5.6.1

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

Answer:

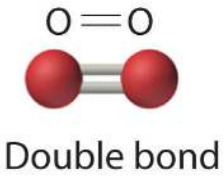


When working with covalent structures, it sometimes looks like you have leftover electrons. You apply the rules you learned so far and there are still some electrons hanging out there unattached. You can't just leave them there. So where do you put them?

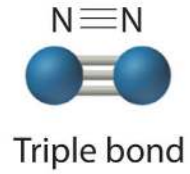
Multiple Covalent Bonds

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***



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



Because each nitrogen contains 5 valence electrons, they need to share 3 pairs to each achieve a valence octet. N_2 is fairly inert, due to the strong triple bond between the two nitrogen atoms.



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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5.7: 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 **5.7.1**.

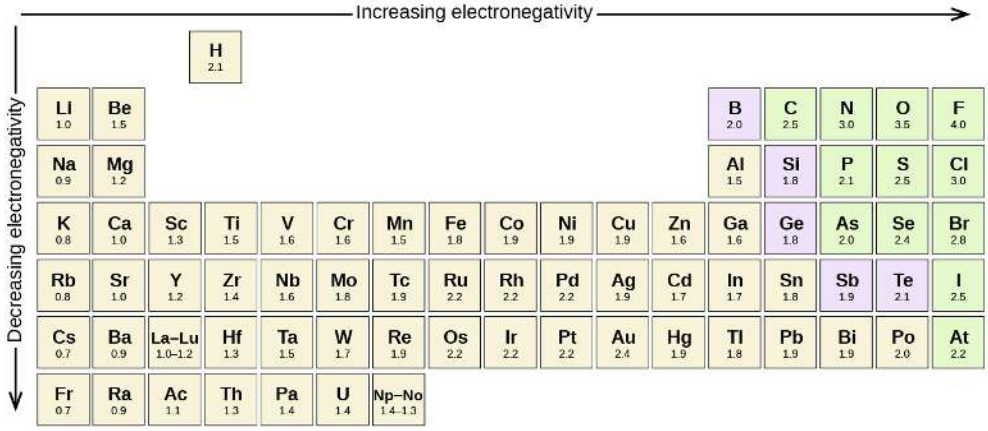


Figure **5.7.1** Electronegativities of the Elements. Electronegativities are used to determine the polarity of covalent bonds.

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 **5.7.1**:Electronegativity differences and bond type

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

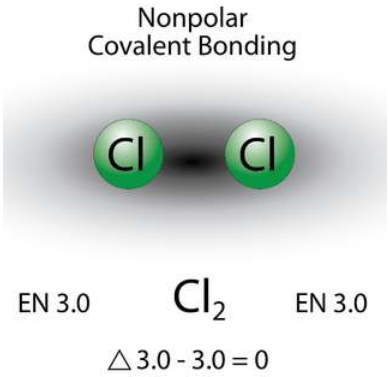


Figure **5.7.2** A nonpolar covalent bond is one in which the distribution of electron density between the two atoms is equal.

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.

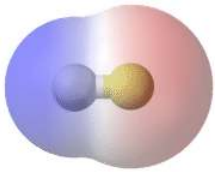


Figure **5.7.3** In the polar covalent bond of **HF**, the electron density is unevenly distributed. There is a higher density (red) near the fluorine atom, and a lower density (blue) near the hydrogen atom.

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

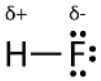


Figure **5.7.4** Use of δ to indicate partial charge.

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 **5.7.5** Use of crossed arrow to indicate polarity



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

Example 5.7.1: Bond Polarity

What is the polarity of each bond?

a. C–H
b. O–H

Solution

Using Figure 5.7.1, 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 5.7.1

What is the polarity of each bond?

a. Rb–F
b. P–Cl

Answer a

likely ionic

Answer b

polar covalent

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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5.8: 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 **5.8.1**).

Table **5.8.1** 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

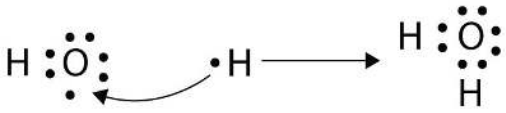
Consider H and O atoms:



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:



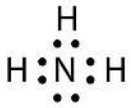
(It does not matter on what side the second H atom is positioned.) Now the O atom has a complete octet around it, and each H atom has two electrons, filling its valence shell. This is how a water molecule, H_2O, is made.

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:

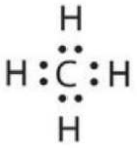


Methane

The C atom has the following Lewis electron dot diagram:

:C:

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:



Writing Lewis Structures with the Octet Rule

For polyatomic molecules, it is helpful to follow the step-by-step procedure outlined here:

1. Determine the total number of valence (outer shell) electrons among all the atoms.
2. Draw a skeleton structure of the molecule, arranging the atoms around a central atom. (Generally, the element closest to the metals should be placed in the center. There are some exceptions) Connect each atom to the central atom with a single bond (one electron pair).
3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen), completing an octet around each atom.
4. Place all remaining electrons on the central atom.
5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

1- Determine the total number of valence (outer shell) electrons in the molecule.

Since OF_2 is a neutral molecule, we simply add the number of valence electrons:

OF_2

O: 6 valence electrons/atom × 1 atom=6

+ F: 7 valence electrons/atom × 2 atoms=14

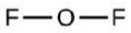
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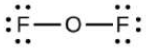
= 20 valence electrons

2- Draw a skeleton structure of the molecule, arranging the atoms around a central atom and connecting each atom to the central atom with a single (one electron pair) bond.

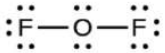
As the closest element to the metals, oxygen will be the central atom. After placing 2 single bonds (20 electrons - 4 electrons), we had 16 electrons remaining.



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



4- For OF_2, we placed 12 electrons between both Fluorine atoms, leaving 4 to be placed on the central atom:



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

In OF_2, each atom has an octet as drawn, so nothing changes.

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Summary

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

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5.9: 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 **5.9.1** lists the most common polyatomic ions.

Table **5.9.1** 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 5.9.1: Calcium Nitrate

Write the formula for calcium nitrate.

Solution

Example 5.9.1: 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.	Ca^{2+} 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 5.9.2

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

Solution

Example 5.9.2: 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 5.9.1

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:

$MgCO_3$

Answer b:

$Al(CH_3COO)_3$

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 5.9.6.

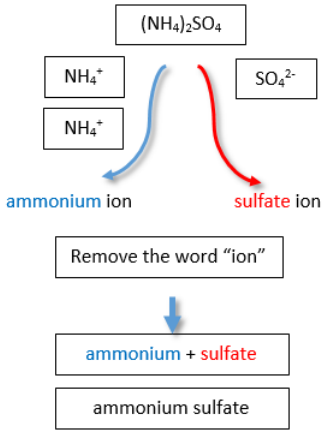


Figure 5.9.2 *Naming Ionic Compounds with Polyatomic Ions*

Example 5.9.3: Naming Ionic Compounds

Write the proper name for each ionic compound.

a. $(NH_4)_2S$
b. $AlPO_4$,
c. $Fe_3(PO_4)_2$

Solution

Example 5.9.3: Explanation for Naming Ionic Compounds

Ionic Compound	Explanation	Answer
a. **$(NH_4)_2S$**	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. $AlPO_4$,	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
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 5.9.2

Write the proper name for each ionic compound.

a. $(NH_4)_3PO_4$

b. $Co(NO_2)_3$

Answer a:

ammonium phosphate

Answer b:

cobalt(III) nitrite

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.

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5.10: 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 5.10.1: Water

Write the Lewis Structure for H_2O.

Solution

Example **5.10.1**: steps for writing the Lewis structure of water

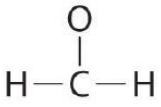
Steps for Writing Lewis Structures	Example 5.10.1:
1. Determine the total number of valence electrons in the molecule or ion.	Each H atom (group 1) has 1 valence electron, and the O atom (group 16) has 6 valence electrons, for a total of 8 valence electrons.
2. Arrange the atoms to show specific connections.	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 5.10.2

Write the Lewis structure for the CH_2O molecule

Solution

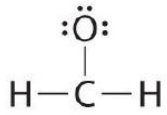
Steps are writing the Lewis structure of the CH_2O molecule

Steps for Writing Lewis Structures	Example 5.10.2
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.

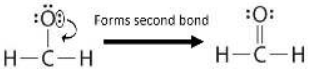
5. If any electrons are left over, place them on the central atom.

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:

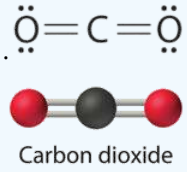


7. Final check Both the oxygen and the carbon now have an octet of electrons, so this is an acceptable Lewis electron structure. The O has two bonding pairs and two lone pairs, and C has four bonding pairs. This is the structure of formaldehyde, which is used in embalming fluid.

? Exercise 5.10.1

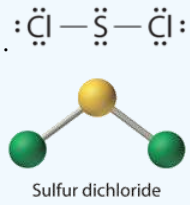
Write Lewis electron structures for CO_2 and SCl_2, a vile-smelling, unstable red liquid that is used in the manufacture of rubber.

Answer CO_2



Carbon dioxide

Answer SCl_2



Sulfur dichloride

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.

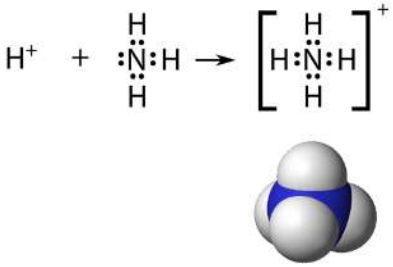


Figure 5.10.3: The ammonium ion.

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:

$1\,\mathrm{N}$ atom $= 5$ valence electrons

$4\,\mathrm{H}$ atoms $= 4 \times 1 = 4$ valence electrons

subtract 1 electron for the $1+$charge of the ion

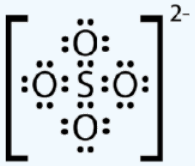
total of 8 valence electrons in the ion

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 5.10.2

Draw the Lewis electron dot structure for the sulfate ion.

Answer



Exceptions to the Octet Rule

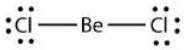
As important and useful as the octet rule is in chemical bonding, there are some well-known violations. This does not mean that the octet rule is useless—quite the contrary. As with many rules, there are exceptions, or violations.

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:

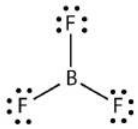


Although the O atom has an octet of electrons, the N atom has only seven electrons in its valence shell. Although NO is a stable compound, it is very chemically reactive, as are most other odd-electron compounds.

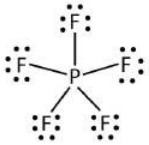
Electron-deficient molecules represent the second violation to the octet rule. These stable compounds have less than eight electrons around an atom in the molecule. The most common examples are the covalent compounds of beryllium and boron. For example, beryllium can form two covalent bonds, resulting 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 5.10.3: Octet Violations

Identify each violation to the octet rule by drawing a Lewis electron dot diagram.

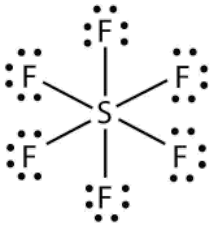
a. ClO
b. SF_6

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 5.10.3: Xenon Difluoride

Identify the violation to the octet rule in XeF_2 by drawing a Lewis electron dot diagram.

Answer:



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

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5.11: 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 **5.11.1** *Beryllium hydride and carbon dioxide bonding.*

The two molecules, shown in the figure below in a "ball and stick" model.

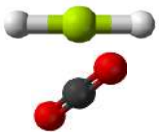


Figure **5.11.2** *Beryllium hydride and carbon dioxide models.*

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:

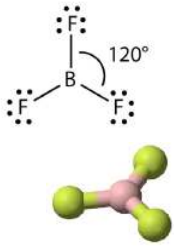


Figure **5.11.3** *Boron trifluoride bonding.*

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:

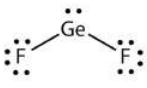


Figure **5.11.4**: Germanium *difluoride bonding.*

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 **5.11.1** 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.

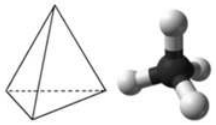


Figure **5.11.5** *Tetrahedral structure of methane.*

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.

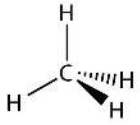


Figure **5.11.6** *Methane bonding.*

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.

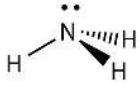


Figure **5.11.7** *Ammonia bonding.*

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 **5.11.8** *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 **5.11.9**.



Figure **5.11.9** *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.

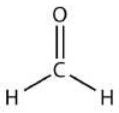


Figure **5.11.10**: Formaldehyde bonding.

(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 5.11.11 illustrates several representations of the water, ammonia, and methane molecules.

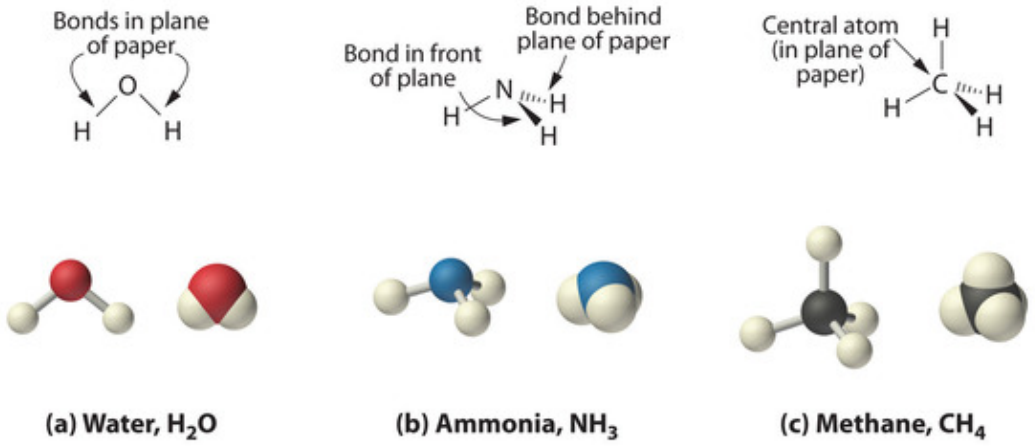


Figure 5.11.11 The three-dimensional structures, ball and stick models,and space filling models of water, ammonia, and methane. *(a) Water is a V-shaped molecule, in which all three atoms lie in a plane. (b) In contrast, ammonia has a pyramidal structure, in which the three hydrogen atoms form the base 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 5.11.1 summarizes the shapes of molecules based on their number of electron groups and surrounding atoms and the common shapes are shown in figure 5.11.1.

Table 5.11.1: 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 5.11.12: Common structures for molecules and Ppolyatomic ions that consist of a central atom bonded to two or three other atoms.

Example 5.11.1:

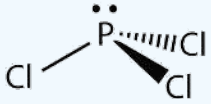
What is the approximate shape of each molecule?

a. PCl_3
b. NOF

Solution

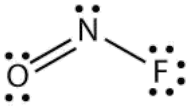
The first step is to draw the Lewis structure of the molecule.

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 5.11.1

What is the approximate molecular shape of CH_2Cl_2?

Answer

Tetrahedral

? Exercise 5.11.2

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

Trigonal planar about both central C atoms

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

-
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5.12: 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 CCl_4 is nonpolar Figure (**5.12.1**. 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.

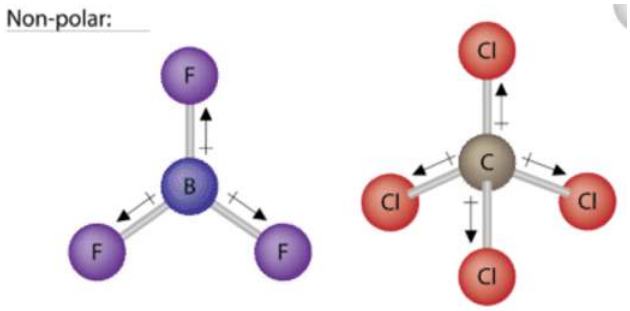
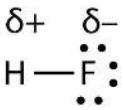


Figure **5.12.1** Some examples of nonpolar molecules based on molecular geometry (BF_3 and CCl_4).

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 **5.12.2** 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.

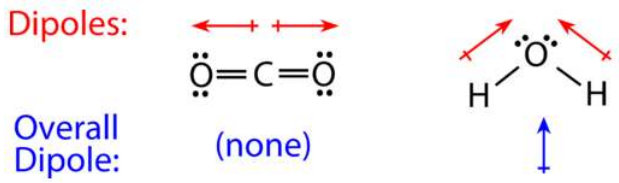


Figure 5.12.3 *The molecular geometry of a molecule affects its polarity. Each CO bond has a dipole moment, but they point in opposite directions so that the net CO2 molecule is nonpolar. In contrast, water is polar because the OH bond moments do not cancel out.*

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.

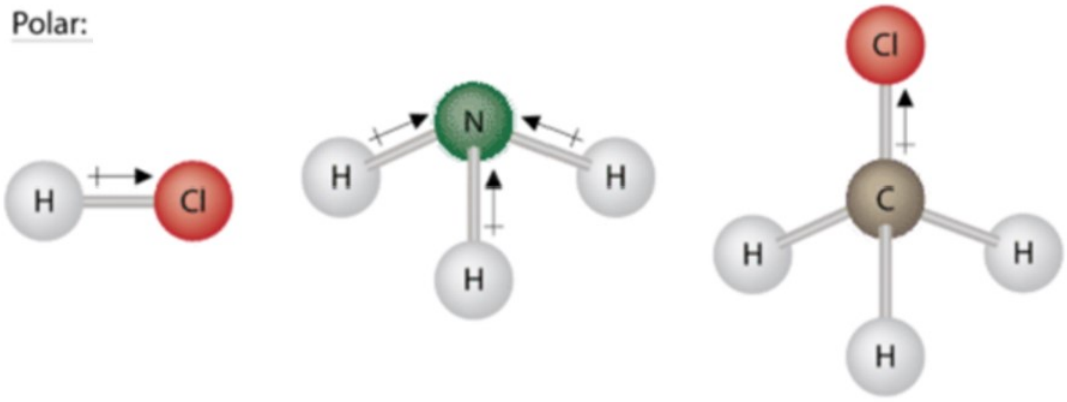


Figure 5.12.4 Some examples of polar molecules based on molecular geometry (HCl, NH3 and CH3Cl).

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 5.12.1:

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 **−OH** side is different from the other 3 **−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 5.12.1

Label each of the following as polar or nonpolar.

a. SO_3

b. NH_3

Answer a

non polar

Answer b

polar

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

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CHAPTER OVERVIEW

6: Chemical Accounting

6.1: Chemical Sentences- Equations

6.2: Volume Relationships in Chemical Equations

6.3: Avogadro's Number and the Mole

6.4: Molar Mass- Mole-to-Mass and Mass-to-Mole Conversions

6.5: Solutions

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6.1: 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, $SO_2 + O_2$, are reactants and sulfur trioxide, SO_3, is the product.

$$\underbrace{2\,SO_2\,(g)+O_2\,(g)}_{\text{Reactants}} \rightarrow \underbrace{2\,SO_3\,(g)}_{\text{Products}}$$

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:

$$\text{Reactants} \rightarrow \text{Products}$$

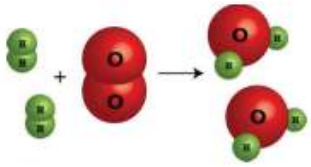
There are a few special symbols that we need to know in order to "talk" in chemical shorthand. In the table below is the summary of the major symbols used in chemical equations. You will find there are others but these are the main ones that we need to know. Table **6.1.1** shows a listing of symbols used in chemical equations.

Table **6.1.1** Symbols Used in Chemical Equations

Symbol	Description
$+$	used to separate multiple reactants or products
$\rightarrow$	yield sign; separates reactants from products
$\rightleftharpoons$	replaces the yield sign for reversible reactions that reach equilibrium
$\xrightarrow{\text{Pt}}$	formula written above the arrow is used as a catalyst in the reaction
$\xrightarrow{\Delta}$	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.

$$2H_2\,(g) + O_2\,(g) \rightarrow 2H_2O\,(g)$$

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:

$$Ca(NO_3)_2\,(aq) + 2NaOH\,(aq) \rightarrow Ca(OH)_2\,(s) + 2NaNO_3\,(aq)$$

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:

$$Cu\,(s) + AgNO_3\,(aq) \rightarrow Cu(NO_3)_2\,(aq) + Ag\,(s)$$

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 **6.1.2** *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 6.1.1

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 6.1.1

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

$H_2(g) + N_2(g) \rightarrow NH_3(g)$

Answer b

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.

Answer c

$Cu(s) + O_2(g) \rightarrow CuO(s)$

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.

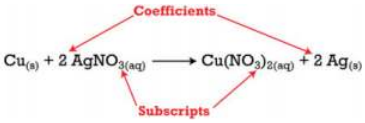


Figure **6.1.1**Balancing Equations. You cannot change subscripts in a chemical formula to balance a chemical equation; you can change only the coefficients. Changing subscripts changes the ratios of atoms in the molecule and the resulting chemical properties. For example, water (H_2O) and hydrogen peroxide (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 **6.1.2**.

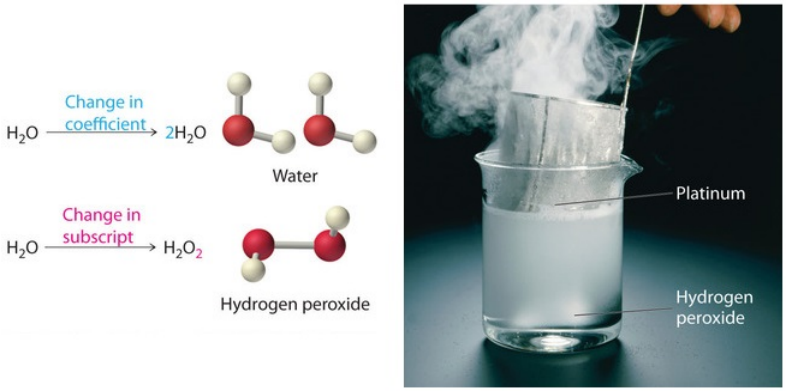


Figure **6.1.2** H_2O_2 decomposes to H_2O and O_2 gas when it comes in contact with the metal platinum (left), whereas no such reaction occurs between water and platinum (right).

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 6.1.2: 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 **6.1.2**: 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 assume initially 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 contains 1 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** | **Products** 7 | C | 7 b. Because one molecule of n-heptane contains 16 hydrogen atoms, we need 8 H_2O molecules, each of which contains 2 hydrogen atoms, on the right side: $$C_7H_{16}(l) + O_2(g) \longrightarrow 7CO_2(g) + \underline{8}H_2O(g)$$ Reactants and Products of Elements **Reactants** | **Element/Polyatomic Ion** | **Products** 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 oxygen atoms on the left. We can balance the oxygen atoms by adjusting the coefficient in front of the least complex substance, O_2, on the reactant side: $$C_7H_{16}(l) + \underline{11}O_2(g) \longrightarrow 7CO_2(g) + 8H_2O(g)$$ Reactants and Products of Elements **Reactants** | **Element/Polyatomic Ion** | **Products** 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 atoms, and

	22 oxygen atoms on each side. Always check to be sure that a chemical equation is balanced.

Example 6.1.3: Combustion of Isooctane

Combustion of Isooctane (C_8H_{18})

$$C_8H_{18}\,(l) + O_2\,(g) \longrightarrow CO_2\,(g) + H_2O\,(g)$$

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 **6.1.3**: 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 C_8H_{18}. We will assume initially 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 there 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** | **Products** 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** | **Products** 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 oxygen atoms on the left. We can balance the least complex substance, O_2, but because there are 2 oxygen atoms per O_2 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** | **Products** 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 eliminate the 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	Products
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 using very large coefficients or if you have spent several minutes without success, go back and make sure that you have written the formulas of the reactants and products correctly.

Example 6.1.4: 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 **6.1.4**: Solution for the combustion of isooctane

Steps for Problem Solving	Example 6.1.4
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 order to 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
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: $\mathrm{Pb(NO_3)_2\,(aq) + 2\,NaCl\,(aq) \longrightarrow \underline{2}\,NaNO_3\,(aq) + PbCl_2\,(s)}$ Reactants and Products of Elements
4. **Balance the remaining atoms**.	There is no need to balance the remaining atoms because they are already balanced.
5. **Check your work.**	$\mathrm{Pb(NO_3)_2\,(aq) + 2\,NaCl\,(aq) \longrightarrow 2\,NaNO_3\,(aq) + PbCl_2\,(s)}$ Reactants and Products of Elements

Reactants	Element/Polyatomic Ion	Products
1	Pb	1
2	Na	1
2	Cl	2

Reactants	Element/Polyatomic Ion	Products
1	Pb	1
2	Na	2
2	Cl	2
2	NO_3^-	2

Reactants	Element/Polyatomic Ion	Products
1	Pb	1
2	Na	2
2	Cl	2
2	NO_3^-	2

? Exercise 6.1.2

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

yes

Answer b

no

Answer c

yes

? Exercise 6.1.3

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

$$N_2\,(g) + 2O_2\,(g) \rightarrow 2NO_2\,(g)$$

Answer b

$$3Pb(NO_3)_2(aq) + 2FeCl_3(aq) \rightarrow 2Fe(NO_3)_3(aq) + 3PbCl_2(s)$$

Answer c

$$2C_6H_{14}(l) + 19O_2(g) \rightarrow 12CO_2(g) + 14H_2O(g)$$

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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6.2: 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 **6.2.1**. 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.

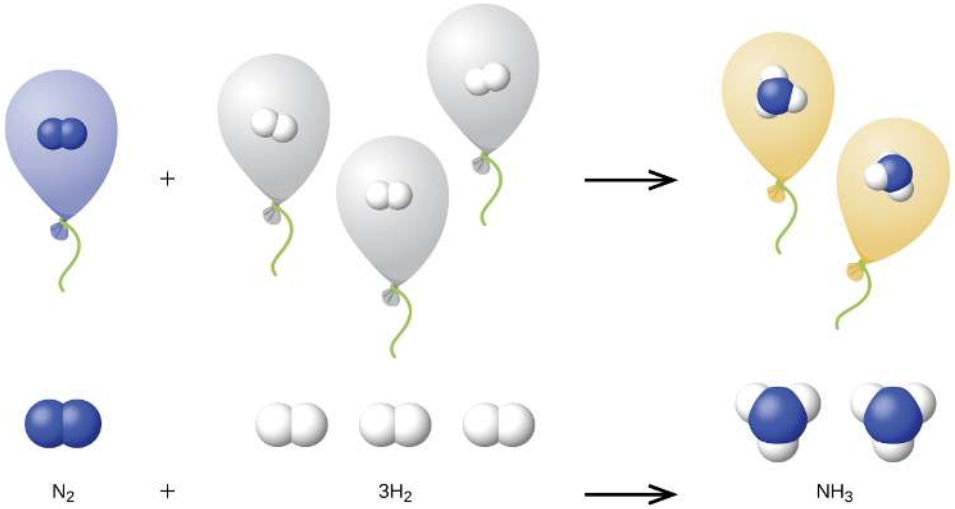


Figure **6.2.1**: *One volume of N_2 combines with three volumes of H_2 to form two volumes of NH_3.*

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 6.2.5: 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:

$$\begin{aligned} &\mathrm{C_3H_8}(g) + 5\,\mathrm{O_2}(g) \longrightarrow && 3\,\mathrm{CO_2}(g) + 4\,\mathrm{H_2O}(l) && (6.2.1)\\ &1\ \text{volume} + 5\ \text{volumes} && 3\ \text{volumes} + 4\ \text{volumes} && (6.2.2)\end{aligned}$$

From the equation, we see that one volume of C_3H_8 will react with five volumes of O_2:

$$2.7\ \mathrm{L}\ \mathrm{C_3H_8} \times \frac{5\ \mathrm{L}\ \mathrm{O_2}}{1\ \mathrm{L}\ \mathrm{C_3H_8}} = 13.5\ \mathrm{L}\ \mathrm{O_2}$$

A volume of 13.5 L of O_2 will be required to react with 2.7 L of C_3H_8.

Exercise 6.2.5

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?

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

Answer

3.34 tanks (2.34×10^4 L)

Example 6.2.6: 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?

$$\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \longrightarrow 2\,\mathrm{NH_3}(g)$$

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:

$$683\ \text{billion ft}^3\ \mathrm{NH_3} \times \frac{3\ \text{billion ft}^3\ \mathrm{H_2}}{2\ \text{billion ft}^3\ \mathrm{NH_3}} = 1.02 \times 10^3\ \text{billion ft}^3\ \mathrm{H_2}$$

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 6.2.6

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

51.0 L

Summary

Avogadro's law may be used to determine the volume of gaseous reactant(s) or product(s) based on a balanced chemical equation.

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6.3: 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:

$$N_A \approx 6.02 \times 10^{23}. \tag{6.3.1}$$

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



***Video* 6.3.1** *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

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

An example on the use of Avogadro's number as a conversion factor is given below for carbon.

Example 6.3.1: Moles of Carbon

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

Solution

Example **6.3.1**:Steps for Problem Solving how many moles of carbon atoms is $\mathbf{4.72 \times 10^{24}}$ atoms of carbon?

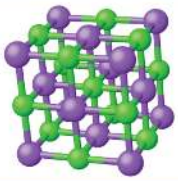
Steps for Problem Solving	Example
Identify the "given"information and what the problem is asking you to "find."	Given: 4.72×10^{24} C atoms Find: mol C
List other known quantities	$1\,mol = 6.022 \times 10^{23}$ C atoms
Prepare a concept map and use the proper conversion factor.	# C atoms → mol C $\frac{1\,mol\,C}{6.022 \times 10^{23} C\,atoms}$
Cancel units and calculate.	$4.72 \times 10^{24}\ \cancel{C\,atoms} \times \frac{1\ mol\ C}{6.02 \times 10^{23}\ \cancel{C\,atoms}} = 7.84\ mol\ C$
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 greater than 1 mole. Since Avogadro's number is a measured quantity with three significant figures, the result of the calculation is rounded 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

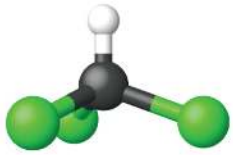


A table and diagram are shown. The table is made up of six columns and four rows. The header row reads: “Element,” “Quantity,” a blank space, “Average atomic mass (a m u),” a blank space and “Subtotal (a m u).” The first column contains the symbols “N a”, “C l,” and a merged cell. The merged cell runs 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 6.3.2 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 6.3.1

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 6.3.3

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 6.3.3: 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.	$$\%Cl = \frac{70.90\text{ g Cl}}{182.90\text{ g}} \times 100\% = 38.76\%\text{ Cl}$$ $$\%\text{ O} = \frac{112.00\text{ g O}}{182.90\text{ g}} \times 100\% = 61.24\%\text{ O}$$ Calculate the percent by mass of each element by dividing the mass of that element in 1 mole of the compound by the 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 $38.76\%\text{ Cl}$ and $61.24\%\text{ O}$. Suppose that you needed to know the masses of chlorine and oxygen present in a 12.50 g sample of dichlorine heptoxide. You can set up a conversion factor based on the percent by mass of each element.

$$12.50\text{ g } Cl_2O_7 \times \frac{38.76\text{ g Cl}}{100\text{ g } Cl_2O_7} = 4.845\text{ g Cl}$$

$$12.50\text{ g } Cl_2O_7 \times \frac{61.24\text{ g O}}{100\text{ g } Cl_2O_7} = 7.655\text{ g O}$$

The sum of the two masses is 12.50 g, the mass of the sample size.

Exercise 6.3.2

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:

78.32% Ba and 21.67% F

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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6.4: 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:

$$\frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \text{ and } \frac{26.98 \text{ g Al}}{1 \text{ mol Al}} \tag{6.4.1}$$

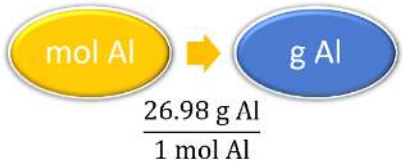
The first conversion factor can be used to convert from mass to moles, and the second converts from moles to mass. Both can be used to solve problems that would be hard to do “by eye.”

Example 6.4.1

What is the mass of 3.987 mol of Al?

Solution

Example **6.4.1**: 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
Prepare a concept map and use the proper conversion factor.	
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 6.4.1

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 **6.4.1** is a chart for determining what conversion factor is needed, and Figure **6.4.2** is a flow diagram for the steps needed to perform a conversion.

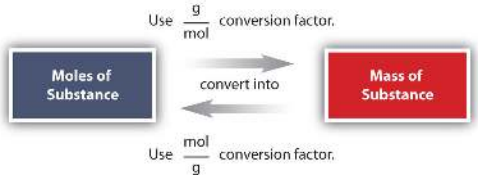


Figure **6.4.1** A Simple Flowchart for Converting between Mass and Moles of a Substance. It takes one mathematical step to convert from moles to mass or from mass to moles.

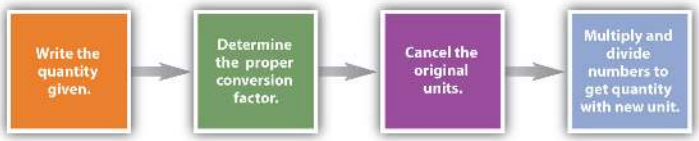


Figure **6.4.2** A Flowchart Illustrating the Steps in Performing a Unit Conversion. When performing many unit conversions, the same logical steps can be taken.

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 **6.4.3**.

Example 6.4.2: Calcium Chloride

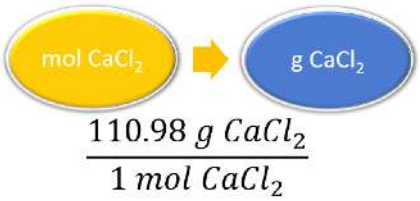
Calculate the mass of 3.00 moles of calcium chloride ($CaCl_2$).



Figure **6.4.1**: Calcium chloride is used as a drying agent and as a road deicer.

Solution

Example **6.4.2**: 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 $CaCl_2$
Prepare a concept map and use the proper conversion factor.	 $\frac{110.98\ g\ CaCl_2}{1\ mol\ CaCl_2}$
Cancel units and calculate.	$3.00\ \cancel{mol\ CaCl_2} \times \frac{110.98\ g\ CaCl_2}{1\ \cancel{mol\ CaCl_2}} = 333\ g\ CaCl_2$
Think about your result.	

Exercise 6.4.2: Calcium Oxide

What is the mass of **7.50 mol** of (calcium oxide) **CaO**?

Answer:

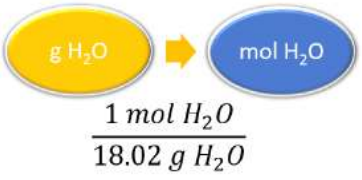
420.60 g

Example 6.4.3: Water

How many moles are present in 108 grams of water?

Solution

Example **6.4.3**: 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	$1\ mol\ H_2O = 18.02\ g\ H_2O$
Prepare a concept map and use the proper conversion factor.	 $\frac{1\ mol\ H_2O}{18.02\ g\ H_2O}$
Cancel units and calculate.	$108\ \cancel{g\ H_2O} \times \frac{1\ mol\ H_2O}{18.02\ \cancel{g\ H_2O}} = 5.99\ mol\ H_2O$
Think about your result.	

Exercise 6.4.3: Nitrogen Gas

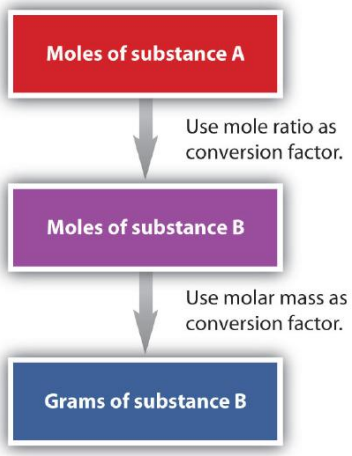
What is the mass of **7.50 mol** of Nitrogen gas N_2?

Answer:

210 g

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:

$$3.59 \ \cancel{\text{mol Fe}_2\text{O}_3} \times \left(\frac{3 \text{ mol SO}_3}{1 \ \cancel{\text{mol Fe}_2\text{O}_3}} \right) = 10.77 \text{ mol SO}_3 \tag{6.4.2}$$

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:

$$10.77 \ \cancel{\text{mol SO}_3} \times \left(\frac{80.06 \text{ g SO}_3}{1 \ \cancel{\text{mol SO}_3}} \right) = 862 \text{ g SO}_3 \tag{6.4.3}$$

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.

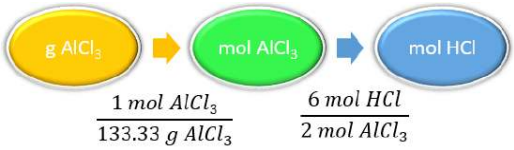
Example 6.4.4: Generation of Aluminum Oxide

How many moles of HCl will be produced when 249 g of $AlCl_3$ are reacted according to this chemical equation?

$$2AlCl_3 + 3H_2O(\ell) \rightarrow Al_2O_3 + 6HCl(g)$$

Solution

Example **6.4.4**: Steps for Problem Solving how many moles are in 249 g of $AlCl_3$?

Steps for Problem Solving	Example
Identify the "given"information and what the problem is asking you to "find."	Given: 249 g $AlCl_3$ Find: moles HCl
List other known quantities	1 mol $AlCl_3$ = 133.33 g/mol 6 mol of HCl to 2 mol $AlCl_3$
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 6.4.4: Generation of Aluminum Oxide

How many moles of Al_2O_3 will be produced when 23.9 g of H_2O are reacted according to this chemical equation?

$$2AlCl_3 + 3H_2O(\ell) \rightarrow Al_2O_3 + 6HCl(g)$$

Answer

0.442 mol Al_2O_3

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:

$$\frac{2\ \text{mol}\ H_2}{1\ \text{mol}\ O_2} \text{ or } \frac{1\ \text{mol}\ O_2}{2\ \text{mol}\ H_2}$$

$$\frac{2\ \text{mol}\ H_2O}{1\ \text{mol}\ O_2} \text{ or } \frac{1\ \text{mol}\ O_2}{2\ \text{mol}\ H_2O}$$

$$\frac{2\ \text{mol}\ H_2}{2\ \text{mol}\ H_2O} \text{ or } \frac{2\ \text{mol}\ H_2O}{2\ \text{mol}\ H_2}$$

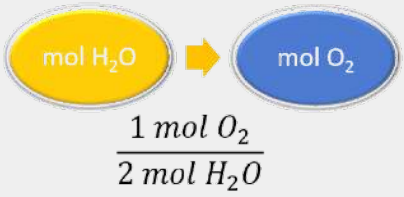
We can use these ratios to determine what amount of a substance, in moles, will react with or produce a given number of moles of a different substance. The study of the numerical relationships between the reactants and the products in balanced chemical reactions is called *stoichiometry*.

Example 6.4.5

How many moles of oxygen react with hydrogen to produce 27.6 mol of H_2O?

Solution

Example **6.4.5**: Steps for Problem Solving how many moles of oxygen react with hydrogen to produce 27.6 mol of H2O?

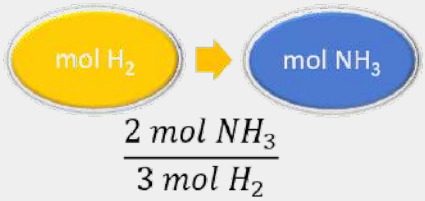
Steps for Problem Solving	Example
Find a balanced equation that describes the reaction	Unbalanced: $H_2 + O_2 \rightarrow H_2O$ Balanced: $\underline{2}H_2 + O_2 \rightarrow \underline{2}H_2O$
Identify the "given"information and what the problem is asking you to "find."	Given: moles H_2O Find: moles 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.	$\cancel{27.6\ mol\ H_2O} \times \frac{1\ mol\ O_2}{\cancel{2\ mol\ H_2O}} = 13.8\ mol\ O_2$ 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 6.4.6

How many moles of ammonia are produced if 4.20 moles of hydrogen are reacted with an excess of nitrogen?

Solution

Example **6.4.6**: 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: $\mathbf{H_2 = 4.20\ mol}$ Find: **mol** of $\mathbf{NH_3}$
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.	$\cancel{4.20\ mol\ H_2} \times \frac{2\ mol\ NH_3}{\cancel{3\ mol\ H_2}} = 2.80\ mol\ NH_3$ The reaction of **4.20 mol** of hydrogen with excess nitrogen produces **2.80 mol** of ammonia
Think about your result.	The result corresponds to the 3:2 ratio of hydrogen to ammonia from the balanced equation.

Exercise 6.4.5

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:

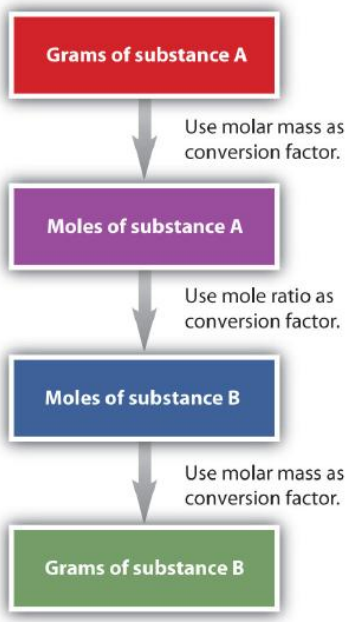
3.14 mol H_2O

Answer b:

$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$; 2.48 mol H_2O

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.

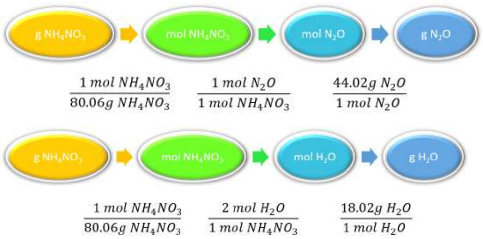
Example 6.4.7: Decomposition of Ammonium Nitrate

Ammonium nitrate decomposes to dinitrogen monoxide and water according to the following equation.

$$NH_4NO_3\,(s) \rightarrow N_2O\,(g) + 2H_2O\,(l)$$

In a certain experiment, **45.7 g** of ammonium nitrate is decomposed. Find the mass of each of the products formed.

Example **6.4.7**: Steps for Problem Solving the Decomposition of Ammonium Nitrate

Steps for Problem Solving	Example 6.4.2
Identify the "given"information and what the problem is asking you to "find."	Given: $45.7\ g\ NH_4NO_3$ Find: Mass $N_2O = ?\ g$ Mass $H_2O = ?\ g$
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.	
Cancel units and calculate.	$45.7\ g\ NH_4NO_3 \times \frac{1\ mol\ NH_4NO_3}{80.06\ g\ NH_4NO_3} \times \frac{1\ mol\ N_2O}{1\ mol\ NH_4NO_3} \times \frac{44.02\ g\ N_2O}{1\ mol\ N_2O} = 25.1\ g\ N_2O$ $45.7\ g\ NH_4NO_3 \times \frac{1\ mol\ NH_4NO_3}{80.06\ g\ NH_4NO_3} \times \frac{2\ H_2O}{1\ mol\ NH_4NO_3} \times \frac{18.02\ g\ H_2O}{1\ mol\ H_2O} = 20.6\ g\ H_2O$
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 6.4.6: 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

908.7g HCl

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

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6.5: Solutions

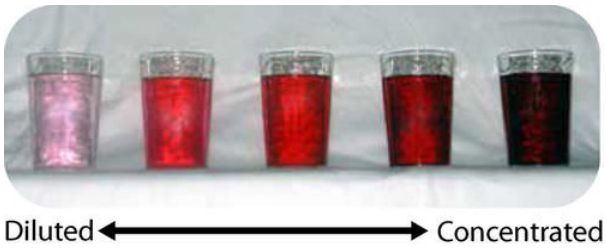
Learning Objectives

- 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 $1\ \text{nm}$ 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.

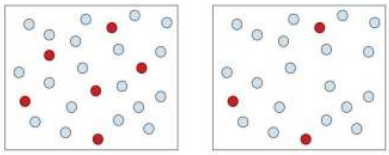


Figure **6.5.2** *The solution on the left is more concentrated than the solution on the right because there is a greater ratio of solute (red balls) to solvent (blue balls) particles. The solution particles are closer together. The solution on the right is more dilute (less concentrated). (CC-SA-BY-3.0 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.

$$\text{molarity} = \frac{\text{number of moles of solute}}{\text{number of liters of solution}} \tag{6.5.1}$$

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 $[Ag^+]$ 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:

$$M = \frac{0.614\ mol\ HCl}{1.56 L\ solution} = 0.394\ M HCl$$

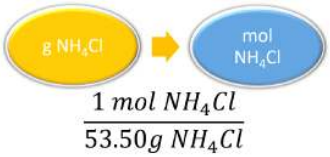
Before a molarity concentration can be calculated, the amount of the solute must be expressed in moles, and the volume of the solution must be expressed in liters, as demonstrated in the following example.

Example 6.5.1

A solution is prepared by dissolving **42.23 g** of NH_4Cl into enough water to make **500.0 mL** of solution. Calculate its molarity.

Solution

Example **6.5.1**: 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 $= 42.23\ \text{g}\ NH_4Cl$ Volume solution $= 500.0\ \text{mL} = 0.5000\ \text{L}$ Find: Molarity = ? M
List other known quantities.	Molar mass $NH_4Cl = 53.50\ \text{g/mol}$
Plan the problem.	1. The mass of the ammonium chloride is first converted to moles.  $\frac{1\ mol\ NH_4Cl}{53.50g\ NH_4Cl}$ 2. Then the molarity is calculated by dividing by liters. Note the given volume has been converted to liters. $\text{M} = \frac{\text{mol NH}_4\text{Cl}}{\text{L solution}}$
Cancel units and calculate.	Now substitute the known quantities into the equation and solve. $42.23\ \cancel{\text{g NH}_4\text{Cl}} \times \frac{1\ \text{mol}\ \cancel{\text{NH}_4\text{Cl}}}{53.50\ \text{g NH}_4\text{Cl}} = 0.7893\ \text{mol NH}_4\text{Cl}$ (6.5.2) $\frac{0.7893\ \text{mol NH}_4\text{Cl}}{0.5000\ \text{L solution}} = 1.579\ \text{M}$ (6.5.3)
Think about your result.	The molarity is $1.579\ \text{M}$, meaning that a liter of the solution would contain $1.579\ \text{mol}\ NH_4Cl$. Four significant figures are appropriate.

? Exercise 6.5.1

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

1.57 M $C_6H_{12}O_6$

? Exercise 6.5.2

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

4.69 M NaCl

Figure **6.5.1** illustrates how a solution is prepared with the measured amount of a solid solute and the desired final volume of the solution.

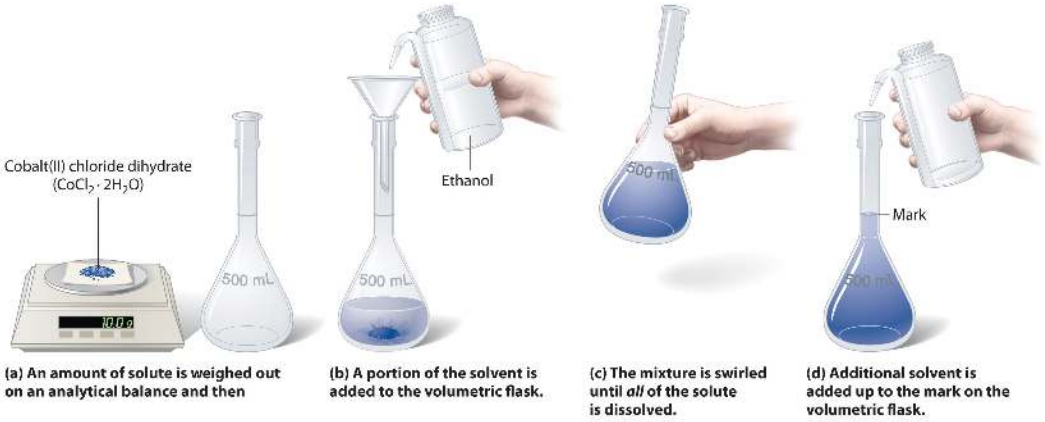


Figure **6.5.3**: Preparation of a solution of known concentration using a solid solute.

(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 $\mathbf{40\ mL}$ of ethanol to $\mathbf{20\ mL}$ of water, the percent by volume is:

$$\text{Percent by volume} = \frac{\text{volume of solute}}{\text{volume of solution}} \times 100\% \tag{6.5.4}$$

$$= \frac{40\ \text{mL ethanol}}{240\ \text{mL solution}} \times 100\% \tag{6.5.5}$$

$$= 16.7\%\ \text{ethanol} \tag{6.5.6}$$

Frequently, ingredient labels on food products and medicines have amounts listed as percentages (see figure below).

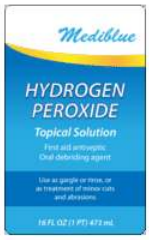


Figure **6.5.4** Hydrogen peroxide is commonly sold as *a* $\mathbf{3\%}$ *by volume solution for use as a disinfectant.*

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 $\mathbf{25.0\ g}$ of sugar into $\mathbf{100.0\ g}$ 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 6.5.2

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:

$$\%\,\text{m/m} = \frac{36.5\text{ g}}{355\text{ g}} \times 100\% = 10.3\%$$

Exercise 6.5.3

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

7.90 %

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 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 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 6.5.4

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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- Marisa Alviar-Agnew (Sacramento City College)
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CHAPTER OVERVIEW

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

7.1: Solids, Liquids, and Gases

7.2: Comparing Ionic and Molecular Substances

7.3: Forces between Molecules

7.4: Forces in Solutions

7.5: Gases- The Kinetic-Molecular Theory

7.6: The Simple Gas Laws

7.7: The Ideal Gas Law

Thumbnail: A water drop. (CC BY 2.0; José Manuel Suárez via Wikipedia).

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7.1: 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.

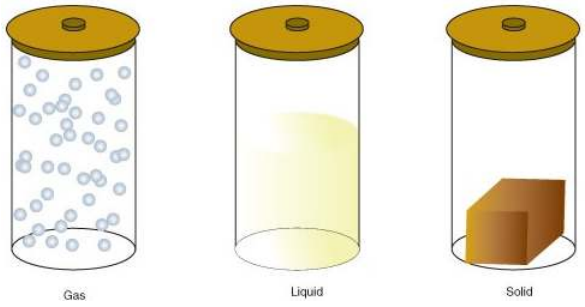
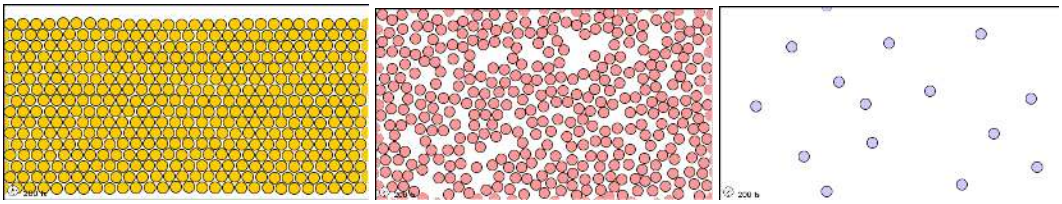


Figure **7.1.1**: States of Matter. All three containers contain a substance with the same mass, but the substances are in different states. In the left-hand container, the substance is a gas, which has spread to fill its container. It takes both the shape and volume of the container. In the middle container, 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 **7.1.2**, 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 LIQUID GAS

***Figure* 7.1.2** *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 **7.1.3** and **7.1.4** show the differences among solids, liquids, and gases at the molecular level, while Table **7.1.1** lists the different characteristics of these states.

Table **7.1.1** 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 7.1.1

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 7.1.1

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

solid

Answer b

gas

Answer c

liquid or gas

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 **7.1.3**).

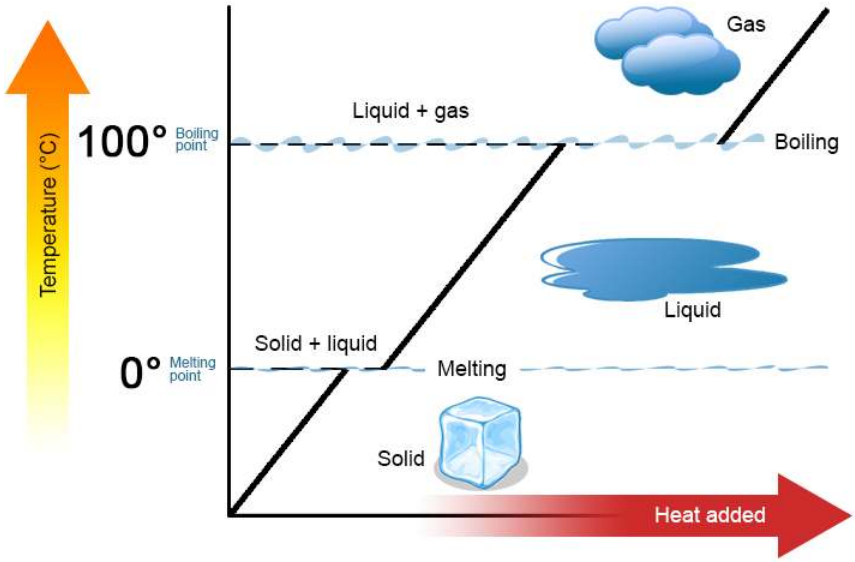


Figure 7.1.3: Heating curve for water. As heat is added to solid water, the temperature increases until it reaches 0 °C, *the melting point. At this point, the phase change, added heat goes into changing the state from a solid to liquid. Only when this phase change is complete, the temperature can increase. (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 **7.1.3**, **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 **7.1.4**: 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

-
- Libretexts: The Basics of GOB (Ball et.al.)
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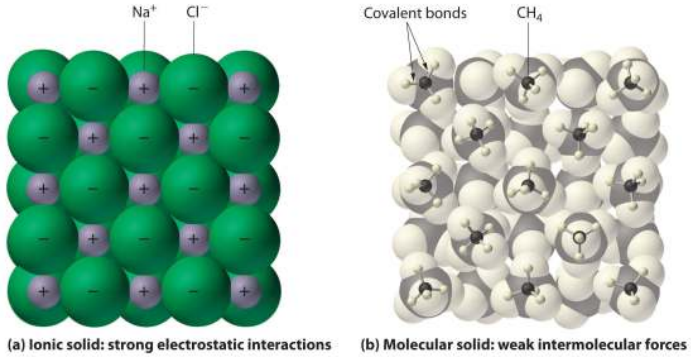
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7.2: Comparing Ionic and Molecular Substances

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 **7.2.1**) . 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* 7.2.1** 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 **7.2.2**; Video **7.2.1**).

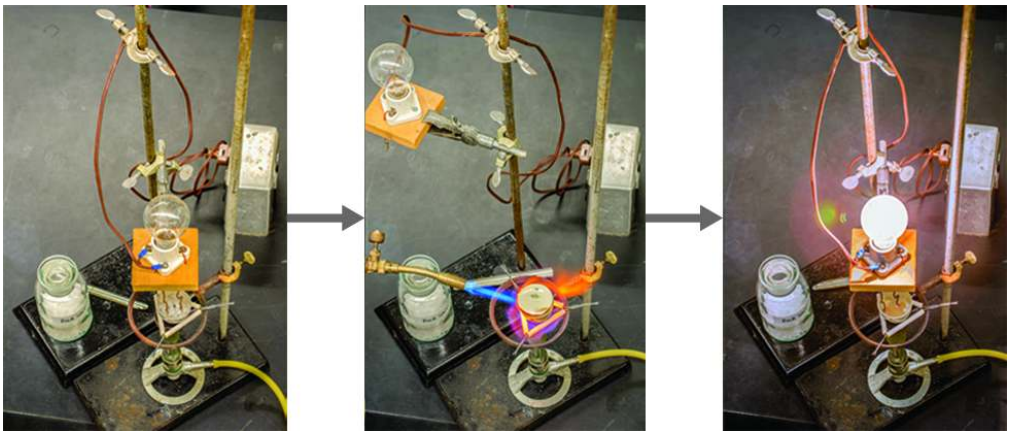


Figure **7.2.2** Sodium chloride melts at 801 °C and conducts electricity when molten. (credit: modification of work by Mark Blaser and Matt Evans)

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



Video **7.2.1** *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* 7.2.1** *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
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°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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7.3: 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 **7.3.1** 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.

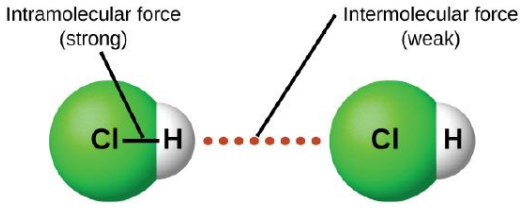


Figure **7.3.1** Intramolecular forces keep a molecule intact. Intermolecular forces hold multiple molecules together and determine many of a substance's properties.

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.

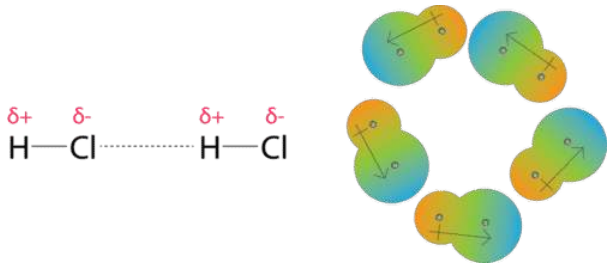


Figure **7.3.2** *Dipole-dipole forces result from the attraction between the positive end of one dipole and the negative end of a neighboring dipole. Dipole-dipole forces are similar to ionic bonds, but because they involve only partial charges, they are much weaker.*

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 **7.3.1**.

Table **7.3.1**: 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 7.3.1 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 7.3.1

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

Answer

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

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 **7.3.3** *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 **7.3.1**.

Table **7.3.2**: 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 **7.3.4** 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).

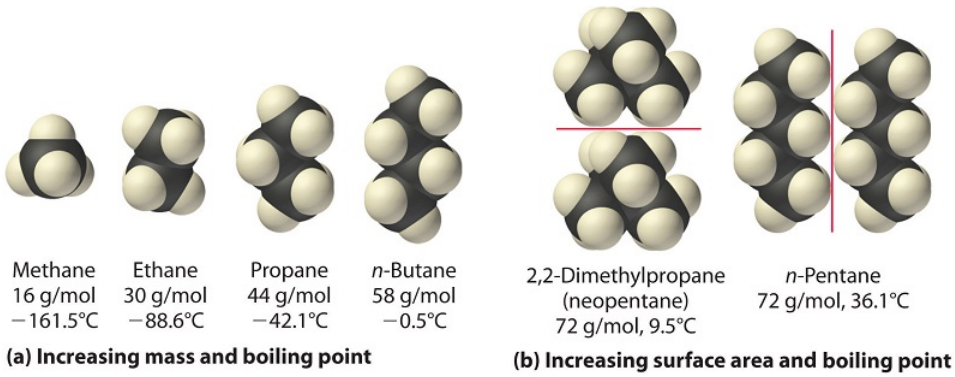


Figure **7.3.4** Mass and Surface Area Affect the Strength of London Dispersion Forces. (a) In this series of four simple alkanes, larger molecules have stronger London forces between them than smaller molecules and consequently higher boiling points. (b) Linear *n*-pentane molecules have a larger surface 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 7.3.2 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:

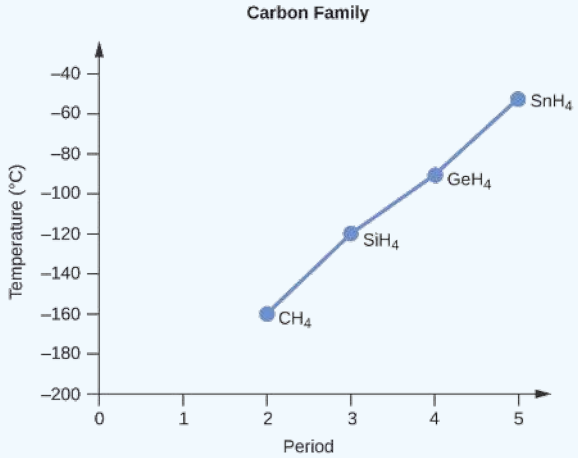
Determine the intermolecular forces in the compound. Also, compare the molar masses and surface area of compounds with similar types of intermolecular force. The substance with the weakest forces and the lowest molar masses and least surface area have the lowest boiling point.

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 7.3.2

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

Answer

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

$$C_2H_6 < C_3H_8 < C_4H_{10}.$$

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).

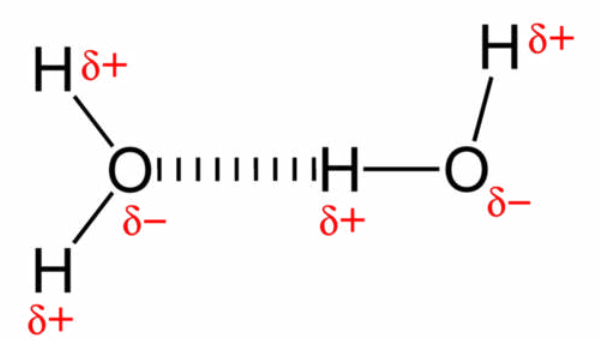


Figure **7.3.5** A hydrogen bond in water occurs between the hydrogen atom of one water molecule and the lone pair of electrons on the oxygen atom of a neighboring water molecule.

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.

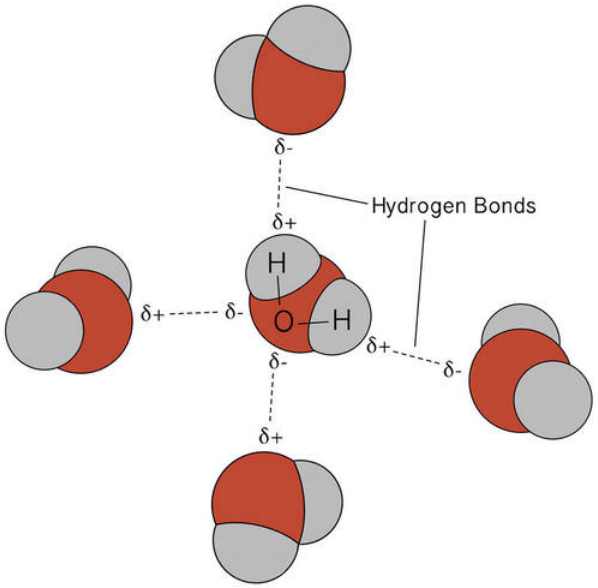


Figure **7.3.6**Multiple hydrogen bonds occur simultaneously in water because of its bent shape and the presence of two hydrogen atoms per molecule.

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 **7.3.7**). 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.

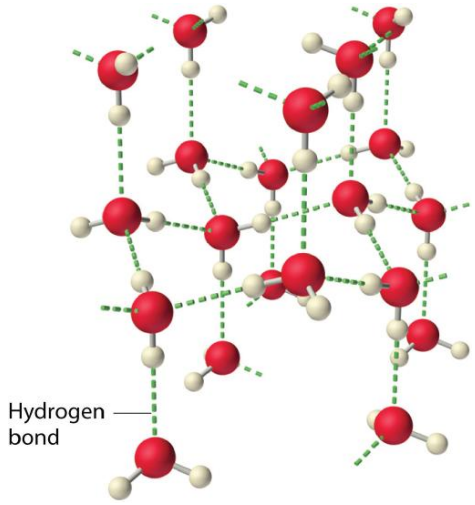


Figure **7.3.7** The Hydrogen-Bonded Structure of Ice.

> *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 **7.3.8**. 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.

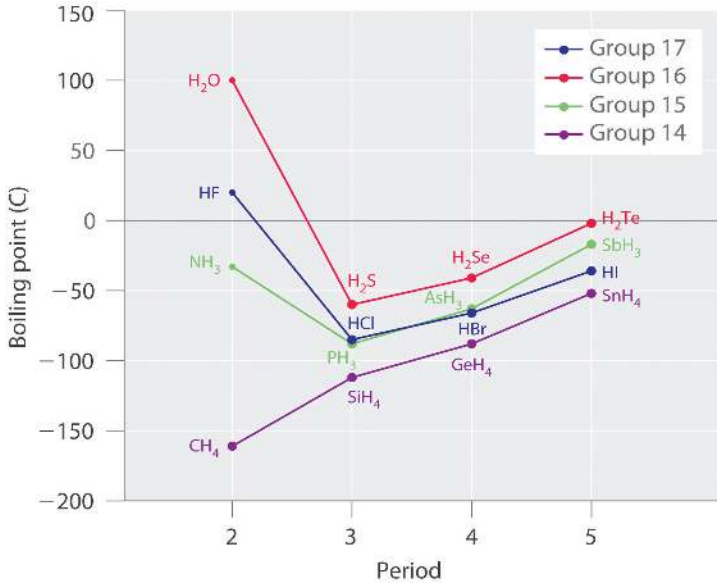


Figure **7.3.8** The Effects of Hydrogen Bonding on Boiling Points. These plots of the boiling points of the covalent hydrides of the elements of groups 14–17 show that the boiling points of the lightest members of each series for which hydrogen bonding is possible (HF, NH_3, and H_2O) are anomalously high for compounds with such low molecular masses.

Example 7.3.3

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:

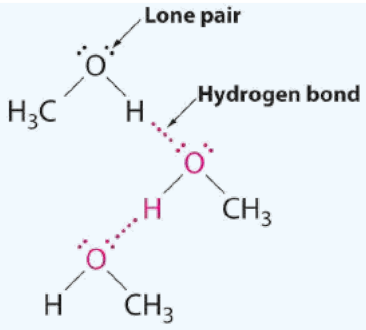
A. Identify the compounds with a hydrogen atom attached to O, N, or F. These are likely to be able to act as hydrogen bond donors.

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:



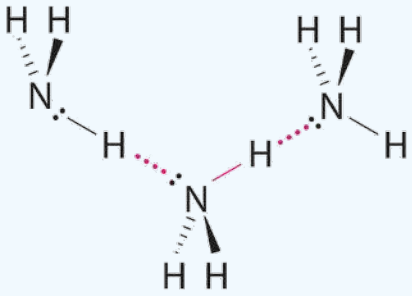
Hydrogen bonding in methanol

Exercise 7.3.3

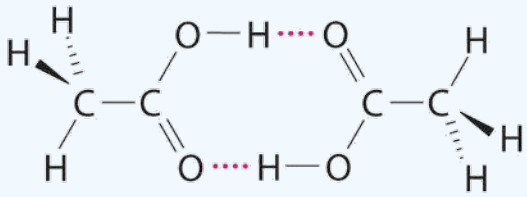
Considering CH_3CO_2H, $(CH_3)_3N$, NH_3, and CH_3F, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Answer

CH_3CO_2H and NH_3;



Hydrogen bonding in ammonia



Hydrogen bonding in acetic acid

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 7.3.4: 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:

$$\text{He } (-269^\circ\text{C}) < \text{Ar } (-185.7^\circ\text{C}) < N_2O\ (-88.5^\circ\text{C}) < C_{60}\ (>280^\circ\text{C}) < \text{NaCl } (1465^\circ\text{C}).$$

? Exercise 7.3.4

Arrange 2,4-dimethylheptane, Ne, CS_2, Cl_2, and KBr in order of decreasing boiling points.

Answer

KBr (1435°C) > 2,4-dimethylheptane (132.9°C) > CS_2 (46.6°C) > Cl_2 (−34.6°C) > Ne (−246°C)

✓ Example 7.3.5:

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 7.3.5

Identify the most significant intermolecular force in each substance.

a. HF
b. HCl

Answer a

hydrogen bonding

Answer b

dipole-dipole interactions

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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7.4: 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 **7.4.1** 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 **7.4.1**.

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 **7.4.1** lists some common types of solutions, with examples of each.

Table **7.4.1** Types of Solutions

Solvent Phase	Solute Phase	Example
gas	gas	air
liquid	gas	carbonated beverages
liquid	liquid	ethanol (C_2H_5OH) in H_2O (alcoholic beverages)
liquid	solid	salt water
solid	gas	H_2 gas absorbed by Pd metal
solid	liquid	Hg(ℓ) in dental fillings
solid	solid	steel alloys

Example 7.4.1: 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 7.4.1

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

solute: HCl(g); solvent: CH_3OH

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 7.4.2 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 **7.4.1** 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 **7.4.2** *Water (clear liquid) and oil (yellow) do not form liquid solutions. (CC BY-SA 1.0 Generic; Victor Blacus)*

Example 7.4.2: 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 7.4.2

Would C_3H_7OH be more soluble in CCl_4 or H_2O? Explain your answer.

Answer

H_2O because both experience hydrogen bonding

Example 7.4.3

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 7.4.3

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

octane (C_8H_{18}) will dissolve. It is also non-polar.

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).

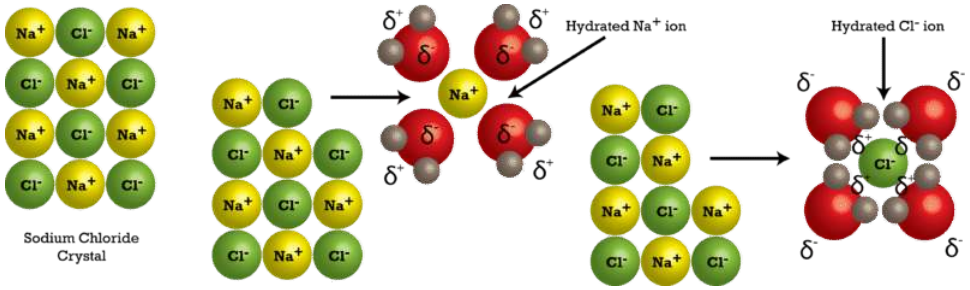


Figure 7.4.3: *The process of an ionic sodium chloride crystal being dissolved and hydrated by water.*

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 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 ($C_{12}H_{22}O_{11}$). 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.

Contributors and Attributions

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7.5: 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 **7.5.1** shows a representation of how we mentally picture the gas phase.

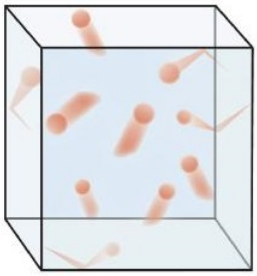


Figure **7.5.1** The kinetic -molecular theory of gases. The kinetic theory of gases describes this state of matter as composed of tiny particles in constant motion with a lot of distance between the particles.

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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7.6: 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 atm** of pressure and is equal to **760 mm Hg** and **101.3 kPa**. Atmospheric pressure is also often stated as pounds per square inch (**psi**). The atmospheric pressure at sea level is **14.7 psi**.

$$\mathbf{1\ atm = 760\ mm\ Hg = 760\ torr = 101.3\ kPa = 14.7\ psi}$$

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 **7.6.1** shows two representations of how Boyle's law works.

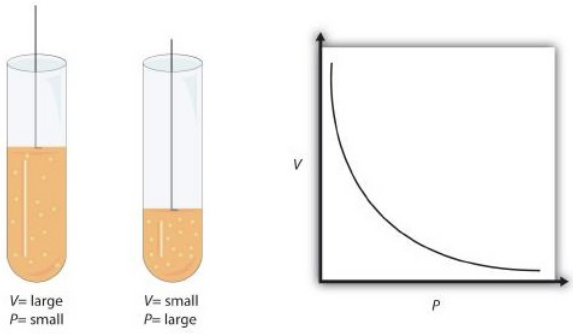


Figure **7.6.1** Boyle's Law. A piston having a certain pressure and volume (left piston) will have half the volume when its pressure is twice as much (right piston). One can also plot P versus V for a given amount of gas at a certain temperature; such a plot will look like the graph on the right.

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 7.6.1

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 **7.6.1**: Steps for Problem Solving volume and pressure changes.

Steps for Problem Solving	**Example 7.6.1**
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
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 decreasing (from 2.44 atm to 1.93 atm), so volume should be increasing to compensate, and it is (from 4.01 L to 5.07 L). So the answer makes sense based on Boyle's law.

? Exercise 7.6.1

If P_1 = 334 torr, V_1 = 37.8 mL, and P_2 = 102 torr, what is V_2?

Answer

124 mL

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 7.6.2:

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 7.6.2:Steps for Problem Solving volume and pressure changes

Steps for Problem Solving	Example 7.6.2
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.
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. $$P_2 = \frac{722\ \text{torr} \times 88.8\ \cancel{mL}}{663\ \cancel{mL}} = 96.7\ \text{torr}$$
Think about your result.	When the volume increased, the pressure decreased, which is as expected for Boyle's law.

? Exercise 7.6.2

If V_1 = 456 mL, P_1 = 308 torr, and P_2 = 1.55 atm, what is V_2?

Answer

119 mL

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.

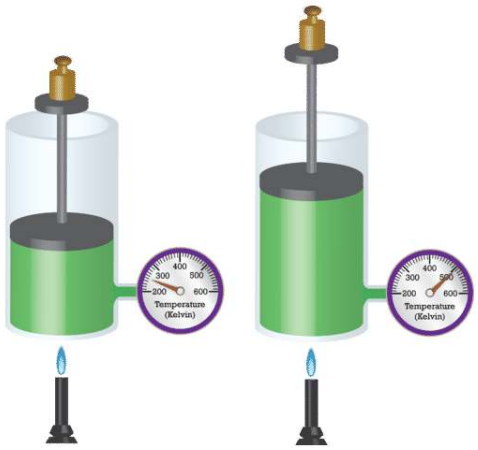


Figure 7.6.2 As a container of confined gas is heated, its molecules increase in kinetic energy and push the movable piston outward, resulting in an increase in volume.

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 7.6.1 Temperature-Volume Data

Temperature (K)	Volume (mL)	$\frac{V}{T} = k\ (\frac{\text{mL}}{\text{K}})$
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.

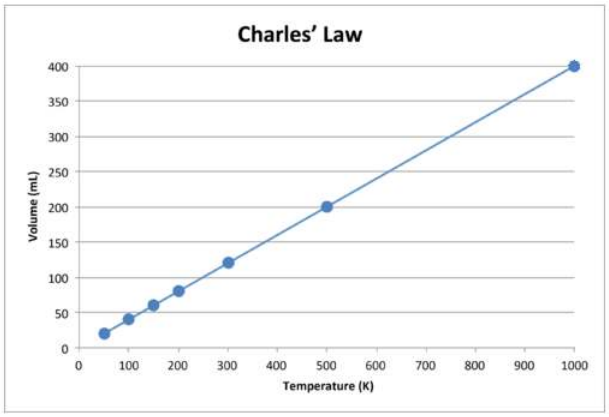


Figure **7.6.3** graph plots how the volume of a gas increases as the Kelvin temperature increases. The increase is linear.

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 7.6.3:

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 7.6.3
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: V_2 = ? L
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. $V_2 = \frac{2.20\ \mathrm{L} \times 344\ \cancel{\mathrm{K}}}{295\ \cancel{\mathrm{K}}} = 2.57\ \mathrm{L}$
Think about your result.	The volume increases as the temperature increases. The result has three significant figures.

Exercise 7.6.3

If V_1 = 3.77 L and T_1 = 255 K, what is V_2 if T_2 = 123 K?

Answer

1.82 L

Example 7.6.4:

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 **7.6.4**: Steps for Problem Solving Volume and Tempature Changes

Steps for Problem Solving	Example 7.6.4
Identify the "given"information and what the problem is asking you to "find."	Given: Given:T_1 = -27°C and V_1 = 34.8 L V_2 = 25.0 L Find: T_2 = ? K
List other known quantities.	K = -27°C + 273
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 7.6.4

If V_1 = 623 mL, T_1 = 255°C, and V_2 = 277 mL, what is T_2?

Answer

235 K, or −38°

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 7.6.4 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 7.6.5

The gas in an aerosol can is under a pressure of $3.00\ \text{atm}$ at a temperature of $25°\text{C}$. It is dangerous to dispose of an aerosol can by incineration. What would the pressure in the aerosol can be at a temperature of $845°\text{C}$?

Solution

Example 7.6.5: Steps for Problem Solving Volume and Tempature Changes

Steps for Problem Solving	Example 7.6.5
Identify the "given"information and what the problem is asking you to "find."	Given: $P_1 = 3.00\ \text{atm}$ $T_1 = 25°\text{C} = 298\ \text{K}$ $T_2 = 845°\text{C} = 1118\ \text{K}$ 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.

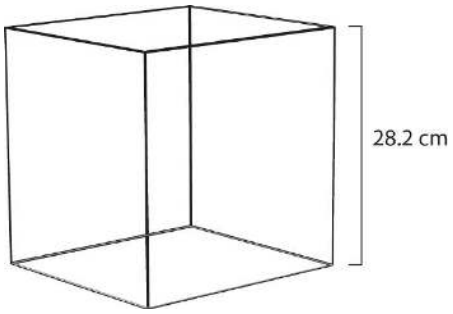


Figure **7.6.5** Molar volume. A mole of gas at STP occupies 22.4 L, the volume of a cube that is 28.2 cm on a side.

Example 7.6.6:

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 7.6.5

What volume does 4.87 mol of Kr have at STP?

Figure **7.6.5** 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.

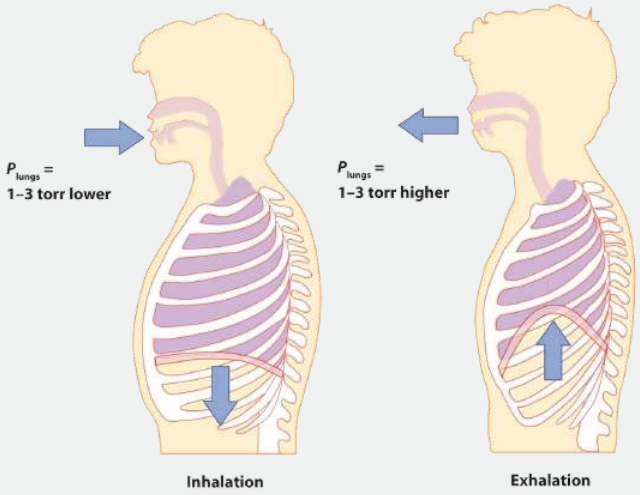


Fig. 6.6.2 Breathing Mechanics. Breathing involves pressure differences between the inside of the lungs and the air outside. The pressure differences are only a few torr.

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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7.7: 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: $\mathbf{kPa}$, $\mathbf{atm}$, or $\mathbf{mm\ Hg}$. Therefore, R can have three different values.

We will demonstrate how R is calculated when the pressure is measured in $\mathbf{kPa}$. The volume of $\mathbf{1.00\ mol}$ of any gas at STP (Standard temperature, 273.15 K and pressure, 1 atm)is measured to be $\mathbf{22.414\ L}$. We can substitute $\mathbf{101.325\ kPa}$ for pressure, $\mathbf{22.414\ L}$ for volume, and $\mathbf{273.15\ K}$ for temperature into the ideal gas equation and solve for R.

$$\begin{aligned} R &= \frac{PV}{nT} \\ &= \frac{101.325\ \text{kPa} \times 22.414\ \text{L}}{1.000\ \text{mol} \times 273.15\ \text{K}} \\ &= 8.314\ \text{kPa} \cdot \text{L/K} \cdot \text{mol} \end{aligned}$$

This is the value of R that is to be used in the ideal gas equation when the pressure is given in $\mathbf{kPa}$. 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 **7.7.1** 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	$8.314\ \text{J/K} \cdot \text{mol}$
atm	L	mol	K	$0.08206\ \text{L} \cdot \text{atm/K} \cdot \text{mol}$
mm Hg	L	mol	K	$62.36\ \text{L} \cdot \text{mm Hg/K} \cdot \text{mol}$

Notice that the unit for R when the pressure is in $\mathbf{kPa}$ has been changed to $\mathbf{J/K \cdot mol}$. A kilopascal multiplied by a liter is equal to the SI unit for energy, a joule ($\mathbf{J}$).

Example 7.7.1 Oxygen Gas

What volume is occupied by **3.76 g** of oxygen gas at a pressure of **88.4 kPa** and a temperature of **19°C**? Assume the oxygen is ideal.

Solution

Example **7.7.1** Steps for Problem Solving volume of oxygen gas

Steps for Problem Solving	**Example 7.7.1**
Identify the "given"information and what the problem is asking you to "find."	Given: • $P = 88.4\ \text{kPa}$ • $T = 19°\text{C} = 292\ \text{K}$ Mass $O_2 = 3.76\ \text{g}$ Find: V = ? L
List other known quantities	$O_2 = 32.00\ \text{g/mol}$ $R = 8.314\ \text{J/K} \cdot \text{mol}$
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. $$3.76\ \cancel{g} \times \frac{1\ \text{mol}\ O_2}{32.00\ \cancel{g}\ O_2} = 0.1175\ \text{mol}\ O_2$$ 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 molar volume $(22.4\ \text{L/mol})$ since the pressure and temperature are reasonably close to standard. The result has three significant figures 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 in liters.

Example 7.7.2: 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 **7.7.2**: Steps for Problem Solving volume of argon gas

Steps for Problem Solving	Example 7.7.2
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\, \cancel{K)}}{1.21\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 7.7.1

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 7.7.2

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 7.7.3:

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 **7.7.3**: Steps for Problem Solving pressure of gas

Steps for Problem Solving	Example 7.7.3
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: $P2$ = ? 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 gas were changing.

? Exercise 7.7.3

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

105 mL

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 $8.314\,J/K \cdot mol$ 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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CHAPTER OVERVIEW

8: Acids and Bases

8.1: Acids and Bases - Experimental Definitions
8.2: Acids and Bases
8.3: Acidic and Basic Anhydrides
8.4: Strong and Weak Acids and Bases
8.5: Neutralization
8.6: The pH Scale
8.7: Buffers and Conjugate Acid-Base Pairs
8.8: Acids and Bases in Industry and in Daily Life

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8.1: 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 **8.1.1** provides some examples of acids and bases.



Figure **8.1.1** 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:

$$\mathrm{Zn}\,(s) + \mathrm{H_2SO_4}\,(aq) \rightarrow \mathrm{ZnSO_4}\,(aq) + \mathrm{H_2}\,(g) \tag{8.1.1}$$

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 8.1.2 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

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8.2: 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.

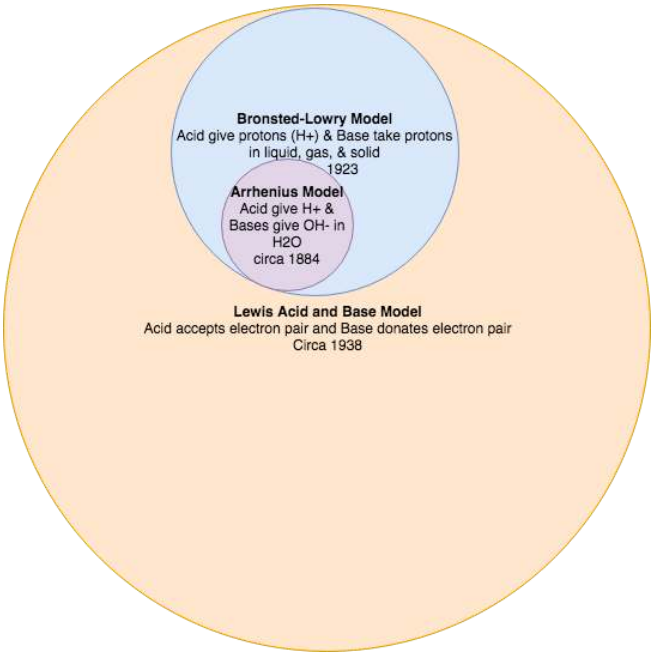


Figure **8.2.1** Acid base reaction theories as superset and subset models.

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 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.

$$HCl\,(aq) \rightarrow H^+\,(aq) + Cl^-\,(aq)$$

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:

$$HCl\,(aq) + H_2O\,(l) \rightarrow H_3O^+\,(aq) + Cl^-\,(aq)$$

An **Arrhenius base** is a compound that **increases the concentration of OH^- ions** that are present when added to water. The dissociation is represented by the following equation:

$$NaOH\ \ (aq) \rightarrow Na^+\ \ (aq) + OH^-\ \ (aq)$$

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:

$$\mathrm{NH_3\,(aq) + H_2O\,(\ell) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)} \tag{8.2.1}$$

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 8.2.2):

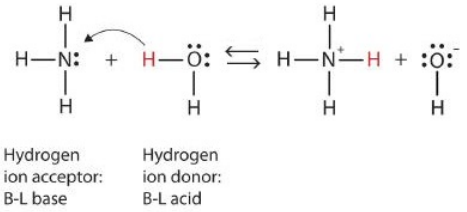


Figure 8.2.2 reaction of ammonia and water.

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 $\mathbf{H_5O_2^+}$ or $\mathbf{H_9O_4^+}$ rather than $\mathbf{H_3O^+}$. It is simpler, however, to use $\mathbf{H_3O^+}$ to represent the hydronium ion.

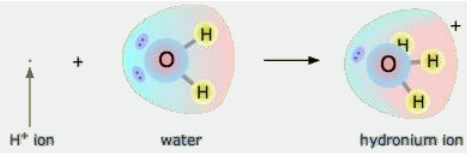


Figure **8.2.3** reaction of hydrogen and water to form hydronium. (CC BY-NC 3.0

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:

$$\mathbf{HCl\,(g) + H_2O\ (\ell)\ \rightarrow H_3O^+\,(aq) + Cl^-\,(aq)} \tag{8.2.2}$$

We can depict this process using Lewis electron dot diagrams (Figure **8.2.4**):

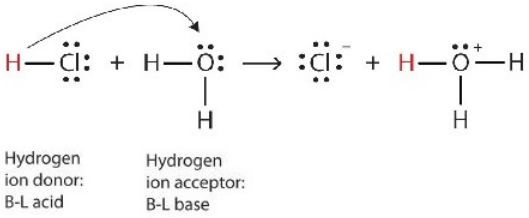


Figure **8.2.4** Lewis electron dot diagram of HCl dissolved in H_2O

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 **8.2.1**.

***Table* 8.2.1** *Acid-Base Definitions*

Type	Acid	Base
Arrhenius	$\mathbf{H^+}$ ions in solution	$\mathbf{OH^-}$ ions in solution
Brønsted-Lowry	$\mathbf{H^+}$ donor	$\mathbf{H^+}$ 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 8.2.1

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:

$$\mathbf{C_6H_5NH_2\,(aq) + H_2O(\ell) \rightleftharpoons C_6H_5NH_3^+\,(aq) + OH^-\,(aq)}$$

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 8.2.1

Identify the Brønsted-Lowry acid and the Brønsted-Lowry base in this chemical equation.

$$\mathbf{H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+}$$

Answer

Brønsted-Lowry acid: $H_2PO_4^-$; Brønsted-Lowry base: H_2O

Exercise 8.2.2

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:

A Brønsted-Lowry Base is a proton acceptor, which means it will take in an H^+. This eliminates $\mathbf{HCl}$, $\mathbf{H_3PO_4}$, $\mathbf{NH_4^+}$ and $\mathbf{CH_3NH_3^+}$ because they are Bronsted-Lowry acids. They all give away protons. In the case of $\mathbf{HPO_4^{2-}}$, consider the following equation:

$$\mathbf{HPO_4^{2-}(aq) + H_2O(l) \rightarrow PO_4^{3-}(aq) + H_3O^+(aq)}$$

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:

$$\mathbf{HPO_4^{2-}(aq) + H_2O(l) \rightarrow H_2PO_4^- + OH^-(aq)}$$

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) $\mathbf{HPO_4^{2-}}$.**

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

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- Marisa Alviar-Agnew (Sacramento City College)
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8.3: 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.

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8.4: 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:

$$HCl \xrightarrow{100\%} H^+(aq) + Cl^-(aq)$$

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:

$$HC_2H_3O_2 \xrightarrow{\sim 5\%} H^+(aq) + C_2H_3O_2^-(aq)$$

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 **8.4.1**. 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 **8.4.1** 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 **8.4.1**); 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 8.4.1: 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 **8.4.1**, it is a strong acid.
b. Because $Mg(OH)_2$ is listed in Table **8.4.1**, 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 8.4.1

Identify each acid or base as strong or weak.

a. **RbOH**
b. $\mathbf{HNO_2}$

Answer a

strong base

Answer b

weak acid

Example 8.4.2: 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:

$$\mathbf{Ca(OH)_2 \longrightarrow Ca^{2+}(aq) + 2\,OH^-(aq)}$$

Because $Ca(OH)_2$ is listed in Table **8.4.1**, this reaction proceeds 100% to products.

Exercise 8.4.2

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

The reaction is as follows:

$$\mathbf{HN_3 \longrightarrow H^+(aq) + N_3^-(aq)}$$

It does not proceed 100% to products because hydrazoic acid is not a strong acid.

Summary

- Strong acids and bases are 100% ionized in aqueous solution.
- Weak acids and bases are less than 100% ionized in aqueous solution.

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

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8.5: 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



***Video* 8.5.1** *Acid-base neutralization reaction.*

Example 8.5.1: 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 **8.5.1**: 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 8.5.1

Write a balanced chemical equation for the reaction of solid barium hydroxide with dilute acetic acid.

Answer

$$\mathbf{Ba(OH)_2\,(s) + 2\,CH_3CO_2H\,(aq) \longrightarrow Ba(CH_3CO_2)_2\,(aq) + 2\,H_2O\,(l)}$$

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 8.5.1 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)
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8.6: 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 **8.6.1** The pH scale.

Figure **8.6.2** 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:

$$[H^+] = 10^{-pH}$$

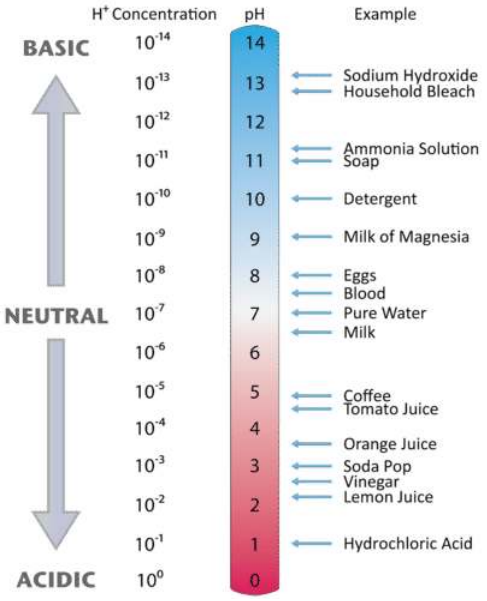


Figure **8.6.2** The ***pH*** values for several common materials with corresponding hydrogen ion concentration, [H+] .

Example 8.6.1

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 8.6.1

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

basic

Answer b

basic

Answer c

acidic

Table **8.6.1**: 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 **8.6.1** 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 8.6.2:

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 8.6.2

What is the $[H^+]$ for an aqueous solution whose pH is 11?

Answer

$[H^+] = 1.0 \times 10^{-11}$ M

Example 8.6.3:

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 1.0×10^{-7}M. The exponent of 10 is -7, which denoted that pH= -(-7) = **7**. The solution is **neutral**.

Exercise 8.6.3

What is the pH of an aqueous solution whose hydrogen ion concentration is 1.0×10^{-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

- Peggy Lawson (Oxbow Prairie Heights School). Funded by Saskatchewan Educational Technology Consortium.
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- Marisa Alviar-Agnew (Sacramento City College)
- Henry Agnew (UC Davis)

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8.7: 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, $\mathbf{OH^-}$, and the conjugate acid of ammonia, $\mathbf{NH_4^+}$:

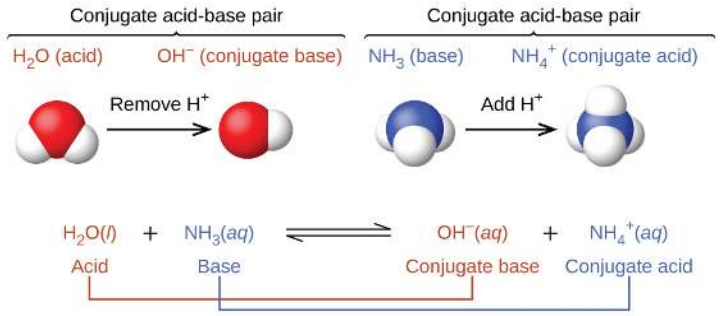


Figure **8.7.2**.This figure has three parts in two rows. In the first row, two diagrams of acid-base pairs are shown. On the left, a space filling model of H subscript 2 O is shown with a red O atom at the center and two smaller white H atoms attached in a bent shape. Above this model is the label “H 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 $\boldsymbol{NH_4^+/NH_3}$ and $\boldsymbol{H_2O/OH^-}$.

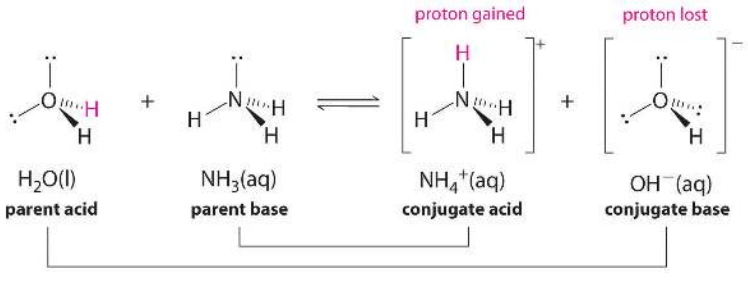


Figure **8.7.2**. The strongest acids are at the bottom left, and the strongest bases are at the top right. The conjugate base of a strong acid is a very weak base, and, conversely, the conjugate acid of a strong base is a very weak acid

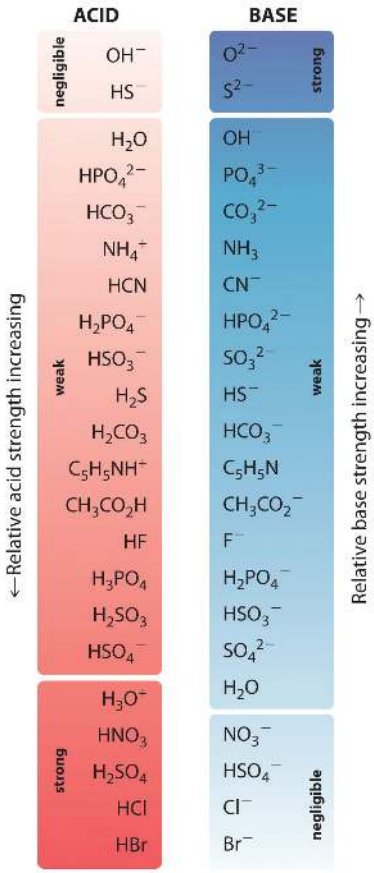


Figure **8.7.3** The Relative Strengths of Some Common Conjugate Acid–Base Pairs

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 8.7.1

Identify the conjugate acid-base pairs in this equilibrium.

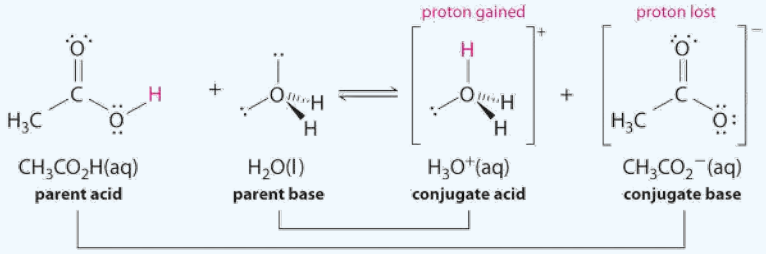
$$\mathbf{CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-}$$

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, $\boldsymbol{H_3O^+}$ 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 ($\boldsymbol{CH_3CO_2H/CH_3CO_2^-}$) and
- the parent base and its conjugate acid ($\boldsymbol{H_3O^+/H_2O}$).



Example **8.7.1** the reaction of acetic acid with water

Example 8.7.2

Identify the conjugate acid-base pairs in this equilibrium.

$$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$$

Solution

One pair is H_2O and OH^-, where H_2O has one more H^+ and is the conjugate acid, while OH^- has one less H^+ and is the conjugate base.

The other pair consists of $(CH_3)_3N$ and $(CH_3)_3NH^+$, where $(CH_3)_3NH^+$ is the conjugate acid (it has an additional proton) and $(CH_3)_3N$ is the conjugate base.

Exercise 8.7.1

Identify the conjugate acid-base pairs in this equilibrium.

$$NH_2^- + H_2O \rightleftharpoons NH_3 + OH^-$$

Answer:

H_2O (acid) and OH^- (base); NH_2^- (base) and NH_3 (acid)

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 $HC_2H_3O_2$ (a weak acid) and $NaC_2H_3O_2$ (the salt derived from that weak acid). Another example of a buffer is a solution containing NH_3 (a weak base) and NH_4Cl (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:

$$HC_2H_3O_2\,(aq) + OH^-\,(aq) \rightarrow H_2O(\ell) + C_2H_3O_2^-\,(aq) \tag{8.7.1}$$

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 $HC_2H_3O_2$:

$$H^+\,(aq) + C_2H_3O_2^-\,(aq) \rightarrow HC_2H_3O_2\,(aq) \tag{8.7.2}$$

Rather than changing the pH dramatically and making the solution acidic, the added H^+ ions react to make molecules of a weak acid. Figure 8.7.2 illustrates both actions of a buffer.

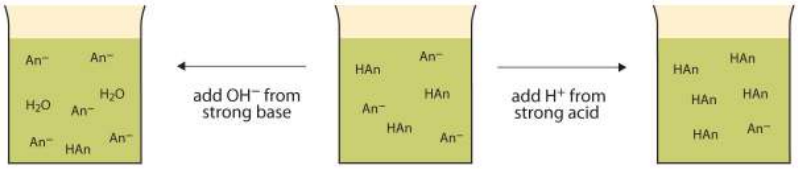


Figure **8.7.4** The actions of buffers. Buffers can react with both strong acids (top) and strong bases (side) to minimize large changes in pH.

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 **8.7.1** Some Common Buffers

Table **8.7.1** *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 8.7.3:

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 **8.7.1**, 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 8.7.2

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

Yes.

Answer b

No. Need a weak acid or base and a salt of its conjugate base or acid.

Answer c

Yes.

Answer d

No. Need a weak base or acid.

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 **8.7.1**, 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.

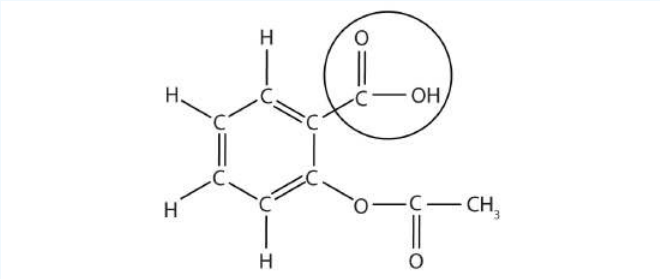


Figure **8.7.5**: The Molecular Structure of Aspirin. The circled atoms are the acid part of the molecule.

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

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

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8.8: Acids and Bases in Industry and in Daily Life

Learning Objective

- Know the many uses of common acids and bases.

Antacids: A Basic Remedy

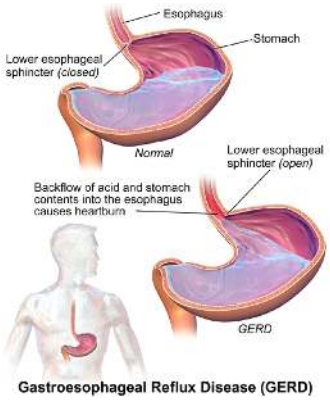


Figure 8.8.1. Antacids are available over the counter and are taken by mouth to quickly relieve occasional heartburn, the major symptom of gastroesophageal reflux disease and also indigestion. Treatment with antacids alone is symptomatic and only justified for minor symptoms.

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 8.8.1 *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 8.8.1 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.
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 **8.8.2**: 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 ($\mathbf{H_2O}$) 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 ($\mathbf{HNO_3}$) 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 **8.8.3**: Second degree burn caused by nitric acid. (CC BY-SA 3.0; Alcamán).

Table **8.8.2** *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 $\mathbf{NaOH}$.

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 **8.8.4** 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 $\mathbf{Ca(OH)_2}$. 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 $\mathbf{NH_3}$ 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.
- Wikipedia
- TextMap: Chemistry-A Molecular Approach (Tro)

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- MedlinePlus

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CHAPTER OVERVIEW

9: Oxidation and Reduction

9.1: Oxidation and Reduction- Four Views
9.2: Oxidizing and Reducing Agents
9.3: Electrochemistry- Cells and Batteries
9.4: Corrosion and Explosion
9.5: Oxygen - An Abundant and Essential Oxidizing Agent
9.6: Some Common Reducing Agents
9.7: Oxidation, Reduction, and Living Things

Thumbnail: Batteries are empowered by REDOX chemistry (Pixabay License; Didgeman via Pixabay).

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9.1: 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.

$$2Mg\,(s) + O_2\,(g) \rightarrow 2MgO\,(s)$$

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.

$$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(g)$$

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: H_2, Br_2, Na, Be, K, O_2, 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 $MgCl_2$, 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 9.1.1

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 9.1.1: Phosphoric Acid

Assign oxidation numbers to the atoms in H_3PO_4.

Answer

H: +1; O: −2; P: +5

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 **9.1.1** The Processes of Oxidation and Reduction.

Oxidation	Reduction
Complete loss of electrons (ionic reaction)	Complete gain of electrons (ionic reaction)
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 9.1.1

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 ($\mathit{CH3CHO}$) 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:

$$\mathbf{CH_3CHO + H_2 \longrightarrow CH_3CH_2OH}$$

Example 9.1.2

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 9.1.2

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 9.1.3:

Identify what is being oxidized and reduced in this redox reaction.

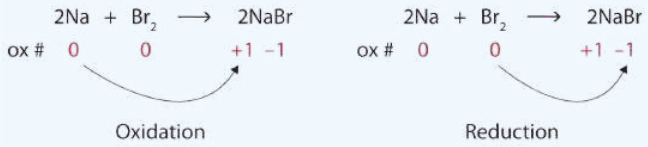
$$\mathbf{2\,Na + Br_2 \longrightarrow 2\,NaBr}$$

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 **9.1.3**

$$2\,Na + Br_2 \longrightarrow 2\,NaBr$$

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 9.1.3

Identify what is being oxidized and reduced in this redox reaction.

$$C + O_2 \longrightarrow CO_2$$

Answer

C is being oxidized from 0 to +4; O is being reduced from 0 to −2.

✔ Example 9.1.4: 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 9.1.4 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 9.1.5: 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:

$$\mathbf{Ag^{+} + Al \longrightarrow Ag + Al^{3+}}$$

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:

$$\mathbf{Ag^{+} + e^{-} \longrightarrow Ag}$$

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

$$\mathbf{Al \longrightarrow Al^{3+} + 3\,e^{-}}$$

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

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

Example **9.1.5** Silver reduction reaction

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

Exercise 9.1.5

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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9.2: 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:

$$\mathrm{Zn + S \rightarrow ZnS}$$

The half-reactions can be written:

$$\mathrm{Oxidation: Zn \rightarrow Zn^{2+} + 2e^-}$$
$$\mathrm{Reduction: S + 2e^- \rightarrow S^{2-}}$$

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 9.2.1 and summarized in Table 9.2.1.

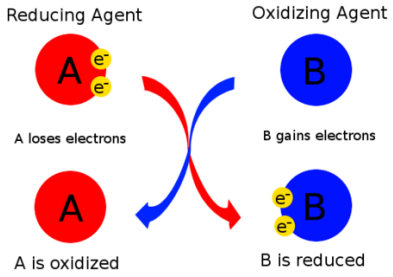


Figure 9.2.1 A reducing agent is oxidized and an oxidizing agent is reduced.

Note

Both the oxidizing and reducing agents are the *reactants* and therefore appear on the *left*-hand side of an equation.

Table 9.2.1: 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 9.2.1 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 9.2.1 : 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 9.2.2: 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 9.2.2: 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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9.3: 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 **9.3.1**: 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 **9.3.1**). 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.

$$\text{oxidation: } \mathrm{Cu}(s) \longrightarrow \mathrm{Cu}^{2+}(aq) + 2\,\mathrm{e}^-$$
$$\text{reduction: } 2 \times (\mathrm{Ag}^+(aq) + \mathrm{e}^- \longrightarrow \mathrm{Ag}(s)) \quad \text{or} \quad 2\,\mathrm{Ag}^+(aq) + 2\,\mathrm{e}^- \longrightarrow 2\,\mathrm{Ag}(s)$$
$$\text{overall: } 2\,\mathrm{Ag}^+(aq) + \mathrm{Cu}(s) \longrightarrow 2\,\mathrm{Ag}(s) + \mathrm{Cu}^{2+}(aq)$$

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.

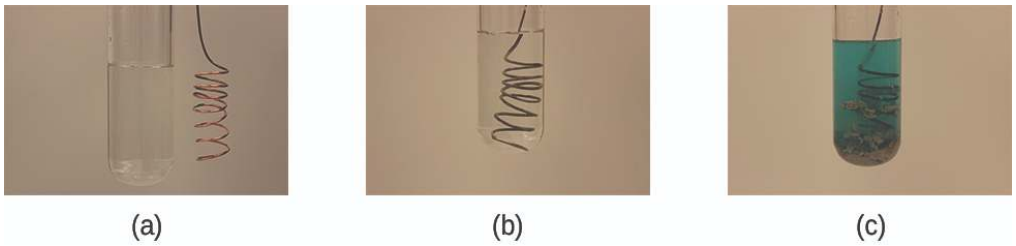


Figure **9.3.1** When a clean piece of copper metal is placed into a clear solution of silver nitrate (a), an oxidation-reduction reaction occurs that results in the exchange of Cu2+ for Ag+ ions in solution. As the reaction proceeds (b), the solution turns blue (c) because of the copper ions present, 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 **9.3.2**) 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.

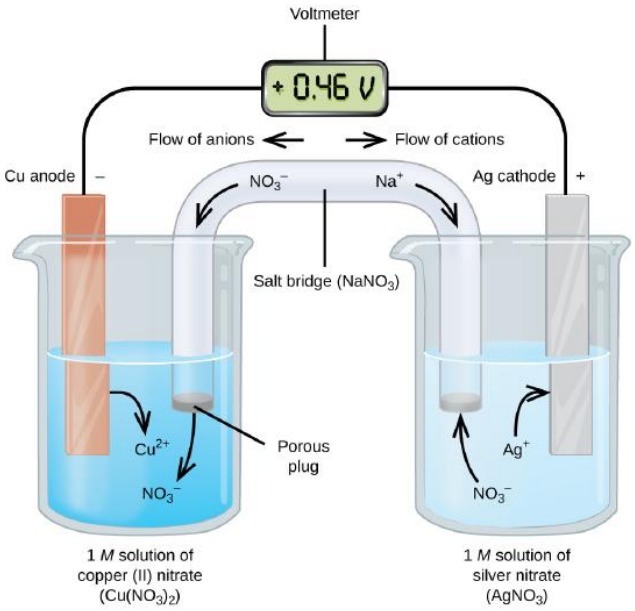


Figure **9.3.2** A standard Cu-Ag galvanic cell.

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 9.3.2

- 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 9.3.1: Chromium-Copper Galvanic Cell

Consider a galvanic cell consisting of

$$2\,Cr(s) + 3\,Cu^{2+}(aq) \longrightarrow 2\,Cr^{3+}(aq) + 3\,Cu(s)$$

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

$$\begin{aligned}&\text{oxidation: } 2\,Cr(s) \longrightarrow 2\,Cr^{3+}(aq) + 6\,e^-\\ &\text{reduction: } 3\,Cu^{2+}(aq) + 6\,e^- \longrightarrow 3\,Cu(s)\\ \hline &\text{overall: } 2\,Cr(s) + 3\,Cu^{2+}(aq) \longrightarrow 2\,Cr^{3+}(aq) + 3\,Cu(s)\end{aligned}$$

Cell notation uses the simplest form of each of the equations, and starts with the reaction at the anode. No concentrations were specified so:

$Cr(s) \mid Cr^{3+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$.

Oxidation occurs at the anode and reduction at the cathode.

? Exercise 9.3.1 Copper-Zinc Galvanic Cell

Consider a galvanic cell consisting of

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

Write the oxidation and reduction half-reactions. Which reaction occurs at the anode? The cathode?

Answer

From the information given in the problem:

$$\begin{aligned}&\text{anode (oxidation): } Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-\\ &\text{cathode (reduction): } Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)\\ \hline &\text{overall: } Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)\end{aligned}$$

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 **9.3.1**). 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:

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-$$

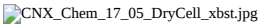


Figure **9.3.3** A diagram of a cross section of a dry cell battery is shown. The overall shape of the cell is cylindrical. The lateral surface of the cylinder, indicated as a thin red line, is labeled “zinc can (electrode).” Just beneath this is a slightly thicker dark grey surface that covers the lateral surface, top, and bottom of the battery, which is labeled “Porous separator.” Inside is a purple region with many evenly spaced small 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, labeled “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 to the bottom of the cylinder. A thin grey line segment at the very bottom of the cylinder is labeled “Metal bottom cover (negative).” The very top of 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. This upper surface is labeled “Metal top cover (positive).” A thin dark grey line just below this surface is labeled “Insulator.” Below this, above the 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

$$2\,MnO_2(s) + 2\,NH_4Cl(aq) + 2\,e^- \longrightarrow Mn_2O_3(s) + 2\,NH_3(aq) + H_2O(l) + 2\,Cl^-$$

The overall reaction for the zinc–carbon battery can be represented as

$$2\,MnO_2(s) + 2\,NH_4Cl(aq) + Zn(s) \longrightarrow Zn^{2+}(aq) + Mn_2O_3(s) + 2\,NH_3(aq) + H_2O(l) + 2\,Cl^-$$

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 **9.3.2**).



Figure **9.3.2** A dry cell with a leak. Source: Photo courtesy of Mitchclanky2008, http://www.flickr.com/photos/25597837@N05/2422765479/.

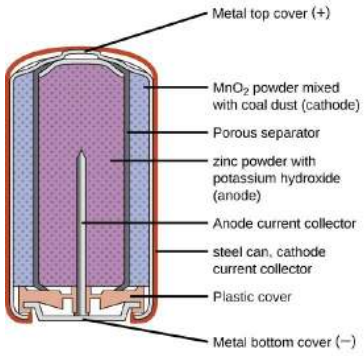


Figure **9.3.4** A cross section of an alkaline battery.

Alkaline batteries (Figure **9.3.4**) 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 **9.3.5**) 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.

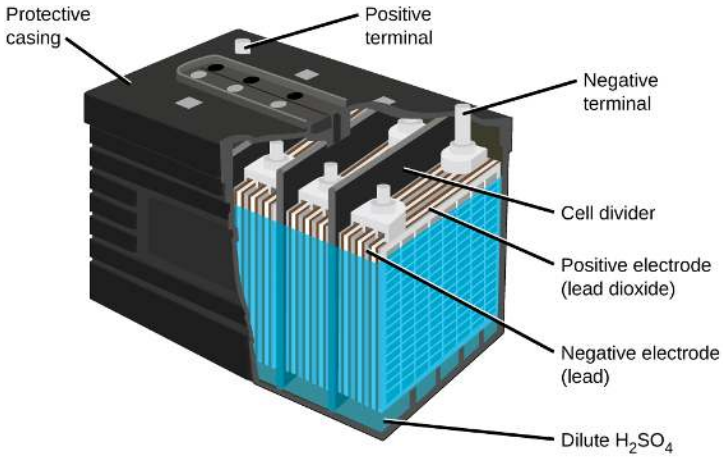


Figure **9.3.5** A lead (acid) storage battery.

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.

$$2PbSO_4\,(s) + 2H_2O\,(l) \rightarrow Pb\,(s) + PbO_2\,(s) + 4H^+\,(aq) + 2SO_4{}^{2-}\,(aq)$$

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 **9.3.6**) is used in small electrical appliances and devices like drills,

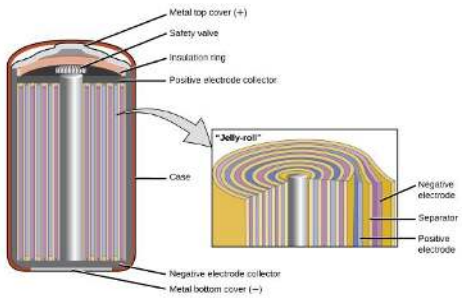


Figure **9.3.6** NiCd battery with “jelly-roll” design.

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 **9.3.7**) 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 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 **9.3.8**).

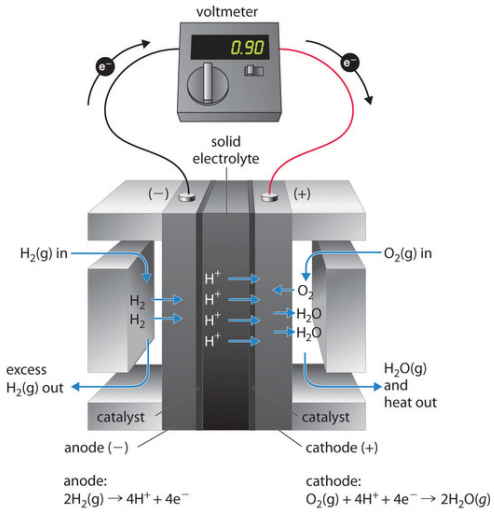


Figure **9.3.8** A hydrogen fuel cell.

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.

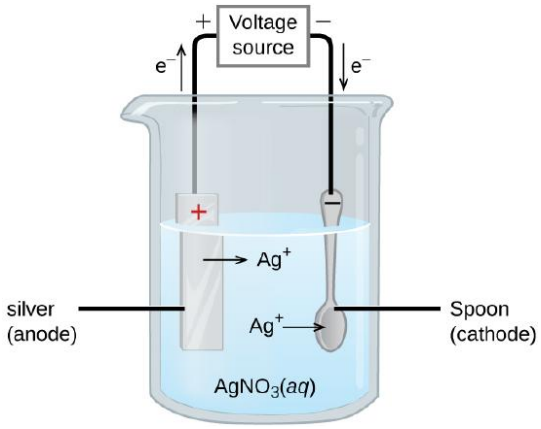


Figure 9.3.9: Silver plating of a spoon.

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 9.3.9).

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)
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9.4: 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.

$$\mathrm{Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-} \qquad \text{(cathode)}$$

The electrons reduce oxygen in the air in acidic solutions.

$$\mathrm{O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)} \qquad \text{(anode)}$$

$$\mathrm{2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O(l)} \qquad \text{(over all)}$$

What we call rust is hydrated iron(III) oxide, which forms when iron(II) ions react further with oxygen.

$$\mathrm{4Fe^{2+}(aq) + O_2(g) + (4+2x)H_2O(l) \longrightarrow 2Fe_2O_3 \cdot xH_2O(s) + 8H^+(aq)}$$

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.

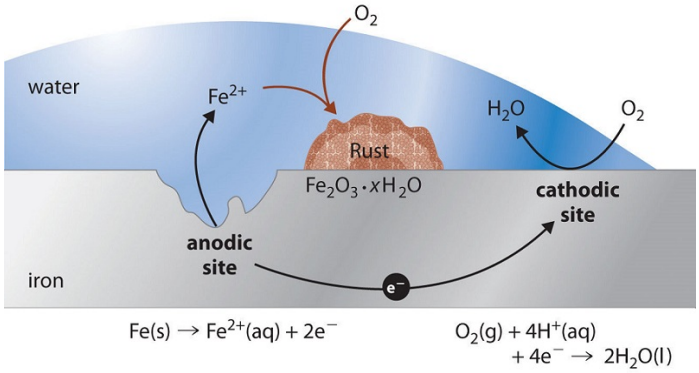


Figure **9.4.1** Rust, the Result of Corrosion of Metallic Iron. Iron is oxidized to Fe2+(aq) at an anodic site on the surface of the iron, which is often an impurity or a lattice defect. Oxygen is reduced to water at a different site on the surface of the iron, which acts as the cathode. Electrons are 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 ($\mathbf{Cu_2O}$), which is red, and then to copper(II) oxide, which is black.

$$2\,\mathrm{Cu\,(s)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)} \rightarrow \underset{\text{red}}{\mathrm{Cu_2O\,(s)}}$$

$$\mathrm{Cu_2O\,(s)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)} \rightarrow 2\,\underset{\text{black}}{\mathrm{CuO\,(s)}}$$

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 $\mathbf{CuO}$.

$$2\,\mathrm{CuO\,(s)} + \mathrm{CO_2\,(g)} + \mathrm{H_2O\,(l)} \rightarrow \underset{\text{green}}{\mathrm{Cu_2CO_3(OH)_2\,(s)}}$$

$$3\,\mathrm{CuO\,(s)} + 2\,\mathrm{CO_2\,(g)} + \mathrm{H_2O\,(l)} \rightarrow \underset{\text{blue}}{\mathrm{Cu_2(CO_3)_2(OH)_2\,(s)}}$$

$$4\,\mathrm{CuO\,(s)} + \mathrm{SO_3\,(g)} + 3\,\mathrm{H_2O\,(l)} \rightarrow \underset{\text{green}}{\mathrm{Cu_4SO_4(OH)_6\,(s)}}$$

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 **9.4.2**: (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 $\mathbf{H_2S\,(g)}$

$$2\,\mathrm{Ag\,(s)} + \mathrm{H_2S\,(g)} \longrightarrow \mathrm{Ag_2S\,(s)} + \mathrm{H_2\,(g)}$$

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:

$$2\,C_7H_5N_3O_6 \longrightarrow 3\,N_2 + 5\,H_2O + 7\,CO + 7\,C$$

$$2\,C_7H_5N_3O_6 \longrightarrow 3\,N_2 + 5\,H_2 + 12\,CO + 2\,C$$

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 (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 (C_nH_{2n+2}) to form nitrogen, carbon dioxide, and water.

$$NH_4NO_3 + C_nH_{2n+2} \longrightarrow x\,N_2 + y\,H_2O + z\,CO_2$$

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).

$$NH_4NO_3 + C_nH_{2n+2} \longrightarrow v\,CO + w\,NOx + y\,H_2O + z\,CO_2$$

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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9.5: 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:

$$2\,Mg\,(s) + O_2\,(g) \longrightarrow 2\,MgO\,(s)$$

$$P_4(s) + 5\,O_2\,(g) \longrightarrow P_4O_{10}\,(s)$$

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:

$$2\,H_2S(g) + 3\,O_2(g) \longrightarrow 2\,H_2O(l) + 2\,SO_2(g)$$

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 **9.5.1** and in the atmosphere near industrial plants that burn fuel containing sulfur compounds.



Figure **9.5.1**: 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 **9.5.2**), 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.

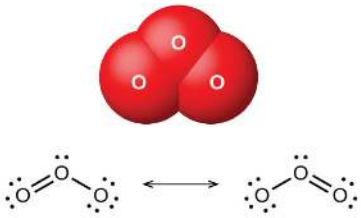


Figure **9.5.2** The image shows the bent ozone (O3) molecule and the resonance structures necessary to describe its bonding.

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:

$$\mathrm{O_3}(g) \xrightarrow{\text{ultraviolet light}} \mathrm{O}(g) + \mathrm{O_2}(g)$$

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.

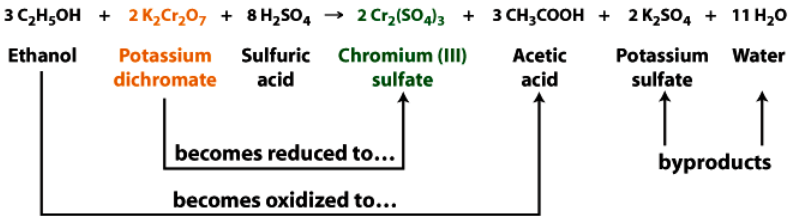


Figure **9.5.3** In this reaction, the chromium atom is reduced from Cr^{6+} to Cr^{3+}, and the ethanol is oxidized to acetic acid.

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 9.5.3: 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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9.6: 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; $\mathbf{C_6H_8O_6}$) is thought to retard potentially damaging oxidation of living cells. In the process, it is oxidized to dehydroascorbic acid ($\mathbf{C_6H_6O_6}$). In the stomach, ascorbic acid reduces the nitrite ion ($\mathbf{NO_2^-}$) to nitric oxide ($\mathbf{NO}$):

$$\mathbf{C_6H_8O_6 + 2\,H^+ + 2\,NO_2^- \rightarrow C_6H_6O_6 + 2\,H_2O + 2\,NO} \tag{9.6.1}$$

> *If reaction in Equation 9.6.1 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 **9.6.2**).



Figure **9.6.2**: 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.



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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- Wikipedia
- Ridhi Sachdev (UC Davis)
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9.7: 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).

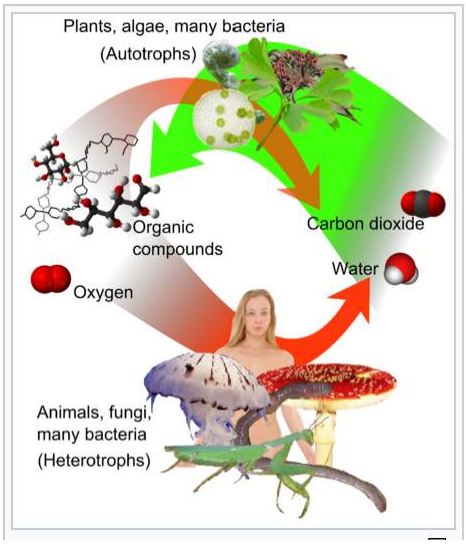


Figure **9.7.1** Aerobic respiration (red arrows) is the main means by which both fungi and animals utilize chemical energy in the form of organic compounds that were previously created through photosynthesis (green arrow). (CC-BY-SA 2.0, Mikael Häggström, Wikimedia)

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 ($\mathbf{C_6H_{12}O_6}$). 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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CHAPTER OVERVIEW

10: 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.

$$AgOCN + NH_4Cl \rightarrow AgCl + NH_4OCN \tag{10.1}$$

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 **10.1** *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 **10.1**.

Table **10.1**: 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 **10.1** 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 **10.1**.

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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- 10.1: Prelude to Organic Chemistry
  10.2: Aliphatic Hydrocarbons
  10.3: Aromatic Compounds- Benzene and Its Relatives
  10.4: Halogenated Hydrocarbons- Many Uses, Some Hazards
  10.5: The Functional Group
  10.6: Alcohols, Phenols, and Ethers
  10.7: Aldehydes and Ketones
  10.8: Carboxylic Acids and Esters
  10.9: Nitrogen-Containing Compounds- Amines and Amides
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10.1: 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.

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- TextMap: The Basics of GOB Chemistry (Ball et al.)

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10.2: 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 *cycloalkenes* or *cycloalkynes*). 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:

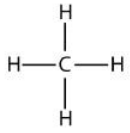


Figure **10.2.1**.

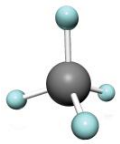


Figure **10.2.1** *Three-dimensional representation of methane © Thinkstock. The methane molecule is three dimensional, with the H atoms in the positions of the four corners of a tetrahedron.*

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

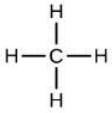
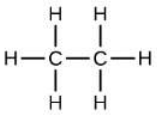
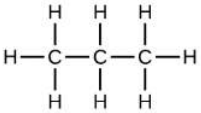
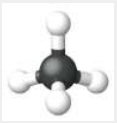
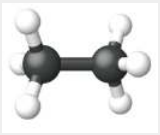
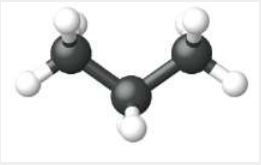
The condensed formulas show hydrogen atoms right next to the carbon atoms to which they are attached, as illustrated for butane:



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:



Pentane Isopentane

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 10.2.1

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

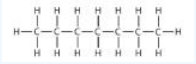
	Explanation	Answer
Molecular Formula	The general formula for an alkane is C_nH_{2n+2} For an alkane with 8 carbon atoms, $C_8H_{(2\times 8)+2} = C_8H_{18}$.	C_8H_{18}.
Complete Structural Formula	Eight carbons first linked together and all remaining bonds to hydrogen to fulfill the octet rule.	C_1-C_2-C_3-C_4-C_5-C_6-C_7-C_8
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 10.2.1

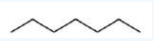
Provide the molecular formula, the complete structural formula, the condensed structural formula, and the line angle formula for a straight chain alkane with 7 carbon atoms.

Answer

molecular formula: C_7H_{16}

complete structural formula: 

condensed structural formula: $CH_3(CH_2)_5CH_3$

line angle drawing: 

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 **10.2.1**.

Table **10.2.1** The First 10 Straight-Chain Alkanes

Molecular Formula	Condensed Structural Formula	Name
CH_4	CH_4	methane
C_2H_6	CH_3CH_3	ethane
C_3H_8	$CH_3CH_2CH_3$	propane
C_4H_{10}	$CH_3CH_2CH_2CH_3$	butane
C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	pentane
C_6H_{14}	$CH_3(CH_2)_4CH_3$	hexane
C_7H_{16}	$CH_3(CH_2)_5CH_3$	heptane
C_8H_{18}	$CH_3(CH_2)_6CH_3$	octane
C_9H_{20}	$CH_3(CH_2)_7CH_3$	nonane
$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	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 **10.2.2**. 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.

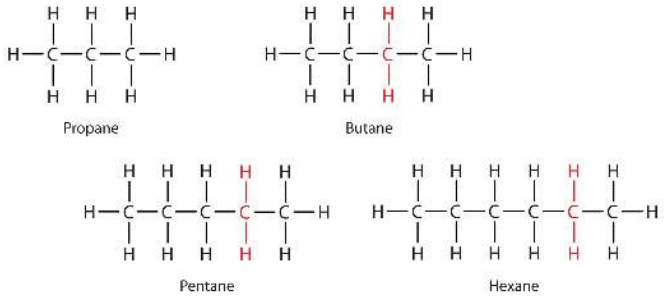


Figure **10.2.2** Members of a homologous series.

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 **10.2.1** 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 **10.2.2***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 10.2.2

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 10.2.2

Provide the name for the following compounds:

a. seven carbon alkane

b. six carbon alkane

Answer

a. heptane

b. hexane

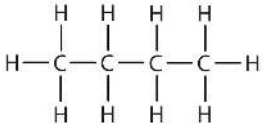
Isomerism-Branched Chain Alkanes - Structural Isomers

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.

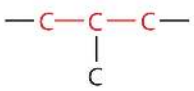
We can write the structure of butane (C_4H_{10}) by stringing four carbon atoms in a row,

–C–C–C–C–

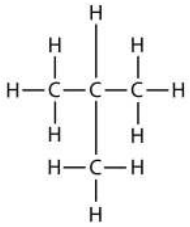
and then adding enough hydrogen atoms to give each carbon atom four bonds:



The compound butane has this structure, but there is another way to put 4 carbon atoms and 10 hydrogen atoms together. Place 3 of the carbon atoms in a row and then branch the fourth one off the middle carbon atom:



Now we add enough hydrogen atoms to give each carbon four bonds.



There is a hydrocarbon that corresponds to this structure, which means that two different compounds have the same molecular formula: C_4H_{10}. The two compounds have different properties—for example, one boils at −0.5°C; the other at −11.7°C. Different compounds having the same molecular formula are called isomers.

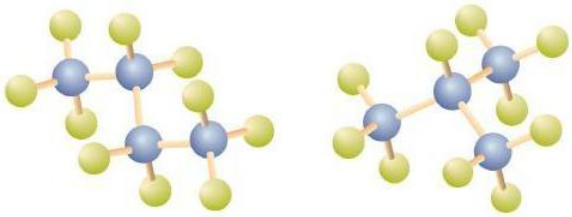
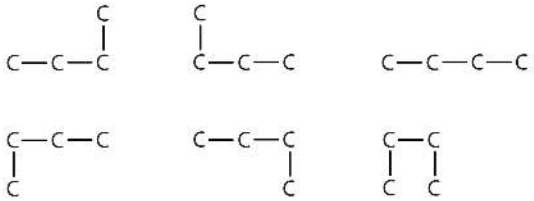


Figure **10.2.3** Butane and isobutane. The ball-and-stick models of these two compounds show them to be isomers; both have the molecular formula C_4H_{10}.

Conformational Isomers

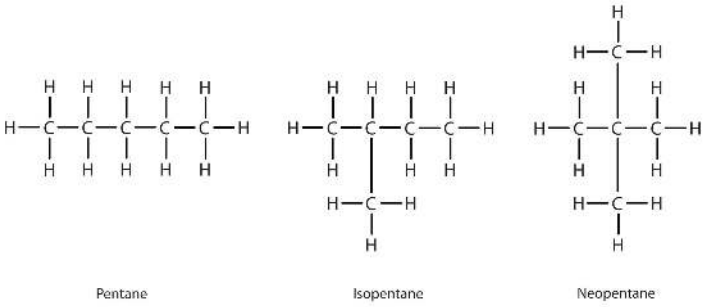
Notice that C_4H_{10} is depicted with a bent chain in Figure **10.2.3**. The four-carbon chain may be bent in various ways because the groups can rotate freely about the C–C bonds. However, this rotation does not change the identity of the compound. It is important to realize that bending a chain does *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 **10.2.3**.

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.

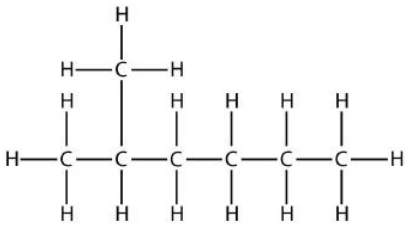
Next beyond C_4H_{10} in the homologous series is pentane. Each compound has the same molecular formula: C_5H_{12}. The compound at the far left is pentane because it has all five carbon atoms in a continuous chain. The compound in the middle is isopentane; like isobutane, it has a one CH_3 branch off 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.



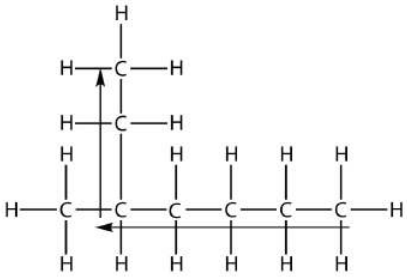
Naming Branched Alkanes

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



the longest chain of carbons has six C atoms. Therefore, it will be named as a hexane. However, in the molecule



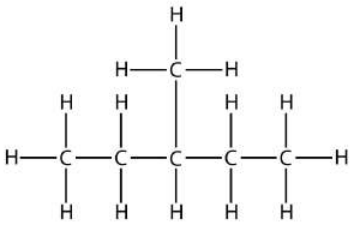
the longest chain of C atoms is not six, but seven, as shown. So this molecule will be named as a heptane.

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 **10.2.3**, lists the substituent names for the five smallest substituents.

***Table* 10.2.3** *Substituent Names.*

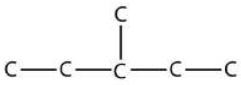
Substituent Formula	Number of C Atoms	Name of Substituent
CH_3	1	*methyl-*
CH_3CH_2	2	*ethyl-*
$CH_3CH_2CH_2$	3	*propyl-*
$CH_3CH_2CH_2CH_2$	4	*butyl-*
$CH_3CH_2CH_2CH_2CH_2$	5	*pentyl-*
and so forth	and so forth	and so forth

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



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!

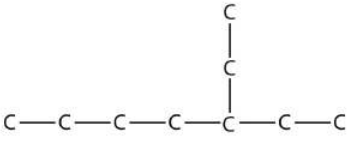
It is common to write the structural formula of a hydrocarbon without the H atoms, for clarity. So we can also represent 3-methylpentane as



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 10.2.3:

Name this molecule.

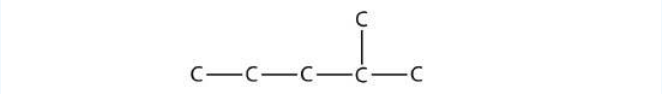


Solution

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 10.2.3

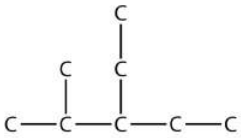
Name this molecule.



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



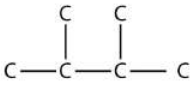
is 3-ethyl-2-methylpentane.

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 **10.2.4**. The number of the position values must agree with the numerical prefix before the substituent.

Table **10.2.4** 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

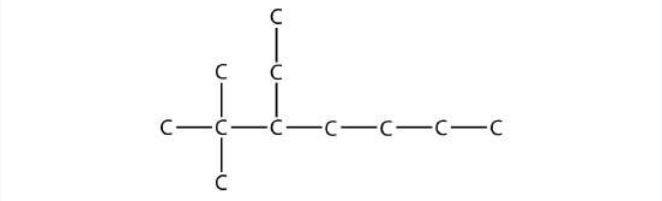
Consider this molecule:



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 10.2.4:

Name this molecule.

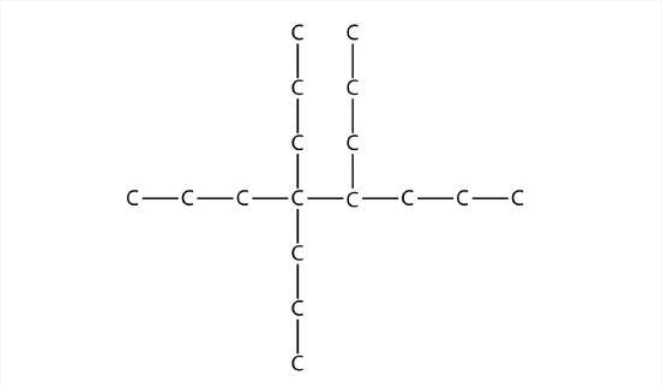


Solution

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 10.2.4

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 **10.2.5**) usually change smoothly and predictably as the number of carbon and hydrogen atoms in the molecules change.

Table **10.2.5** Properties of Some Alkanes

Alkane	Molecular Formula	Melting Point (°C)	Boiling Point (°C)	Phase at STP[4]	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:

$$\mathrm{CH_4}(g) + 2\,\mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(g) \tag{10.2.1}$$

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 **10.2.4**). You may recall that boiling point is a function of intermolecular interactions, which was discussed in the chapter on solutions and colloids.

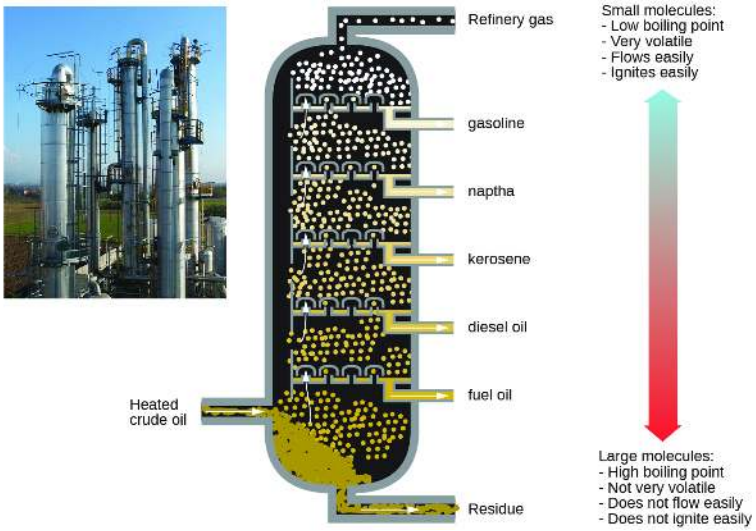
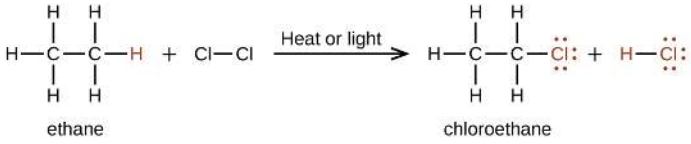


Figure **10.2.4** In a column for the fractional distillation of crude oil, oil heated to about 425 °C in the furnace vaporizes when it enters the base of the tower. The vapors rise through bubble caps in a series of trays in the tower. As the vapors gradually cool, fractions of higher, then of lower, 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:



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 C_nH_{2n}. The simplest cycloalkane shown below is cyclopropane, a three-carbon ring.

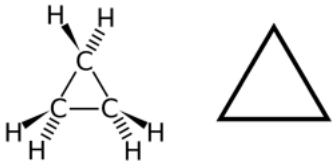
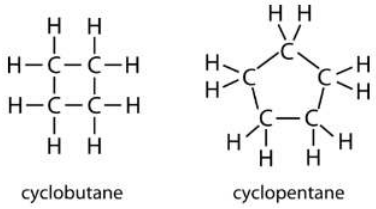


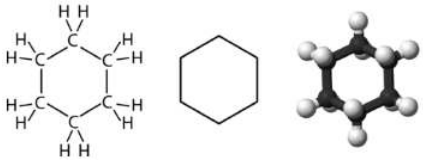
Figure **10.2.5** *Cyclopropane the simplest cycloalkane.*

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 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.



Cyclohexane is a six-carbon cycloalkane shown below



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.

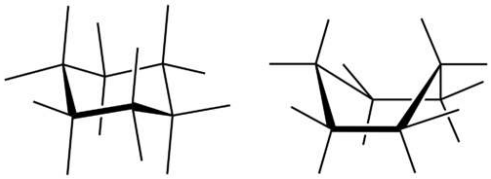
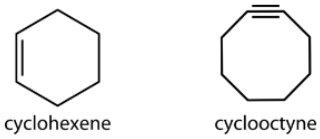


Figure 10.2.6 *Chair (left) and boat (right) conformations for cyclohexane.*

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.



Unsaturated Hydrocarbons: Alkenes and Alkynes

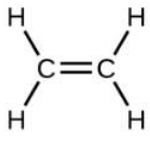
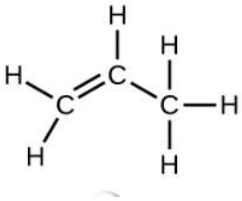
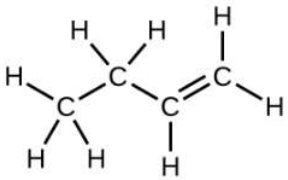
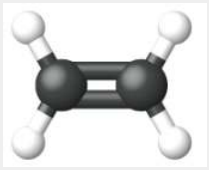
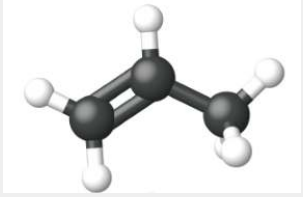
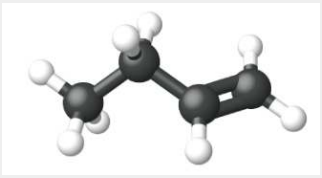
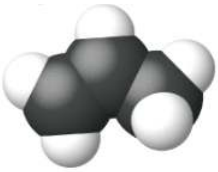
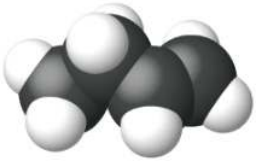
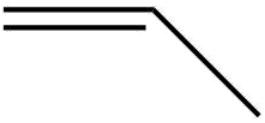
Alkenes

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.

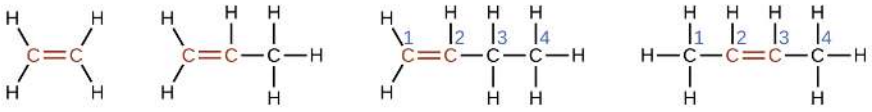
Note

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 **10.2.6**); 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 Formula			
Ball and Stick Model			
Space Filling model			
Name	ethene	propene	1-butene
Condensed Structural Formula	CH_2CH_2	CH_2CHCH_3	$CH_3CH_2CHCH_2$
Molecular Formula	C_2H_2	C_3H_6	C_4H_8
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:



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:

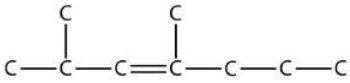


ethyne (acetylene)

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, $\mathbf{CH_3CH_2C \equiv CH}$ is called 1-butyne.

Naming Alkenes and Alkynes

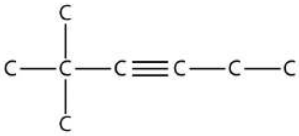
Alkenes and alkynes are named in a similar fashion. The biggest difference is that when identifying the longest carbon chain, it *must* contain the C–C double or triple bond. Furthermore, when numbering the main chain, the double or triple bond gets the lowest possible number. This means that there may be longer or higher-numbered substituents than may be allowed if the molecule were an alkane. For example, this molecule



is 2,4-dimethyl-3-heptene (note the number and the hyphens that indicate the position of the double bond).

Example 10.2.5

Name this molecule.

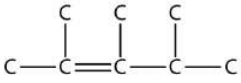


Solution

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 10.2.5

Name this molecule.

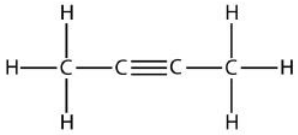


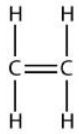
Answer

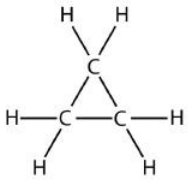
2,3,4-trimethyl-2-pentene

Example 10.2.6

Identify the molecule as an alkane, an alkene, or an alkyne.

1. 

2. 

3. 

Solution

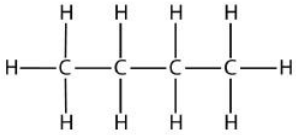
1. The molecule has at least one carbon-to-carbon triple bond (C≡C) so it is an **alkyne**.

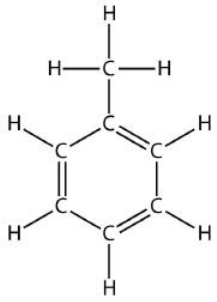
2. The molecule has a one carbon-to-carbon double bond (C=C) so it is an **alkene**.

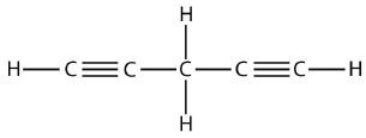
3. The molecule only has carbon-to-carbon single bonds so it is an **alkane**.

Exercise 10.2.6

Identify the molecule as an alkane, an alkene, or an alkyne.

1. 

2. 

3. 

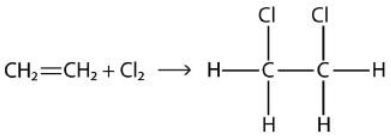
Answer

1. alkane, 2. alkene, 3. alkyne

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



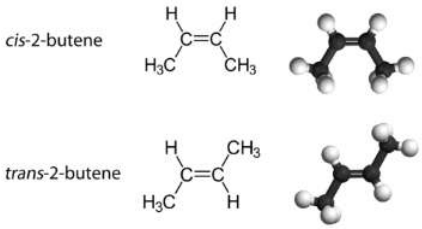
The reaction conditions are usually mild; in many cases, the halogen reacts spontaneously with an alkene or an alkyne.

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:

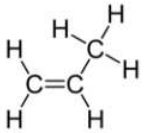
$$CH_2 = CH_2 + H_2 \overset{metal\ catalyst}{\rightarrow} CH_3CH_3 \tag{10.2.2}$$

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.



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.



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)

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10.3: 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.

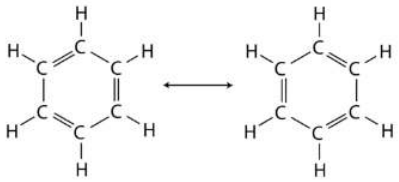


Figure **10.3.1** benzene

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 **10.3.2** 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:

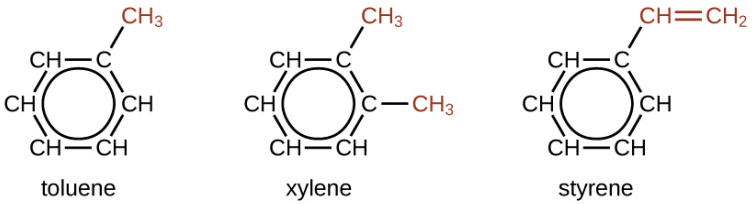


Figure **10.3.3** Three structural formulas are shown. The first is labeled toluene. This molecule has a six carbon hydrocarbon ring in which five of the C atoms are each bonded to only one H atom. At the upper right of the ring, the C atom that does not have a bonded H atom has a red C H subscript 3 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.

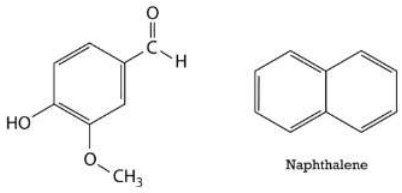


Figure 10.3.4 (left) vanilla molecule ; (right) naphthalene

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.

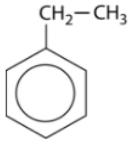


Figure 10.3.5 ethylbenzene

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.

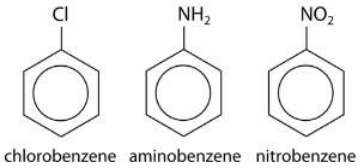


Figure 10.3.6 from left to right: chlorobenzene; aminobenzene; nitrobenzene

If more than one substituent is present, their location relative to each other can be indicated by numbering the positions on the benzene ring.

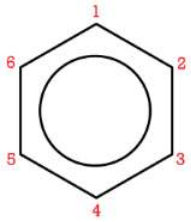


Figure 10.3.7 substituent locations relative to each other can be indicated by numbering the positions on the benzene ring

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.

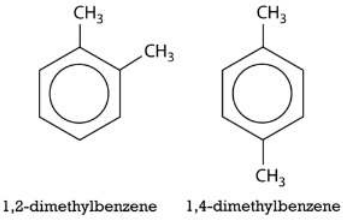


Figure 10.3.8 1,2-dimethylbenzene (left); 1-ethyl-4-methylbenzene (right)

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.

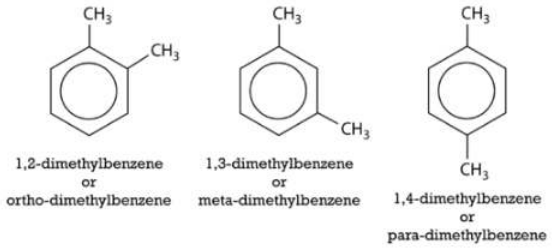


Figure **10.3.9** from left to right: ortho-dimethylbenzene; meta-dimethylbenzene ; para-dimethylbenzene

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.

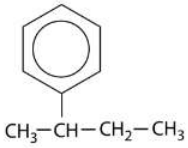


Figure **10.3.10** 2-phenylbutane

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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10.4: 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 **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.

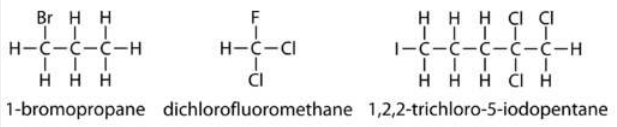


Figure **10.4.1** from left to right: 1-bromopropane; dichlorofluoromethane; 1,2,2-trichloro-5-iodpentane

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 10.4.1

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 10.4.1

Give common and IUPAC names for each compound.

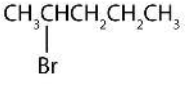
a. CH_3CH_2I
b. $CH_3CH_2CH_2CH_2F$

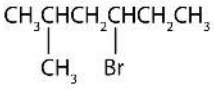
Answers

a. 1-iodoethane, ethyl iodide
b. 1-fluorobutane, butyl fluoride

Example 10.4.2

Give the IUPAC name for each compound.

1. 

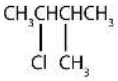


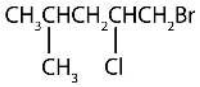
Solution

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 10.4.2

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 **10.4.1**, along with some of their uses.

Table **10.4.1**: 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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- Marisa Alviar-Agnew (Sacramento City College)
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10.5: 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.

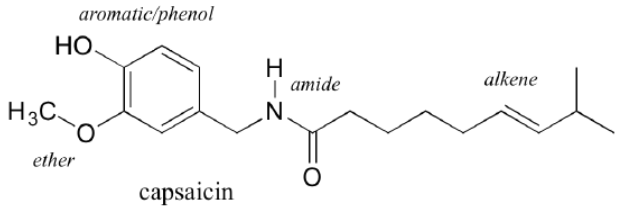


Figure **10.5.1** The structure of capsaicin

The table below summarizes the structures that will be discussed in this chapter:

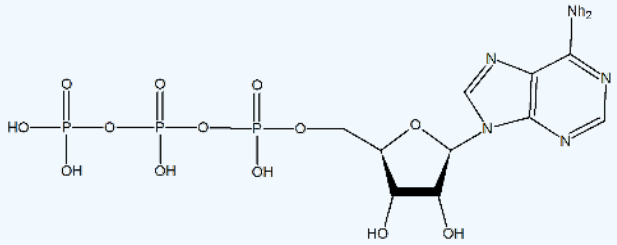
Table **10.5.1** Selected Organic Functional Groups

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—O—H	CH_3CH_2OH	ethanol
ether	R—O—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)—O—H	CH_3COOH	acetic acid
ester	R—C(=O)—O—R′	$CH_3CO_2CH_2CH_3$	ethyl acetate
amine	R—N(—H)—H; R—N(—H)—R′; R—N(—R′)—R″	$C_2H_5NH_2$	ethylamine
amide	R—C(=O)—N(—H)—R′	CH_3CONH_2	acetamide

Figure **10.5.1**

Example 10.5.1

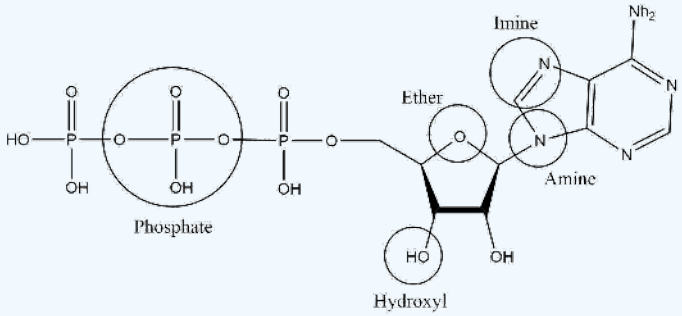
Identify the common functional groups for ATP.



Example **10.5.1**

Solution

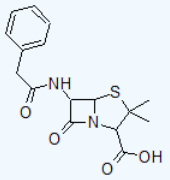
The common functional groups for ATP are **hydroxyl**, **ether** and **amine**. The other functional groups are covered in higher organic chemistry courses.



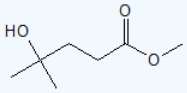
Example **10.5.1** ATP

Exercise 10.5.1

Identify the functional groups (other than alkanes) in the following organic compounds. State whether alcohols and amines are primary, secondary, or tertiary.



penicillin

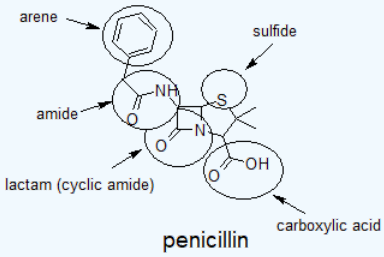




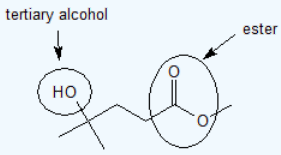
pyruvic acid

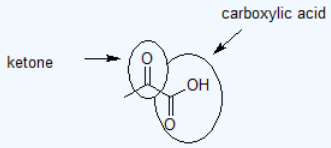


Answer

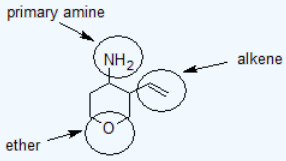


penicillin





pyruvic acid



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.

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10.6: 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*:

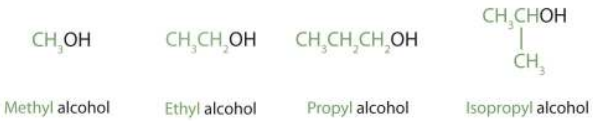
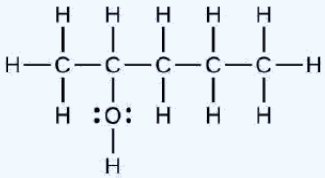


Figure **10.6.1**:left to right: methyl alcohol; ethyl alcohol; propyl alcohol; isopropyl alcohol

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 10.6.1: Naming Alcohols

Consider the following example. How should it be named?

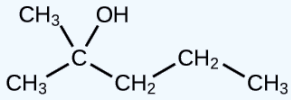


Solution

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 10.6.1

Name the following molecule:



Exercise **10.6.1**: 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

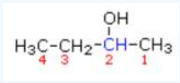
2-methyl-2-pentanol

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 10.6.2: Naming Alcohols

Consider the following example. How should it be named according to the guidelines adopted in 2013?



Example **10.6.2**:

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

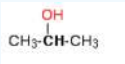
"Always place the OH on the lowest possible number for the chain."

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 10.6.2: Naming Alcohols

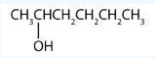
Name the following molecules according to the guidelines adopted in 2013?

a.



Exercise **10.6.2**:

b.



Exercise **10.6.2**:

Answer

a. propan-2-ol

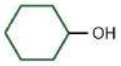
b. hexan-2-ol

Table **10.6.1** 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 **10.6.2**: from left to right: isobutyl alcohol press; sec-butyl alcohol;tert-butyl alcohol

Table **10.6.1**: 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
	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:

$$\underset{\text{glucose}}{C_6H_{12}O_6(aq)} \xrightarrow{\text{Yeast}} \underset{\text{ethanol}}{2C_2H_5OH(aq)} + 2CO_2(g)$$

Figure **10.6.3**: 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:

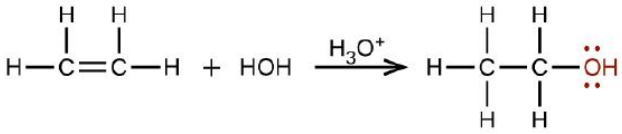


Figure **10.6.4** This reaction shows two carbons connected by a double bond, each with two bonded H atoms plus H O H arrow labeled “H subscript 3 O superscript plus” followed by two carbon atoms connected with a single bond with 5 bonded H atoms and an O H group shown in red at the right end of the 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 **10.6.2** 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 **10.6.2** 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):

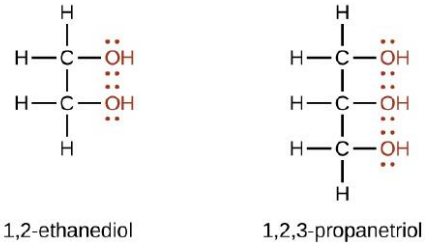


Figure **10.6.5**1,2-ethanediol; 1,2,3-propanetriol

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.



Figure **10.6.6** 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 **10.6.7** *A bottle of flavored "e-liquid" for "vaping" shows propylene glycol as the main ingredient. Source: Wikipedia*



Figure **10.6.8** **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 (/ˈɡlɪsərɒl/; 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 **10.6.9** 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 \(\PageIndex{2}\) Blood Alcohol Levels and Effects Source: Wikipedia.

Figure **10.6.10** *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.

$$\mathbf{ArOH\,(aq) + NaOH\,(aq) \rightarrow ArONa\,(aq) + H_2O}$$

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.

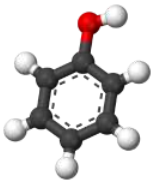


Figure **10.6.11** *Structure of phenol*



Figure **10.6.12**
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 **10.6.13** *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.

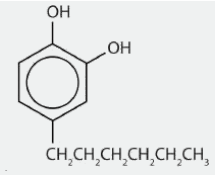


Figure **10.6.14** The compound 4-hexylresorcinol is mild enough to be used as the active ingredient in antiseptic preparations for use on the skin.

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.

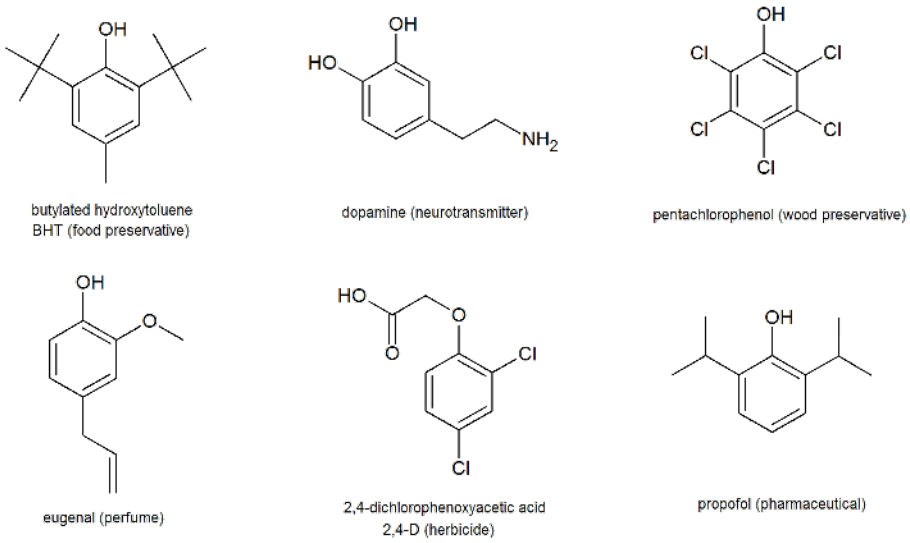


Figure **10.6.15** Top from left to right: line models of BHT; dopamine; pentachlorophenol; Bottom: eugenal; 2,4-dichlorophenoxyacetic acid; propofol

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.”

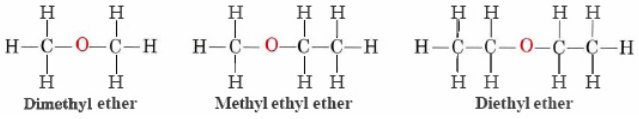


Figure **10.6.16** from left to right: Dimethyl ether; methyl ethyl ether; Diethyl ether

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 **10.6.3**).

Table **10.6.3** 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
$CH_3CH_2CH_2CH_2CH_3$	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 **10.6.17** *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.

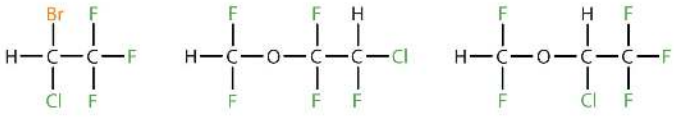


Figure **10.6.18** from left to right: halothane, enflurane, isoflurane. *These three modern, inhalant, halogen-containing, anesthetic compounds are less flammable than diethyl ether.*

A list of important ethers and their uses are given in Table **10.6.4**

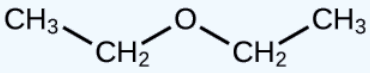
Table **10.6.4** Important Ethers and Their Uses

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 **10.6.2**: classifying functional groups

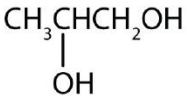
Identify the following compounds as alcohol, phenol or ether.

a.



Example **10.6.2**:

b.



Example **10.6.2**:

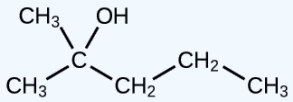
Solution

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 10.6.2

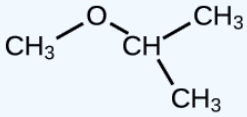
Identify the following compounds as alcohol, phenol or ether.

a.



Exercise **10.6.2**: 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 **10.6.2**: 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

a. alcohol b. ether

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

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- TextMap: The Basics of GOB Chemistry (Ball et al.)
- Marisa Alviar-Agnew (Sacramento City College)
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10.7: 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 **10.7.1** are found chiefly in plants or microorganisms and those in Figure **10.7.2** 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.

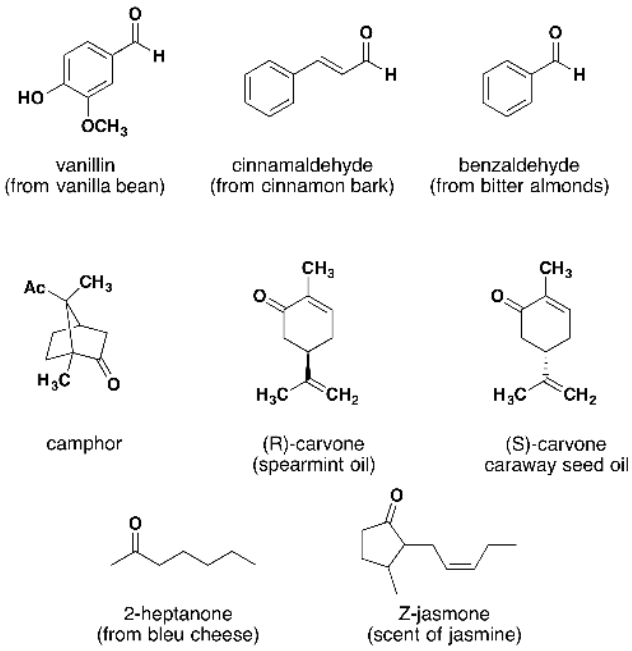


Figure **10.7.1** Aldehyde and ketone containing molecules isolated from plant sources.

Figure **10.7.1**

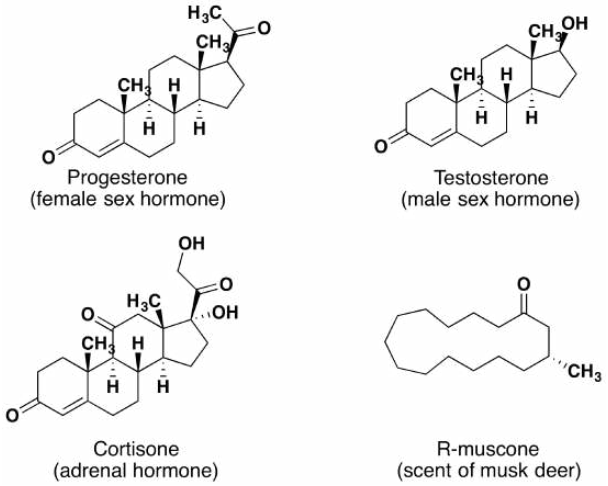


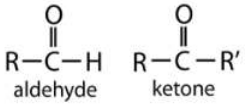
Figure **10.7.2** Aldehyde and ketone containing molecules isolated from animal sources.

Figure **10.7.1**

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.



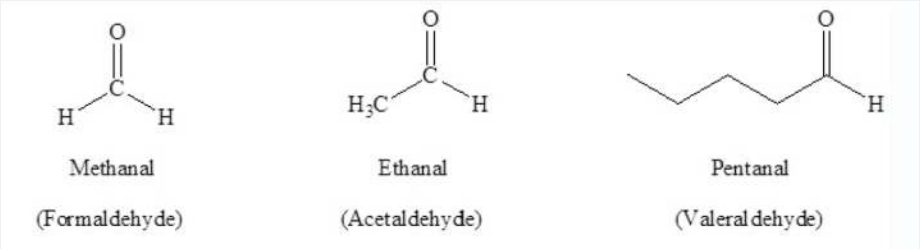
For aldehydes, the **R** group may be a hydrogen atom or any length carbon chain.

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.



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.

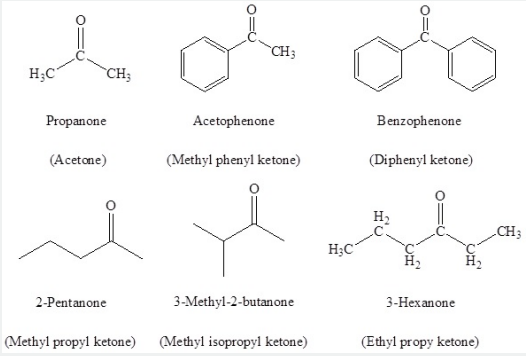
1. Name the parent compound by finding the longest continuous chain that contains the carbonyl group. Change the *-e* at the end of the name of the alkane to *-one*.
2. Number the carbon atoms in the chain in a way that the carbonyl group has the lowest possible number.

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 $-89°C$, ethanal is $20°C$, and ethanol is $78°C$.

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

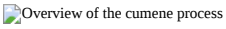
Traces of many aldehydes are found in essential oils and often contribute to their favorable odors, e.g. cinnamaldehyde, cilantro, and vanillin.

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:



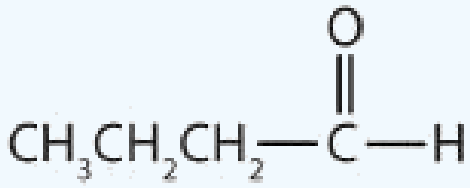
Other processes involve the direct oxidation of propylene (Wacker-Hoechst process), or the hydration of propylene to give 2-propanol, which is oxidized to acetone.

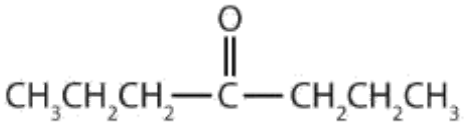
Butanone, also known as **methyl ethyl ketone** (**MEK**), is an organic compound with the formula $CH_3C(O)CH_2CH_3$. This colorless liquid ketone has a sharp, sweet odor reminiscent of butterscotch and acetone. It is produced industrially on a large scale, and also occurs in trace amounts in nature. 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.

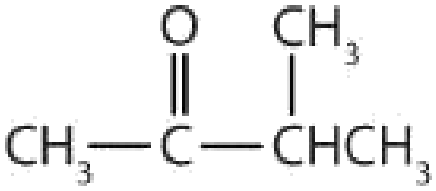
Cyclohexanone is the organic compound with the formula $(CH_2)_5CO$. The molecule consists of six-carbon cyclic molecule with a ketonefunctional group. This colorless oil has an odor reminiscent of that of acetone. Over time, samples of cyclohexanone assume a yellow color. Cyclohexanone is slightly soluble in water and miscible with common organic solvents. Billions of kilograms are produced annually, mainly as a precursor to nylon.

Example 10.7.1

Classify each compound as an aldehyde or a ketone.

a. 

b. 

c. 

Solution

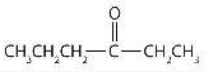
a. This compound has the carbonyl group on an end carbon atom, so it is an aldehyde.

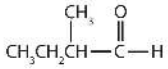
b. This compound has the carbonyl group on an interior carbon atom, so it is a ketone.

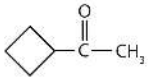
c. This compound has the carbonyl group between two alkyl groups, so it is a ketone.

? Exercise 10.7.1

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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- Prof. Steven Farmer (Sonoma State University(opens in new window))

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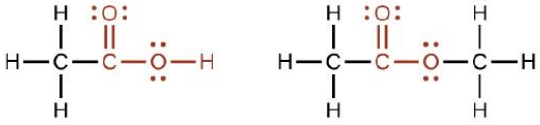
10.8: Carboxylic Acids and Esters

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):



ethanoic acid (acetic acid)

methyl ethanoate (methyl acetate)

Figure **10.8.1** 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

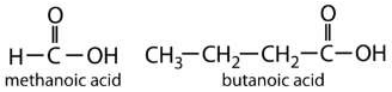
Carboxylic acids occur widely in nature, often combined with alcohols or other functional groups, as in fats, oils, and waxes. They are components of many foods, medicines, and household products (Figure **10.8.1**). Not surprisingly, many of them are best known by common names based on Latin and Greek words that describe their source.



Figure 10.8.2 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 C=O of the carbonyl group, with the carbon atom also being bonded to a hydroxyl (–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 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:

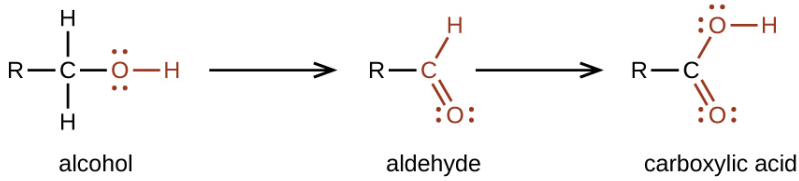
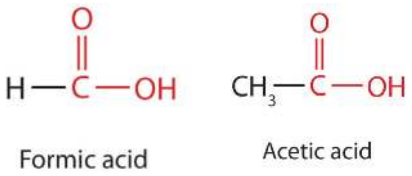


Figure **10.8.3** A chemical reaction with two arrows is shown. On the left, an alcohol, indicated with a C atom to which an R group is bonded to the left, H atoms are bonded above and below, and in red, a single bonded O atom with an H atom bonded to the right is shown. Following the first reaction 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.



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 **10.8.4**). Ethanoic and citric acids are frequently added to foods to give them a tart flavor.

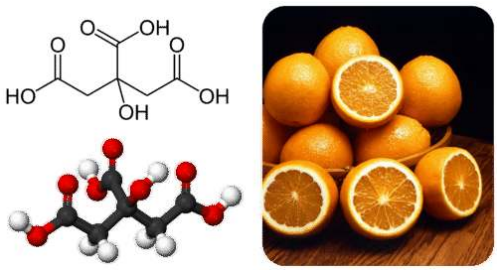
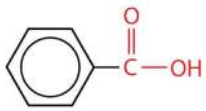


Figure **10.8.4**: Citric acid is a large carboxylic acid with three ionizable hydrogen atoms. It is found in citrus fruits and gives them their sour or tart flavor.

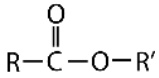
Benzoic, propanoic, and sorbic acids are used as food preservatives because of their ability to kill microorganisms that can lead to spoilage. Methanoic and ethanoic acids are widely used in industry as starting points for the manufacture of paints, adhesives, and coatings.



Benzoic acid

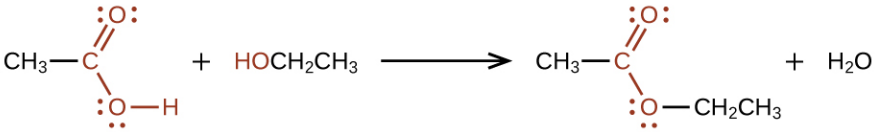
Esters: The Sweet Smell of RCOOR'

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.



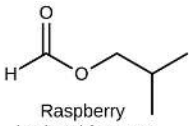
The **R** group can either be a hydrogen or a carbon chain. The **R′** group must be a carbon chain since a hydrogen atom would make the molecule a carboxylic acid.

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:

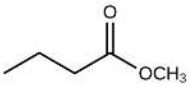


acetic acid ethanol ethyl acetate

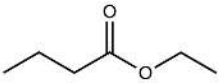
Figure **10.8.5**). Once a flower or fruit has been chemically analyzed, flavor chemists can attempt to duplicate the natural odor or taste. Both natural and synthetic esters are used in perfumes and as flavoring agents.A chemical reaction is shown. On the left, a C H subscript 3 group bonded to a red 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.



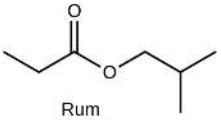
Raspberry
iso-butyl formate



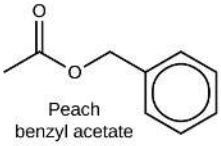
Apple
butyl acetate



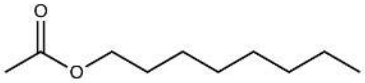
Pineapple
ethyl butyrate



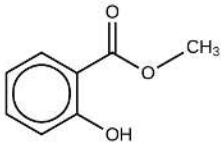
Rum
propyl isobutyrate



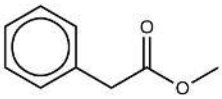
Peach
benzyl acetate



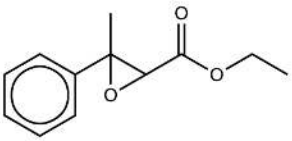
Orange
octyl acetate



Wintergreen
methyl salicylate



Honey
methyl phenylacetate



Strawberry
ethyl methylphenylglycidate

Figure **10.8.6** 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 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 **10.8.1**: 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, $\mathbf{CH_3(CH_2)_7CH=CH(CH_2)_7CO_2H}$. Oleic acid is an unsaturated acid; it contains a $\mathbf{C=C}$ 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 $\mathbf{R{-}COOH}$.
- 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.

Contributors and Attributions

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10.9: Nitrogen-Containing Compounds- Amines and Amides

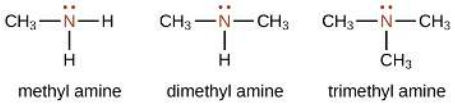
Learning Objectives

- 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:



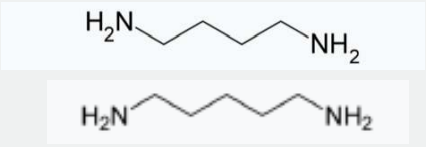
The name of larger molecules involve the class-identifying suffix *–ine* as you will see later in this section(e.g. caffeine and nicotine).

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.

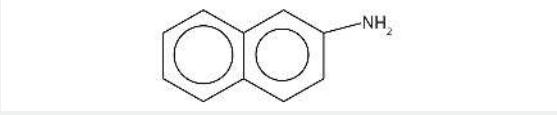
To Your Health: Amines in Death and Life

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.



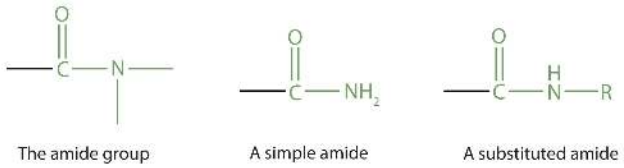
(Figure **10.9.1**) Putrescine(left) Cadaverine (right)

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

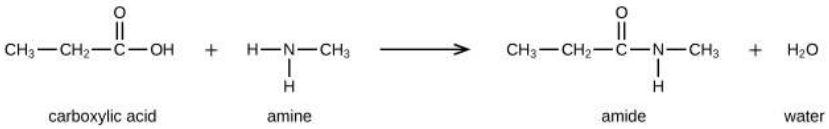
The amide functional group has an nitrogen atom attached to a carbonyl carbon atom. If the two remaining bonds on the nitrogen atom are attached to hydrogen atoms, the compound is a *simple amide*. If one or both of the two remaining bonds on the atom are attached to alkyl or aryl groups, the compound is a *substituted amide*.



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*.



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):



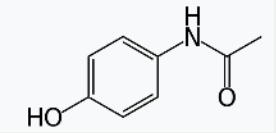
(Figure **10.9.2**) reaction between carboxylic acid and amine to form amide and water

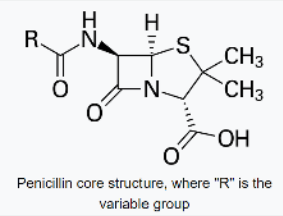
The reaction between amines and carboxylic acids to form amides is biologically important. It is through this reaction that amino acids (molecules containing both amine and carboxylic acid substituents) link together in a polymer to form proteins.

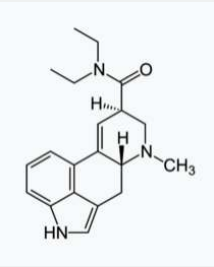
> The carbonyl carbon-to-nitrogen bond is called an *amide linkage*. This bond is quite stable and is found in the repeating units of protein molecules, where it is called a *peptide linkage*.

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 **10.9.3**) Paracetamol (acetaminophen) LSD (Lysergic diethylamide)

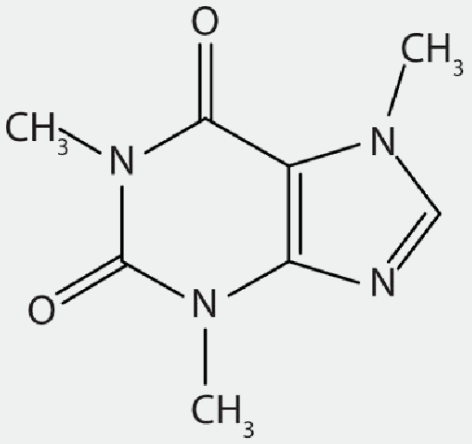
Heterocyclic Compounds: Alkaloids and Others

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.

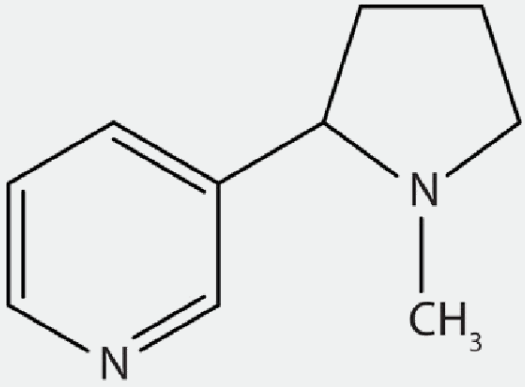
To Your Health: Three Well-Known Alkaloids

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

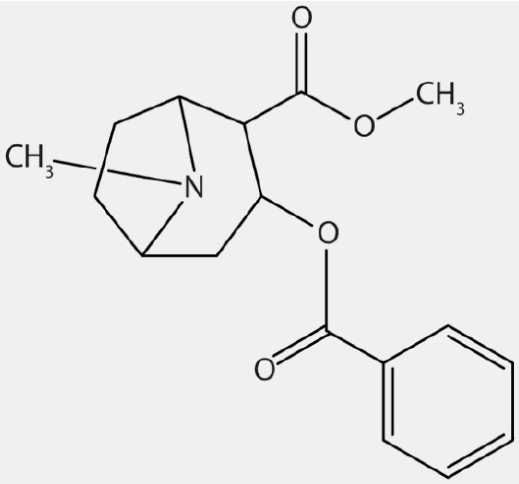
Nicotine acts as a stimulant by a different mechanism; it probably mimics the action of the neurotransmitter acetylcholine. People ingest this drug by smoking or chewing tobacco. Its stimulant effect seems transient, as this initial response is followed by depression. Nicotine is highly toxic to animals. 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.



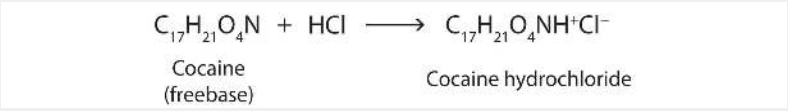
Nicotine

Cocaine acts as a stimulant by preventing nerve cells from taking up dopamine, another neurotransmitter, from the synapse. 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*.



Cocaine



Because it is soluble in water, cocaine hydrochloride is readily absorbed through the watery mucous membranes of the nose when it is snorted. Crack cocaine is more volatile than cocaine hydrochloride. It vaporizes at the temperature of a burning cigarette. When smoked, cocaine reaches the brain in 15 s.

Morphine and Heroin

Morphine, a strong narcotic used to relieve pain, contains two hydroxyl functional groups, located at the bottom of the

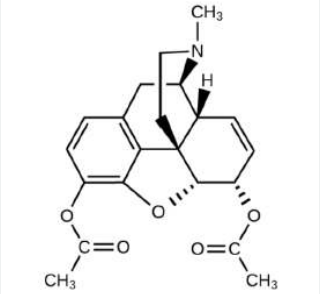


Figure **10.9.4** Poppies can be used in the production of opium, a plant latex that contains morphine from which other opiates, such as heroin, can be synthesized. (credit: Karen Roe)

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 **10.9.4**).



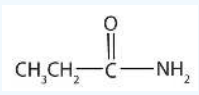
morphine

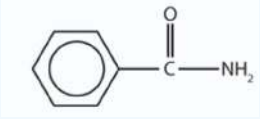


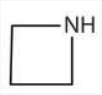
heroin

Example 10.9.1: Amines and Amides

Identify whether each compound is an amide or an amine.

a. 

b. 

c. 

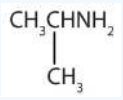
Solutions

a. The compound has the $CONH_2$ functional group so it is an amide.

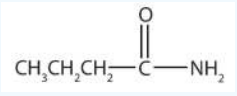
b. The compound has the $CONH_2$ functional group so it is an amide.

c. The compound has the NH functional group so it is an amine.

? Exercise 10.9.1

a. 

b. $CH_3CH_2CH_2CH_2CH_2CH_2NH_2$

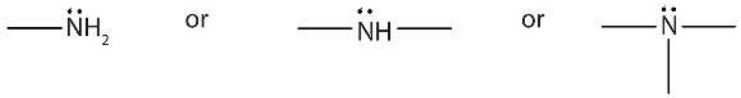
c. 

Answer

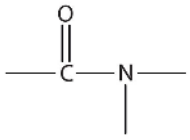
a. amine b. amine c. amide

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 **10.9.5**) 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

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CHAPTER OVERVIEW

11: Air

11.1: Earth's Atmosphere- Divisions and Composition
11.2: Chemistry of the Atmosphere
11.3: Outdoor Air Pollution
11.4: Automobile Emissions
11.5: Photochemical Smog- Making Haze While the Sun Shines
11.6: Acid Rain- Air Pollution Water Pollution
11.7: Indoor Air Pollution
11.8: Stratospheric Ozone- Earth's Vital Shield
11.9: Carbon Dioxide and Climate Change
11.10: Who Pollutes? Who Pays?

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11.1: 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 **11.1.1**). 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).

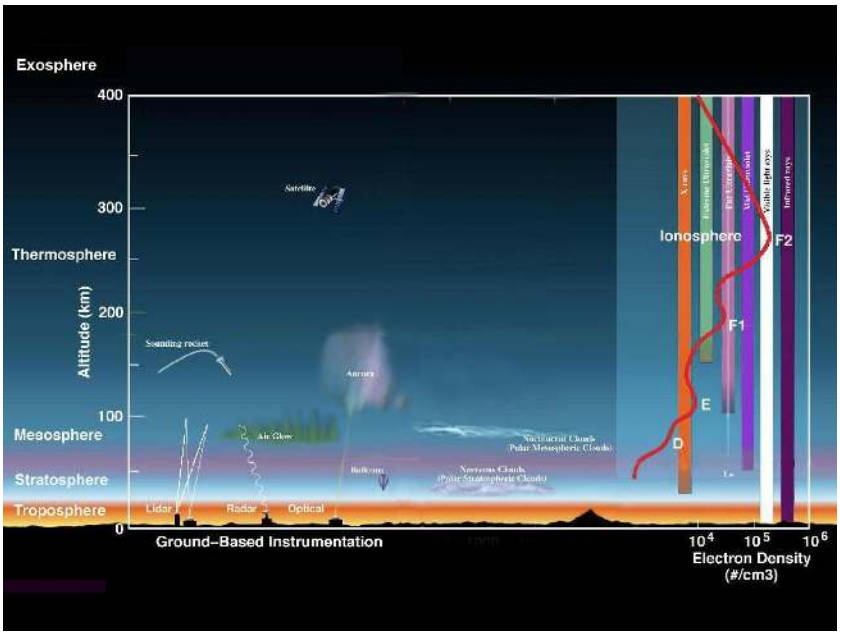


Figure* 11.1.1** *The Earth's atmosphere* ***Credit: *NASA/Goddard*

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 **11.1.1**). 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 **11.1.1** *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 **11.1.2**). 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 **11.1.2** *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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11.2: 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 **11.2.1** 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).

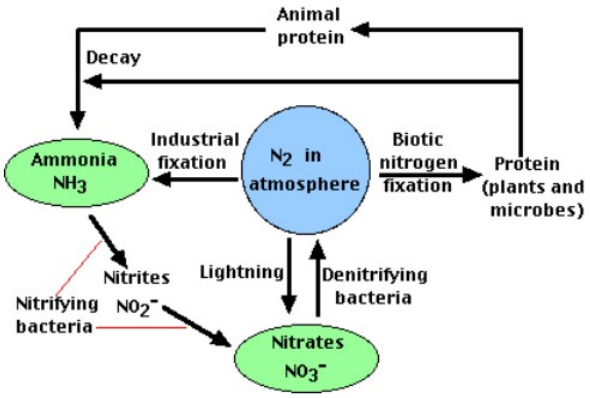


Figure **11.2.1** Nitrogen cycle

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 (NH_3). Ammonia can be used directly as fertilizer, but most of its is further processed to urea and ammonium nitrate (NH_4NO_3).

Biological Fixation

The ability to fix nitrogen in the soil (Figure **11.2.2**) 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 $\mathbf{NH_3}$ to **nitrites** ($\mathbf{NO_2^-}$).
2. Bacteria of the genus *Nitrobacter* oxidize the nitrites to **nitrates** ($\mathbf{NO_3^-}$).

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.

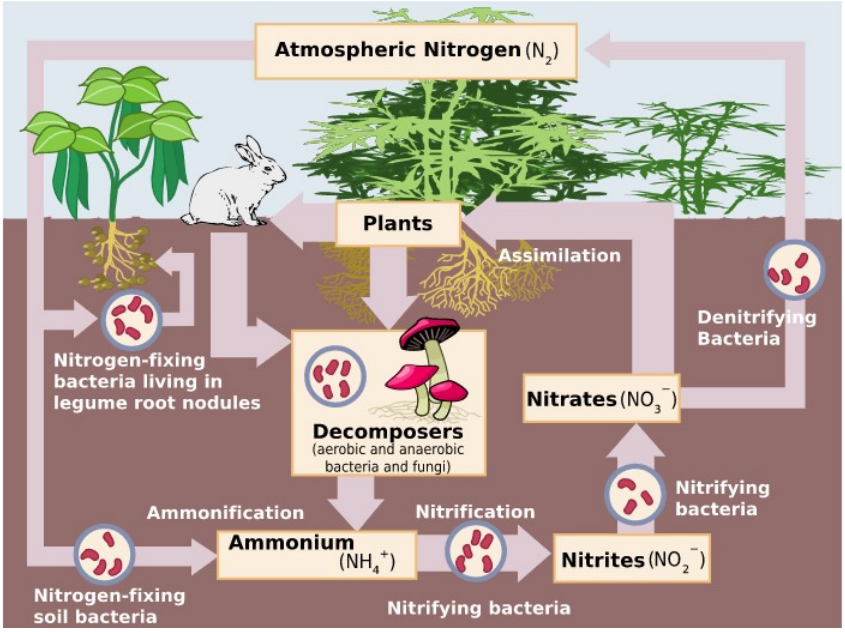


Figure **11.2.2** The role of soil bacteria in the Nitrogen cycle: Nitrogen transitions between various biologically useful forms.

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* **11.2.4**). 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* **11.2.3***)* . 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:

$$6\,CO_2(g) + 6\,H_2O(l) \xrightarrow[\text{light}]{\text{chlorophyll}} C_6H_{12}O_6(aq) + 6\,O_2(g) \tag{11.2.1}$$

$$\underset{\text{dioxide}}{\text{carbon}} \quad \text{water} \quad \text{glucose} \quad \text{oxygen} \tag{11.2.2}$$

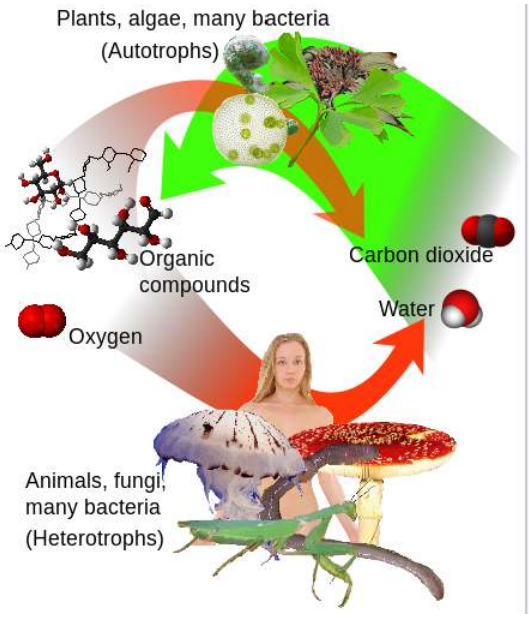


Figure **11.2.3**

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:

$$4\,FeO + O_2 \longrightarrow 2\,Fe_2O_3$$

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:

$$O_3(g) \xrightarrow{\text{ultraviolet light}} O(g) + O_2(g)$$

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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11.3: 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 **11.3.1**). 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.

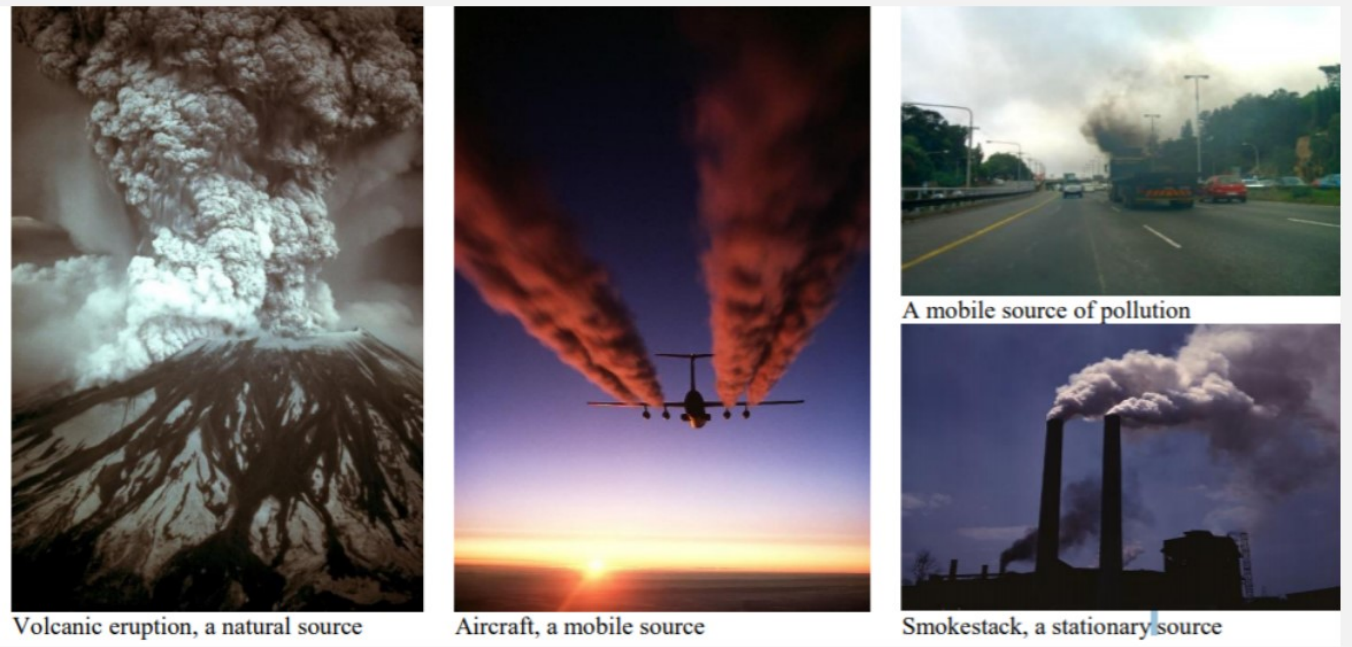


Figure **11.3.1**: Images showing various sources of air pollution, including natural and anthropogenic, stationary and mobile. Source: All images obtained from Wiki Commons commons.wikimedia.org/wiki/Air_pollution

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 **11.3.2**). 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.

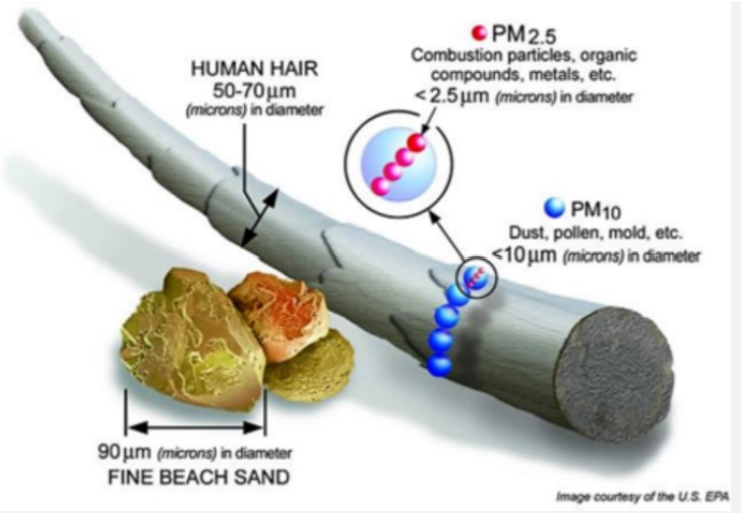


Figure **11.3.2** Graphic showing size comparison of particulate material (PM_{10} and $PM_{2.5}$) compared to fine beach sand and human hair. Source: US EPA http://www.epa.gov/air/particlepollution/basic.html

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 **11.3.3** and **11.3.4**). 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 **11.3.3**: Smog over Almaty city, Kazakhstan. Photo by Igors Jefimovs. Source: Wikicommons commons.wikimedia.org/wiki/C...dia/File:Smog_ over_Almaty.jpg



Figure **11.3.4**: Smog over Santiago in Chile. Source: German Wikipedia commons.wikimedia.org/wiki/C...#/media/File:Santiago30std.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.

$$SO_2 + OH \rightarrow HOSO_2 \tag{11.3.1}$$

$$HOSO_2 + O_2 \rightarrow HO_2 + SO_3 \tag{11.3.2}$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \tag{11.3.3}$$

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 11.3.5).

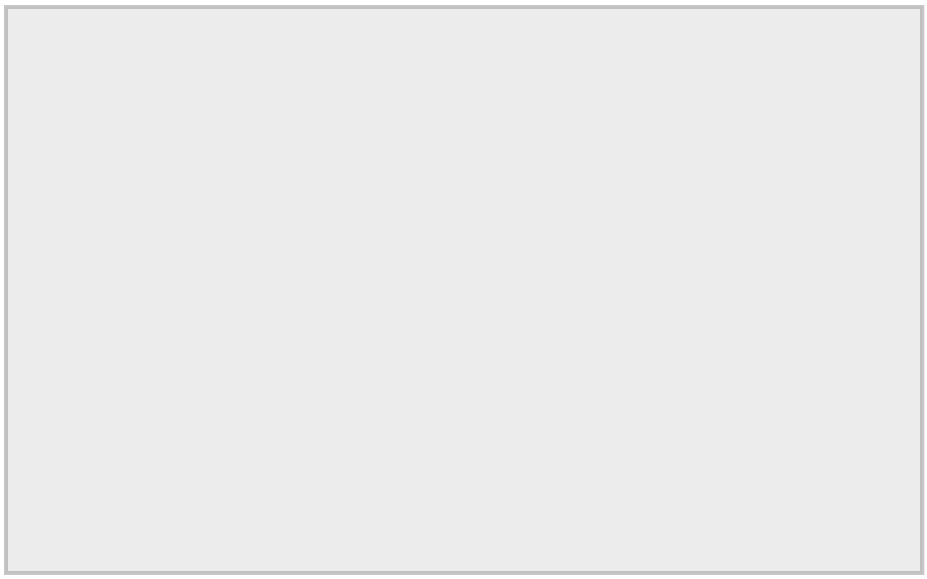


Figure 11.3.5: Schematic Diagram of a Wet Scrubber System. In coal-burning power plants, SO_2 can be removed ("scrubbed") from exhaust gases by its reaction with a lime (CaO) and water spray to produce calcium sulfite dihydrate ($CaSO_3 \cdot 2H_2O$). Removing SO_2 from the gases prevents its conversion 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 11.3.1) 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 **11.3.1**: 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)
- Marisa Alviar-Agnew (Sacramento City College)
- Wikipedia

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11.4: 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.

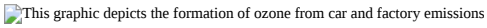
Called stratospheric ozone, good ozone occurs naturally in the upper atmosphere, where it forms a protective layer that shields us from the sun's harmful ultraviolet rays. This beneficial ozone has been partially destroyed by manmade chemicals, causing what is sometimes called a "hole in the ozone." 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.

Contributor

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11.5: 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.

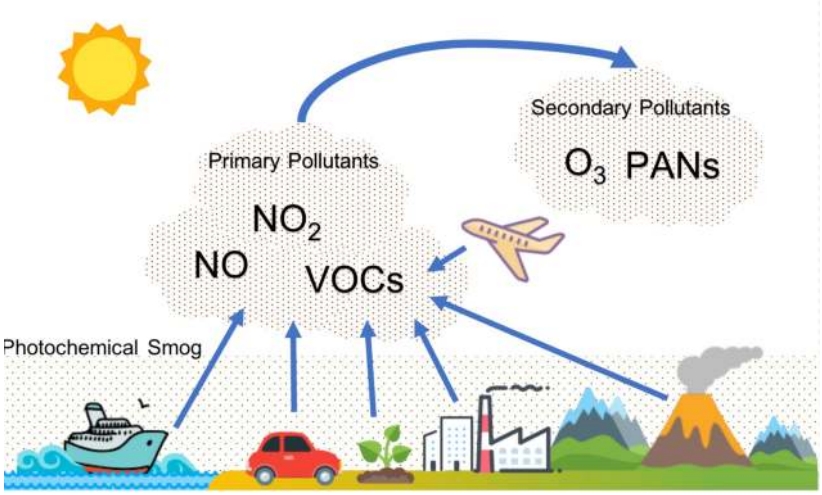


Figure **11.5.1** The photochemical smog formation diagram. Source: Wikipedia

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.

Contributors and Attributions

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- Marisa Alviar-Agnew (Sacramento City College)
- Wikipedia

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11.6: 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 **11.6.1**) 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.

$$SO_2 + HOH \rightarrow H_2SO_3 \tag{11.6.1}$$

$$2NO_2 + HOH \rightarrow HNO_2 + HNO_3 \tag{11.6.2}$$

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.

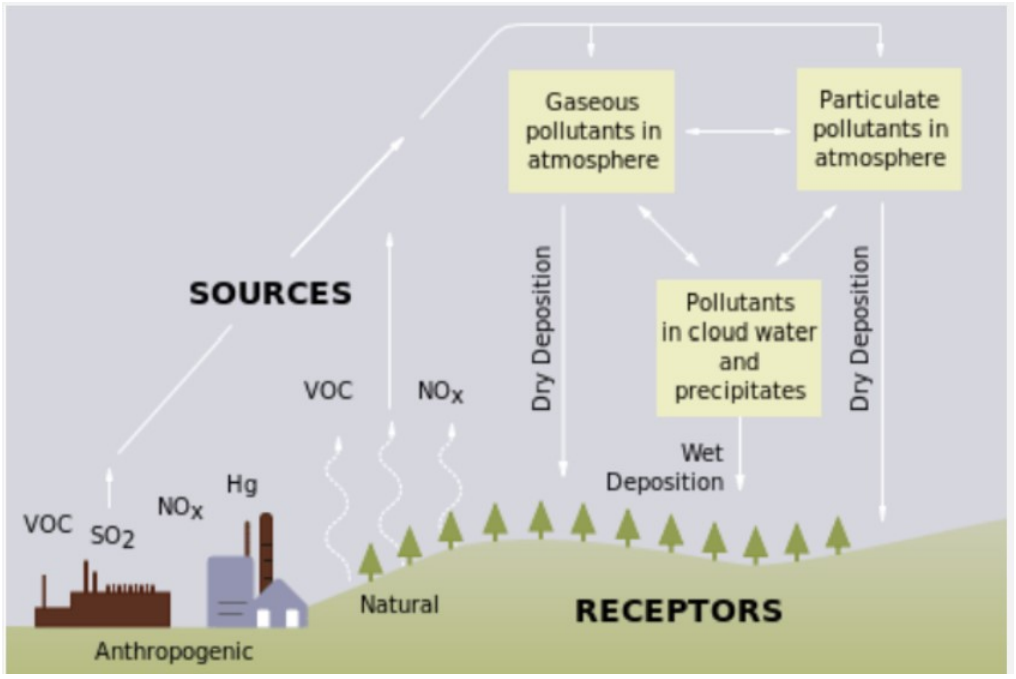


Figure **11.6.1** Processes involved in acid deposition.

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 **11.6.2**. 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 **11.6.2**. 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:

$$CaCO_{3(s)} + H_2SO_{4(aq)} \rightarrow CaSO_{4(s)} + H_2O_{(l)} + CO_{2(g)} \tag{11.6.3}$$

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 **11.6.3**).



Figure **11.6.3**. 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).

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11.7: 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 **11.7.1**). 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.

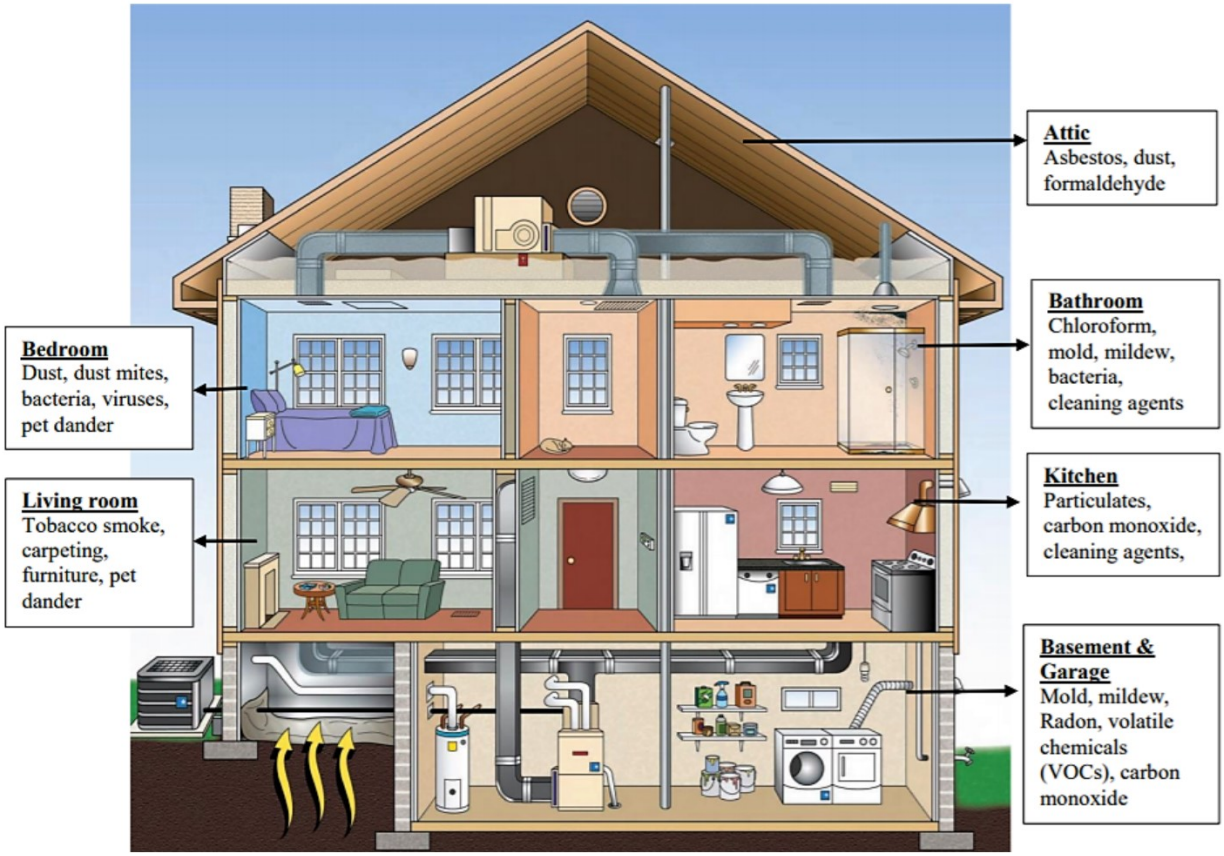


Figure 11.7.1: Sources of indoor air pollution. Image source: EPA http://www.epa.gov/iaq/pdfs/careforyourair.pdf

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.

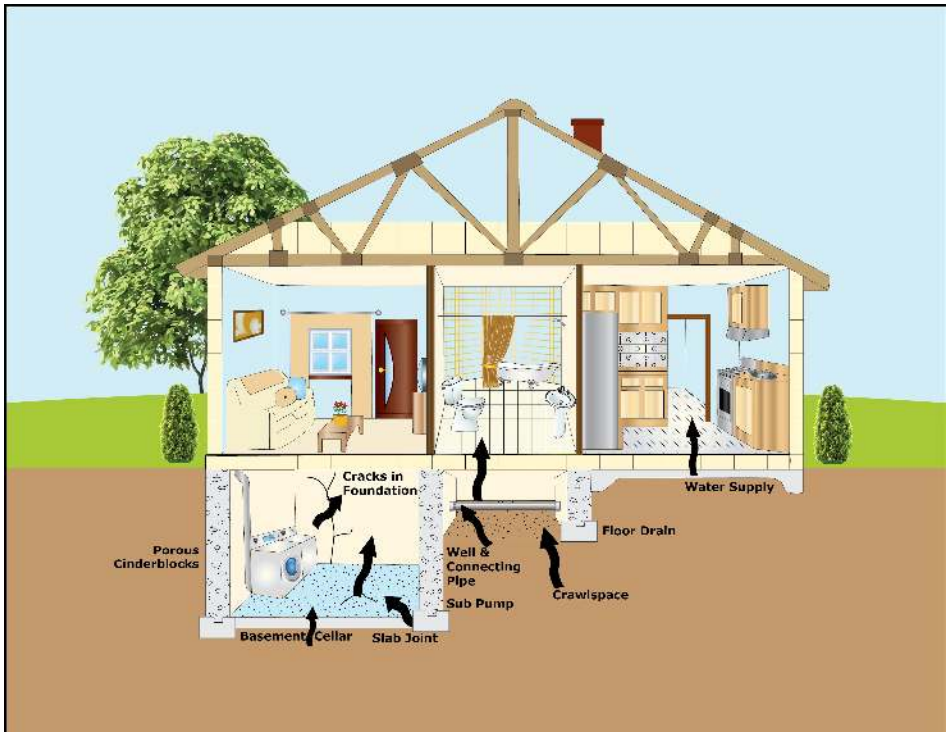


Figure* 11.7.2*: *Sources of Radon. Image source: EPA*https://www.epa.gov/radiation/radionuclide-basics-radon

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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11.8: 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.

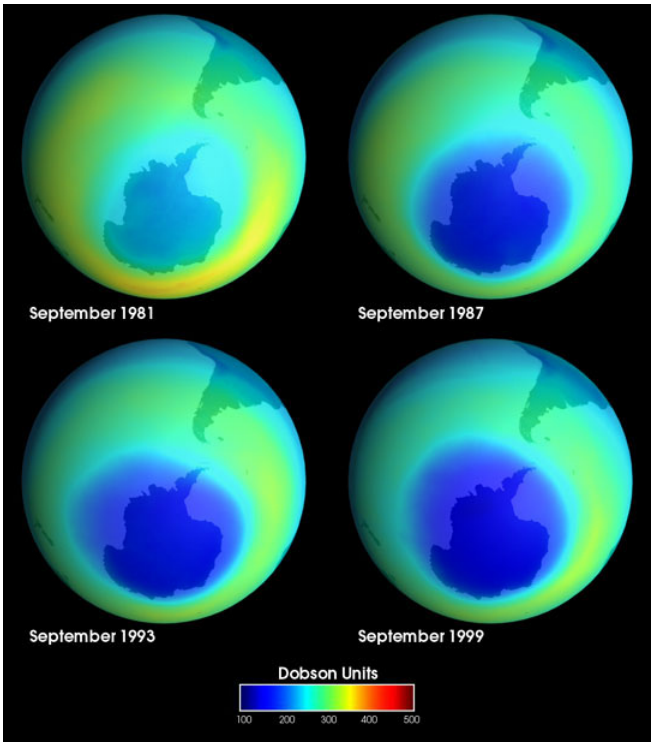


Figure courtesy of NASA.

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:

$$Cl + O_3 \rightarrow ClO + O_2 \qquad \textbf{(step 1)}$$

$$ClO + O^{\cdot} \rightarrow Cl + O_2 \qquad \textbf{(step 2)}$$

$$O_3 + O^{\cdot} \rightarrow 2O_2 \qquad \textbf{(Overall reaction)}$$

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.

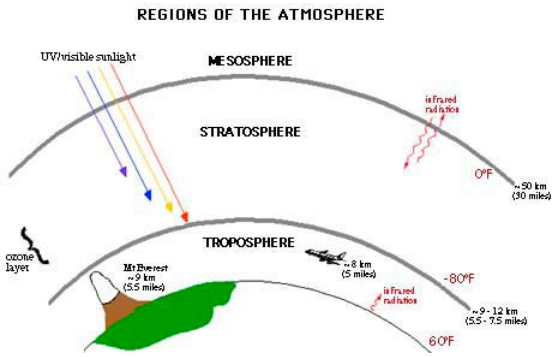


Figure courtesy of NOAA.

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 **11.8.1**: 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
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.

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11.9: 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.

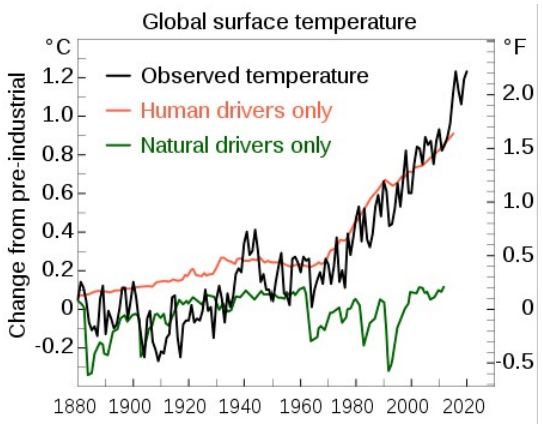


Figure **11.9.1** Observed temperature from NASA versus the 1850-1900 average as a pre-industrial baseline.

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 **11.9.2**). 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.

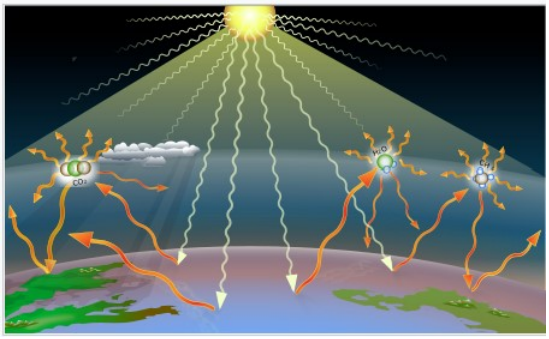


Figure 11.9.2 The greenhouse effect of solar radiation on the Earth's surface caused by emission of greenhouse gases. Source: Wikipedia

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 **11.9.1** 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 **11.9.2** 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.

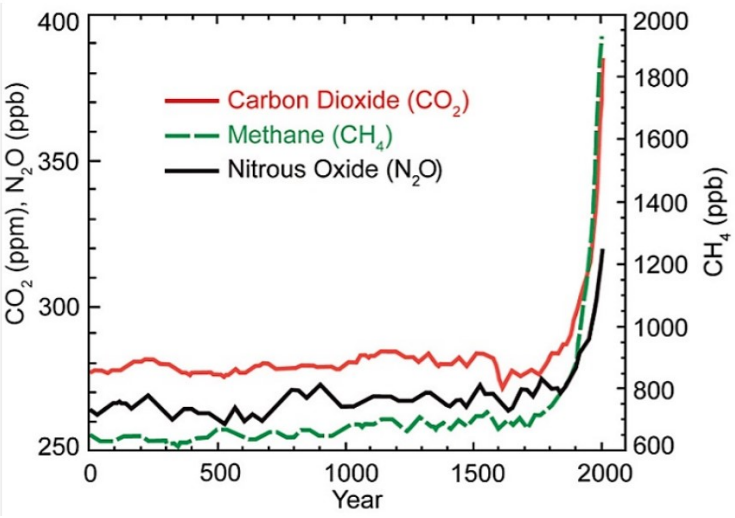


Figure **11.9.2**: Increase in greenhouse gas concentrations in the atmosphere over the last 2,000 years. Increases in concentrations of these gases since 1750 are due to human activities in the industrial era. Concentration units are parts per million (ppm) or parts per billion (ppb), indicating the 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 **11.9.1**. 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 **11.9.1**. 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 **11.9.1**. 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 **11.9.3**.



Figure **11.9.3**: 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 **11.9.4**, 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?

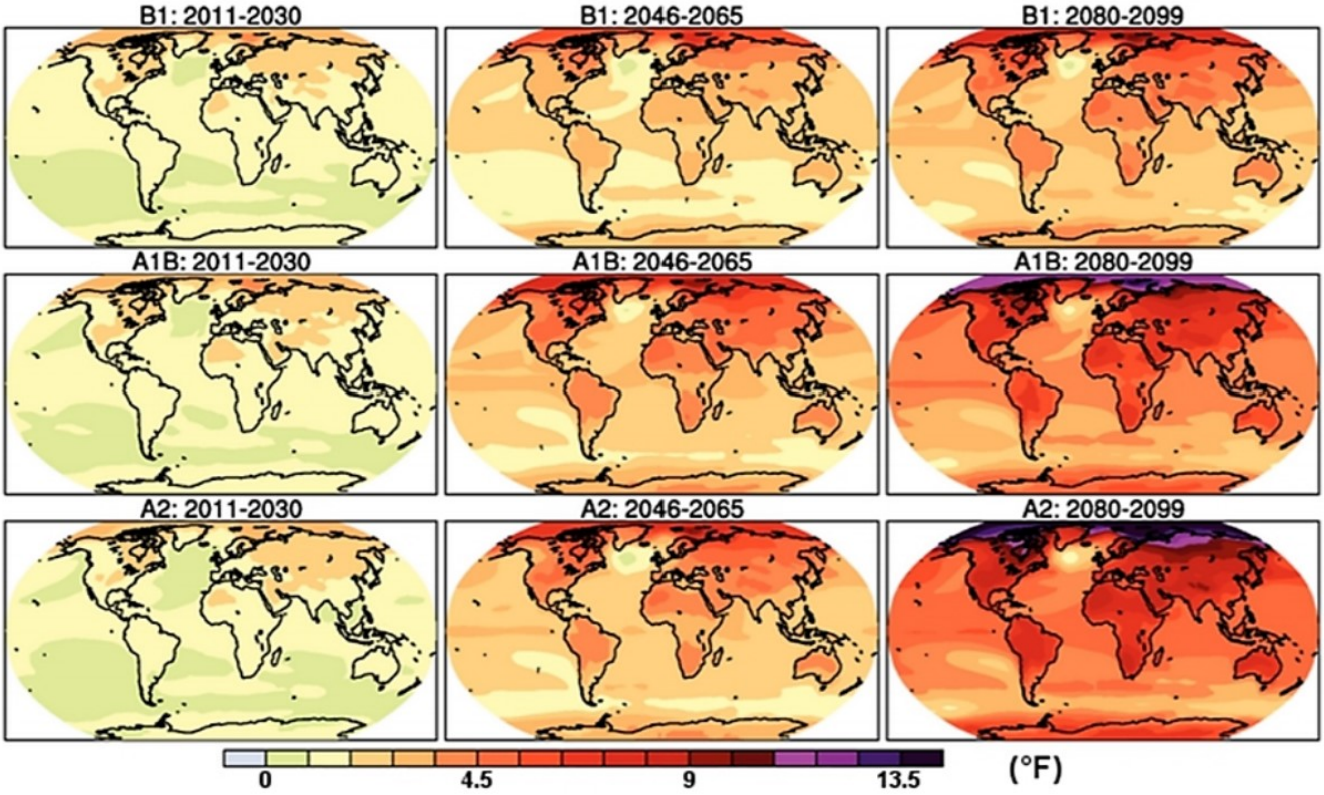


Figure **11.9.4**: Projected changes in global average temperatures under three emissions scenarios (rows) for three different time periods (columns). Changes in temperatures are relative to 1961- 1990 averages. The scenarios come from the IPCC Special Report on Emissions Scenarios: B1 is a low emissions 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 **11.9.5**, 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?

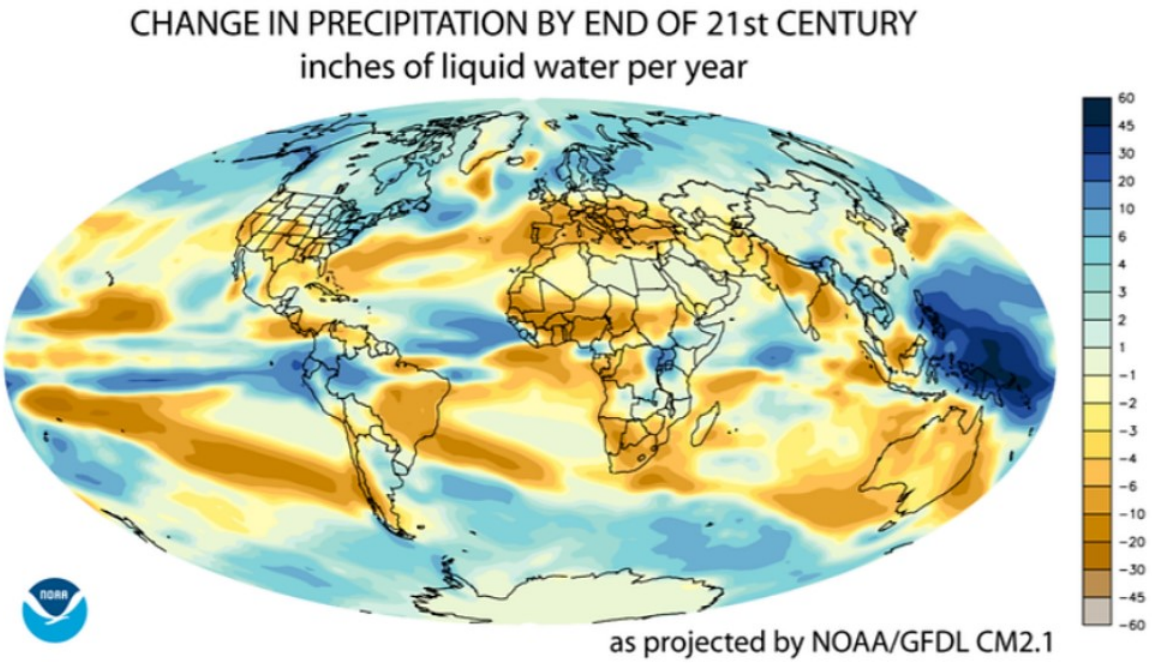


Figure **11.9.5** The plotted precipitation differences were computed as the difference between the 2081 to 2100 20-year averages minus the 1951 to 2000 50-year average. Blue areas project increases in precipitation; brown areas project decreases.

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 **11.9.6**).

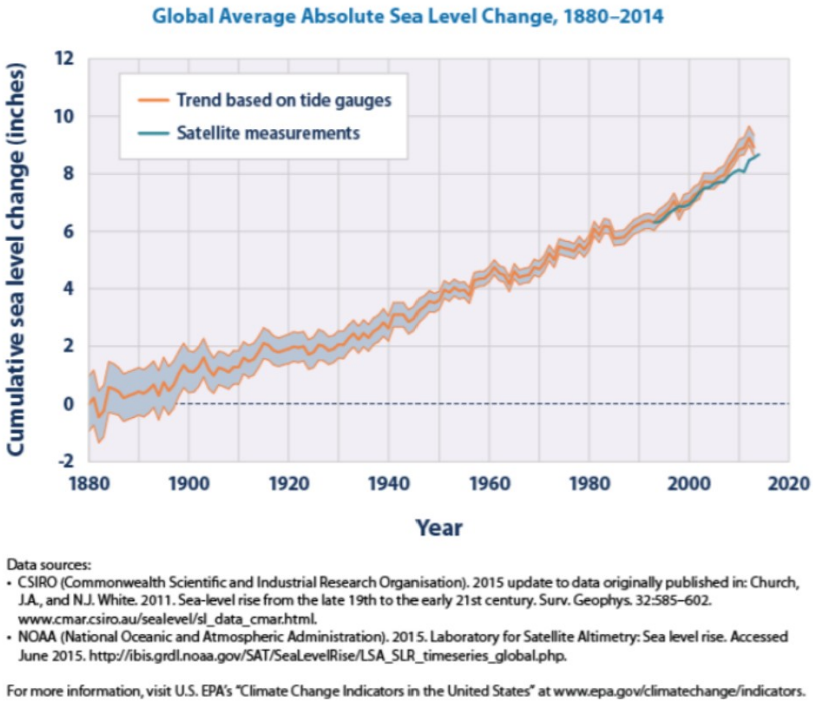


Figure **11.9.6**: *This graph shows average absolute cumulative changes in sea level for the world's oceans since 1880, based on a combination of tide gauge measurements and recent satellite measurements. The shaded band shows the likely range of values, based on the number of measurements collected and the precision of the methods used.*

From the data in Figure **11.9.6**, 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 **11.9.7**) 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 11.9.7: 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 **11.9.8** 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.

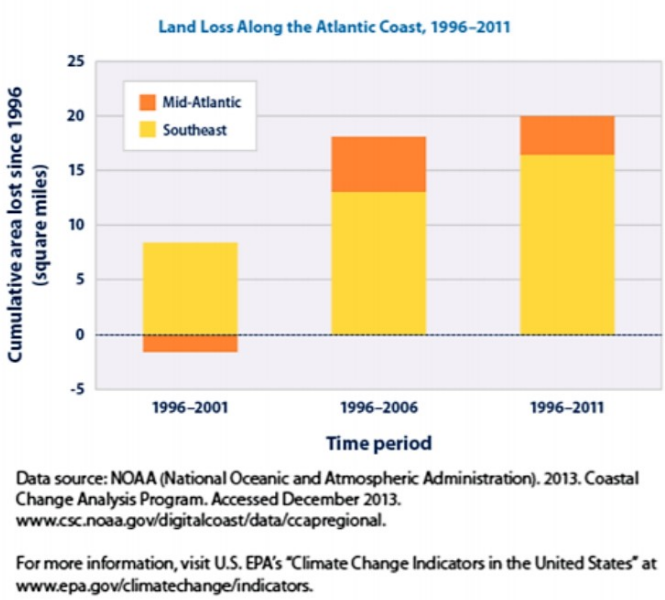


Figure **11.9.8**: This graph shows the net amount of land converted to open water along the Atlantic coast during three time periods: 1996–2001, 1996–2006, and 1996–2011. The results are divided into two regions: the Southeast and the Mid-Atlantic. Negative numbers show where land loss is outpaced by 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 **11.9.1** and **11.9.2**).

$$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^-$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$$

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 **11.9.1** and **11.9.2** 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 **11.9.9** 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.

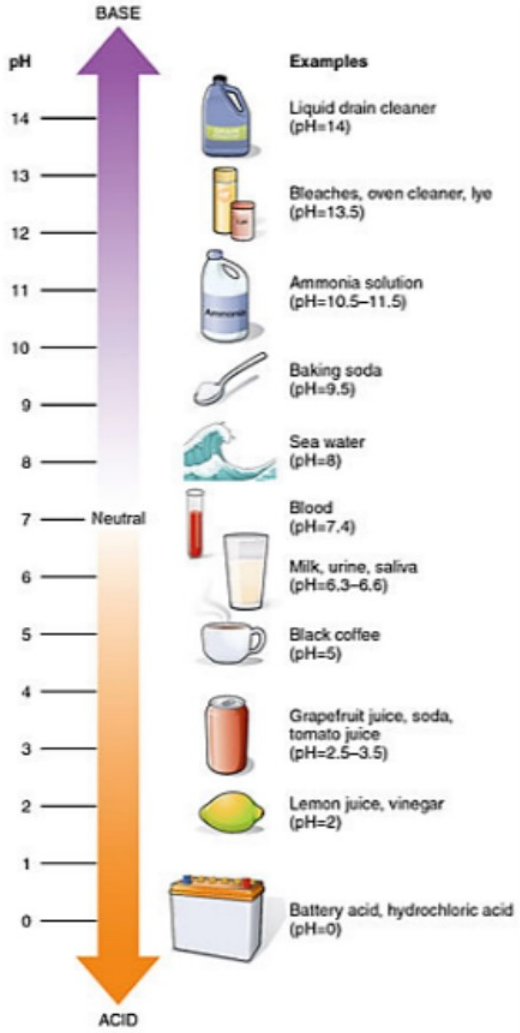


Figure **11.9.9**: The pH scale and relative acidity. Illustration from Anatomy & Physiology, Connexions Web site. http://cnx.org/content/col11496/1.6/, Jun 19, 2013.

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 **11.9.10**.

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/.

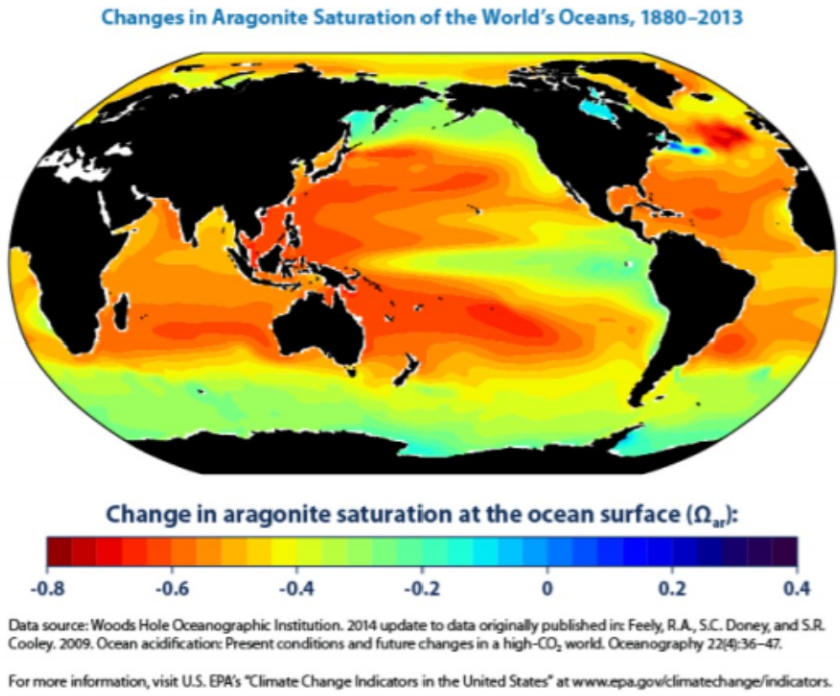


Figure **11.9.10**: This map shows changes in the aragonite saturation level of ocean surface waters between the 1880s and the most recent decade (2004–2013). Aragonite is a form of calcium carbonate that many marine animals use to build their skeletons and shells. A negative change represents a decrease 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 11.9.11).

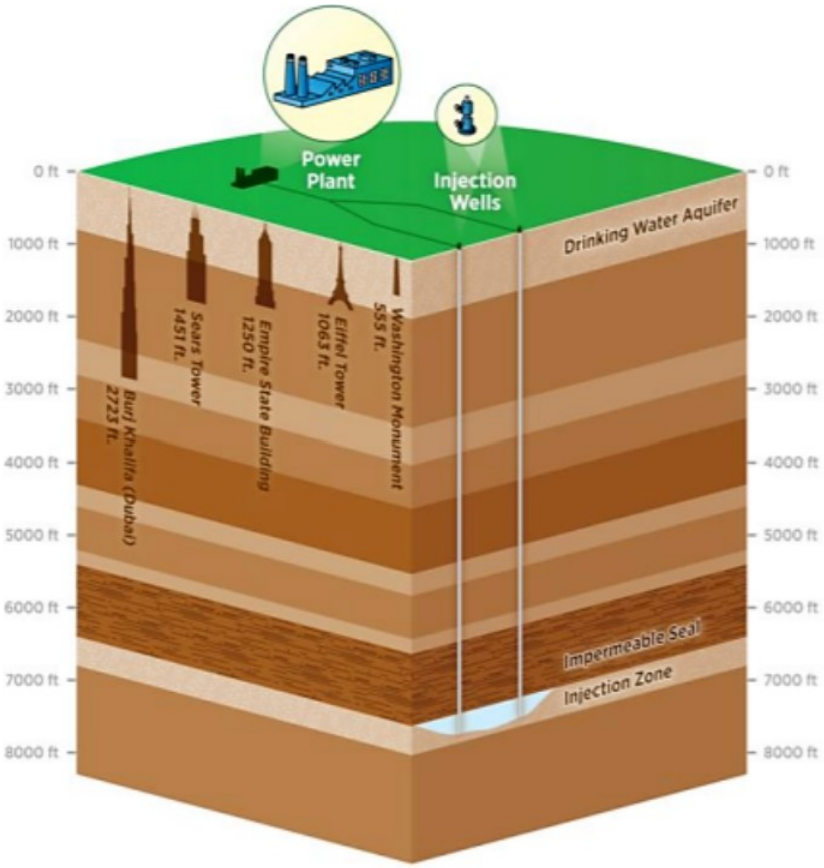


Figure 11.9.11: Carbon capture and sequestration schematic with landmarks shown to scale for depth reference. Source: US EPA.

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 **11.9.12** 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

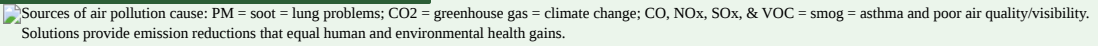


Figure **11.9.6** *Sources and solutions for transportation air pollution. Image: EPA*

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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11.10: 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 **11.10.1**. 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 **11.10.1** 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 µg/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 µg/m^3	annual mean, averaged over 3 years
		secondary	1 year	15.0 µg/m^3	annual mean, averaged over 3 years
		primary and secondary	24 hours	35 µg/m^3	98th percentile, averaged over 3 years
	PM_{10}	primary and secondary	24 hours	150 µg/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
		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 **11.10.2** list the sources and harmful effects of criteria pollutants.

Table **11.10.2** 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	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

		renal effects in adults and early effects related to anemia.	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

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CHAPTER OVERVIEW

12: Water

12.1: Water - Some Unique Properties
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12.3: Chemical and Biological Contamination
12.4: Groundwater Contamination to Tainted Tap Water
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12.8: Wastewater and Sewage Treatment

Thumbnail: Acid mine drainage in the Rio Tinto River. (Public Domain; Carol Stoker @ NASA via).

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12.1: 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 12.1.1). 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 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 O–H bonds do not cancel one another and the molecule as a whole is polar.

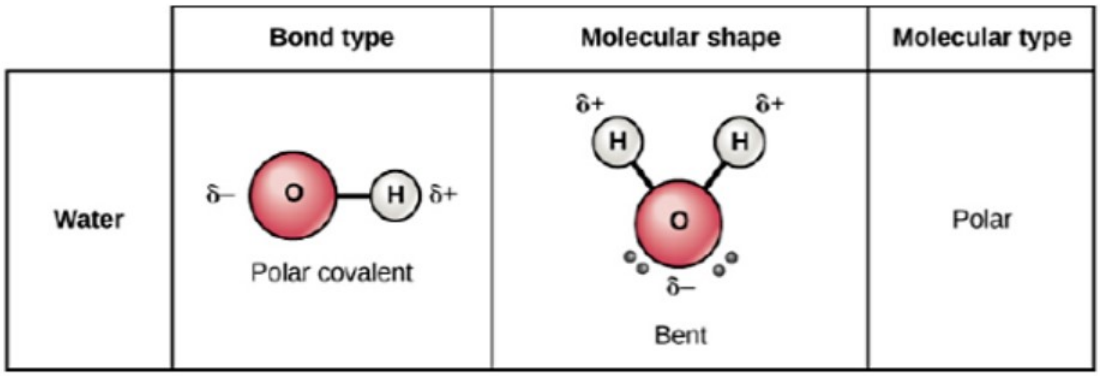


Figure 12.1.1 *Polarity of the water molecule due to the uneven distribution of electrons in its covalent bond. C (From OpenStax Concepts of Biology text)*

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 **12.1.1**) . It actually reaches its highest density at about **4°C**.

Table **12.1.1** *Density of Water and Ice*

Temperature (°C)	Density $\left(g/cm^3\right)$
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°C** and **0°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 **12.1.2**).

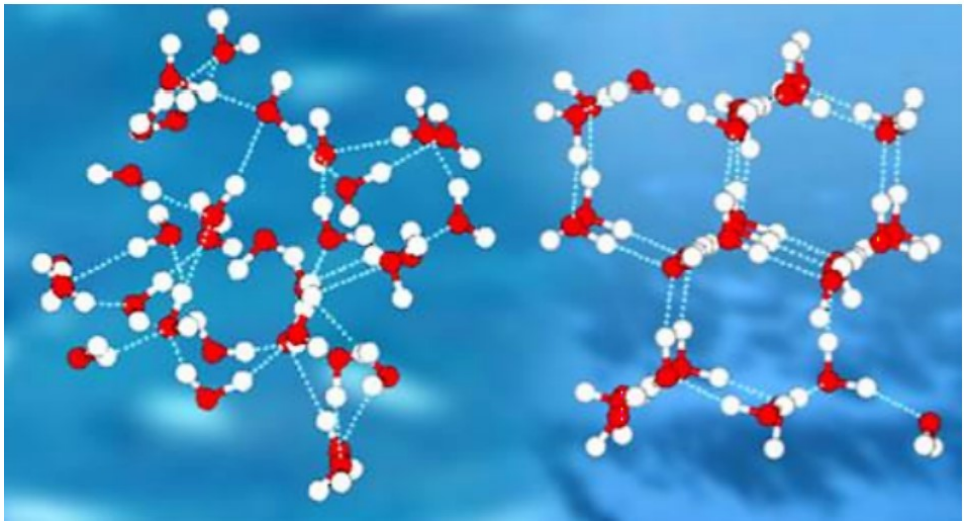


Figure **12.1.2** *Hydrogen bonding makes ice less dense than liquid water. The lattice structure water is more condensed (left structure) than that of ice (right structure). The lattice structure of ice makes it less dense than freely flowing molecules of liquid water, enabling ice to float on liquid 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 **12.1.3**) .

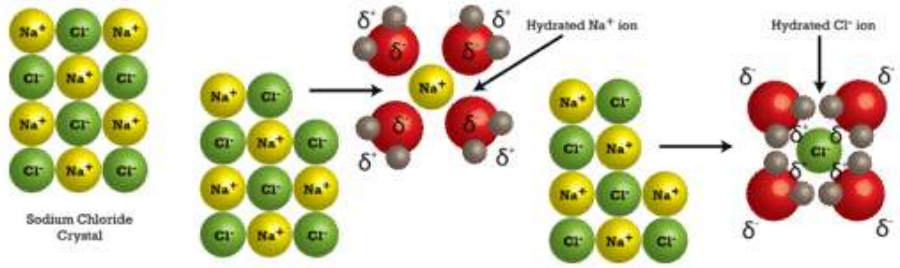


Figure **12.1.3** *The dissolving of sodium chloride in water.*

After coming apart from the crystal, the individual ions are then surrounded by solvent particles in a process called **solvation**. Note that the individual $\mathbf{Na^+}$ 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 ($\mathbf{C_{12}H_{22}O_{11}}$) 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 $\mathbf{-OH}$ 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:

$$HCl(acid) + H_2O(base) \rightleftharpoons H_3O^+ + Cl^-$$

In the reaction with ammonia, NH_3, water donates a H^+ ion, and is thus acting as an acid:

$$NH_3(base) + H_2O(acid) \rightleftharpoons NH^+_4 + OH^-$$

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 **12.1.2** 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 ($\mathbf{J/g°C}$) or calories per gram per degree ($\mathbf{cal/g°C}$). This text will use $\mathbf{J/g°C}$ for specific heat.



Figure 12.1.4 *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 12.1.4). 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 12.1.2 *Specific Heats of Some Common Substances*

Substance	Specific Heat (J/g°C)
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°C**).
- The specific heat of a substance is the amount of energy required to raise the temperature of 1 gram of the substance by **1°C**.
- 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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12.2: 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 **12.2.1**). 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**.

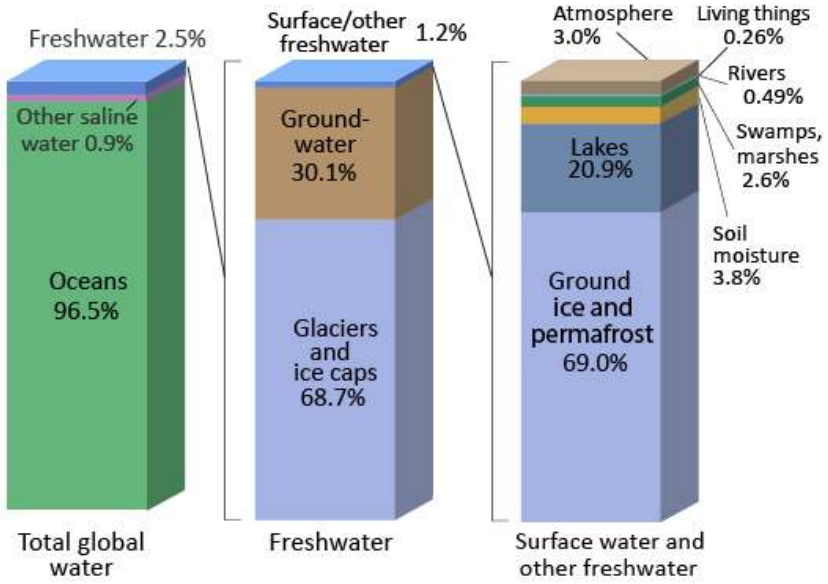


Figure **12.2.1** The distribution of Earth’s water. In the first bar, notice how only 2.5% of Earth's water is freshwater - the amount needed for life to survive. The middle bar shows the breakdown of freshwater. Almost all of it is locked up in ice and in the ground. Only a little more than 1.2% of 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 **12.2.2**).

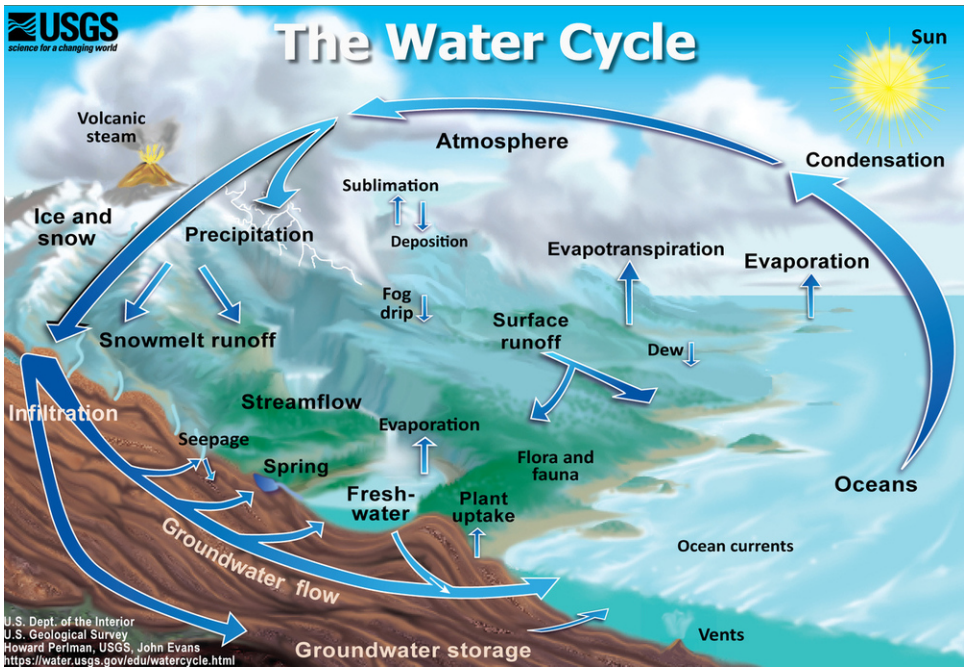


Figure **12.2.2** Because it is a cycle, the water cycle has no beginning and no end. Earth's water is always in movement, and the natural water cycle, also known as the hydrologic cycle, describes the continuous movement of water on, above, and below the surface of the Earth. Water is always changing 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.

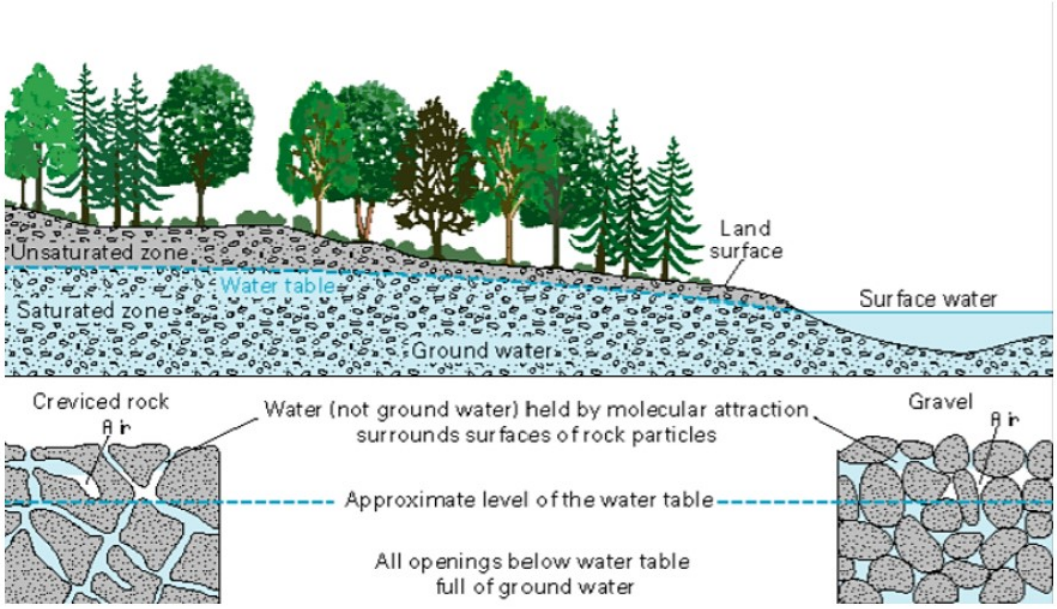


Figure Extra close brace or missing open brace *Model of groundwater system showing the different components of an unconfined groundwater system:* *http://water.usgs.gov/edu/earthgwaquifer.html*

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 **12.2.1** 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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12.3: 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 12.3.1) . 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 12.3.1

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 **12.3.2**) . 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 12.3.2 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 12.3.3 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.

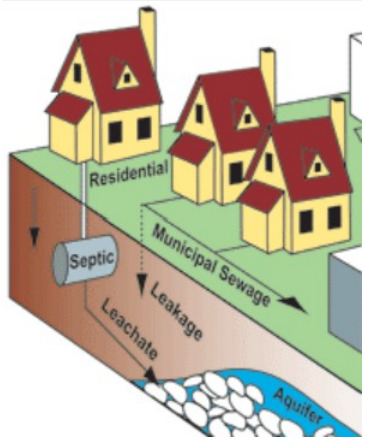


Figure 12.3.3 Methods of PPCP entry into the environment from residential homes via septic and sewage systems.[11]

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.



***Video* 12.3.1** *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 **12.3.1** 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 **12.3.4**) 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.

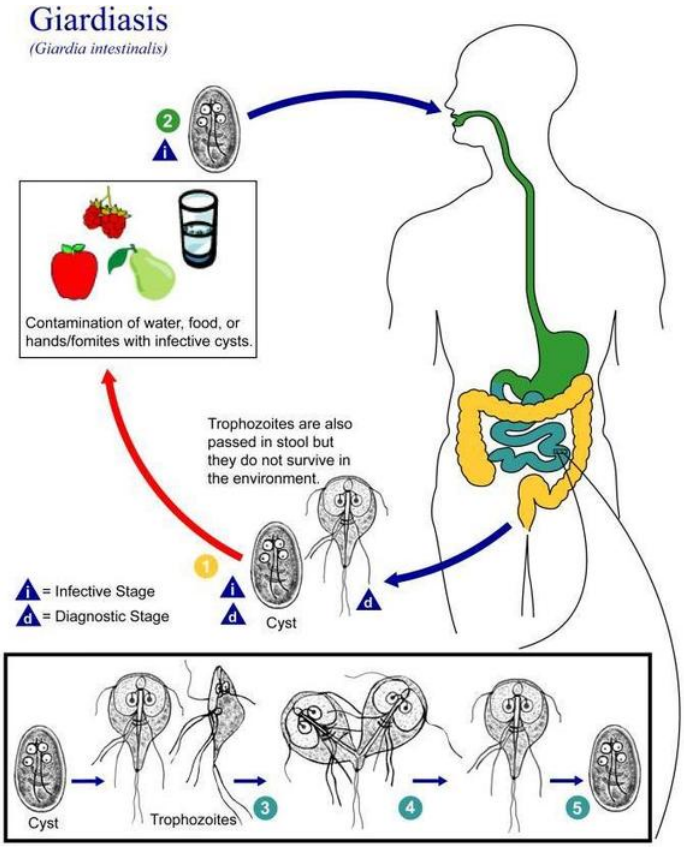


Figure **12.3.4** The life cycle of Giardia.



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 **12.3.2**). 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 **12.3.2**: 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

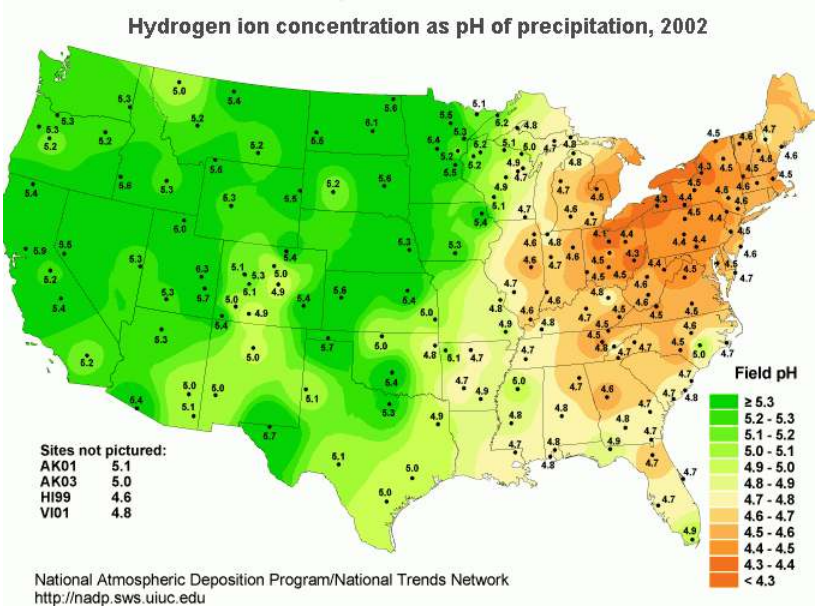


Figure **12.3.5**: pH of rainwater over the continental United States.

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 **12.3.5**). 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.

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12.4: 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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12.5: 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.

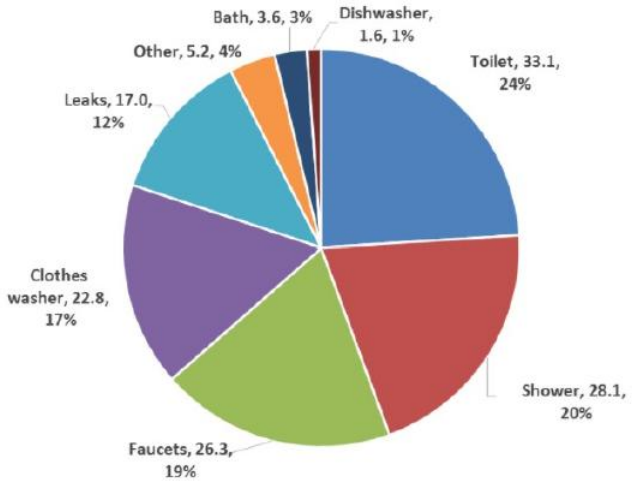


Figure **12.5.1** End uses of water for households in the U.S.in gallons per household per day and percent of indoor use.

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 **12.5.2**). 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* 12.5.2** *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).

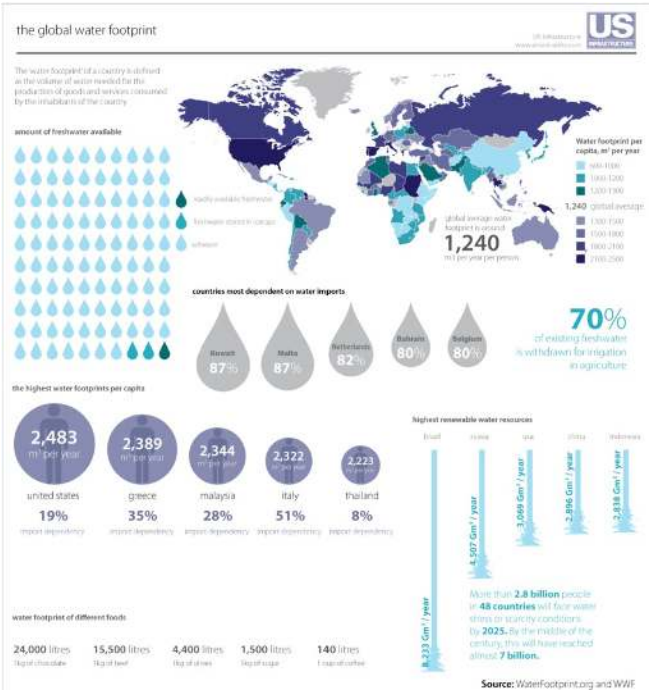


Figure **12.5.3** *The global water footprint.*

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 **12.5.3** *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.

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- Marisa Alviar-Agnew (Sacramento City College)
- Wikipedia

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12.6: 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 **12.6.1**: 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 **12.6.1**

***Table* 12.6.1** *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
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.

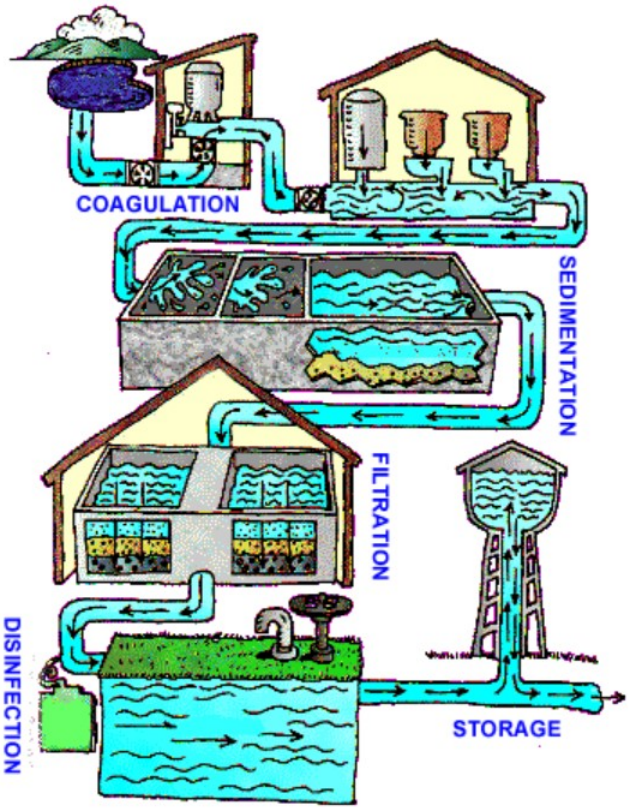


Figure 12.6.1 The common steps in water treatment. Source: US EPA

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 12.6.1) 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.



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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- Wikipedia

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12.8: 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.

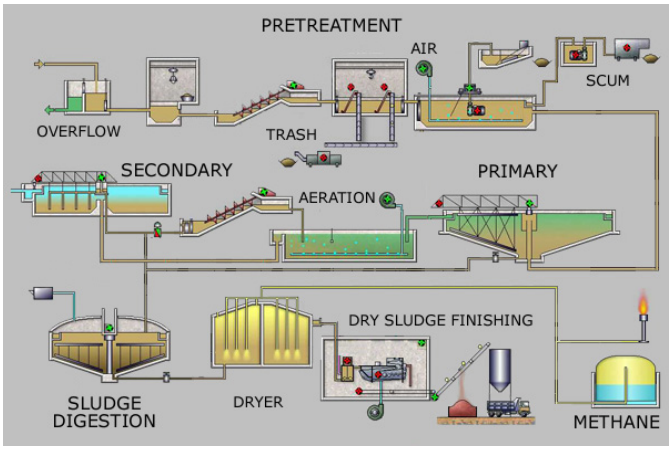


***Figure* 12.8.1 Diagram of Sewage Treatment Process**: Sewage passes through primary, secondary, and tertiary treatment.

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.

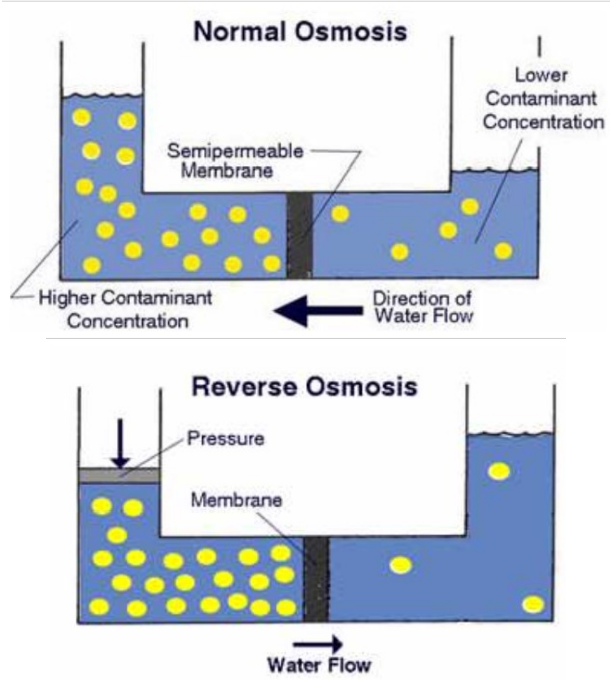


Figure **12.8.2** Comparison of normal osmosis and reverse osmosis. Source: PurePro.

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.



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.

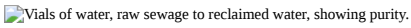


Figure **12.8.3** *The Sequence of reclamation from left: raw sewage, plant effluent, and finally reclaimed water (after several treatment steps). (Credit: Wikipedia)*

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.

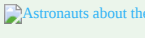
The main reclaimed water applications in the world are shown below:

Table **12.8.1** 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 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

- Libretexts: Microbioloy (Boundless)
- USGS
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- Marisa Alviar-Agnew (Sacramento City College)
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CHAPTER OVERVIEW

13: Biochemistry

13.1: Energy and the Living Cell
13.2: Carbohydrates- A Storehouse of Energy
13.3: Fats and Other Lipids
13.4: Proteins- Polymers of Amino Acids
13.5: Structure and Function of Proteins
13.6: Nucleic Acids- Parts, Structure, and Function
13.7: The Human Genome
13.8: RNA Protein Synthesis and the Genetic Code

Thumbnail: DNA double helix. (public domain; NIH - Genome Research Institute).

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13.1: 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 13.1.1) 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.

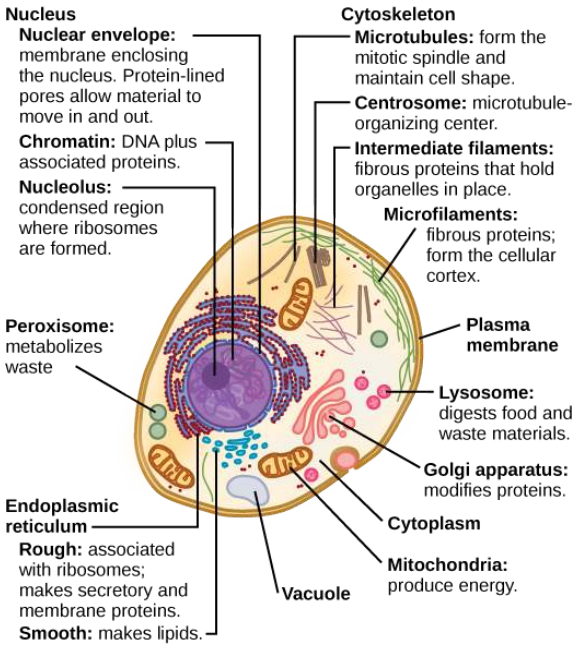
Ribosomes

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* 13.1.1*: *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:

$$6\,CO_2 + 6\,H_2O + 686\ \text{kcal} \rightarrow C_6H_{12}O_6 + 6\,O_2 \tag{13.1.1}$$

(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 **13.1.1**) 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.

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13.2: 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 **13.2.1**.

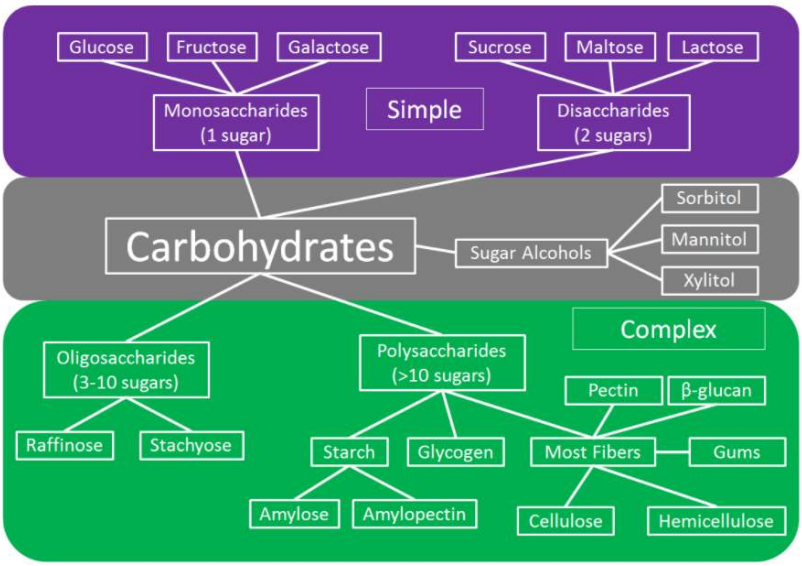
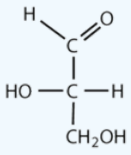
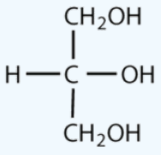


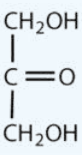
Figure **13.2.1** *Overview of carbohydrates*

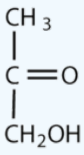
Example 13.2.1

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.

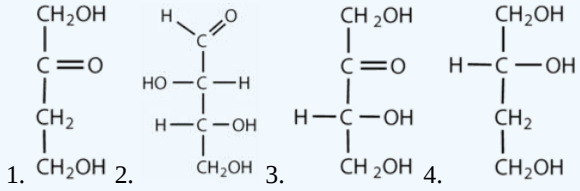
b. This is not a carbohydrate because the molecule does not contain an aldehyde or a ketone functional group.

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 13.2.1

Which compounds would be classified as carbohydrates?



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 **13.2.2**). Glucose and galactose are both aldohexoses, while fructose is a ketohexose.

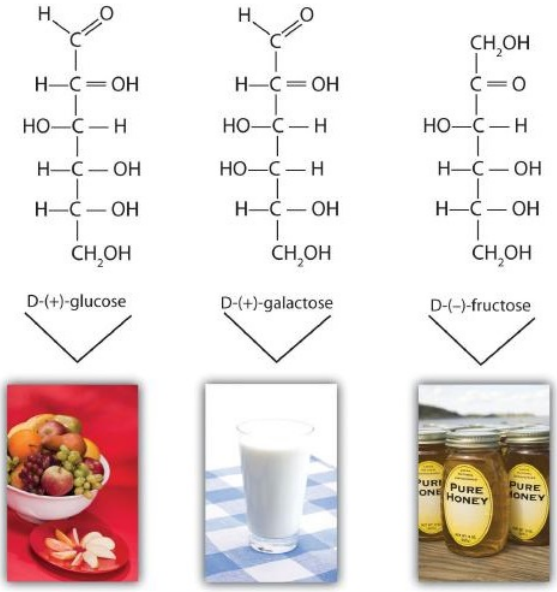


Figure **13.2.2**: Structures of Three Important Hexoses. Each hexose is pictured with a food source in which it is commonly found. Source: Photos © Thinkstock.

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 **13.2.3**. 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.

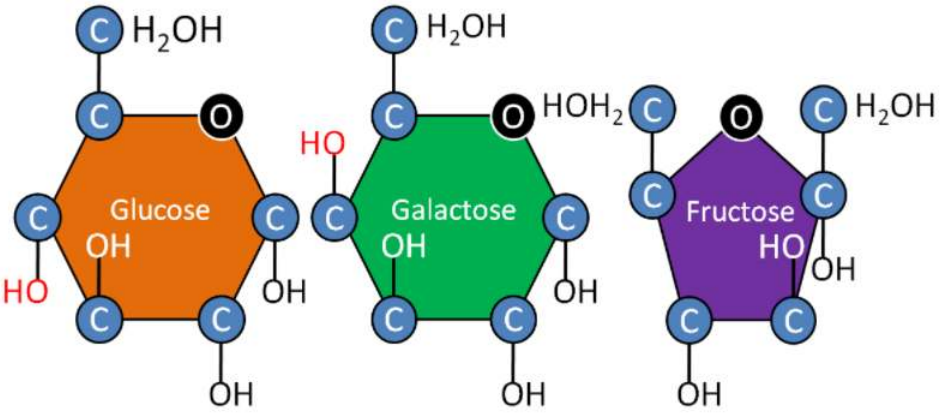


Figure **13.2.3** *The ring structures of glucose, galactose, and fructose.*

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 **13.2.4**.

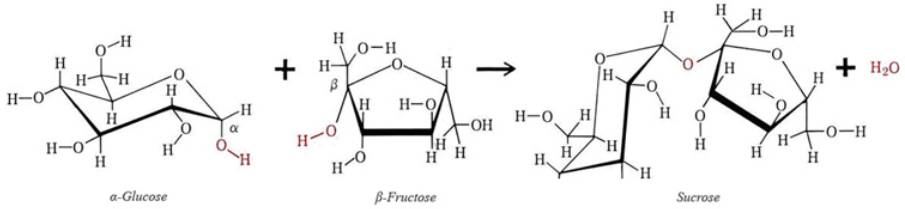


Figure **13.2.4** *The formation of sucrose from glucose and fructose.*

Other, less familiar, examples of disaccharides are lactose, which occurs in milk, and maltose, which are shown in Figure **13.2.5**. 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.

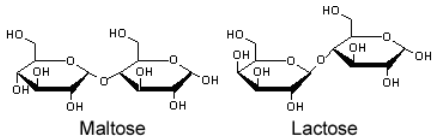


Figure **13.2.5** Two other common disaccharides, maltose and lactose.

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 **13.2.6**). 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 **13.2.6**). 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.

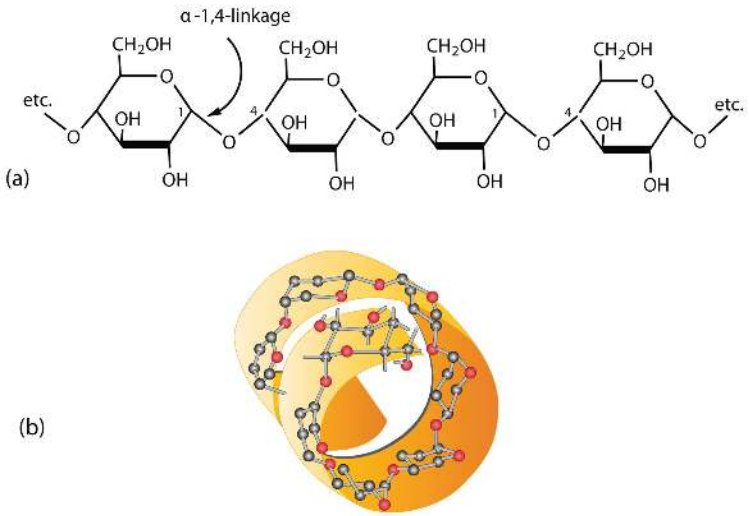


Figure **13.2.6** Amylose. (a) Amylose is a linear chain of α-D-glucose units joined together by α-1,4-glycosidic bonds. (b) Because of hydrogen bonding, amylose acquires a spiral structure that contains six glucose units per turn.

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 **13.2.7**). 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.

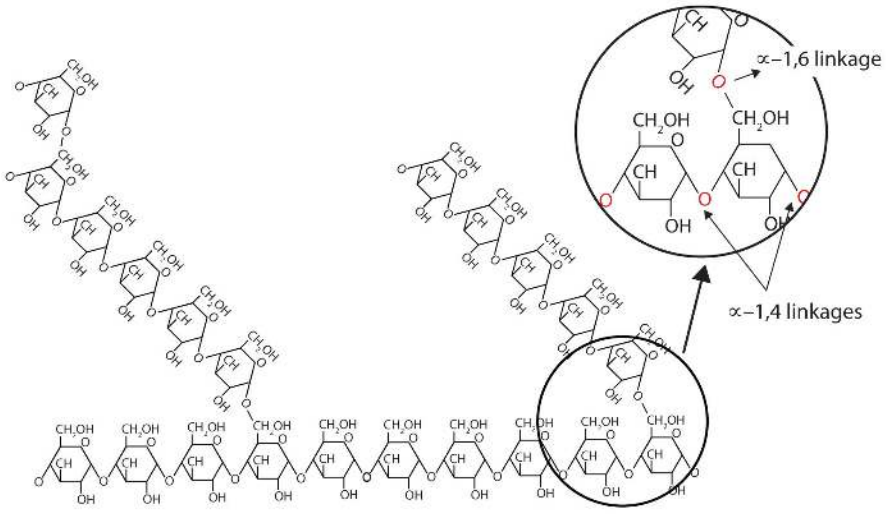


Figure **13.2.7** Representation of the Branching in Amylopectin and Glycogen. Both amylopectin and glycogen contain branch points that are linked through α-1,6-linkages. These branch points occur more often in glycogen.

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 **13.2.8**). 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 **13.2.8**). 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.

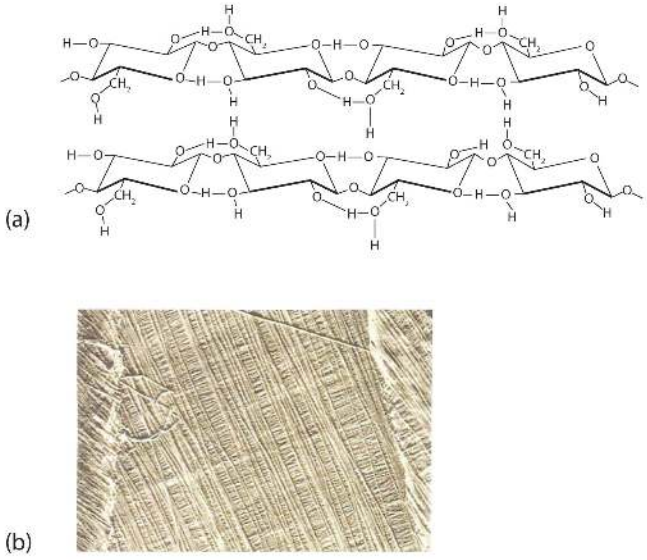


Figure **13.2.8** Cellulose. (a) There is extensive hydrogen bonding in the structure of cellulose. (b) In this electron micrograph of the cell wall of an alga, the wall consists of successive layers of cellulose fibers in parallel arrangement.

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.)
- Ed Vitz (Kutztown University), John W. Moore (UW-Madison), Justin Shorb (Hope College), Xavier Prat-Resina (University of Minnesota Rochester), Tim Wendorff, and Adam Hahn.
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13.3: 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 **13.3.1** 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.

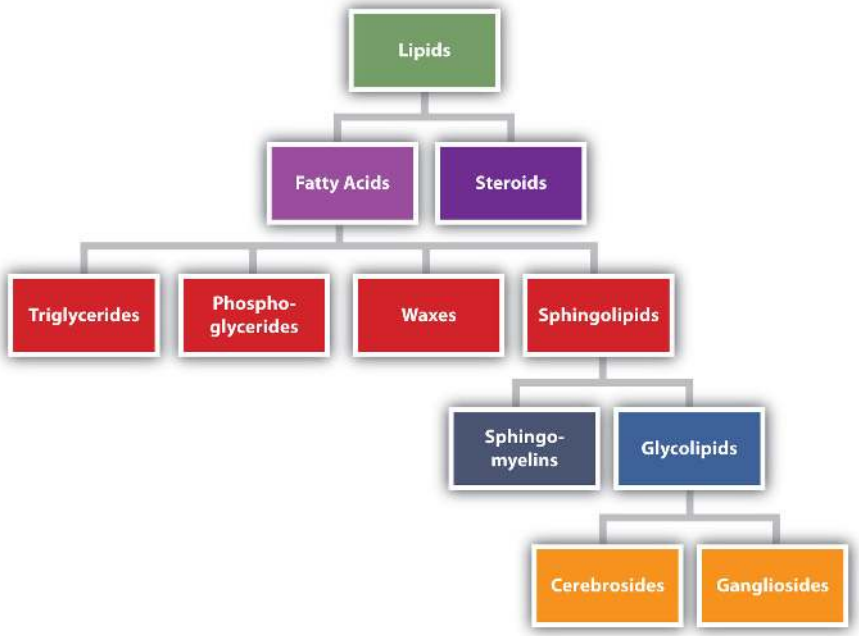
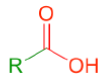


Figure **13.3.1** *Lipid organization based on structural relationships*

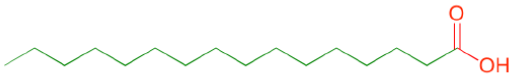
Fatty Acids

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. Saturated fatty acids contain only alkane carbons (single bonds only), mononsaturated fatty acids contain a single double bond, and

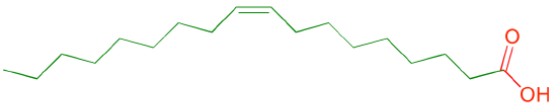
polyunsaturated fatty acids contain two or more double bonds. The double bonds in naturally occurring fatty acids are predominantly in the *cis* configuration.



fatty acid



palmitic acid
(a 16-carbon saturated fatty acid)

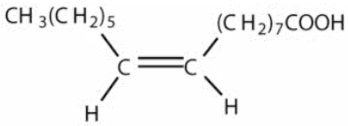


oleic acid
(an 18-carbon monounsaturated fatty acid)

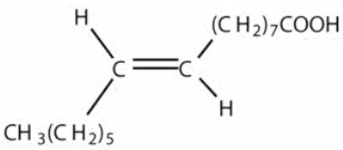
Double bonds on Fatty Acids

Note that all naturally occurring double bonds are cis (E), with a methylene spacer between double bonds - i.e. the double bonds are not conjugated. For saturated fatty acids, the melting point increases with C chain length, owing to increased likelihood of van der Waals (London or induced dipole) interactions between the overlapping and packed chains. Within chains of the same number of Cs, melting point decreases with increasing number of double bonds, owing to the kinking of the acyl chains, followed by decreased packing and reduced intermolecular forces (IMFs). Fatty acid composition differs in different organisms:

- animals have 5-7% of fatty acids with 20-22 carbons, while fish have 25-30%
- animals have <1% of their fatty acids with 5-6 double bonds, while plants have 5-6% and fish 15-30%



cis fatty acid



trans fatty acid

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 **13.3.2*a***). Viewed as a whole, however, the saturated fatty acid molecule is relatively straight (Figure **13.3.2*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.

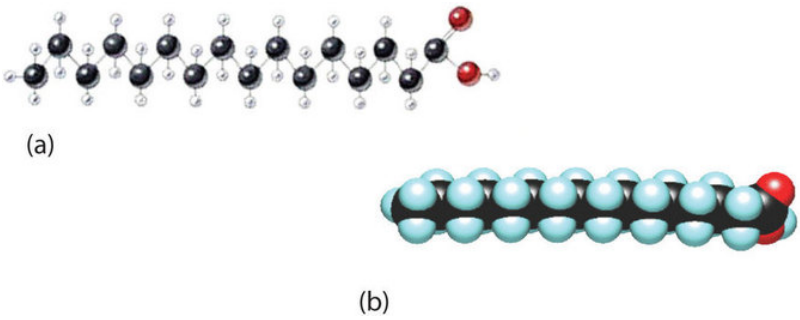


Figure **13.3.2** The Structure of Saturated Fatty Acids. (a) There is a zigzag pattern formed by the carbon-to-carbon single bonds in the ball-and-stick model of a palmitic acid molecule. (b) A space-filling model of palmitic acid shows the overall straightness of a saturated fatty acid molecule.

Essential Fatty Acids

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.

Table **13.3.1** Some Common Fatty Acids Found in Natural Fats.

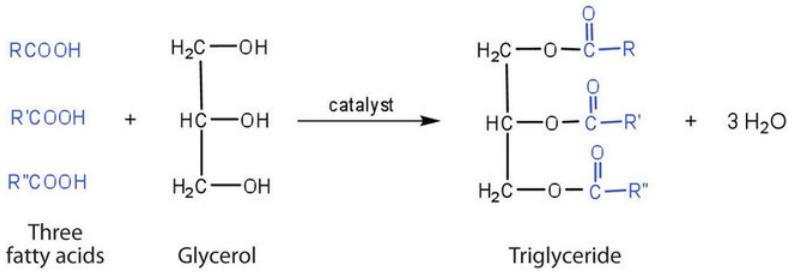
Name	Abbreviated Structural Formula	Condensed Structural Formula	Melting Point (°C)	Source
lauric acid	$C_{11}H_{23}COOH$	$CH_3(CH_2)_{10}COOH$	44	palm kernel oil
myristic acid	$C_{13}H_{27}COOH$	$CH_3(CH_2)_{12}COOH$	58	oil of nutmeg
palmitic acid	$C_{15}H_{31}COOH$	$CH_3(CH_2)_{14}COOH$	63	palm oil
palmitoo	$C_{15}H_{29}COOH$	$CH_3(CH_2)_5CH=CH(CH_2)_7COOH$	0.5	macadam

Name	Abbreviated Structural Formula	Condensed Structural Formula	Melting Point (°C)	Source
linolenic acid				linseed 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-li	$C_{17}H_{29}COOH$	$CH_3(CH_2CH{=}CH)_3(CH_2)_7COOH$	−11	flax

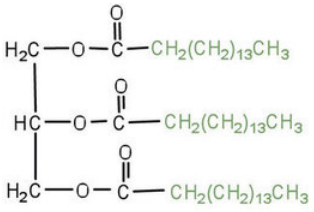
Name	Abbreviated Structural Formula	Condensed Structural Formula	Melting Point (°C)	Source
nolenic acid				seed
arachidonic acid	$C_{19}H_{31}COOH$	$CH_3(CH_2)_4(CH_2CH{=}CH)_4(CH_2)_2COOH$	−50	liver

Triglycerides

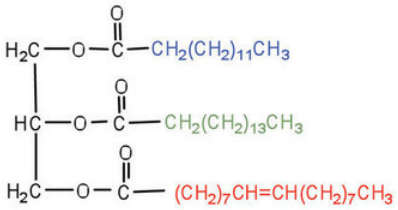
Triglycerides (or *triacylcylgerols*) are esters composed of three fatty acid units joined to *glycerol*, a trihydroxy alcohol:



If all three OH groups on the glycerol molecule are esterified with the same fatty acid, the resulting ester is called a *simple triglyceride*. Although simple triglycerides have been synthesized in the laboratory, they rarely occur in nature. Instead, a typical triglyceride obtained from naturally occurring fats and oils contains two or three different fatty acid components and is thus termed a *mixed triglyceride*.



Tristearin
a simple triglyceride



a mixed triglyceride

A triglyceride is called a fat if it is a solid at 25°C; it is called an oil if it is a liquid at that temperature. These differences in melting points reflect differences in the degree of unsaturation and number of carbon atoms in the constituent fatty acids. Triglycerides obtained from animal sources are usually solids, while those of plant origin are generally oils. Therefore, we commonly speak of animal fats and vegetable oils.

No single formula can be written to represent the naturally occurring fats and oils because they are highly complex mixtures of triglycerides in which many different fatty acids are represented. Table **13.3.2** 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 **13.3.2** 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.

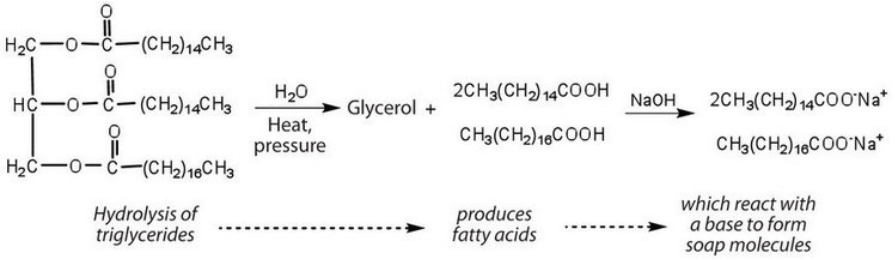


Diacetyl 3-hydroxy-2-butanone

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.

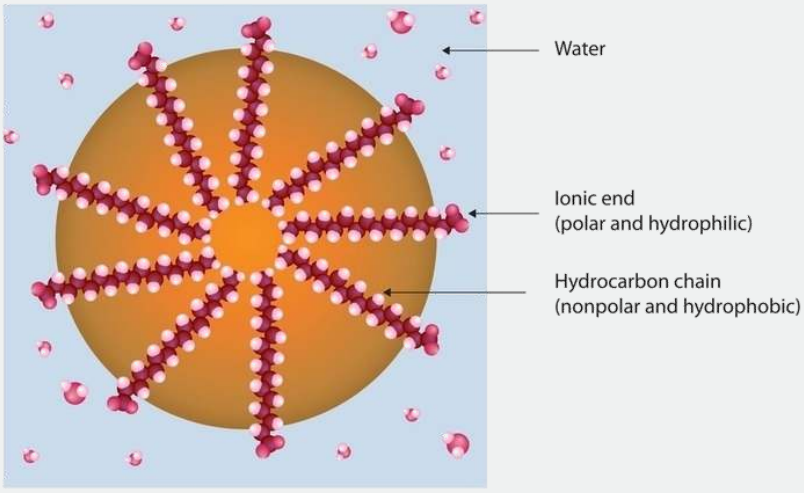
Chemical Reactions of Fats and Oils

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):



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

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13.4: Proteins- Polymers of Amino Acids

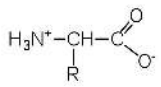
Learning Objectives

- Identify different amino acids.
- Describe how short chain proteins (polypeptides) are formed from amino acids.

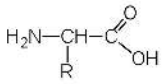
Proteins may be defined as compounds of high molar mass consisting largely or entirely of chains of amino acids. Their masses range from several thousand to several million daltons (Da). In addition to carbon, hydrogen, and oxygen atoms, all proteins contain nitrogen and sulfur atoms, and many also contain 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

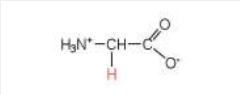
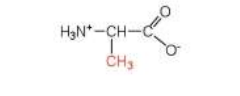
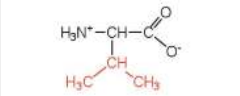
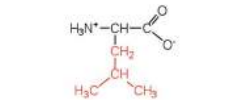
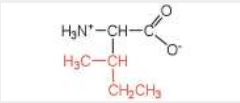
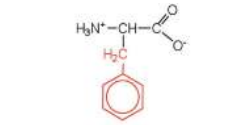
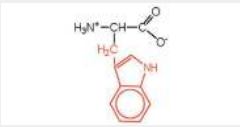
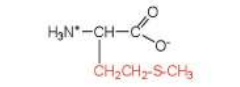
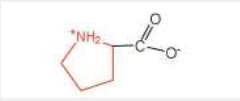
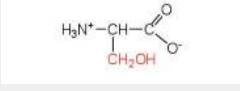
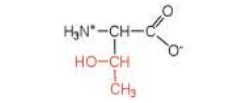
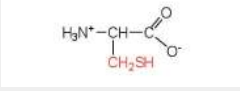


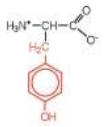
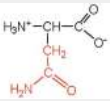
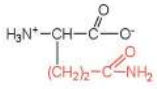
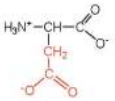
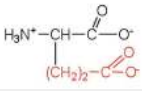
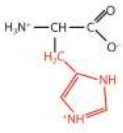
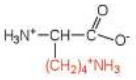
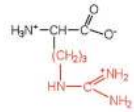
α-Amino acid drawn as an uncharged molecule; not an accurate respresentation of amino acid structure

Classification

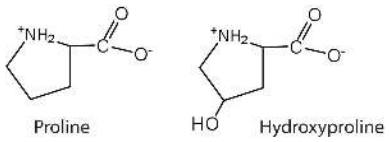
In addition to the amino and carboxyl groups, amino acids have a side chain or R group attached to the α-carbon. Each amino acid has unique characteristics arising from the size, shape, solubility, and ionization properties of its R group. As a result, the side chains of amino acids exert a profound 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 **13.4.1**.

Table **13.4.1**: Common Amino Acids Found in Proteins

Common Name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
Amino acids with a nonpolar R group				
glycine	gly (G)		75	the only amino acid lacking a chiral carbon
alanine	ala (A)		89	—
valine	val (V)		117	a branched-chain amino acid
leucine	leu (L)		131	a branched-chain amino acid
isoleucine	ile (I)		131	an essential amino acid because most animals cannot synthesize branched-chain amino acids
phenylalanine	phe (F)		165	also classified as an aromatic amino acid
tryptophan	trp (W)		204	also classified as an aromatic amino acid
methionine	met (M)		149	side chain functions as a methyl group donor
proline	pro (P)		115	contains a secondary amine group; referred to as an *α-imino acid*
Amino acids with a polar but neutral R group				
serine	ser (S)		105	found at the active site of many enzymes
threonine	thr (T)		119	named for its similarity to the sugar threose
cysteine	cys (C)		121	oxidation of two cysteine molecules yields *cystine*

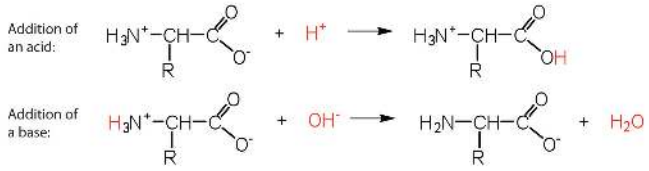
Common Name	Abbreviation	Structural Formula (at pH 6)	Molar Mass	Distinctive Feature
tyrosine	tyr (Y)		181	also classified as an aromatic amino acid
asparagine	asn (N)		132	the amide of aspartic acid
glutamine	gln (Q)		146	the amide of glutamic acid
Amino acids with a negatively charged R group				
aspartic acid	asp (D)		132	carboxyl groups are ionized at physiological pH; also known as aspartate
glutamic acid	glu (E)		146	carboxyl groups are ionized at physiological pH; also known as glutamate
Amino acids with a positively charged R group				
histidine	his (H)		155	the only amino acid whose R group has a pK_a (6.0) near physiological pH
lysine	lys (K)		147	—
arginine	arg (R)		175	almost as strong a base as sodium hydroxide

The first amino acid to be isolated was asparagine in 1806. It was obtained from protein found in asparagus juice (hence the name). Glycine, the major amino acid found in gelatin, was named for its sweet taste (Greek *glykys*, meaning “sweet”). In some cases an amino acid found in a protein is actually a derivative of one of the common 20 amino acids (one such derivative is hydroxyproline). The modification occurs *after* the amino acid has been assembled into a protein.



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 **13.4.1**

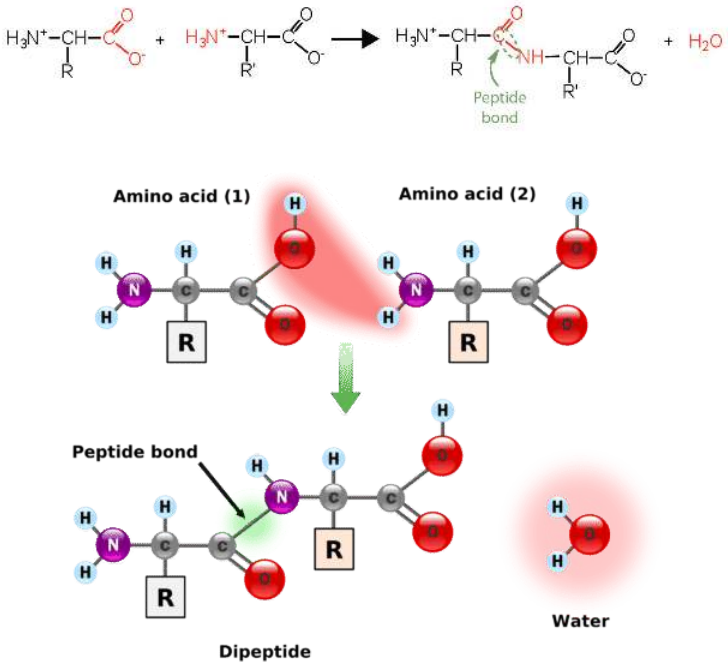
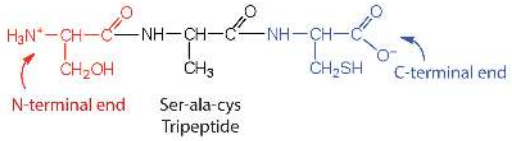


Figure **13.4.1** *Amino acids undergo condensation to form a molecule called a dipeptide. The* **C–N** *bond is called a peptide bond.*

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.

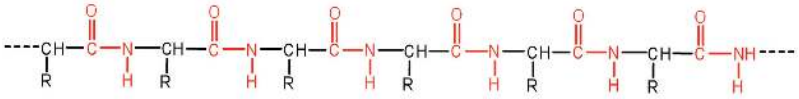


The general term *peptide* refers to an amino acid chain of unspecified length. However, chains of about 50 amino acids or more are usually called proteins or polypeptides. In its physiologically active form, a protein may be composed of one or more polypeptide chains.

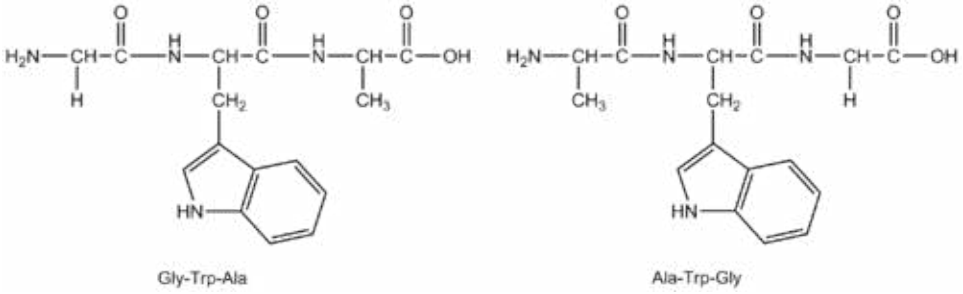
Peptide cells in our bodies have an intricate mechanism for the manufacture of proteins. Humans have to use other techniques in order to synthesize the same proteins in a lab. The chemistry of peptide synthesis is complicated. Both active groups on an amino acid can react and the amino acid sequence 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.



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 **13.4.2**) 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.

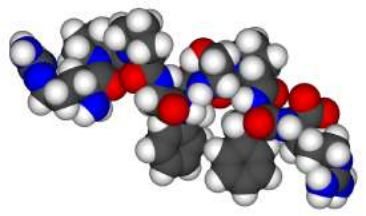


Figure **13.4.2** Space-filling model of bradykinin. (Public Domain; Fvasconcellos)

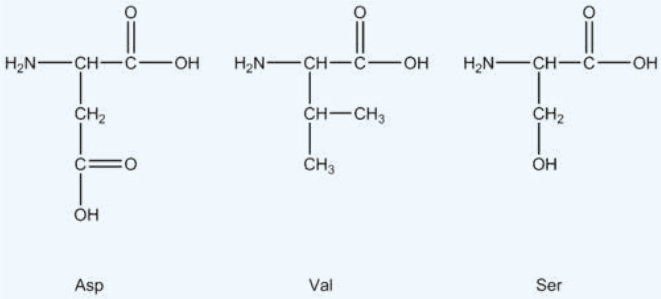
Just as millions of different words are spelled with our 26-letter English alphabet, millions of different proteins are made with the 20 common amino acids. However, just as the English alphabet can be used to write gibberish, amino acids can be put together in the *wrong sequence* to produce nonfunctional 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 13.4.1

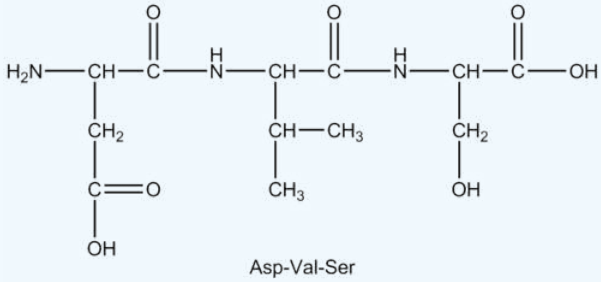
Draw the polypeptide Asp-Val-Ser.

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.



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 13.4.2

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

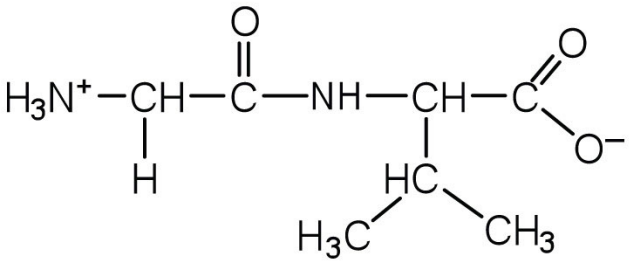
Exercise 13.4.1

Draw the structure for each peptide.

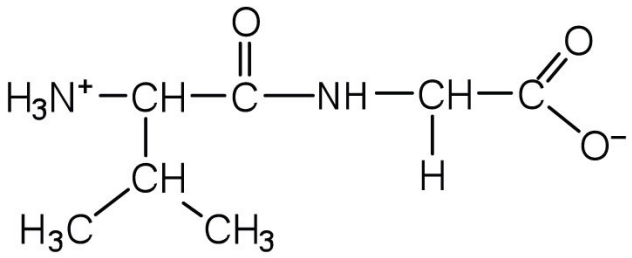
a. gly-val
b. val-gly

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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13.5: 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 **13.5.1**.

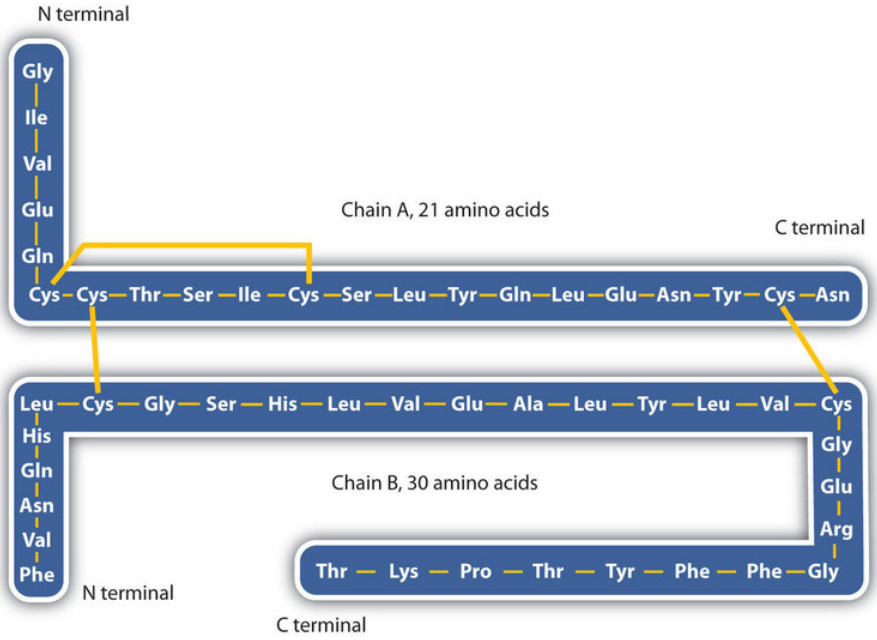


Figure **13.5.1** Primary Structure of Human Insulin. Human insulin, whose amino acid sequence is shown here, is a hormone that is required for the proper metabolism of glucose.

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 **13.5.2**). 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.

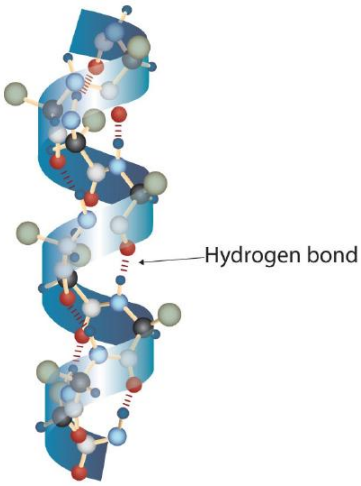


Figure **13.5.2** A Ball-and-Stick Model of an α-Helix. This ball-and-stick model shows the intrachain hydrogen bonding between carbonyl oxygen atoms and amide hydrogen atoms. Each turn of the helix spans 3.6 amino acids. Note that the side chains (represented as green spheres) point out from the helix.

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 **13.5.3**). 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.

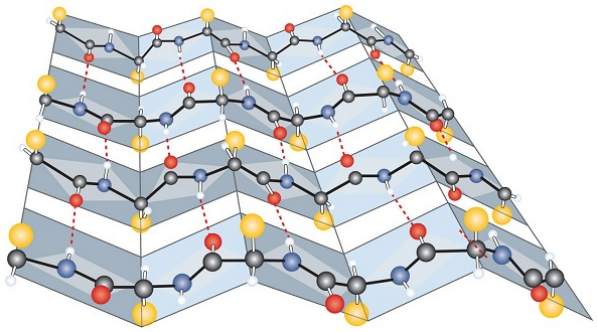


Figure **13.5.3** A Ball-and-Stick Model of the β-Pleated Sheet Structure in Proteins. The side chains extend above or below the sheet and alternate along the chain. The protein chains are held together by interchain hydrogen bonding.

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 **13.5.4** shows a depiction of the three-dimensional structure of insulin.

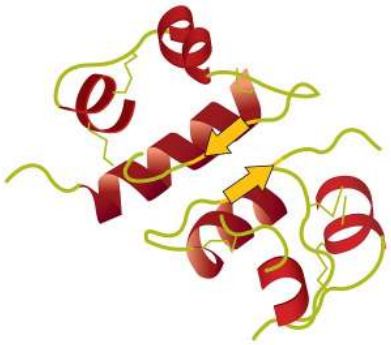
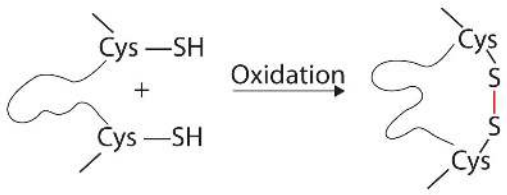


Figure **13.5.4** A Ribbon Model of the Three-Dimensional Structure of Insulin. The spiral regions represent sections of the polypeptide chain that have an α-helical structure, while the broad arrows represent β-pleated sheet structures.

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 **13.5.5**).
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 **13.5.5**).
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 **13.5.5**). Intrachain disulfide linkages are found in many proteins, including insulin (yellow bars in Figure **13.5.1**) 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 **13.5.5**). 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.

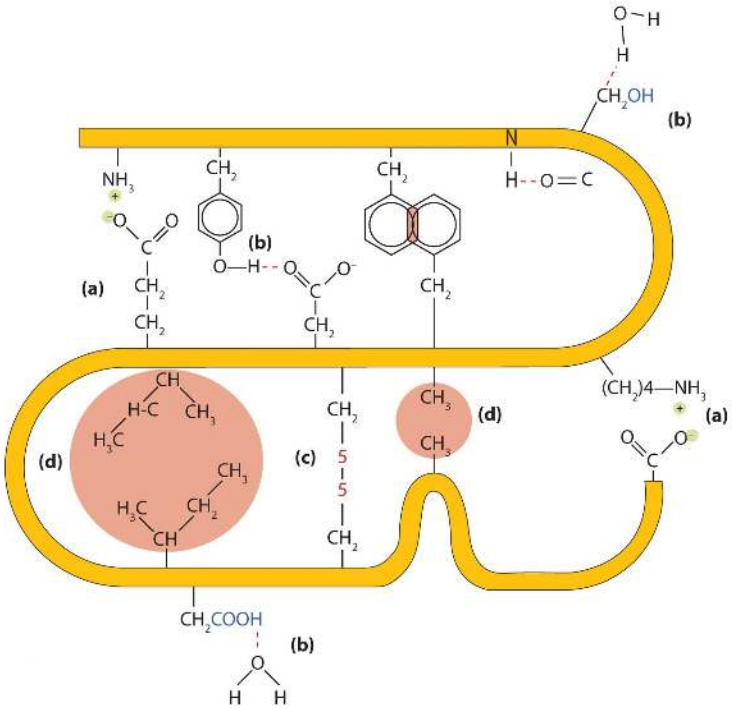


Figure **13.5.5** Tertiary Protein Structure Interactions. Four interactions stabilize the tertiary structure of a protein: (a) ionic bonding, (b) hydrogen bonding, (c) disulfide linkages, and (d) dispersion forces.

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 **13.5.6**). 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 **13.5.7**.

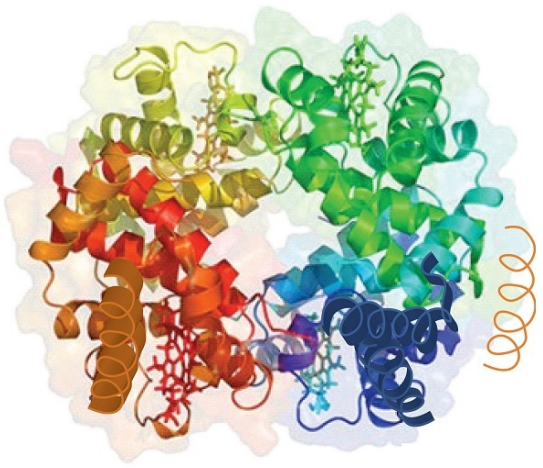


Figure **13.5.6** The Quaternary Structure of Hemoglobin. Hemoglobin is a protein that transports oxygen throughout the body.

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).

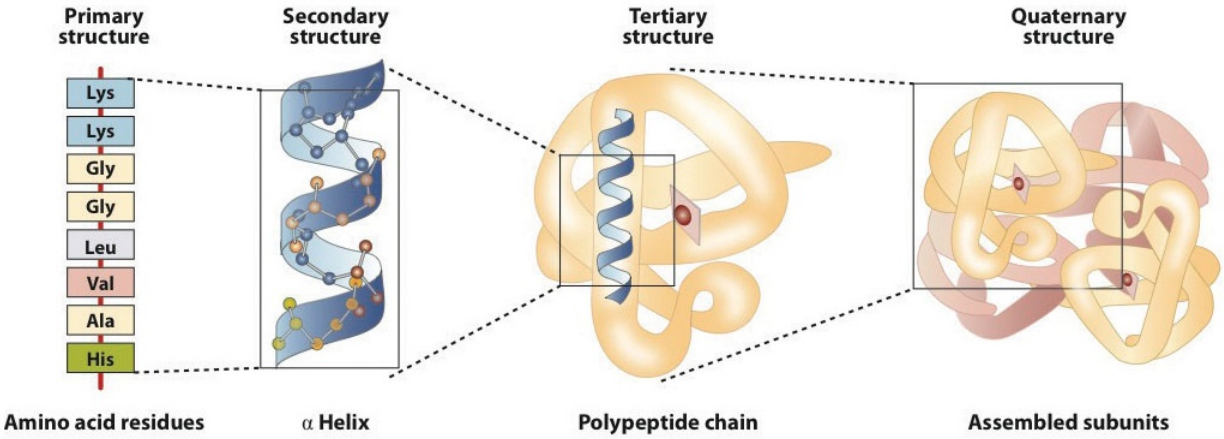


Figure **13.5.7** Levels of Structure in Proteins.

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.

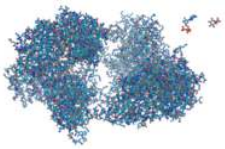


Figure **13.5.8** Globular protein.

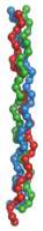


Figure **13.5.9** Fibrous protein.

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 **13.5.10** 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.

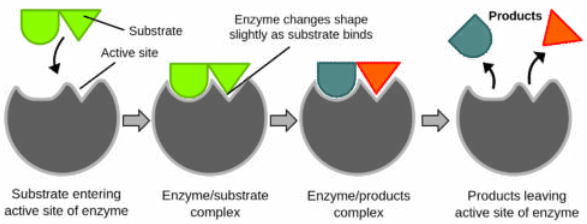


Figure **13.5.10** The sequence of steps for a substrate binding to an enzyme in its active site, reacting, then being released as products.

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 **13.5.11*A***) 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 **13.5.11*B***) 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.

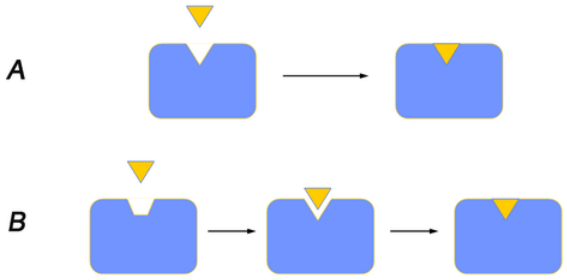


Figure **13.5.11** (A) Lock and key enzyme model and (B) induced fit enzyme model.

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.

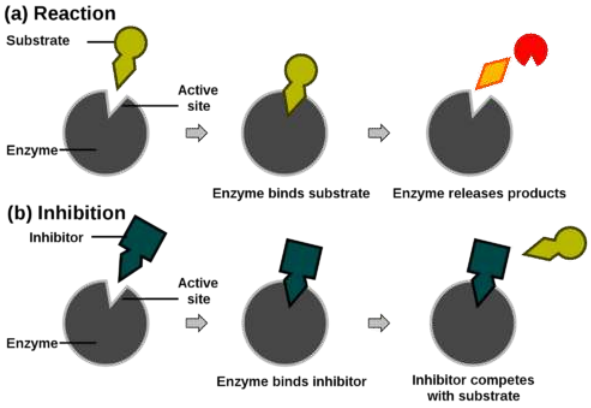


Figure **13.5.12** A competitive inhibitor is a molecule that binds to the active site of an enzyme without reacting, thus preventing the substrate from binding.

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).

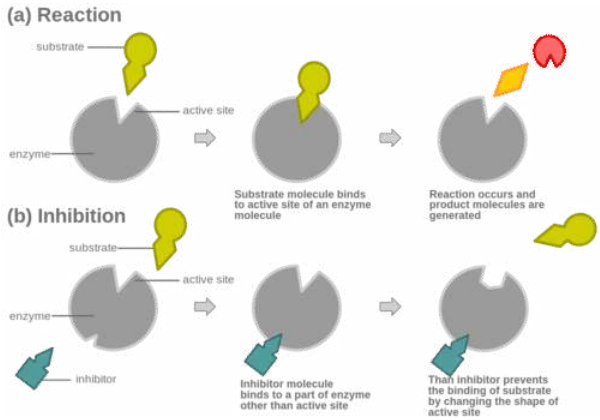


Figure 13.5.13 Non-competitive inhibition.

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.

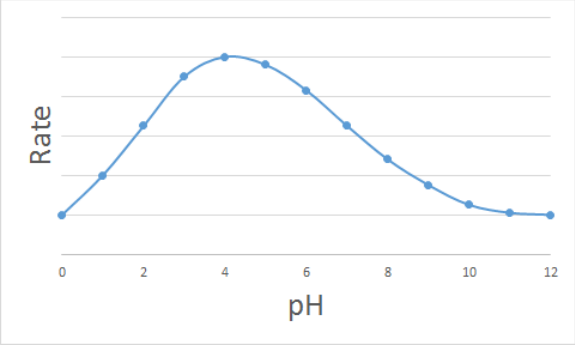


Figure **13.5.14** Relationship between rate and pH.

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°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.

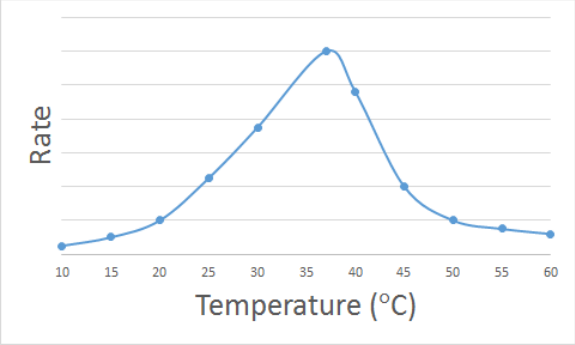


Figure **13.5.15** *Relationship between temperature and rate*.

Applications of Enzymes

Enzymes are used in the and other industrial applications when extremely specific catalysts are required (Table **13.5.1**). 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 **13.5.1** *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.



https://www.youtube.com/watch?v=E90D4BmaVJM

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.)
-
- Allison Soult, Ph.D. (Department of Chemistry, University of Kentucky)
- Wikipedia
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13.6: Nucleic Acids- Parts, Structure, and Function

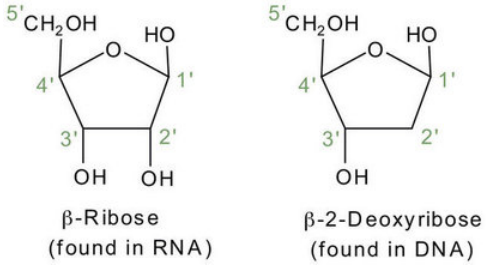
Learning Objectives

- 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 **13.6.1**).

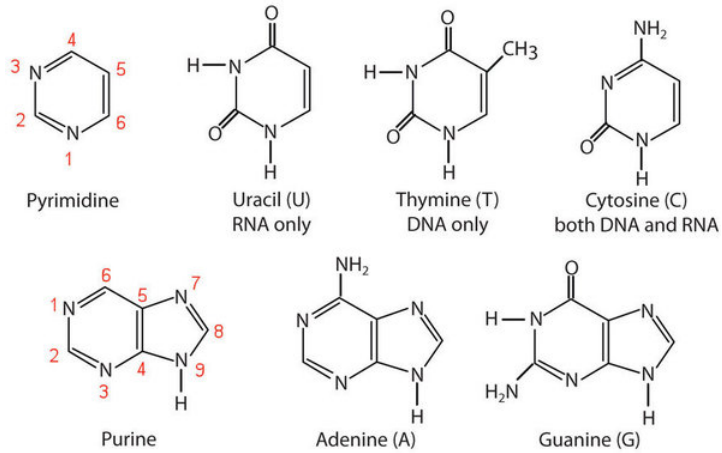


Figure **13.6.1** The Nntrogenous bases found in DNA and RNA.

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 **13.6.1** 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 **13.6.1** 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 **13.6.2**.

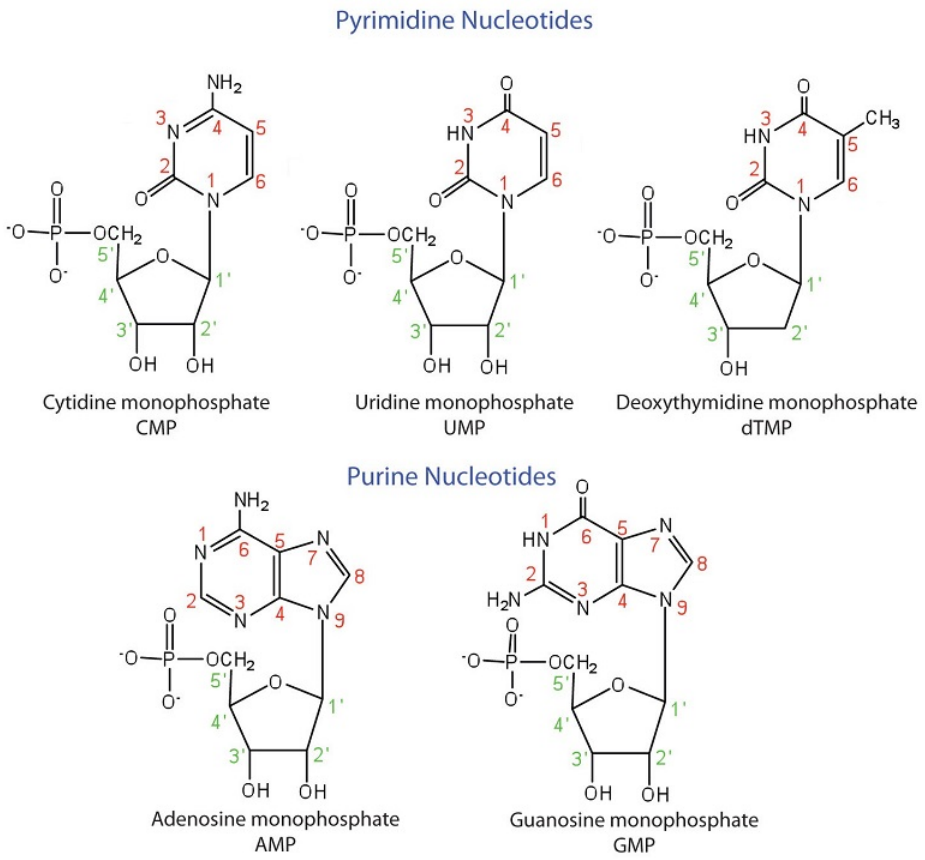


Figure **13.6.2** The pyrimidine and purine nucleotides

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 **13.6.3**, 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.

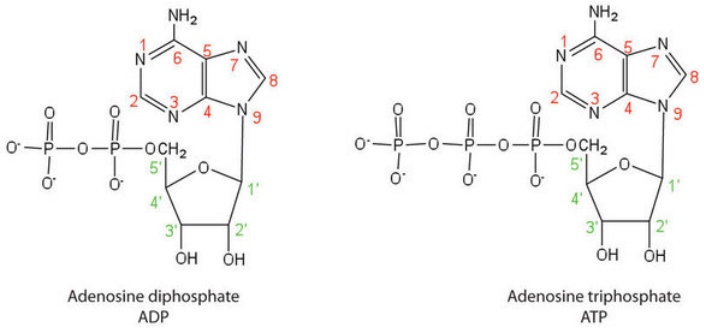


Figure **13.6.3** *Structures of two important adenine-containing nucleotides.*

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 **13.6.4**). 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.*

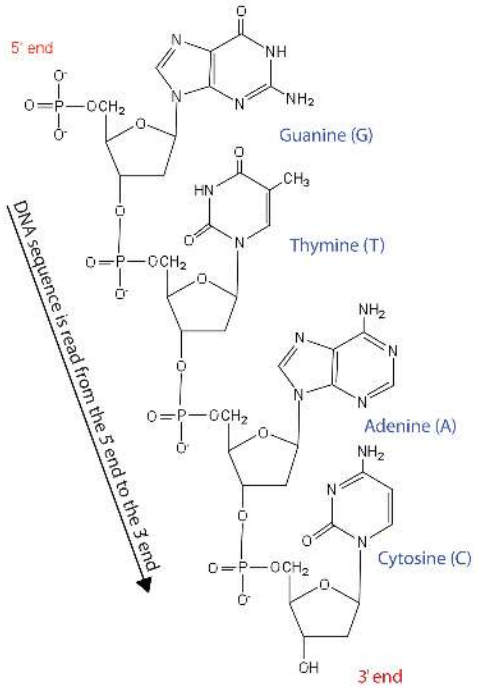


Figure **13.6.4** Structure of a segment of DNA. A similar segment of RNA would have OH groups on each C2′, and uracil would replace thymine.

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 **13.6.4**) 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 **13.6.4** 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 **13.6.5**).

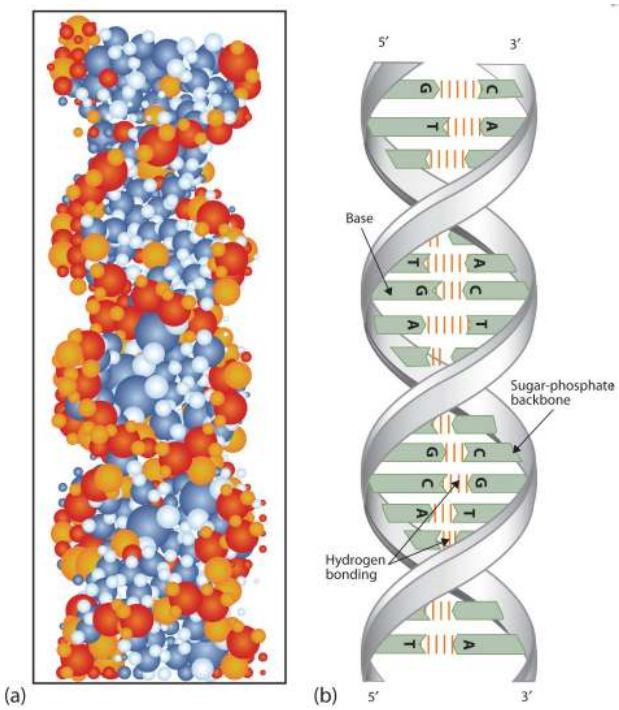


Figure **13.6.5** DNA Double Helix. (a) This represents a computer-generated model of the DNA double helix. (b) This represents a schematic representation of the double helix, showing the complementary bases.

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 **13.6.6** 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).

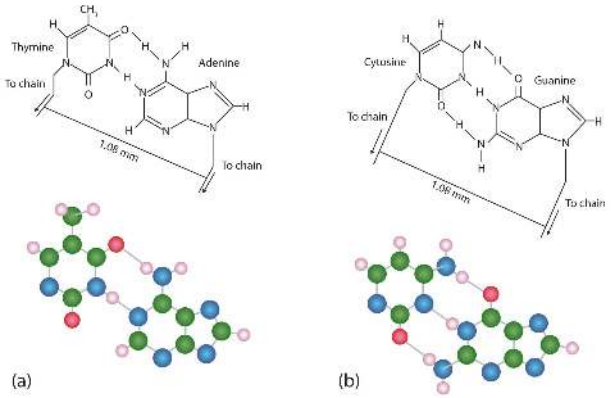


Figure **13.6.6** Complementary Base Pairing. Complementary bases engage in hydrogen bonding with one another: (a) thymine and adenine; (b) cytosine and guanine.

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 **13.6.7**. 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 **13.6.6** 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.

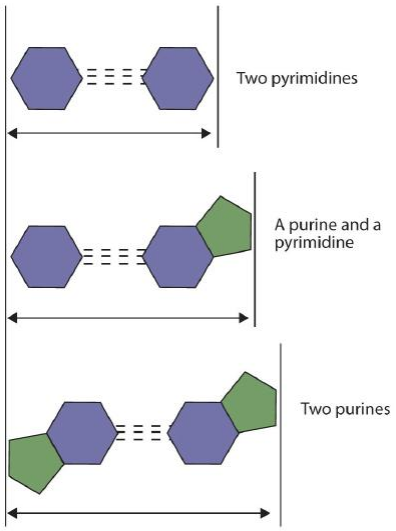


Figure **13.6.7** Difference in Widths of Possible Base Pairs

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 **13.6.8**). 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.

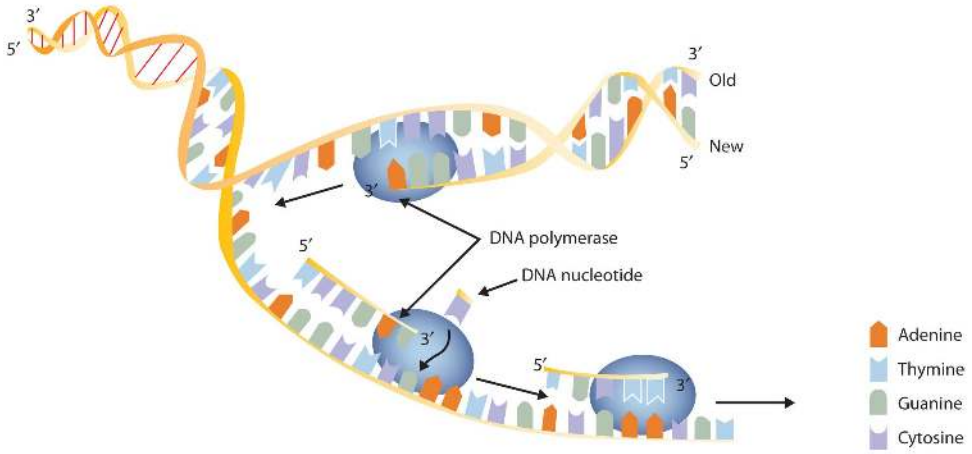


Figure **13.6.8** A Schematic Diagram of DNA Replication. DNA replication occurs by the sequential unzipping of segments of the double helix. Each new nucleotide is brought into position by DNA polymerase and is added to the growing strand by the formation of a phosphate ester bond. Thus, two double helixes form from one, and each consists of one old strand and one new strand, an outcome called *semiconservative replications*. (This representation is simplified; many more proteins are involved in replication.)

✔ Example 13.6.1

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 13.6.1

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.

Contributors and Attributions

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13.7: The Human Genome

Learning Objectives

- Describe the human genome project.
- Describe the advances made possible by recombinant DNA technology.

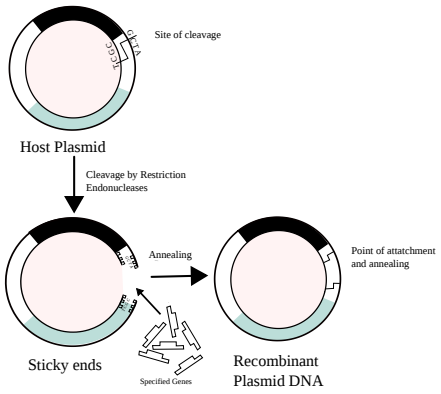
The Human Genome

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 **13.7.1**) **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.

Contributors and Attributions

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13.8: 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.



***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.

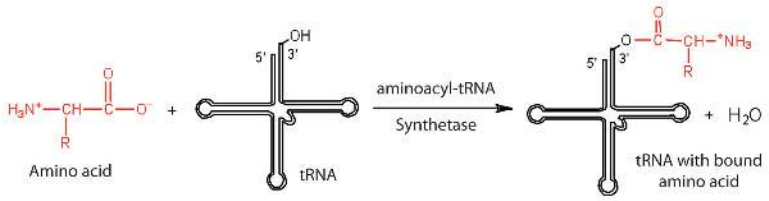
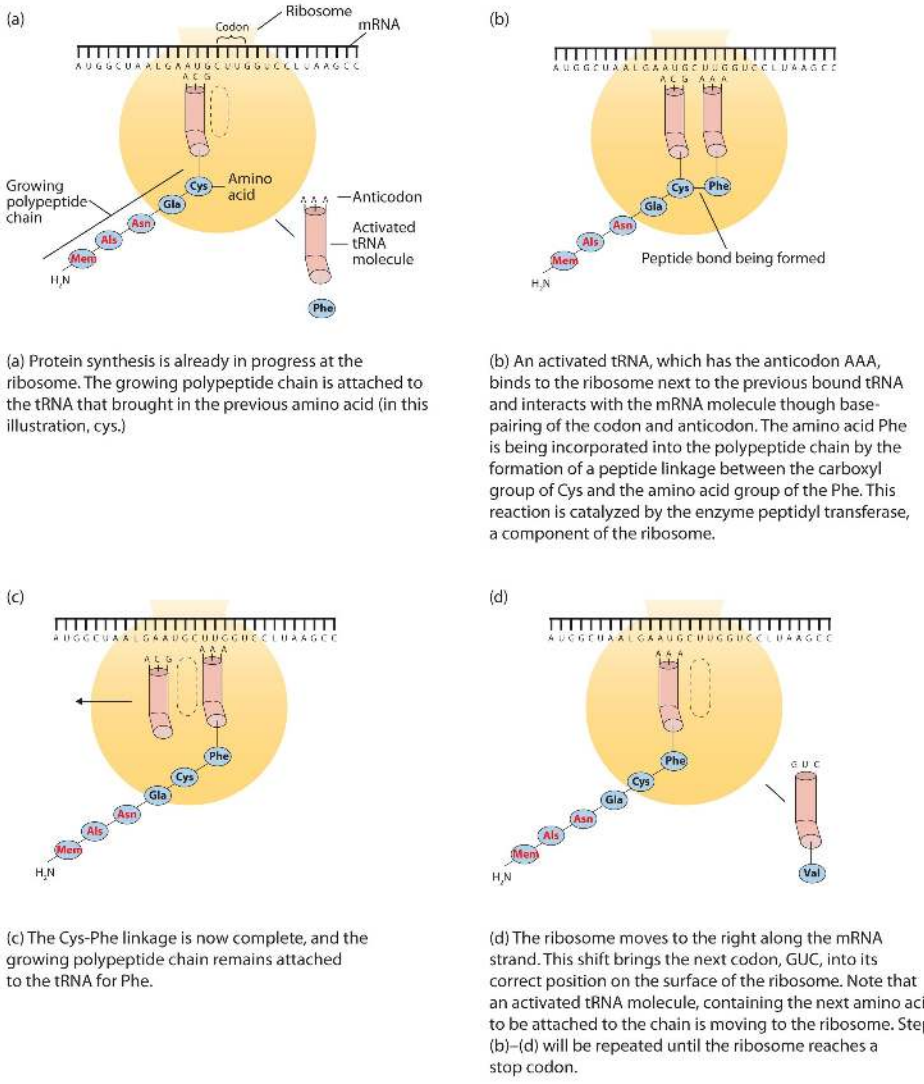


Figure **13.8.1**: Binding of an Amino Acid to Its tRNA

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 **13.8.1**). 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 **13.8.2** depicts a schematic stepwise representation of this all-important process.



(a) Protein synthesis is already in progress at the ribosome. The growing polypeptide chain is attached to the tRNA that brought in the previous amino acid (in this illustration, cys.)

(b) An activated tRNA, which has the anticodon AAA, binds to the ribosome next to the previous bound tRNA and interacts with the mRNA molecule though base-pairing of the codon and anticodon. The amino acid Phe is being incorporated into the polypeptide chain by the formation of a peptide linkage between the carboxyl group of Cys and the amino acid group of the Phe. This reaction is catalyzed by the enzyme peptidyl transferase, a component of the ribosome.

(c) The Cys-Phe linkage is now complete, and the growing polypeptide chain remains attached to the tRNA for Phe.

(d) The ribosome moves to the right along the mRNA strand. This shift brings the next codon, GUC, into its correct position on the surface of the ribosome. Note that an activated tRNA molecule, containing the next amino acid to be attached to the chain is moving to the ribosome. Steps (b)–(d) will be repeated until the ribosome reaches a stop codon.

Figure **13.8.2**: 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 **13.8.3**, 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 **13.8.3**: The Genetic Code

Example 13.8.1: 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 **13.8.3** 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 13.8.1

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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CHAPTER OVERVIEW

14: Carbohydrates

14.1: Overview of Carbohydrates
14.2: Classifying Monosaccharides
14.3: Important Monosaccharides
14.4: Reactions of Monosaccharides
14.5: Disaccharides
14.6: Oligosaccharides
14.7: Polysaccharides
14.E: Carbohydrates (Exercises)
14.S: Carbohydrates (Summary)

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14.1: Overview of Carbohydrates

Learning Objectives

- To recognize carbohydrates and classify them as mono-, di-, oligo- or polysaccharides.

Carbohydrates are biological molecules composed of carbon, hydrogen and oxygen atoms. The term carbohydrate is generally applied to the group of polyhydroxy aldehydes or polyhydroxy ketones commonly known as sugars.

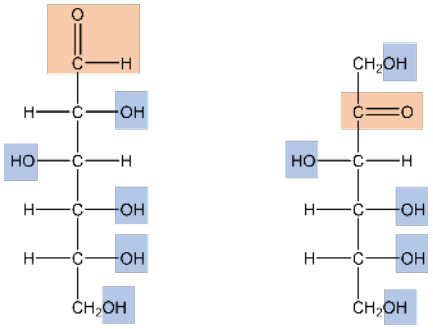


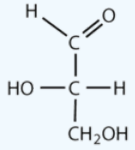
Figure **14.1.1**: Structures of a polyhydroxy aldehyde (left) and polyhydroxy ketone (right).

Examples of carbohydrates include starch, fiber, the sweet-tasting compounds called sugars, and structural materials such as cellulose. The term *carbohydrate* had its origin in a misinterpretation of the molecular formulas of many of these substances. For example, because its formula is $C_6H_{12}O_6$, glucose was once thought to be a "carbon hydrate" with the structure $C_n{\cdot}(H_2O)_n$ or $C_6{\cdot}6H_2O$ molecular formula.

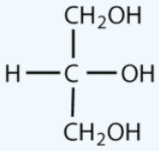
Example 14.1.1

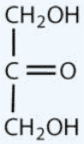
Which compounds would be classified as carbohydrates?

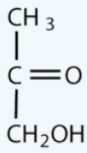
a.



b.



c. 

d. 

Solution

a. This is a carbohydrate because the molecule contains an aldehyde functional group with OH groups on the other two carbon atoms.

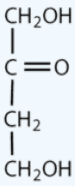
b. This is not a carbohydrate because the molecule does not contain an aldehyde or a ketone functional group.

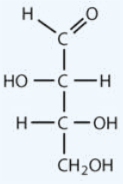
c. This is a carbohydrate because the molecule contains a ketone functional group with OH groups on the other two carbon atoms.

d. This is not a carbohydrate; although it has a ketone functional group, one of the other carbons atoms does not have an OH group attached.

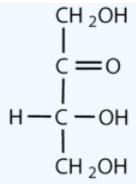
Exercise 14.1.1

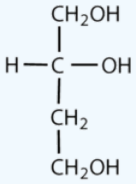
Which compounds would be classified as carbohydrates?

a. 

b. 

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c. 

d. 

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**:

$$6\,CO_2 + 6\,H_2O + 686\text{ kcal} \rightarrow C_6H_{12}O_6 + 6\,O_2 \tag{14.1.1}$$

(The 686 kcal come from solar energy.) Plants can use the glucose for energy or convert it to larger carbohydrates, such as starch or cellulose. Starch provides energy for later use, perhaps as nourishment for a plant's seeds, while cellulose is the structural material of plants. We can gather and eat the parts of a plant that store energy—seeds, roots, tubers, and fruits—and use some of that energy ourselves. Carbohydrates are also needed for the synthesis of nucleic acids and many proteins and lipids.

Animals, including humans, cannot synthesize carbohydrates from carbon dioxide and water and are therefore dependent on the plant kingdom to provide these vital compounds. We use carbohydrates not only for food (about 60%–65% by mass of the average diet) but also for clothing (cotton, linen, rayon), shelter (wood), fuel (wood), and paper (wood).

Carbohydrates are classified based on the number of sugar units combined to make the molecule. The simplest carbohydrates—those that cannot be hydrolyzed to produce even smaller carbohydrates—are called **monosaccharides**. Two or more monosaccharides can link together to form chains that contain from two to several hundred or thousand monosaccharide units. Prefixes are used to indicate the number of such units in the chains. **Disaccharides** (meaning two sugars) consist of two monosaccharides joined together; **oligosaccharides** (meaning a few sugars) contain anywhere from three to nine monosaccharides; and **polysaccharides** (meaning many sugars) are biological polymers containing 10 or more monosaccharide units. All these so-called higher saccharides can be hydrolyzed back to their constituent monosaccharides.

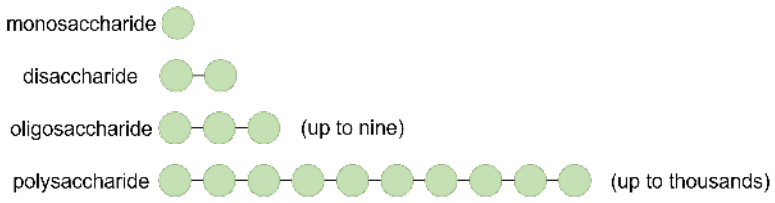


Figure 14.1.2: Types of carbohydrates categorized based on the number of sugar units present.

> *Compounds that cannot be hydrolyzed will not react with water to form two or more smaller compounds.*

Example 14.1.1

When an aqueous solution of trehalose is hydrolyzed, two molecules of glucose are produced for each molecule of trehalose. Is trehalose a monosaccharide, a disaccharide, an oligosaccharide, or a polysaccharide?

Solution

Trehalose is a disaccharide because it is hydrolyzed into two molecules of glucose (a monosaccharide)

Exercise 14.1.1

When an aqueous solution of arabinose is hydrolyzed, no other molecules are produced. Is arabinose a monosaccharide, a disaccharide, an oligosaccharide, or a polysaccharide

Summary

- Carbohydrates are an important group of biological molecules that includes sugars and starches.
- Photosynthesis is the process by which plants use energy from sunlight to synthesize carbohydrates.
- Carbohydrates are classified based on the number of sugar units. A monosaccharide is the simplest carbohydrate and cannot be hydrolyzed to produce a smaller carbohydrate molecule. Disaccharides contain two monosaccharide units, oligosaccharides contain between three and nine monosaccharide units, and polysaccharides contain ten or more monosaccharide units.

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14.2: Classifying Monosaccharides

Learning Objectives

- Classify monosaccharides based on the carbonyl group.
- Classify monosaccharides based on the number of carbon atoms.
- Distinguish between a D sugar and an L sugar.

Types of Monosaccharides

The naturally occurring monosaccharides contain three to seven carbon atoms per molecule. Monosaccharides of specific sizes may be indicated by names composed of a stem denoting the number of carbon atoms and the suffix ***-ose***. For example, the terms *triose*, *tetrose*, *pentose*, and *hexose* signify monosaccharides with, respectively, three, four, five, and six carbon atoms.

Monosaccharides are also classified as **aldoses** or **ketoses** to indicate the carbonyl-containing group that is present. Those that contain an aldehyde functional group are called aldoses; those containing a ketone functional group on the second carbon atom are ketoses. Combining these classification systems gives general names that indicate both the type of carbonyl group *and* the number of carbon atoms in a molecule. Thus, monosaccharides are described as aldotetroses, aldopentoses, ketopentoses, ketoheptoses, and so forth. Glucose and fructose are specific examples of an aldohexose and a ketohexose, respectively.

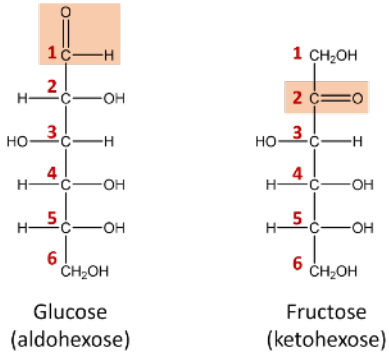


Figure **14.2.1**: Structures of glucose (left) and fructose.

Example 14.2.1

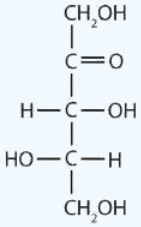
Draw an example of each type of compound.

a. a ketopentose

b. an aldotetrose

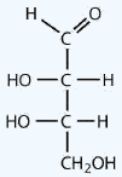
Solution

a. The structure must have five carbon atoms with the second carbon atom being a carbonyl group and the other four carbon atoms each having an OH group attached. Several structures are possible, but one example is shown.



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b. The structure must have four carbon atoms with the first carbon atom part of the aldehyde functional group. The other three carbon atoms each have an OH group attached. Several structures are possible, but one example is shown.



Exercise 14.2.1

Draw an example of each type of compound.

a. an aldohexose

b. a ketotetrose

Stereochemistry of Monosaccharides

The simplest sugars are the trioses. The possible trioses are shown in part (a) of Figure **14.2.2**; glyceraldehyde is an aldotriose, while dihydroxyacetone is a ketotriose. Notice that two structures are shown for glyceraldehyde. These structures are stereoisomers, and hence are isomers having the same structural formula but differing in the arrangement of atoms or groups of atoms in three-dimensional space. If you make models of the two stereoisomers of glyceraldehyde, you will find that you cannot place one model on top of the other and have each functional group point in the same direction. However, if you place one of the models in front of a mirror, the image in the mirror will be identical to the second stereoisomer in part (b) of Figure **14.2.2**. Since these molecules are nonsuperimposable mirror images of each other, they represent enantiomers.

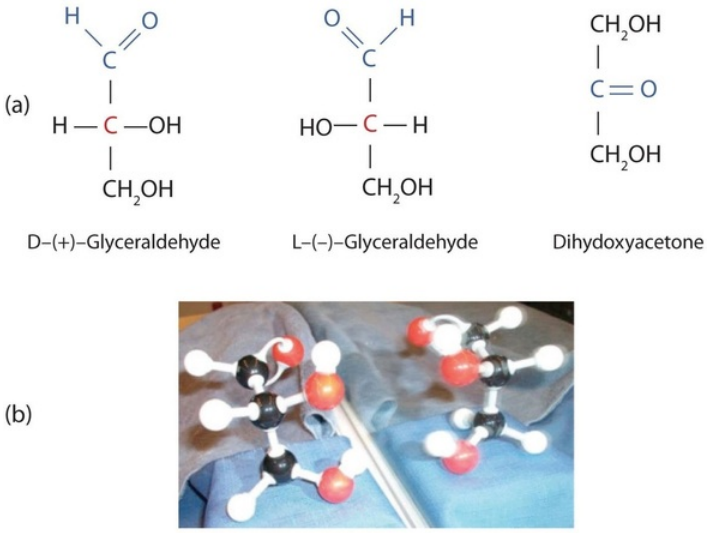


Figure **14.2.2**: Structures of the Trioses. (a) D- and L-glyceraldehyde are mirror images of each other and represent a pair of enantiomers. (b) A ball-and-stick model of D-glyceraldehyde is reflected in a mirror. Note that the reflection has the same structure as L-glyceraldehyde.

A key characteristic of enantiomers is that they have a chiral carbon. If a molecule contains one or more chiral carbons, it is likely to exist as two or more stereoisomers. Dihydroxyacetone does not contain a chiral carbon and thus does not exist as a pair of stereoisomers. Glyceraldehyde, however, has a chiral carbon and exists as a pair of enantiomers. Except for the direction in which

each enantiomer rotates plane-polarized light, these two molecules have identical physical properties. One enantiomer has a specific rotation of +8.7°, while the other has a specific rotation of −8.7°.

H. Emil Fischer, a German chemist, developed the convention commonly used for drawing monosaccharides. These structural formulas, known as **Fischer projections**, use horizontal and vertical lines to indicate the three–dimensional structure of a molecule. The horizontal lines project forward (coming towards you), while the vertical lines project backward (going away from you). Where the lines intersect represents a carbon atom that is usually chiral.

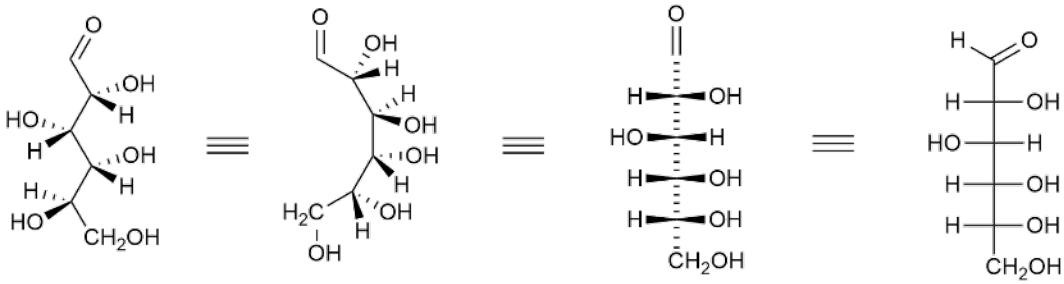


Figure 14.2.3: Projection of Glucose to the Fischer Projection. Choutkaj, CC BY-SA 4.0 <https://creativecommons.org/licenses/by-sa/4.0>, via Wikimedia Commons

When drawing Fischer projections, the aldehyde group is written at the top, and the H and OH groups that are attached to each chiral carbon are written to the right or left. The arrange of the atoms distinguishes one stereoisomer from the other.

The two enantiomers of glyceraldehyde are especially important because monosaccharides with more than three carbon atoms can be considered as being derived from them. Thus, D- and L-glyceraldehyde provide reference points for designating and drawing all other monosaccharides. Sugars whose Fischer projections terminate in the same configuration as D-glyceraldehyde are designated as **D sugars**; those derived from L-glyceraldehyde are designated as **L sugars**. D and L designations of sugars are based on the position of the hydroxyl on the chiral carbon farthest from the carbonyl group in the Fischer projection of the molecule. All D-sugars have the –OH on the right side and L-sugars have the –OH on the left side.

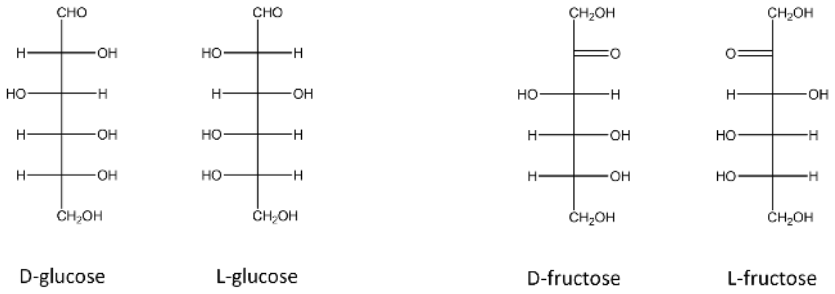


Figure 14.2.4: Fischer projections of enantiomers of glucose (left) and fructose (right).

> *By convention, the penultimate (next-to-last) carbon atom has been chosen as the carbon atom that determines if a sugar is D or L. It is the chiral carbon farthest from the aldehyde or ketone functional group.*

D and L sugars of the same monosaccharide are enantiomers of one another (Figure 14.2.4). When comparing the Fischer projections of monosaccharides, if the arrangement around all of the chiral centers (horizontal lines) are the exact opposite, then the molecules are enantiomers. However, molecules are not “perfect” mirror images are diastereomers. When comparing Fischer

projections of monosaccharides, if the arrangement is different at one or more (but not all) chiral centers, then the molecules are diastereomers (Figure 14.2.5).

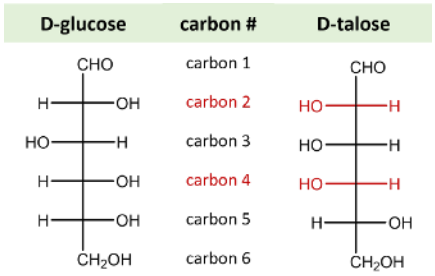


Figure 14.2.5: Fischer projections of diastereomers: D-glucose and D-talose.

The arrangement of H and OH around each chiral center gives the identity of the carbohydrate. Since diastereomers have different arrangements, they will also have different names. Since epimers are a type of diastereomers, they will also have dfiferent names. When comparing Fischer projections, if the arrangement is different at only one chiral center, the molecules are epimers. For example, D-glucose and D-galactose are epimers because the molecules are identical, except for the arrangement of the H and OH around carbon 4 Figure 14.2.6.

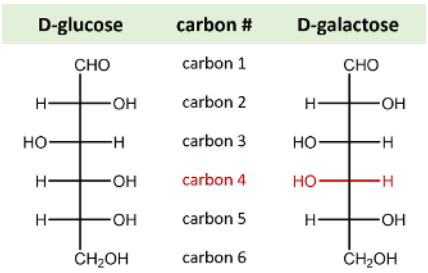


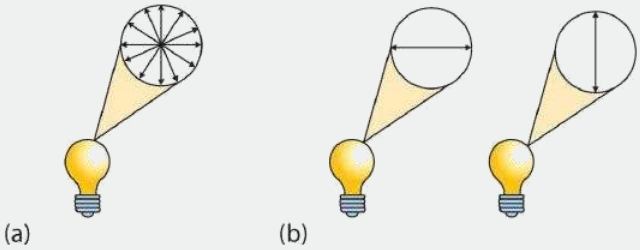
Figure 14.2.1: Fischer projections of epimers: D-glucose and D-galactose.

The general formula for determining the maximum number of stereoisomers of a molecule is 2^n, where n is the number of chiral centers present in the molecule. IN the case of glucose, carbons 2, 3, 4, and 5 are chiral centers. Therefore, there are $2^4 = 2 \times 2 \times 2 \times 2 = 16$ stereoisomers of the molecule. Only two can represent enatiomers, while the others would represent diastereomers (or epimers).

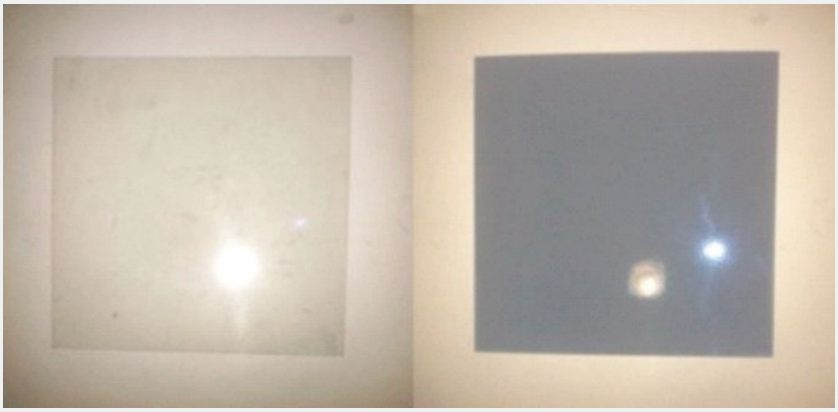
Looking Closer: Polarized Light

A beam of ordinary light can be pictured as a bundle of waves; some move up and down, some sideways, and others at all other conceivable angles. When a beam of light has been polarized, however, the waves in the bundle all vibrate in a single plane. Light altered in this way is called *plane-polarized light*. Much of what chemists know about stereoisomers comes from studying the effects they have on plane-polarized light. In this illustration, the light on the left is not polarized, while that on the right is polarized.

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Sunlight, in general, is not polarized; light from an ordinary light bulb or an ordinary flashlight is not polarized. One way to polarize ordinary light is to pass it through Polaroid sheets, special plastic sheets containing carefully oriented organic compounds that permit only light vibrating in a single plane to pass through. To the eye, polarized light doesn't "look" any different from nonpolarized light. We can detect polarized light, however, by using a second sheet of polarizing material, as shown here.



In the photo on the left, two Polaroid sheets are aligned in the same direction; plane-polarized light from the first Polaroid sheet can pass through the second sheet. In the photo on the right, the top Polaroid sheet has been rotated 90° and now blocks the plane-polarized light that comes through the first Polaroid sheet.

Certain substances act on polarized light by rotating the plane of vibration. Such substances are said to be optically active. The extent of optical activity is measured by a polarimeter, an instrument that contains two polarizing lenses separated by a sample tube, as shown in the accompanying figure. With the sample tube empty, maximum light reaches the observer's eye when the two lenses are aligned so that both pass light vibrating in the same plane. When an optically active substance is placed in the sample tube, that substance rotates the plane of polarization of the light passing through it, so that the polarized light emerging from the sample tube is vibrating in a different direction than when it entered the tube. To see the maximum amount of light when the sample is in place, the observer must rotate one lens to accommodate the change in the plane of polarization.

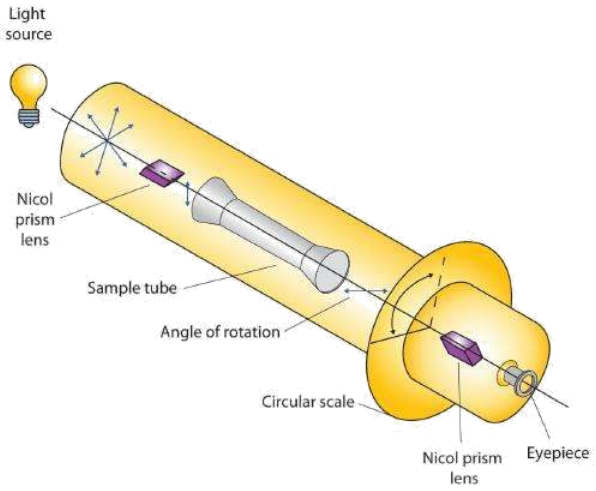


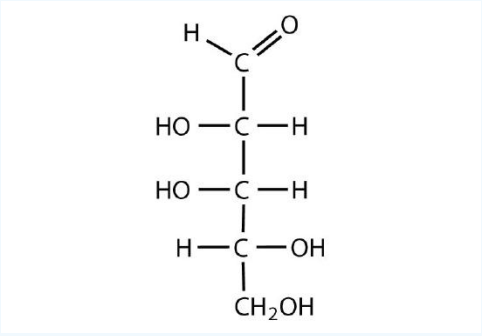
Figure 14.2.5: Diagram of a Polarimeter

Some optically active substances rotate the plane of polarized light to the right (clockwise) from the observer's point of view. These compounds are said to be **dextrorotatory (d)** and the direction of rotation is denoted with a positive sign (+). Substances that rotate light to the left (counterclockwise) are said to be **levorotatory (l)** and the direction of rotation is denoted with a negative sign (−). Achiral compounds are optically inactive because they do not rotate plane-polarized light. **Racemic mixtures**, mixtures containing a 50:50 mix of both enantiomers, are also optically inactive.

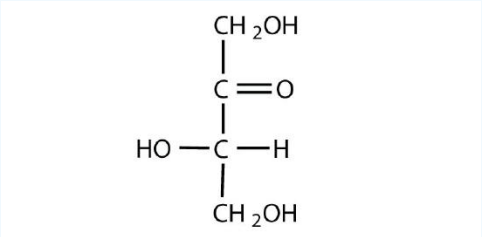
Example 14.2.2

Identify each sugar as an aldose or a ketose and then as a D sugar or an L sugar.

a.



b.



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Solution

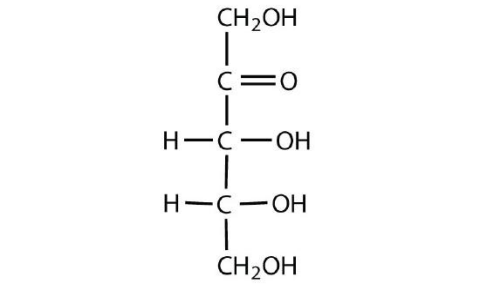
a. aldose; D sugar. The carbonyl group is on carbon 1 which indicates the presence of an aldehyde. The hydroxyl on the chiral carbon farthest from the carbonyl group is pointing to the right, making it a D-sugar.

b. ketose; L sugar. The carbonyl group is on carbon 2 which indicates the presence of an ketone. The hydroxyl on the chiral carbon farthest from the carbonyl group is pointing to the left, making it an L-sugar.

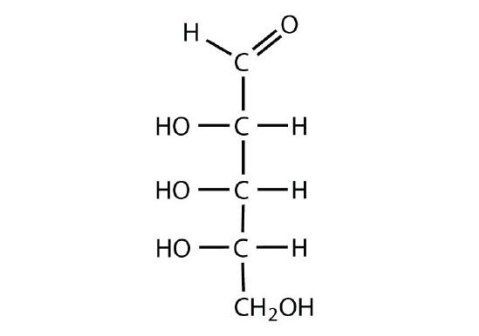
Exercise 14.2.2

Identify each sugar as an aldose or a ketose and then as a D sugar or an L sugar.

a.



b.



Summary

- Monosaccharides can be classified based on their chemical composition (number of carbon atoms and/or the type of carbonyl group).
- Fischer projections are commonly used to draw monosaccharides. The intersection of the horizontal and veritical lines represents a carbon, which is typically a chiral center.
- Most monosaccharides contain at least one chiral carbon and can form 2^n possible stereoisomers.
- Three types of stereoisomers present in monosaccharides can be identified by comparing the chiral centers in Fischer Projections:
  o all opposite = enantiomers
  o only 1 opposite = epimers
  o more than 1, but less than all opposite = diastereomers
- Enantiomers are a specific type of stereoisomers that are mirror images of each other and rotate plane polarized light in opposite directions.

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14.3: Important Monosaccharides

Learning Objectives

- Identify the structures of glucose, galactose, and fructose.
- Contrast structures of the important monosaccharides.
- Classify monosaccharides as D- or L-sugars.

Important Hexoses

Although a variety of monosaccharides are found in living organisms, three hexoses are particularly abundant: D-glucose, D-galactose, and D-fructose (Figure **14.3.1**). Glucose and galactose are both aldohexoses, while fructose is a ketohexose.

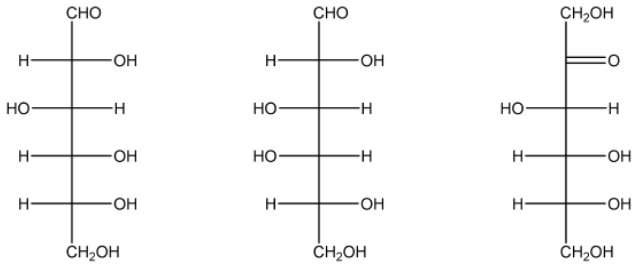


Figure \(\PageIndex{1}\): Structures of three important hexoses: D-glucose (left), D-galactose (middle), and D-fructose (right).

Glucose

D-Glucose, generally referred to simply as glucose, is the most abundant sugar found in nature. Most of the carbohydrates we eat are eventually converted to glucose in a series of biochemical reactions that produce energy for our cells. Glucose is also known by three other names: *dextrose*, from the fact that it rotates plane-polarized light in a dextrorotatory (clockwise) direction; *corn sugar* because in the United States cornstarch is used in the commercial process that produces glucose from the hydrolysis of starch; and *blood sugar* because it is the carbohydrate found in the circulatory system of animals. Normal blood sugar values range from 70 to 105 mg glucose/dL plasma, and normal urine may contain anywhere from a trace to 20 mg glucose/dL urine.

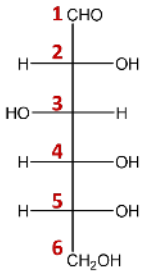


Figure **14.3.2**: Fischer projection of D-glucose

The Fischer projection of D-glucose is given in Figure **14.3.2**. Glucose is a D sugar because the OH group on the fifth carbon atom (the chiral center farthest from the carbonyl group) is on the right. In fact, all the OH groups except the one on the third carbon atom are to the right. If the direction of any of these groups change, it will no longer represent D-glucose.

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*.

Galactose is an epimer of glucose because the arrangement of the molecules are identical, except around one chiral center (Figure **14.3.3**).

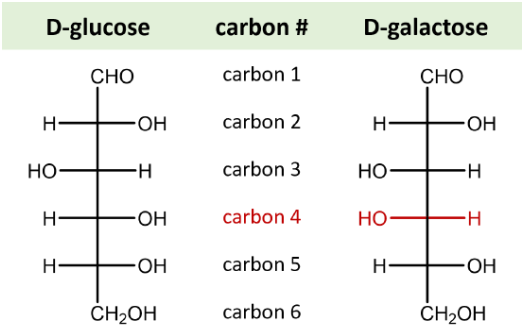


Figure **14.3.3**: Fischer projections of D-Glucose and D-Galactose.

Fructose

D-Fructose, also shown in Figure **14.3.1**, is the most abundant ketohexose. Glucose and fructose are not epimers. Instead, these molecules are structural isomers of one another. They both have the $C_6H_{12}O_6$ molecular formula, but differ in the arrangement of atoms around carbons 1 and 2. Note that from the third through the sixth carbon atoms, the structures are the same.

Fructose occurs, along with glucose and sucrose, in honey (which is 40% fructose) and sweet fruits. D-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°). Fructose is the sweetest sugar, being 1.7 times sweeter than sucrose (table sugar), although many nonsugars are several hundred or several thousand times as sweet (Table **14.3.1**).

Table **14.3.1**: The Relative Sweetness of Some Compounds (Sucrose = 100)

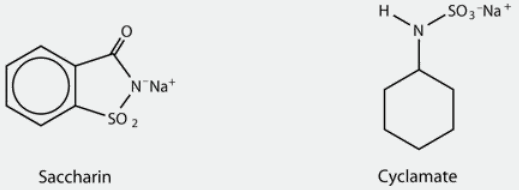
Compound	Relative Sweetness
lactose	16
maltose	32
glucose	74
sucrose	100
fructose	173
aspartame	18,000
acesulfame K	20,000
saccharin	30,000
sucralose	60,000

Looking Closer: Artificial Sweeteners

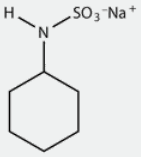
Although sweetness is commonly associated with mono- and disaccharides, it is not a property found only in sugars. Several other kinds of organic compounds have been synthesized that are far superior as sweetening agents. These so-called high-intensity or artificial sweeteners are useful for people with diabetes or other medical conditions that require them to control their carbohydrate intake. The synthetic compounds are noncaloric or used in such small quantities that they do not add significantly to the caloric value of food.

The first artificial sweetener—saccharin—was discovered by accident in 1879. It is 300 times sweeter than sucrose, but it passes through the body unchanged and thus adds no calories to the diet. After its discovery, saccharin was used until it was banned in the early 1900s. However, during the sugar-short years of World War I, the ban was lifted and was not reinstated at the war's end. One drawback to the use of saccharin is its bitter, metallic aftertaste. The initial solution to this problem was to combine saccharin with cyclamate, a second artificial sweetener discovered in 1937.

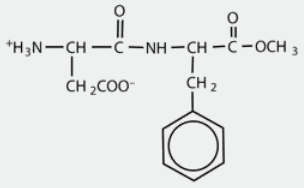
In the 1960s and 1970s, several clinical tests with laboratory animals implicated both cyclamate and saccharin as carcinogenic (cancer-causing) substances. The results from the cyclamate tests were completed first, and cyclamate was banned in the United States in 1969. Then a major study was released in Canada in 1977 indicating that saccharin increased the incidence of bladder cancer in rats. The US Food and Drug Administration (FDA) proposed a ban on saccharin that raised immediate public opposition because saccharin was the only artificial sweetener still available. In response, Congress passed the Saccharin Study and Labeling Act in 1977, permitting the use of saccharin as long as any product containing it was labeled with a consumer warning regarding the possible elevation of the risk of bladder cancer. Today this warning is no longer required; moreover, the FDA is currently reviewing the ban on cyclamate, as 75 additional studies and years of usage in other countries, such as Canada, have failed to show that it has any carcinogenic effect.



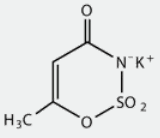
Saccharin



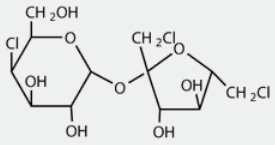
Cyclamate



Aspartame



Acesulfame K



Sucralose

A third artificial sweetener, aspartame, was discovered in 1965. This white crystalline compound is about 180 times sweeter than sucrose and has no aftertaste. It was approved for use in 1981 and is used to sweeten a wide variety of foods because it blends well with other food flavors. Aspartame is not used in baked goods, however, because it is not heat stable.

In the body (or when heated), aspartame is initially hydrolyzed to three molecules: the amino acids aspartic acid and phenylalanine and an alcohol methanol. Repeated controversy regarding the safety of aspartame arises partly from the fact that the body metabolizes the released methanol to formaldehyde. It should be noted, though, that a glass of tomato juice has six times as much methanol as a similar amount of a diet soda containing aspartame. The only documented risk connected to aspartame use is for individuals with the genetic disease *phenylketonuria* (PKU); these individuals lack the enzyme needed to

metabolize the phenylalanine released when aspartame is broken down by the body. Because of the danger to people with PKU, all products containing aspartame must carry a warning label.

Acesulfame K, discovered just two years after aspartame (1967), was approved for use in the United States in 1988. It is 200 times sweeter than sugar and, unlike aspartame, is heat stable. It has no lingering aftertaste.

One of the newest artificial sweeteners to gain FDA approval (April 1998) for use in the United States is sucralose, a white crystalline solid approximately 600 times sweeter than sucrose. Sucralose is synthesized from sucrose and has three chlorine atoms substituted for three OH groups. It is noncaloric because it passes through the body unchanged. It can be used in baking because it is heat stable.

All of the extensive clinical studies completed to date have indicated that these artificial sweeteners approved for use in the United States are safe for consumption by healthy individuals in moderate amounts.

Important Pentoses

Ribose and 2-deoxyribose are pentoses which are parts of larger biomolecules that make up our genetic material called nucleic acids. Ribonucleic acid (RNA) contains the sugar ribose and deoxyribonucleic acid (DNA) contains 2-deoxyribose.

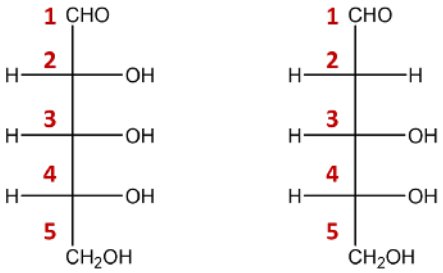


Figure 14.3.1: Fischer projections of D-ribose (left) and D-2-deoxyribose (right).

Example 14.3.1

Describe the similarities and differences in the structures of D-glucose and D-galactose.

Solution

D-glucose and D-galactose are similar because they are both monosaccharides that are classified as aldohexoses. However, these two monosaccharides differ in the arrangement of the H and OH around the fourth carbon atom.

Exercise 14.3.1

Describe similarities and differences in the structures of D-glucose and D-fructose

Summary

- Three abundant hexoses in living organisms are the aldohexoses D-glucose and D-galactose and the ketohexose D-fructose.
- D-glucose and D-galactose are epimers because the molecules are identical, except at C4.
- D-glucose and D-fructose are structural isomers that both have the $C_6H_{12}O_6$ molecular formula.

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14.4: Reactions of Monosaccharides

Learning Objectives

- Distinguish between the oxidation and reduction of monosaccharides.
- Define what is meant by anomers.
- Predict the product of the ring formation of a monosaccharide.

Monosaccharide Redox Reactions

The chemical reactions of carbohydrates are largely that of the hydroxyl and carbonyl groups. The aldehyde and ketone groups in sugars undergo redox reactions to produce new substances. Recall, redox (reduction-oxidation) reactions involve a transfer of electrons. The substance losing electrons is said to undergo oxidation, while the substance gaining electrons is said to undergo reduction. In the case of organic molecules, this process is often distinguished based on the change in hydrogen and/or oxygen atoms. An increase in O and/or decrease in H represents oxidation. While a decrease in O and/or increase in H represents reduction. These processes result in a change in the carbonyl functional group present in the molecule Figure **14.4.1**.

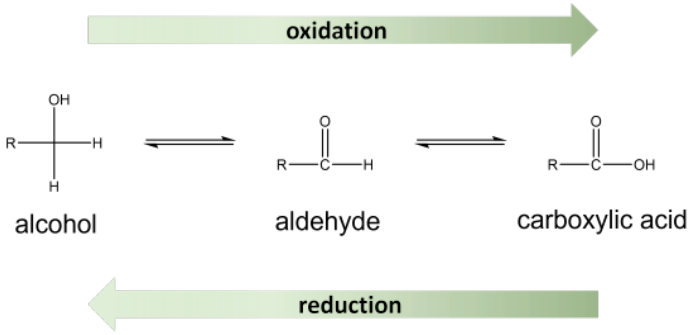


Figure **14.4.1**: Oxidation and reduction of organic functional groups.

The oxidation of monosaccharides, results in the aldehyde functional group being converted into a carboxylic acid. This compound is then referred to as a **sugar acid**. The same process will occur if the monosaccharide is a ketose. In the presence of an oxidizing agent, the ketose can rearrange to an aldose and then undergo oxidation to form the sugar acid. Carbohydrates that are able to undergo oxidation are referred to as **reducing sugars** (sugars that are reducing agents). The **Benedict's test** is a useful test to determine the presence of reducing sugars. In the reaction between a reducing sugar and Benedict's reagent, copper (II) ion is reduced to copper (I) by the aldehyde functional group Figure **14.4.2**:.

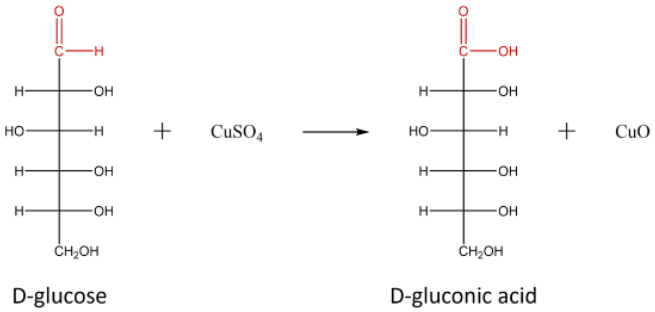


Figure **14.4.2**: Chemical reaction for the reduction of Cu (II) by glucose. Note the oxidation of the aldehyde to a carboxylic acid.

The reduction of monosaccharides can also occur. This reaction results in the aldehyde functional group being converted to an alcohol, in a compound referred to as a **sugar alcohol**.

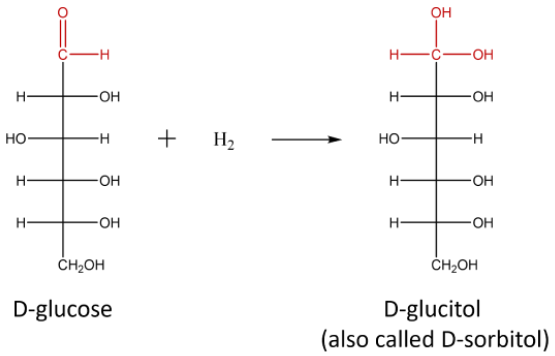


Figure **14.4.3**: Copy and Paste Caption here. (Copyright; author via source)

Monosaccharide Ring Formation

So far we have represented monosaccharides as linear molecules, but many of them also adopt cyclic structures. This conversion occurs because of the ability of aldehydes and ketones to react with alcohols. When the alcohol and aldehyde combine, a **hemiacetal** is formed. When an alcohol and ketone combine, a **hemiketal** is formed.

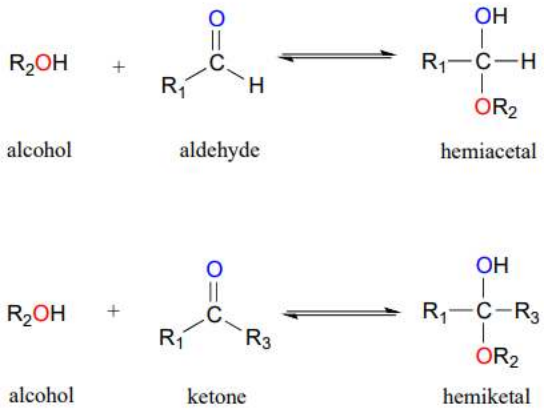


Figure **14.4.4**: Formation of a hemiacetal and hemiketal. " Hemiacetals, Hemiketals, and Hydrates" by Tim Soderberg, LibreTexts is licensed under CC BY-NC-SA .

You might wonder why the aldehyde reacts with the OH group on the fifth carbon atom rather than the OH group on the second carbon atom next to it. Recall that cyclic alkanes containing five or six carbon atoms in the ring are the most stable. The same is true for monosaccharides that form cyclic structures: rings consisting of five or six carbon atoms are the most stable.

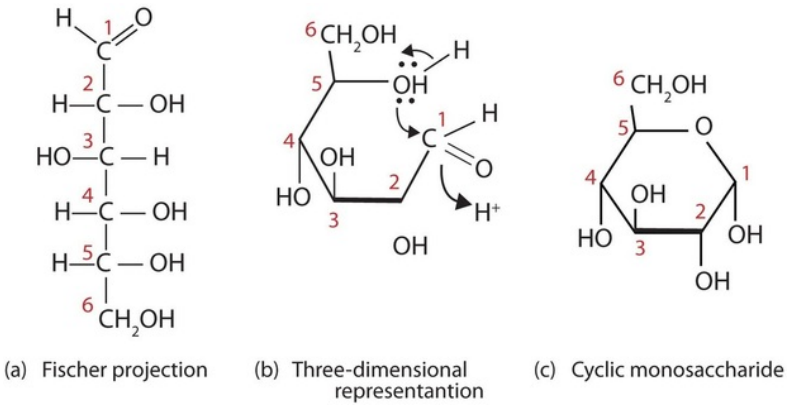


Figure **14.4.5**: Ring formation of D-glucose. D-Glucose can be represented with a Fischer projection (a) or three dimensionally (b). By reacting the OH group on the fifth carbon atom with the aldehyde group, the cyclic monosaccharide (c) is produced.

When a straight-chain monosaccharide forms a cyclic structure, the carbonyl oxygen atom may be pushed either up or down, giving rise to two **anomers**. Anomers are a type of diastereomer (technically epimer) that differ only around the **anomeric carbon**. The anomeric carbon is the carbonyl carbon that reacts to form the cyclic structure. The two possible arrangements, termed *anomers*, are referred to as the alpha (α) and beta (β) anomers. The **a anomer** is formed when the hydroxyl group bonded to the anomeric carbon is trans (opposite side) to the carbon outside the ring (carbon 6). The **β anomer** is formed when the hydroxyl group bonded to the anomeric carbon is cis (same side) to the carbon outside the ring. Note that this hydroxyl group on the anomeric carbon is formed during the hemiacetal/hemiketal reaction.

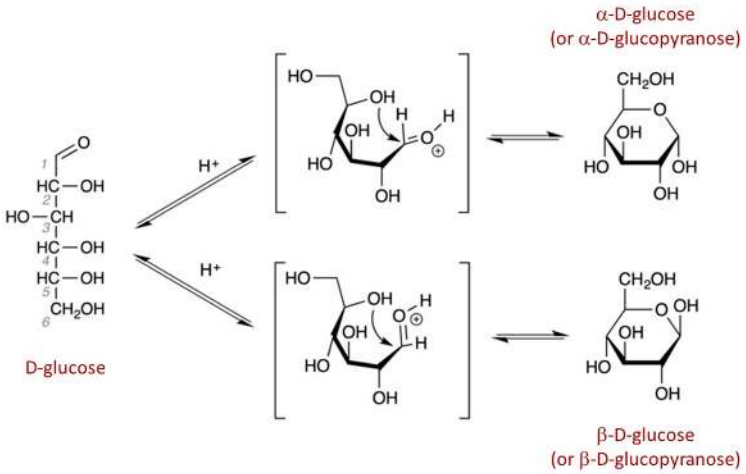


Figure **14.4.6**: . Ring formation in D–glucose (left) to form α–D–glucose (top) and β–D–glucose (bottom). Steff-X, CC BY-SA 4.0 <https://creativecommons.org/licenses/by-sa/4.0>, via Wikimedia Commons (changes made to include molecule names).

It is possible to obtain a sample of crystalline glucose in which all the molecules have the α structure or all have the β structure. The α form melts at 146°C and has a specific rotation of +112°, while the β form melts at 150°C and has a specific rotation of +18.7°. When the sample is dissolved in water, however, a mixture is soon produced containing both anomers as well as the straight-chain form, in dynamic equilibrium (part (a) of Figure **14.4.7**). You can start with a pure crystalline sample of glucose consisting entirely of either anomer, but as soon as the molecules dissolve in water, they open to form the carbonyl group and then reclose to form either the α or the β anomer. The opening and closing repeats continuously in an ongoing interconversion between anomeric forms and is referred to as **mutarotation** (Latin *mutare*, meaning “to change”). At equilibrium, the mixture consists of

about 36% α-D-glucose, 64% β-D-glucose, and less than 0.02% of the open-chain aldehyde form. The observed rotation of this solution is +52.7°.

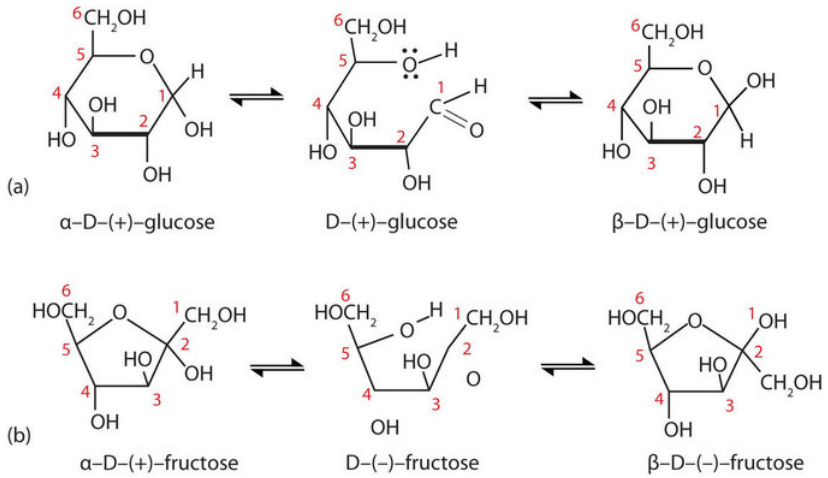


Figure 14.4.7: Monosaccharides. In an aqueous solution, monosaccharides exist as an equilibrium mixture of three forms. The interconversion between the forms is known as *mutarotation*, which is shown for D-glucose (a) and D-fructose (b).

Even though only a small percentage of the molecules are in the open-chain aldehyde form at any time, the solution will nevertheless exhibit the characteristic reactions of an aldehyde. As the small amount of free aldehyde is used up in a reaction, there is a shift in the equilibrium to yield more aldehyde. Thus, all the molecules may eventually react, even though very little free aldehyde is present at a time.

Drawing Cyclic Structures of Monosaccharides

The cyclic forms of sugars are commonly depicted as **Haworth projections**. This convention, first suggested by the Englis chemist Walter N. Haworth, shows molecules drawn as planar rings with darkened edges representing the side facing toward the viewer. The structure is simplified to show only the functional groups attached to the carbon atoms. Any group written to the *right* in a Fischer projection appears *below (bottom face)* the plane of the ring in a Haworth projection, and any group written to the *left* in a Fischer projection appears *above* (top face) the plane in a Haworth projection.

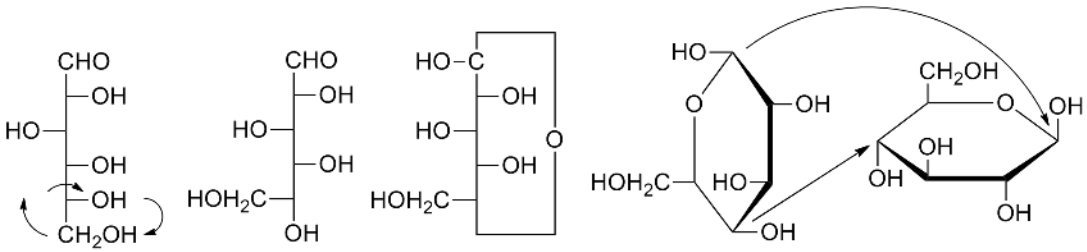


Figure 14.4.8: Conversion of the Fischer projection of D-glucose to the Haworth projection of ß-D-glucose.

1. When converting a Fischer projection (line) to a Haworth projection, you must first identify the type of monosaccharide involved. If the carbohydrate represents an aldohexose, the **pyranose** ring is typically used. A pyranose is a cyclic structure that contains five carbon atoms and an oxygen. If the carbohydrate represents a ketohexose, the **furanose** ring is typically used. The furanose ring contains four carbon atoms and an oxygen.

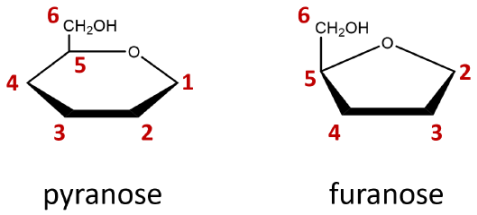


Figure 14.4.9: Haworth projections of a pyranose and furanose ring.

2. Indicate the arrangement of the hydroxyl group attached to the anomeric carbon to identify the sugar as an alpha or beta anomer. The α and β anomers are determined with respect to carbon 6. If the molecule represents a D-sugar, carbon 6 will be above the plane of the ring (top face) and forn an L-sugar, carbon 6 will be below the plane of the ring (ring). The α anomer occurs when the OH on the anomeric carbon is trans to carbon 6 and the β anomer occurs when the OH on the anomeric carbon is cis to carbon 6. If the cyclic structure contains a furanose, since carbon 1 is not included within the ring, that carbon group would be arranged in the opposite direction of the OH group (Figure \(\PageIndex{10}\)).

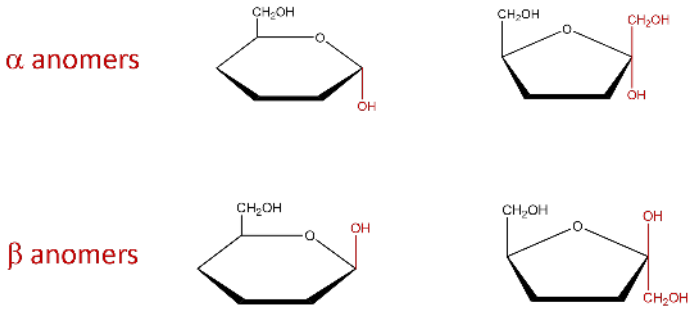


Figure 14.4.10: Arrangement of groups around the anomeric carbon to designate the molecule as an alpha or beta anomer.

3. The remaining chiral centers (carbons 2, 3 and 4 of the pyranose or carbons 3 and 4 of the furanose) are arranged based on the directions of the hydroxyl from the Fischer projection structures. Groups to the left of the Fischer projection would point up (top face), while groups to the right would point down (bottom face).

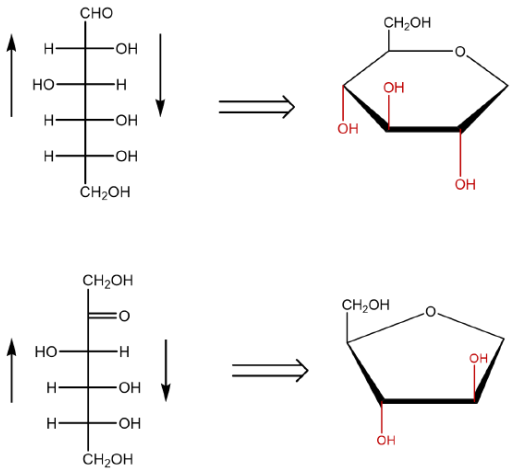


Figure 14.4.11: Fischer projections (left) and incomplete Haworth projections (right) of D-glucose (top) and D-fructose (bottom).

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Since the Fischer Projection of any given carbohydrate is always the same, the Haworth Projection is essentially always the same. The only differences between the Haworth Projection of the alpha or beta form of a single carbohydrate, is how the OH (and carbon 1 if a furanose ring) is arranged around the anomeric carbon to determine whether the molecule is alpha or beta.

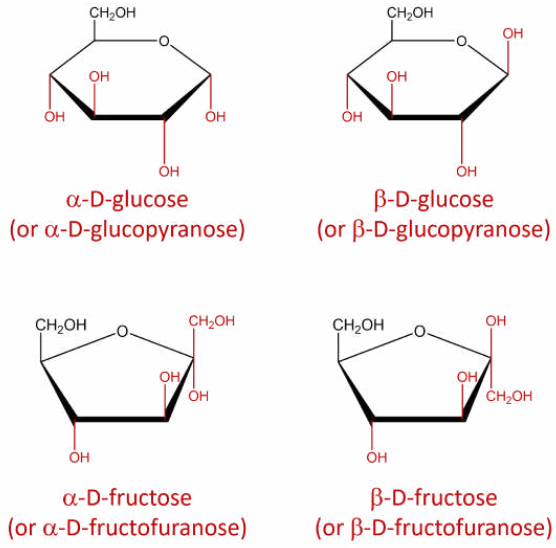


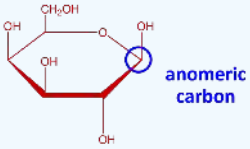
Figure 14.4.12: Haworth projections of D-glucose (top) and D-fructose (bottom).

The difference between the α and the β forms of sugars may seem trivial, but such structural differences are often crucial in biochemical reactions. This explains why we can get energy from the starch in potatoes and other plants but not from cellulose, even though both starch and cellulose are polysaccharides composed of glucose molecules linked together.

Example 14.4.1

Draw the cyclic structure for β-D-galactose. Identify the anomeric carbon.

Solution



To identify the structure, we should first start with the Fischer projection of D-galactose. Since it is an aldohexose, we will start with the pyranose ring. The beta anomer was requested, so the OH on the anomeric carbon (C1) is cis to C6. Since C6 is top face (pointing up), the OH will be top face. Carbons 2, 3, and 4 are then arranged based on the Fischer projection arrangement at those carbons (C2 right, C3 left, and C4 left).

Exercise 14.4.1

Draw the cyclic structure for α-D-galactose. Identify the anomeric carbon

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Summary

- Monosaccharides can be oxidized to produce sugar acids or reduced to form sugar alcohols.
- Monosaccharides commonly exist in the cyclic form and are shown as Haworth projections.
- Two cyclic stereoisomers can form from each straight-chain monosaccharide; these are known as anomers. The alpha (α) anomer is trans to carbon 6 and the beta (ß) anomer is cis to carbon 6.

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14.5: Disaccharides

Learning Objectives

- Identify the structures of sucrose, lactose, and maltose.
- Identify the monosaccharides that are needed to form sucrose, lactose, and maltose

Previously, you learned that monosaccharides can form cyclic structures by the reaction of the carbonyl group with an OH group. These cyclic molecules can in turn react with another alcohol. **Disaccharides** ($C_{12}H_{22}O_{11}$) are sugars composed of two monosaccharide units that are joined by a carbon–oxygen-carbon linkage known as a **glycosidic linkage (or glycosidic bond)**. This linkage is formed from the reaction of the anomeric carbon of one cyclic monosaccharide with the OH group of a second monosaccharide. If one anomeric carbon is free (not part of a glycosidicbond), the sugar is a reducing sugar. If there is no free anomeric carbon, the sugar is a nonreducing sugar.

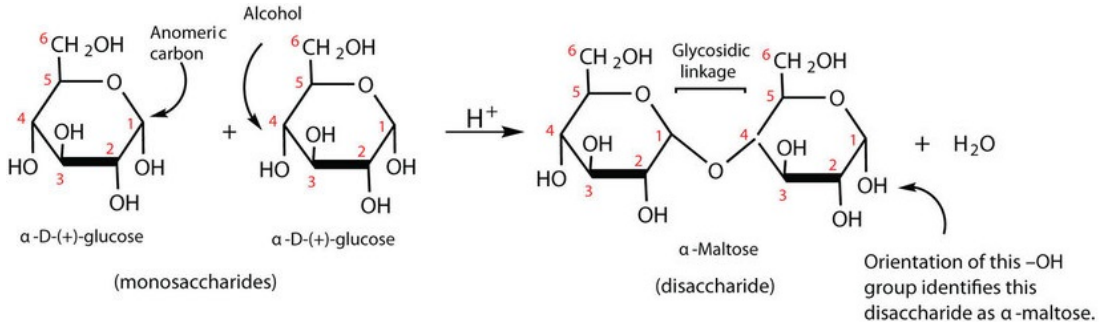


Figure 14.5.1: Formation of the maltose disaccharide.

The disaccharides differ from one another in their monosaccharide constituents and in the specific type of glycosidic linkage connecting them. There are three common disaccharides: maltose, lactose, and sucrose. All three are white crystalline solids at room temperature and are soluble in water. We'll consider each sugar in more detail.

Maltose

Maltose occurs to a limited extent in sprouting grain. It is formed most often by the partial hydrolysis of starch and glycogen. In the manufacture of beer, maltose is liberated by the action of malt (germinating barley) on starch; for this reason, it is often referred to as *malt sugar*. Maltose is about 30% as sweet as sucrose. The human body is unable to metabolize maltose or any other disaccharide directly from the diet because the molecules are too large to pass through the cell membranes of the intestinal wall. Therefore, an ingested disaccharide must first be broken down by hydrolysis into its two constituent monosaccharide units.

In the body, such hydrolysis reactions are catalyzed by enzymes such as *maltase*. The same reactions can be carried out in the laboratory with dilute acid as a catalyst, although in that case the rate is much slower, and high temperatures are required. Whether it occurs in the body or a glass beaker, the hydrolysis of maltose produces two molecules of D-glucose.

$$\text{maltose} \xrightarrow{H^+ \text{ or maltase}} 2\ \text{D-glucose} \tag{16.6.2}$$

Maltose is a reducing sugar. Thus, its two glucose molecules must be linked in such a way as to leave one anomeric carbon that can open to form an aldehyde group. The glucose units in maltose are joined in a *head-to-tail* fashion through an α-linkage from the first carbon atom of one glucose molecule to the fourth carbon atom of the second glucose molecule (that is, an α-1,4-glycosidic

linkage; see Figure 14.5.1). The bond from the anomeric carbon of the first monosaccharide unit is directed downward, which is why this is known as an α-glycosidic linkage. The OH group on the anomeric carbon of the second glucose can be in either the α or the β position, as shown in Figure 14.5.2.

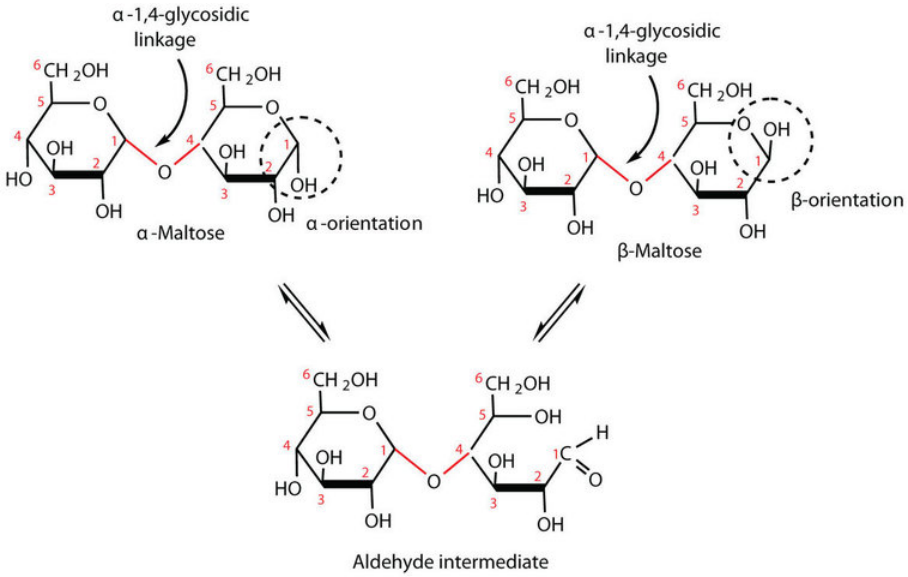


Figure 14.5.2: An Equilibrium Mixture of Maltose Isomers.

Lactose

Lactose is known as *milk sugar* because it occurs in the milk of humans, cows, and other mammals. In fact, the natural synthesis of lactose occurs only in mammary tissue, whereas most other carbohydrates are plant products. Human milk contains about 7.5% lactose, and cow's milk contains about 4.5%. This sugar is one of the lowest ranking in terms of sweetness, being about one-sixth as sweet as sucrose. Lactose is produced commercially from whey, a by-product in the manufacture of cheese. It is important as an infant food and in the production of penicillin.

Lactose is a reducing sugar composed of one molecule of ß-D-galactose and one molecule of D-glucose joined by a β-1,4-glycosidic bond (the bond from the anomeric carbon of the first monosaccharide unit being directed upward). The two monosaccharides are obtained from lactose by acid hydrolysis or the catalytic action of the enzyme *lactase*:

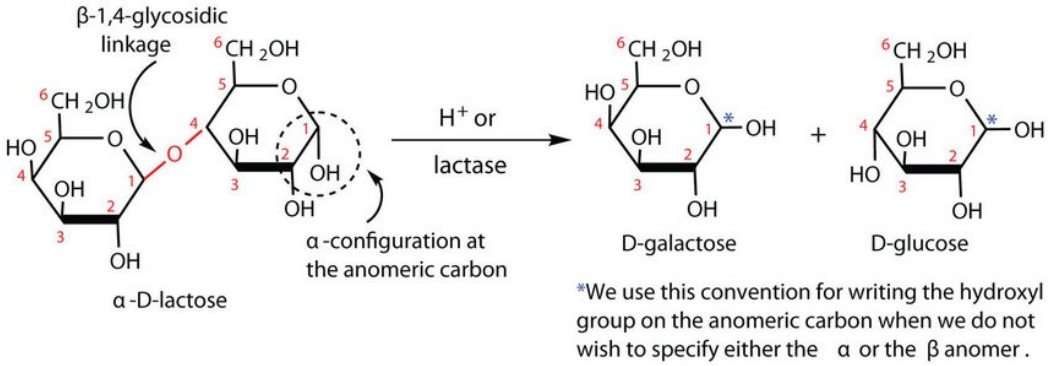


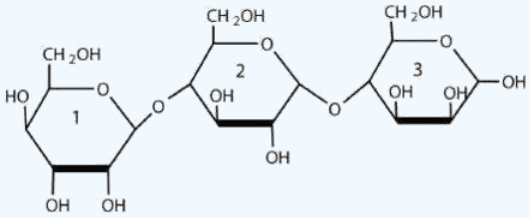
Figure 14.5.3: Hydrolysis of of the alpha lactose disaccharide.

Many adults and some children suffer from a deficiency of lactase. These individuals are said to be lactose intolerant because they cannot digest the lactose found in milk. A more serious problem is the genetic disease galactosemia, which results from the absence

of an enzyme needed to convert galactose to glucose. Certain bacteria can metabolize lactose, forming lactic acid as one of the products. This reaction is responsible for the “souring” of milk.

Example 14.5.1

For this trisaccharide, indicate whether each glycosidic linkage is α or β.

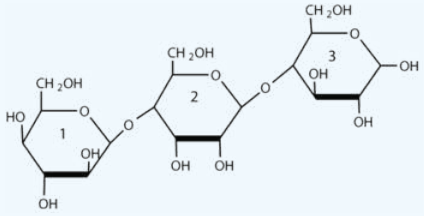


Solution

The glycosidic linkage between sugars 1 and 2 is β because the bond is directed up from the anomeric carbon. The glycosidic linkage between sugars 2 and 3 is α because the bond is directed down from the anomeric carbon.

Exercise 14.5.1

For this trisaccharide, indicate whether each glycosidic linkage is α or β.



To Your Health: Lactose Intolerance and Galactosemia

Lactose makes up about 40% of an infant’s diet during the first year of life. Infants and small children have one form of the enzyme lactase in their small intestines and can digest the sugar easily; however, adults usually have a less active form of the enzyme, and about 70% of the world’s adult population has some deficiency in its production. As a result, many adults experience a reduction in the ability to hydrolyze lactose to galactose and glucose in their small intestine. For some people the inability to synthesize sufficient enzyme increases with age. Up to 20% of the US population suffers some degree of lactose intolerance.

In people with lactose intolerance, some of the unhydrolyzed lactose passes into the colon, where it tends to draw water from the interstitial fluid into the intestinal lumen by osmosis. At the same time, intestinal bacteria may act on the lactose to produce organic acids and gases. The buildup of water and bacterial decay products leads to abdominal distention, cramps, and diarrhea, which are symptoms of the condition.

The symptoms disappear if milk or other sources of lactose are excluded from the diet or consumed only sparingly. Alternatively, many food stores now carry special brands of milk that have been pretreated with lactase to hydrolyze the lactose. Cooking or fermenting milk causes at least partial hydrolysis of the lactose, so some people with lactose intolerance are still able to enjoy cheese, yogurt, or cooked foods containing milk. The most common treatment for lactose intolerance, however, is the use of lactase preparations (e.g., Lactaid), which are available in liquid and tablet form at drugstores and grocery stores. These are taken orally with dairy foods—or may be added to them directly—to assist in their digestion.

Galactosemia is a condition in which one of the enzymes needed to convert galactose to glucose is missing. Consequently, the blood galactose level is markedly elevated, and galactose is found in the urine. An infant with galactosemia experiences a lack of appetite, weight loss, diarrhea, and jaundice. The disease may result in impaired liver function, cataracts, mental retardation, and even death. If galactosemia is recognized in early infancy, its effects can be prevented by the exclusion of milk and all other sources of galactose from the diet. As a child with galactosemia grows older, he or she usually develops an alternate pathway for metabolizing galactose, so the need to restrict milk is not permanent. The incidence of galactosemia in the United States is 1 in every 65,000 newborn babies.

Sucrose

Sucrose, probably the largest-selling pure organic compound in the world, is known as *beet sugar*, *cane sugar*, *table sugar*, or simply *sugar*. Most of the sucrose sold commercially is obtained from sugar cane and sugar beets (whose juices are 14%–20% sucrose) by evaporation of the water and recrystallization. The dark brown liquid that remains after the recrystallization of sugar is sold as molasses.

The sucrose molecule is unique among the common disaccharides in having an α-1,β-2-glycosidic (head-to-head) linkage. Because this glycosidic linkage is formed by the OH group on the anomeric carbon of α-D-glucose and the OH group on the anomeric carbon of β-D-fructose, it ties up the anomeric carbons of both glucose and fructose.

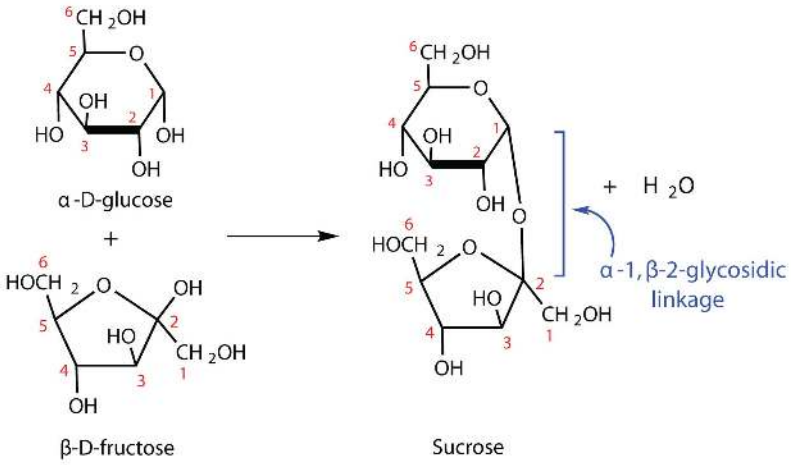


Figure **14.5.4**: Formation of the sucrose disaccharide.

This linkage gives sucrose certain properties that are quite different from those of maltose and lactose. As long as the sucrose molecule remains intact, neither monosaccharide “uncyclizes” to form an open-chain structure. Thus, sucrose is incapable of mutarotation and exists in only one form both in the solid state and in solution. In addition, sucrose does not undergo reactions that are typical of aldehydes and ketones. Therefore, sucrose is a nonreducing sugar.

The hydrolysis of sucrose in dilute acid or through the action of the enzyme *sucrase* (also known as invertase) gives an equimolar mixture of glucose and fructose. This 1:1 mixture is referred to as *invert sugar* because it rotates plane-polarized light in the opposite direction than sucrose. The hydrolysis reaction has several practical applications. Sucrose readily recrystallizes from a solution, but invert sugar has a much greater tendency to remain in solution. In the manufacture of jelly and candy and in the canning of fruit, the recrystallization of sugar is undesirable. Therefore, conditions leading to the hydrolysis of sucrose are employed in these processes. Moreover, because fructose is sweeter than sucrose, the hydrolysis adds to the sweetening effect. Bees carry out this reaction when they make honey.

The average American consumes more than 100 lb of sucrose every year. About two-thirds of this amount is ingested in soft drinks, presweetened cereals, and other highly processed foods. The widespread use of sucrose is a contributing factor to obesity and tooth

decay. Carbohydrates such as sucrose, are converted to fat when the caloric intake exceeds the body's requirements, and sucrose causes tooth decay by promoting the formation of plaque that sticks to teeth.

Example 14.5.2

Identify each sugar by its common chemical name.

a. milk sugar

b. table sugar

Solution

a. lactose

b. sucrose

Exercise 14.5.2

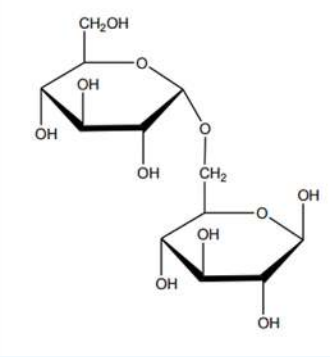
Identify each sugar by its common chemical name.

a. cane sugar

b. malt sugar

Example 14.5.3

Using the structure of the discaccharide shown below to answer the questions that follow:



a. What are the identities of the monosaccharides present in the molecule?

b. What type of glycosidic linkage is present?

c. Would this be a reducing sugar?

Solution

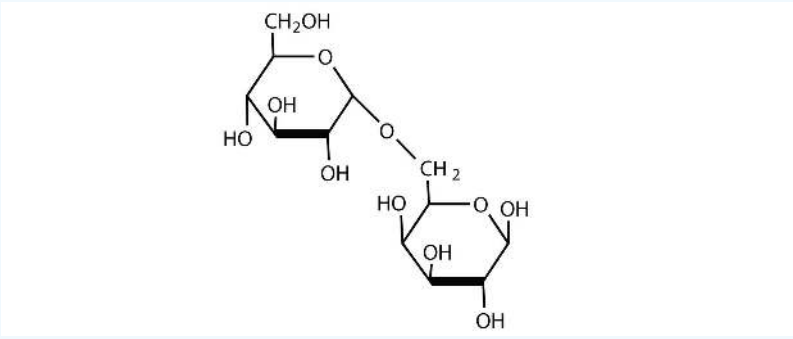
a. These are both D-glucose molecules. The monosaccharide to the left is α-D-glucose and the right unit is β-D-glucose.

b. The glycosidic linkage present in the disaccharide is an α-1,6-glycosidic linkage.

c. This molecule would be a reducing sugar, because the anomeric carbon on the glucose to the right is free.

Exercise 14.5.1

Using the structure of the discaccharide shown below to answer the questions that follow:



a. What are the identities of the monosaccharides present in the molecule?

b. What type of glycosidic linkage is present?

c. Would this be a reducing sugar?

Summary

- Maltose is composed of two molecules of D-glucose (one has to be alpha and the other can be either) joined by an α-1,4-glycosidic linkage. It is a reducing sugar that is found in sprouting grain.
- Lactose is composed of a molecule of ß-D-galactose joined to a molecule of glucose (either alpha or beta) by a β-1,4-glycosidic linkage. It is a reducing sugar that is found in milk.
- Sucrose is composed of a molecule of α-D-glucose joined to a molecule of β-fructose by an α-1,β-2-glycosidic linkage. It is a nonreducing sugar that is found in sugar cane and sugar beets.

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14.6: Oligosaccharides

Learning Objectives

- Describe the role of carbohydrates as cell markers.
- Identify the blood type classified as the universal donor/acceptor.

Oligosaccharides

An **oligosaccharide** is a saccharide polymer containing a small number (typically two to ten) of monosaccharides. Oligosaccharides can have many functions; for example, they are commonly found on the plasma membrane of animal cells where they can play a role in cell-cell recognition. In general, they are found attached to compatible amino acid side-chains in proteins or to lipids.

Oligosaccharides are often found as a component of **glycoproteins** or **glycolipids**. They are often used as chemical markers on the outside of cells, often for cell recognition. Oligosaccharides are also responsible for determining blood type.

Blood Type

Cell markers are carbohydrate chains on the surface of cells where they act as “road signs” allowing molecules to distinguish one cell from another. ABO blood markers found on red blood cells are made up of oligosaccharides that contain either three or four sugar units (Figure 14.6.1).

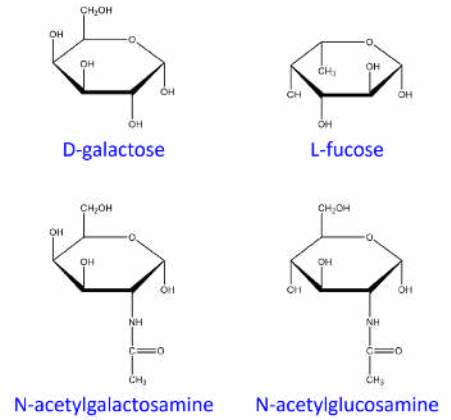


Figure 14.6.1: Structures of monosaccharide units present in ABO blood markers.

Carbohydrates attached to red blood cells determine the ABO blood type (Figure 14.6.2).

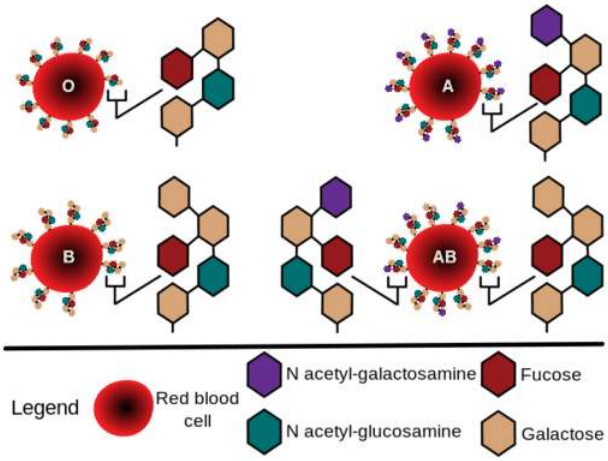


Figure 14.6.2: ABO blood types.

Of the four blood types, type O has the fewest types of saccharides attached to it while type AB has the most. As a result, type O blood is considered the **universal donor** because it doesn't have any saccharides present that will appear as foreign when transfused into blood of another type. The reverse is not true. For example, if type A blood is given to a patient with type O blood, it will be rejected by the body because there is an unknown species being introduced to the body. Type A blood cells contain N-acetylgalactosamine which is not present in type O blood. A person with type O blood would undergo rejection upon receiving type A blood. Since type AB blood has all possible saccharides, type AB blood is considered the **universal acceptor**. The Rhesus factor (Rh) in blood also affects donor and acceptor properties but it does not depend on carbohydrates. The Rh factor is determined by the presence (Rh+) or absence (Rh-) of a specific protein on the surface of red blood cells.

Example 14.6.1

Indicate whether the following blood types could be accepted by a person with type A blood:

a. Type AB

b. Type O

Solution

a. No, because type AB blood has saccharides that are not present in type A blood. Therefore, the presence of this foreign substance would be rejected.

b. Yes, this is the universal donor. Although it does not have all of the same saccharides as type A, no foreign substances are introduced.

Exercise 14.6.1

Indicate whether the following blood types could be accepted by a person with type AB blood:

a. Type B

b. Type O

Summary

- All blood types include the N-acetylglucosamine, galactose, and fucose; but differ in the absence or presence of additional units.
- Type O blood is considered the universal donor.
- Type AB blood is considered the universal acceptor.

Contributors and Attributions

-
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14.7: Polysaccharides

Learning Objectives

- Compare and contrast the structures and uses of starch, glycogen, and cellulose.

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 polysaccharides: **amylose** and **amylopectin**. Natural starches consist of about 10%–30% amylose and 70%–90% amylopectin. Amylose is a straight-chain polysaccharide composed entirely of D-glucose units joined by the α-1,4-glycosidic linkages we saw in maltose (Figure **14.7.1*a***). 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 (Figure **14.7.1*b***). 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.

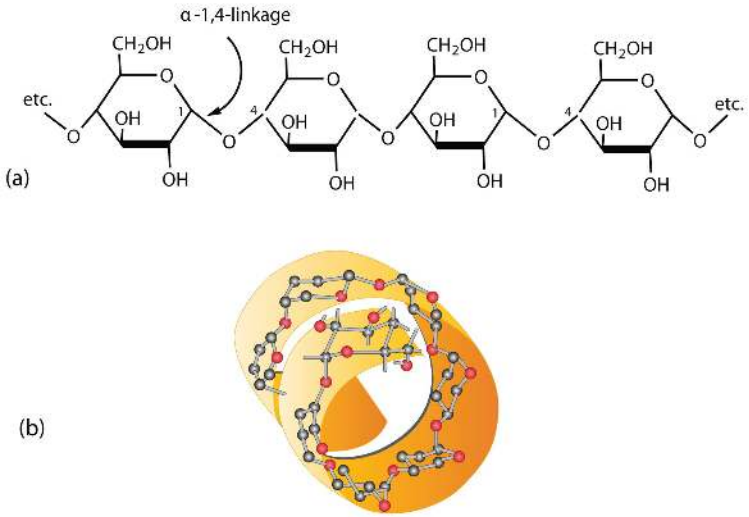


Figure **14.7.1**: Amylose. (a) Amylose is a linear chain of α-D-glucose units joined together by α-1,4-glycosidic bonds. (b) Because of hydrogen bonding, amylose acquires a spiral structure that contains six glucose units per turn.

Amylopectin is a branched-chain polysaccharide composed of glucose units linked primarily by α-1,4-glycosidic bonds but with occasional α-1,6-glycosidic bonds, which are responsible for the branching. A molecule of amylopectin may contain many thousands of glucose units with branch points occurring about every 25–30 units (Figure **14.7.2**). The helical structure of amylopectin is disrupted by the branching of the chain, so instead of the deep blue-violet color amylose gives with iodine, amylopectin produces a less intense reddish brown.

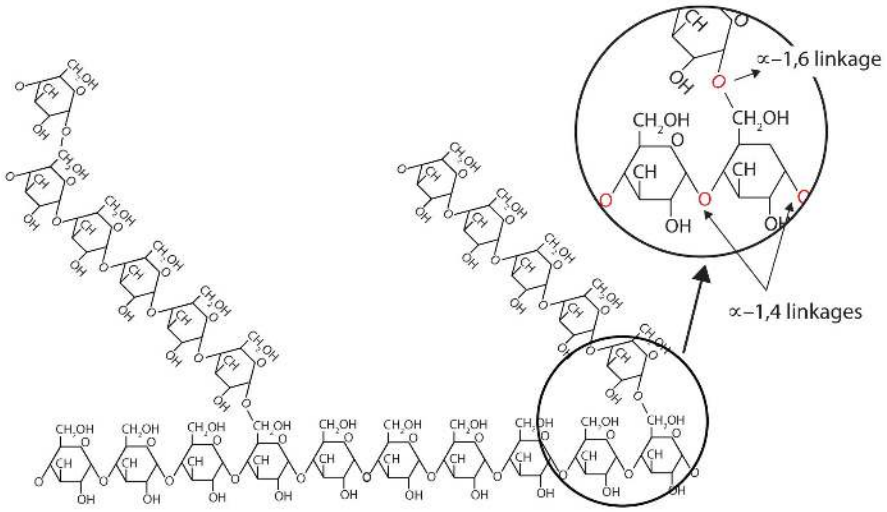


Figure **14.7.2**: Representation of the Branching in Amylopectin and Glycogen. Both amylopectin and glycogen contain branch points that are linked through α-1,6-linkages. These branch points occur more often in glycogen.

Dextrins are glucose polysaccharides of intermediate size. The shine and stiffness imparted to clothing by starch are due to the presence of dextrins formed when clothing is ironed. Because of their characteristic stickiness with wetting, dextrins are used as adhesives on stamps, envelopes, and labels; as binders to hold pills and tablets together; and as pastes. Dextrins are more easily digested than starch and are therefore used extensively in the commercial preparation of infant foods.

The complete hydrolysis of starch yields, in successive stages, glucose:

$$\text{starch} \rightarrow \text{dextrins} \rightarrow \text{maltose} \rightarrow \text{glucose}$$

In the human body, several enzymes known collectively as amylases degrade starch sequentially into usable glucose units.

Glycogen

Glycogen is the energy storage 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 (Figures **14.7.3**). This extreme linearity allows a great deal of hydrogen bonding between OH groups on adjacent chains, causing them to pack closely into fibers (Figure **14.7.3**). As a result, cellulose exhibits little interaction with water or any other solvent. Cotton and wood, for example, are completely insoluble in water and have considerable mechanical strength. Because cellulose does not have a helical structure, it does not bind to iodine to form a colored product.

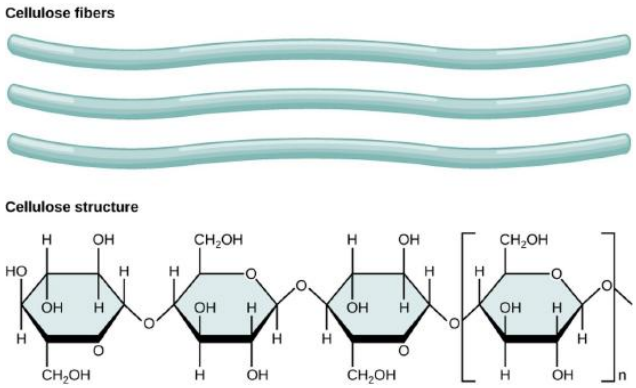


Figure **14.7.3**: Cellulose. In cellulose, glucose monomers are linked in unbranched chains by *β-1*,4 glycosidic linkages. Because of the way the glucose subunits are joined, every glucose monomer is flipped relative to the next one resulting in a linear, fibrous structure.

Cellulose yields D-glucose after complete acid hydrolysis, yet humans are unable to metabolize cellulose as a source of glucose. Our digestive juices lack enzymes that can hydrolyze the β-glycosidic linkages found in cellulose, so although we can eat potatoes, we cannot eat grass. However, certain microorganisms can digest cellulose because they make the enzyme cellulase, which catalyzes the hydrolysis of cellulose. The presence of these microorganisms in the digestive tracts of herbivorous animals (such as cows, horses, and sheep) allows these animals to degrade the cellulose from plant material into glucose for energy. Termites also contain cellulase-secreting microorganisms and thus can subsist on a wood diet. This example once again demonstrates the extreme stereospecificity of biochemical processes.

Career Focus: Certified Diabetes Educator

Certified diabetes educators come from a variety of health professions, such as nursing and dietetics, and specialize in the education and treatment of patients with diabetes. A diabetes educator will work with patients to manage their diabetes. This involves teaching the patient to monitor blood sugar levels, make good food choices, develop and maintain an exercise program, and take medication, if required.



A certified diabetes educator at Naval Medical Center Portsmouth (left) and a registered dietician at the medical center (center), provide nutritional information to a diabetes patient and her mother at the Diabetes Boot Camp.

Diabetes educators also work with hospital or nursing home staff to improve the care of diabetic patients. Educators must be willing to spend time attending meetings and reading the current literature to maintain their knowledge of diabetes medications, nutrition, and blood monitoring devices so that they can pass this information to their patients.

Example 14.7.1

What monosaccharide is obtained from the hydrolysis of cellulose?

Solution

Glucose (more specifically, *β-D-glucose)*

Exercise 14.7.1

What monosaccharide is obtained from the hydrolysis of each carbohydrate?

a. starch

b. cellulose

Summary

- Starch is a storage form of energy in plants. It contains two polysaccharides composed of alpha-D-glucose units:
  - amylose - linear with α-1,4-glycosidic bonds.
  - amylopectin - branched polysaccharide with α-1,4 and α-1,6-glycosidic bonds.
- Glycogen is a storage form of energy in animals. It is a branched polysaccharide composed of alpha-D-glucose units with α-1,4 and α-1,6-glycosidic bonds. It is more highly branched than amylopectin.
- Cellulose is a structural polysaccharide of glucose units found in plants. It is a linear polysaccharide with the glucose units linked through β-1,4-glycosidic bonds.

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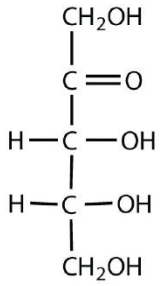
14.E: Carbohydrates (Exercises)

Additional Exercises

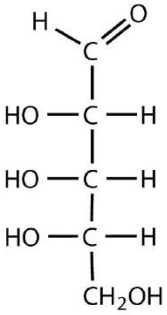
1. When an aqueous solution of an unknown carbohydrate was heated, four molecules of glucose were produced. What type of carbohydrate does this compound represent?

2. Classify the following based on the chemical composition (functional group and number of carbon) and then as a D sugar or an L sugar.

a.



b.



3. Use the structures shown above in problem 2 to answer the following problems:

   a. How many chiral centers are present in the molecule shown in 2a?

   b. What is the maximum number of stereoisomers possible for the molecule shown in 2a?

   c. Draw the enantiomer of the molecule shown in 2a. Is this a D-sugar or L-sugar?

4. What hexose would you expect to be most abundant in each food?

   a. honey

   b. milk

5. Given that the aldohexose D-mannose differs from D-glucose only in the configuration at the second carbon atom, draw the cyclic structure for α-D-mannose.

6. Indicate whether the following would yield a positive Benedict's test

   a. L-galactose

b. levulose

c. D-glucose

7. Cellobiose is a disaccharide composed of two glucose units joined by a β-1,4-glycosidic linkage.

a. Draw the structures of α-cellobiose and β-cellobiose.

b. Is cellobiose a reducing or nonreducing sugar? Justify your answer.

8. Describe the similarities and differences between amylose and cellulose.

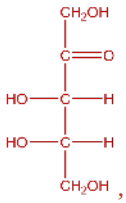
Answers

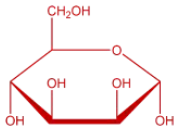
1. Oligosaccharide because four monosaccharides are present.

3.

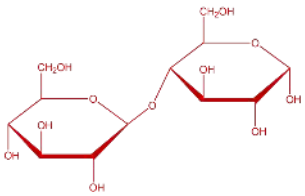
a. 2 chiral centers (carbons 3 and 4)

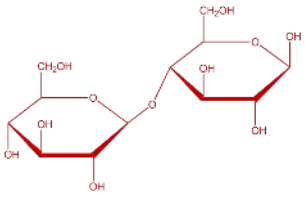
b. 8 possible stereoisomers. There are 3 chiral centers and using $2^n = 2^3 = 8$ possible arrangements that will result in molecules that have the same connectivity around the chiral centers, but with different arrangements.

c.  , this is an L-sugar.

5. 

7.

a. α-cellobiose 

β-cellobiose 

b. Cellobiose is a reducing sugar because it has a free anomeric carbon on the second glucose molecule.

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14.S: Carbohydrates (Summary)

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

Carbohydrates, a large group of biological compounds containing carbon, hydrogen, and oxygen atoms, include sugars, starch, glycogen, and cellulose. All carbohydrates contain alcohol functional groups, and either an aldehyde or a ketone group (or a functional group that can be converted to an aldehyde or ketone). The simplest carbohydrates are **monosaccharides**. Monosaccharrides can be classified based on the carbonyl functional group and number of carbon atoms present. These compounds can combine to form more complex carbohydrates. Those with two monosaccharide units are **disaccharides**, those with three to nine monosaccharide units are **oligosaccharides**, and those with ten or more monosaccharide units are **polysaccharides**. Most sugars are either monosaccharides or disaccharides. Cellulose, glycogen, and starch are polysaccharides.

Many carbohydrates exist as **stereoisomers**, in which the three-dimensional spatial arrangement of the atoms in space is the only difference between the isomers. These particular stereoisomers contain at least one **chiral carbon**, a carbon atom that has four different groups bonded to it. A molecule containing a chiral carbon is nonsuperimposable on its mirror image, and two molecules that are nonsuperimposable mirror images of each other are a special type of stereoisomer called **enantiomers**. Enantiomers have the same physical properties, such as melting point, but differ in the direction they rotate polarized light.

A sugar is designated as being a D sugar or an L sugar according to how, in a Fischer projection of the molecule, the hydrogen atom and OH group are attached to the *penultimate* carbon atom, which is the carbon atom immediately before the terminal alcohol carbon atom. If the structure at this carbon atom is the same as that of D-glyceraldehyde (OH to the right), the sugar is a **D sugar**; if the configuration is the same as that of L-glyceraldehyde (OH to the left), the sugar is an **L sugar**.

Monosaccharides of five or more carbons atoms readily form cyclic structures when the carbonyl carbon atom reacts with an OH group on a carbon atom three or four carbon atoms distant. Consequently, glucose in solution exists as an equilibrium mixture of three forms, two of them cyclic (α- and β-) and one open chain. In Haworth projections, the ***alpha*** form is drawn with the OH group on the "former" carbonyl carbon atom (**anomeric carbon**) is trans (opposite) to carbon 6; the ***beta*** form, with the OH group is cis (same) to carbon 6; these two compounds are stereoisomers and are given the more specific term of **anomers**. Any solid sugar can be all alpha or all beta. Once the sample is dissolved in water, however, the ring opens up into the open-chain structure and then closes to form either the α- or the β-anomer. These interconversions occur back and forth until a dynamic equilibrium mixture is achieved in a process called **mutarotation**.

Three abundant hexoses in living organisms are the aldohexoses **D-glucose** and **D-galactose** and the ketohexose **D-fructose**. D-glucose and D-galactose are **epimers** because the molecules are identical, except at C4. D-glucose and D-fructose are structural isomers that both have the $C_6H_{12}O_6$ molecular formula.

The carbonyl group present in monosaccharides is easily oxidized by Tollens' or Benedict's reagents (as well as others). Any mono- or disaccharide containing a free anomeric carbon is a **reducing sugar**. The disaccharide *maltose* contains two glucose units joined in an α-1,4-glycosidic linkage. The disaccharide *lactose* contains a galactose unit and a glucose unit joined by a β-1,4-glycosidic linkage. Both maltose and lactose contain a free anomeric carbon that can convert to an aldehyde functional group, so they are reducing sugars; they also undergo mutarotation. Many adults, and some children, have a deficiency of the enzyme lactase (which is needed to break down lactose) and are said to be **lactose intolerant**. A more serious problem is the genetic disease **galactosemia**, which results from the absence of an enzyme needed to convert galactose to glucose.

The disaccharide ***sucrose*** (table sugar) consists of a glucose unit and a fructose unit joined by a **glycosidic linkage**. The linkage is designated as an α-1,β-2-glycosidic linkage because it involves the OH group on the first carbon atom of glucose and the OH group on the second carbon atom of fructose. Sucrose is not a reducing sugar because it has no anomeric carbon that can reform a carbonyl group, and it cannot undergo mutarotation because of the restrictions imposed by this linkage.

Oligosaccharides play important roles in the blood markers. The types of monosaccharide units present in the oligosaccharide attached to the red blood cell indicates the ABO blood type. All blood types include the N-

acetylglucosamine, galactose, and fucose; but differ in the absence or presence of additional units. Type O blood is considered the **universal donor**, while Type AB blood is considered the **universal acceptor**.

Starch, the principal carbohydrate of plants, is composed of the polysaccharides **amylose** (10%–30%) and **amylopectin** (70%–90%). When ingested by humans and other animals, starch is hydrolyzed to glucose and becomes the body's energy source. *Glycogen* is the polysaccharide animals use to store excess carbohydrates from their diets. Similar in structure to amylopectin, glycogen is hydrolyzed to glucose whenever an animal needs energy for a metabolic process. The polysaccharide *cellulose* provides structure for plant cells. It is a linear polymer of glucose units joined by β-1,4-glycosidic linkages. It is indigestible in the human body but digestible by many microorganisms, including microorganisms found in the digestive tracts of many herbivores.

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CHAPTER OVERVIEW

15: Food

15.1: Carbohydrates in the Diet
15.2: Fats and Cholesterol
15.3: Proteins- Muscle and Much More
15.4: Minerals, Vitamins, and Other Essentials
15.5: Starvation, Fasting, and Malnutrition
15.6: Flavorings- Spicy and Sweet
15.7: Other Food Additives- Beneficial or Dangerous
15.8: Problems with our Food

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15.1: 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 **15.1.1**.

***Table* 15.1.1** *The Major Dietary Carbohydrates. Source: Wikipedia*

Class (DP*)	Subgroup	Components
Sugars (1–2)	Monosaccharides	Glucose, galactose, fructose, xylose
	Disaccharides	Sucrose, lactose, maltose, trehalose
	Polyols	Sorbitol, mannitol
Oligosaccharides (3–9)	Malto-oligosaccharides	Maltodextrins
	Other oligosaccharides	Raffinose, stachyose, fructo-oligosaccharides
Polysaccharides (>9)	Starch	Amylose, amylopectin, modified starches
	Non-starch polysaccharides	Glycogen, Cellulose, Hemicellulose, Pectins, Hydrocolloids

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 **15.1.1**) 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.

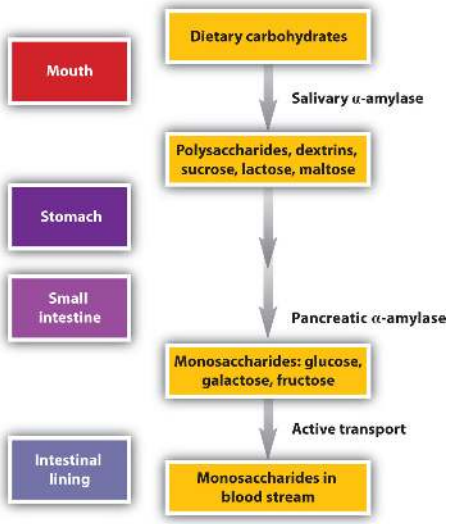


Figure **15.1.1** The Principal events and sites of carbohydrate digestion.

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 **15.1.2**) . Because carbohydrates are easily digested, athletes often rely on carbohydrate rich foods to enable a high level of performance.



Figure **15.1.2** *Foods that serve as carbohydrate sources.*

Common Monosaccharides and Disaccharides

Monosaccharides and disaccharides commonly found in our diets are listed in Table **15.1.3**. Although a variety of monosaccharides are found in living organisms, three hexoses are particularly abundant: D-glucose, D-galactose, and D-fructose (Figure **15.1.3**). Glucose and galactose are both aldohexoses, while fructose is a ketohexose.

Table **15.1.2** . 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

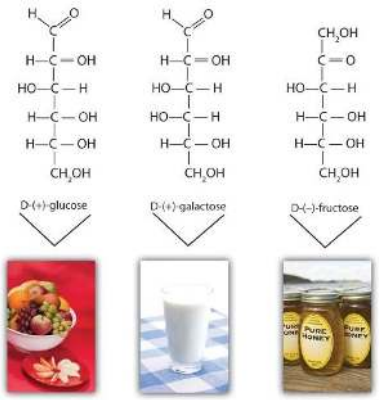


***Figure* 15.1.3** *Structures of three important hexoses. Each hexose is pictured with a food source in which it is commonly found. Source: Photos © Thinkstock.*

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 **15.1.3**. Notice that the configuration differs from that of glucose only at the fourth carbon atom.

Fructose

D-Fructose, also shown in Figure **15.1.3**, 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 **15.1.1**).

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 **15.1.4** below.

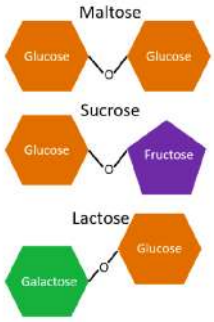


Figure **15.1.4** The three disaccharides.

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 **15.1.3**.

Table **15.1.3**: 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 **15.1.5**U.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 **15.1.6**) 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 15.1.6 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. 15.1.6.

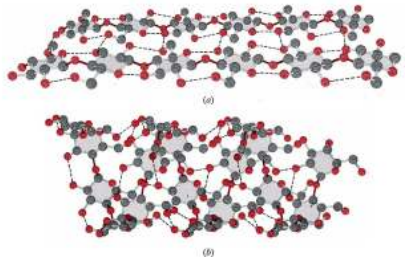


Figure 15.1.6 Structures of (a) cellulose and (b) amylose (starch). The C—O bonds linking glucose units are shown in color and hydrogen bonds are shown as single black lines. Hydrogen atoms have been omitted to simplify the structure. Note how the β-glucose units in cellulose form a linear chain because 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.

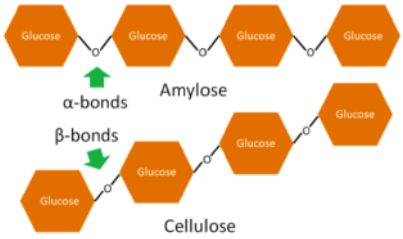


Figure 15.1.7 Structures of amylose and cellulose

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 15.1.4 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 15.1.4 Common Types of Fermentable (Soluble) Fiber and Non-Fermentable (Insoluble) Fiber.

Fermentable (Soluble) Fiber	Description	Non-Fermentable (Insoluble Fiber)	Description
Hemicellulose (soluble type)	Surround cellulose in plant cell walls	Cellulose	Main component of plant cell walls
Pectin	Found in cell walls and intracellular tissues of fruits and berries	Hemicellulose (insoluble type)	Surround cellulose in plant cell walls
Beta-glucans	Found in cereal brans	Lignin	Non carbohydrate found within "woody" plat cell walls
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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15.2: 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 15.2.1). 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.

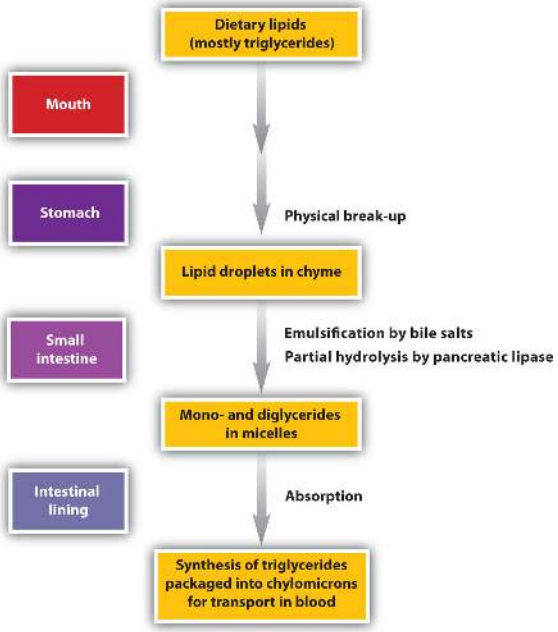
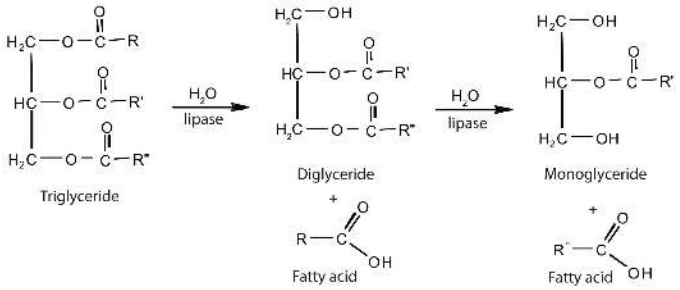


Figure 15.2.1 The principal events and sites of lipid (primarily triglyceride) digestion.

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.

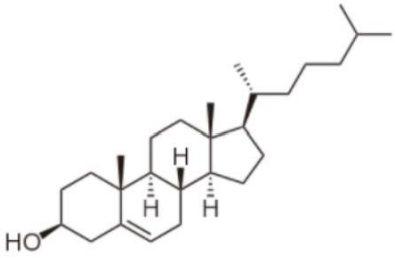


Figure **15.2.2** *The carbon ring structure of cholesterol*[1]

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* 15.2.3** *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.

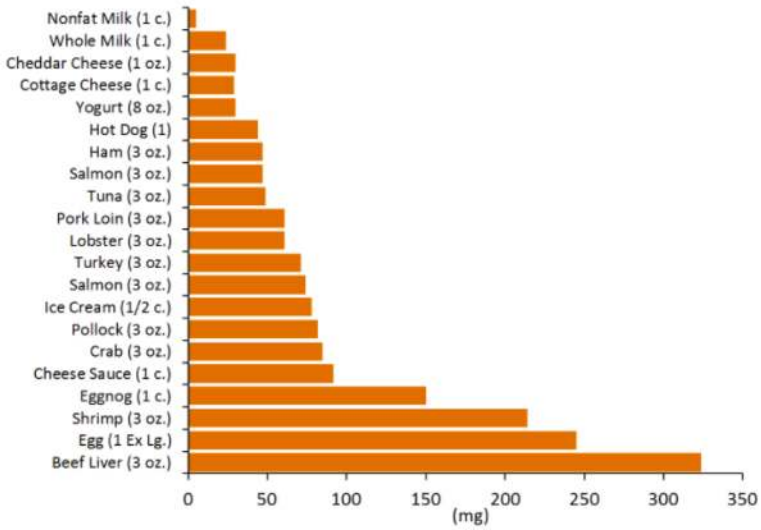


Figure **15.2.4** *The cholesterol content (mg) of foods*[4]

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)	Purpose
HDL (high-density lipoproteins)	1.063-1.21	5-12	It is sometimes called "good" cholesterol because it carries cholesterol from other parts of your body back to your liver. Your liver then removes the cholesterol from your body.
LDL (low-density lipoproteins)	1.019-1.063	18-25	It is sometimes called "bad" cholesterol because a high LDL level leads to the buildup of plaque in your arteries.
VLDL (very low-density lipoproteins)	0.95-1.006	30-80	Some people also call VLDL a "bad" cholesterol because it too contributes to the buildup of plaque in your arteries. But VLDL and LDL are different; VLDL mainly carries triglycerides and LDL mainly carries cholesterol.

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.

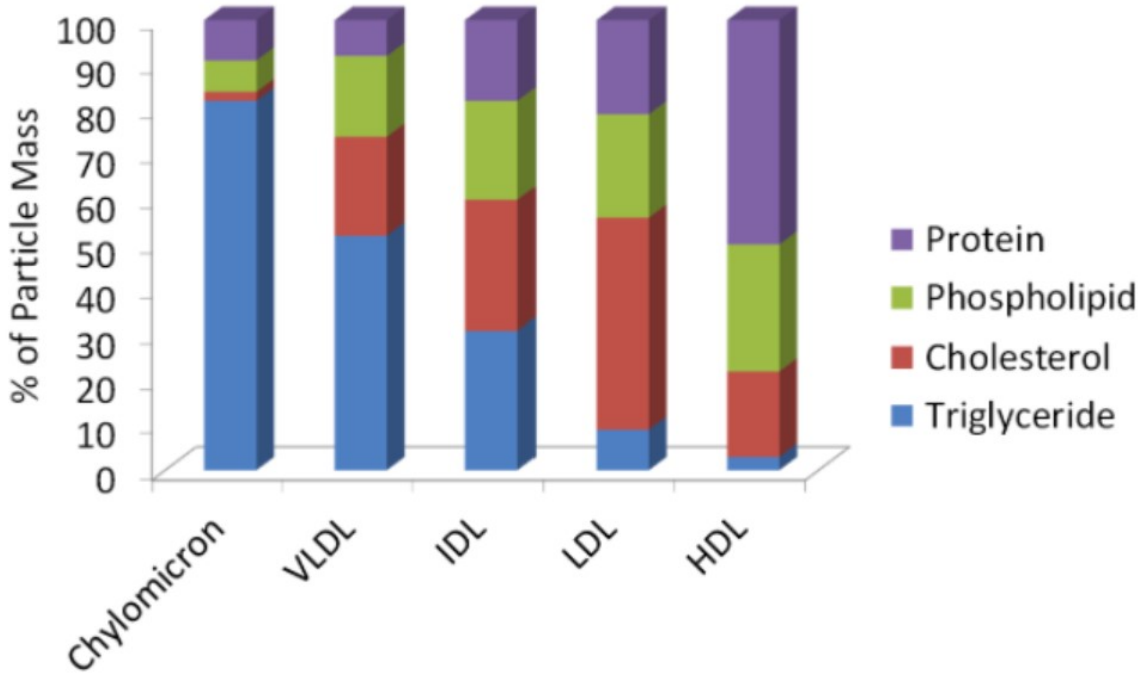


Figure **15.2.5** *Composition of lipoproteins*

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.

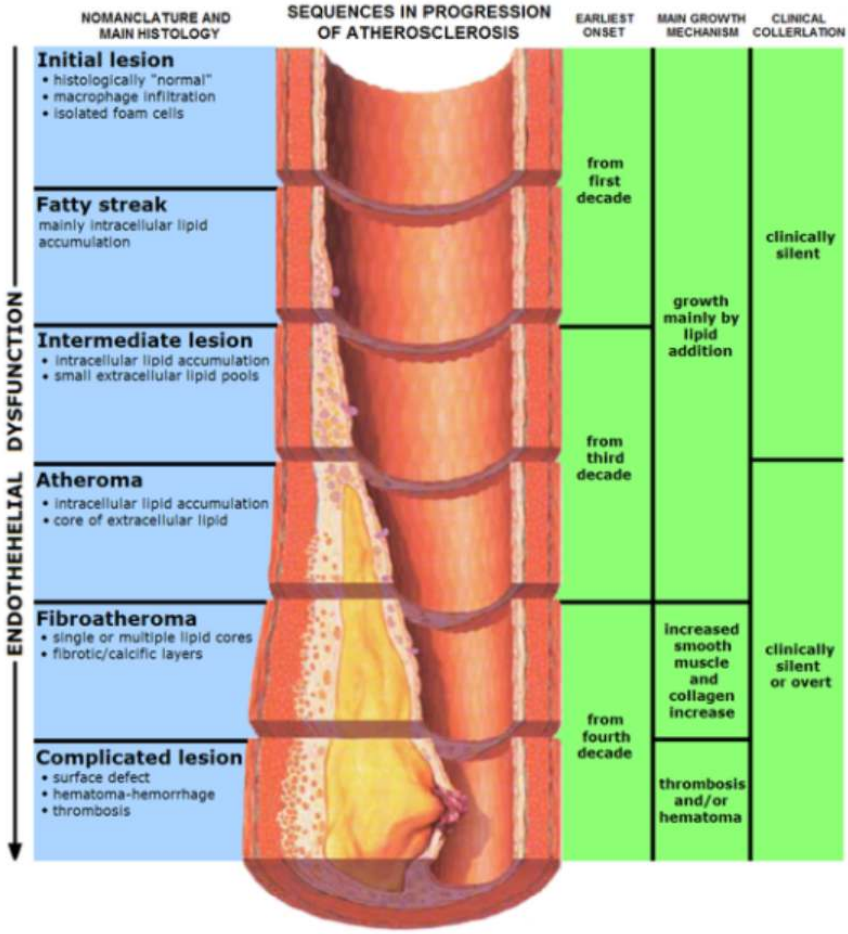


Figure **15.2.6** *The formation of a lesion in an artery*[5]

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.

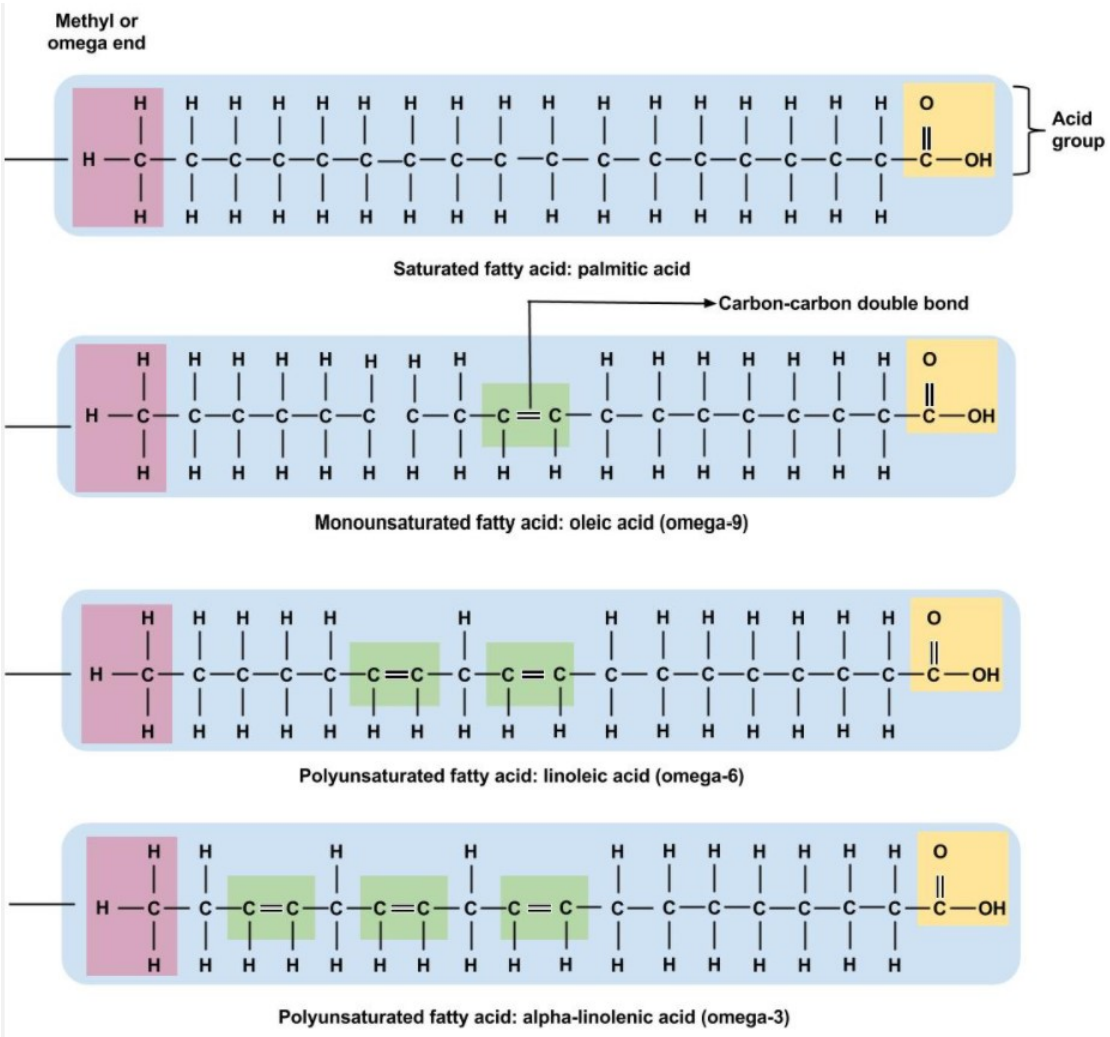


Figure **15.2.1**: The structures of a saturated, monounsaturated, and polyunsaturated fat. Note the differences in points of unsaturation (C=C double bonds) on some of the fatty acids.

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.

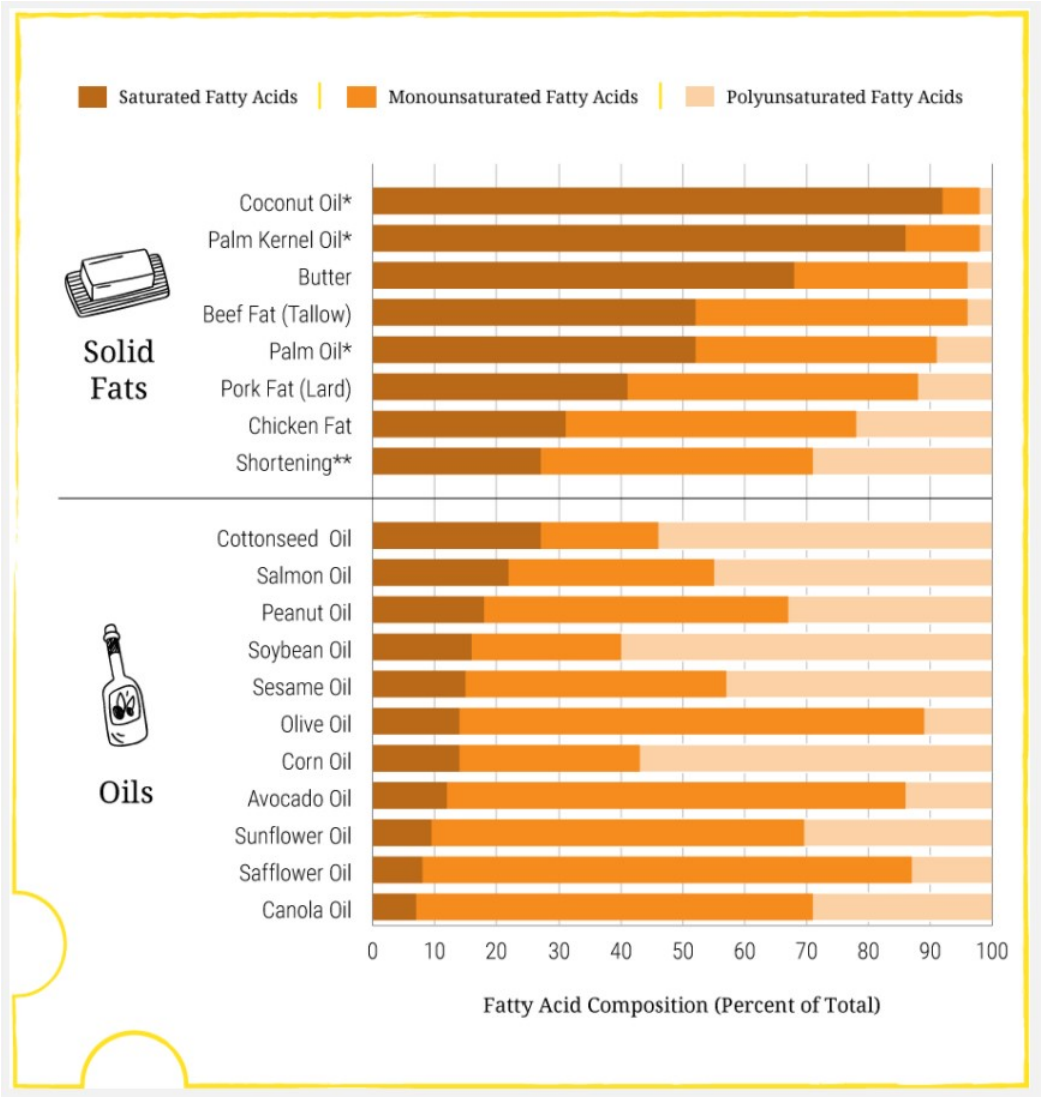


Figure **15.2.2**: Dietary fats contain a mixture of saturated, monounsaturated, and polyunsaturated fatty acids. Foods are often categorized by the predominant type of fatty acids they contain, even though foods contain all three types. (Copyright; author via source)

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 **15.2.3**: 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.

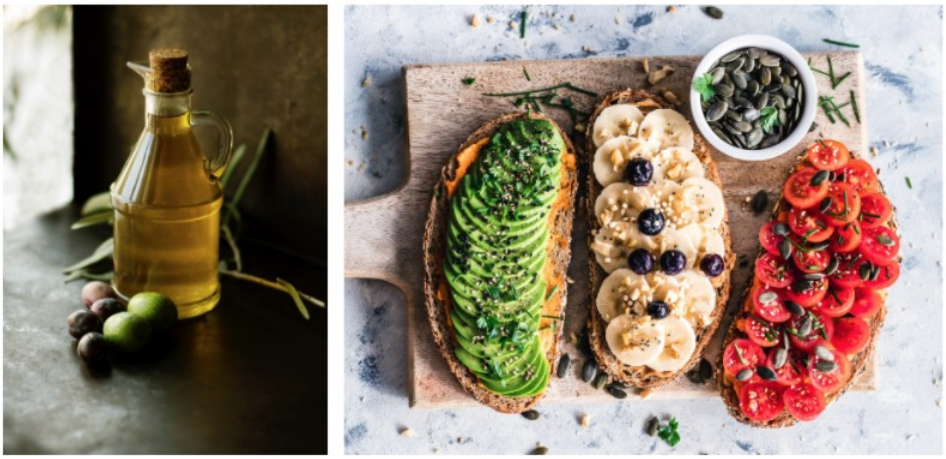


Figure **15.2.4**: Examples of foods high in monounsaturated fat, such as olive oil, avocado, nut butters, and seeds. (Copyright; author via source).

Food sources of predominately polyunsaturated fats include plant oils (soybean, corn); fish; flaxseed; and some nuts like walnuts and pecans.



Figure **15.2.5**: 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.)

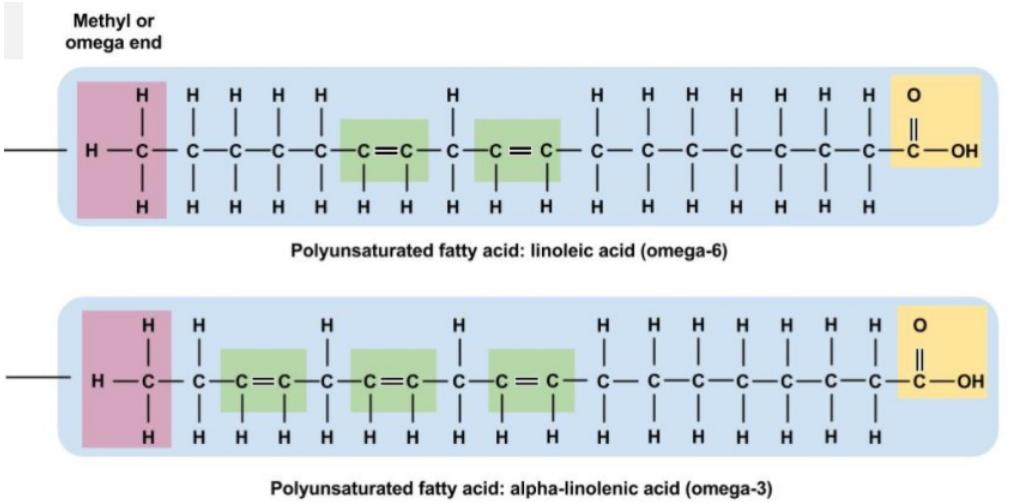
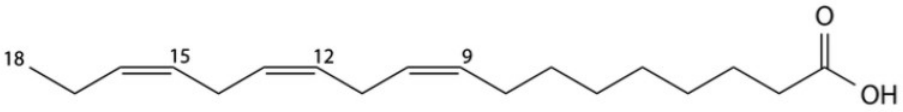
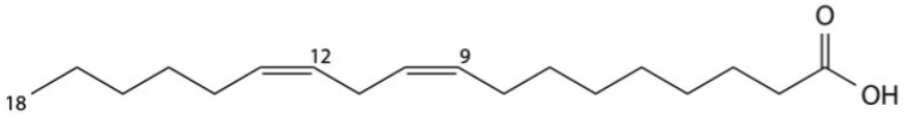


Figure **15.2.6**: The position of the first C=C double bond determines whether an unsaturated fatty acid is classified as omega-3 or omega-6. The two essential fatty acids, linoleic acid (an omega-6) and alpha-linolenic acid (an omega-3) are shown here.

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 **15.2.7**: The chemical structure of the essential fatty acids shown in shorthand, without individual carbon and hydrogen atoms marked.

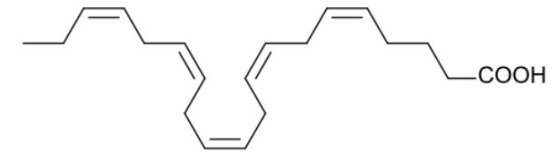
Most Americans easily consume enough linoleic acid and other omega-6 fatty acids, because corn and soybean oil are common ingredients in our food supply. However, sources of ALA and other omega-3 fatty acids are less common in the American diet, and many people could benefit from incorporating more sources 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]

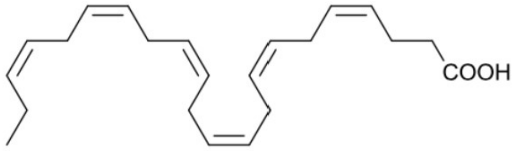
Omega-3 and omega-6 fatty acids are precursors to a large family of important signaling molecules called ***eicosanoids*** (prostaglandins are one type of eicosanoid). Among the many functions of eicosanoids in the body, one of the most important is to regulate inflammation. Without these hormone-like 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.



Eicosapentaenoic acid (EPA)



Docosahexaenoic acid (DHA)

Figure 15.2.8: 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.**

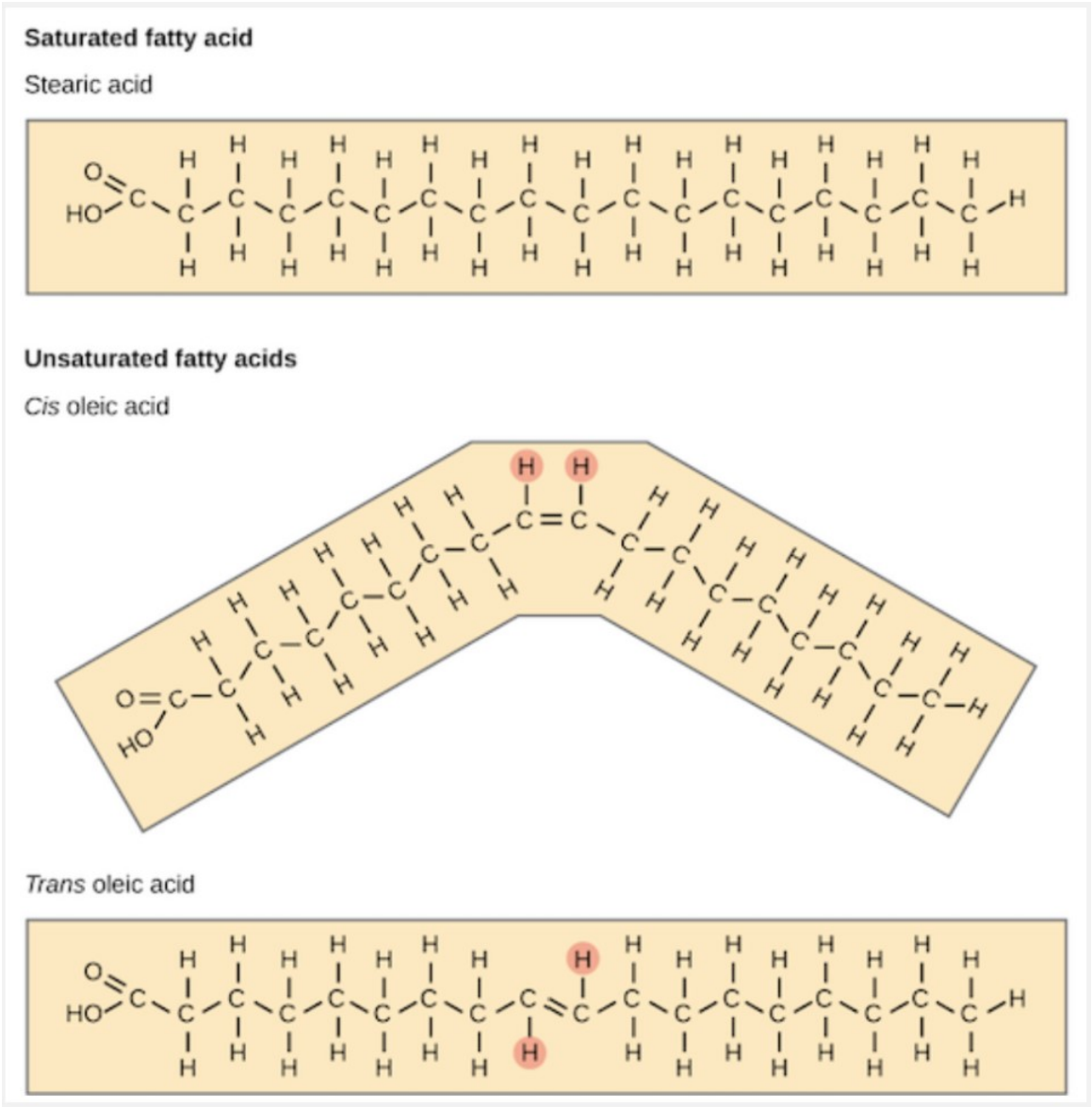


Figure **15.2.9**: Comparison of a saturated fatty acid to both the cis and trans forms of an unsaturated fatty acid.

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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15.3: 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 **15.3.3**), 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.

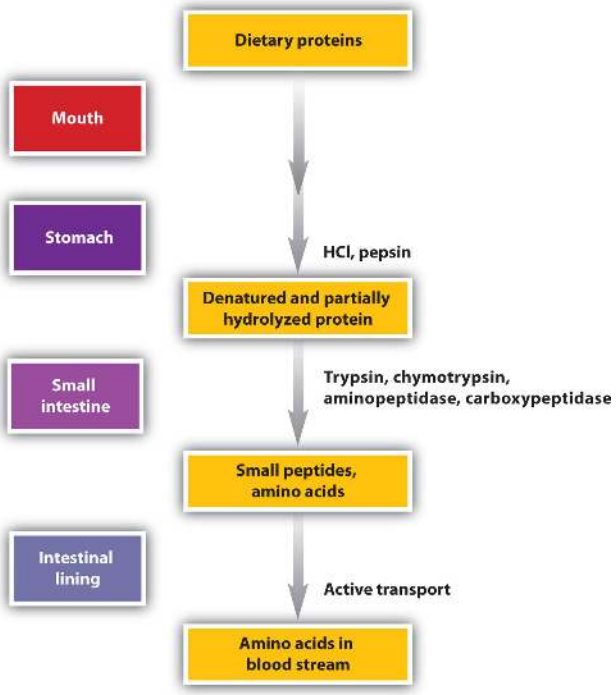


Figure **15.3.1** The principal events and Sites of Protein Digestion

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 **15.3.1**: 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.

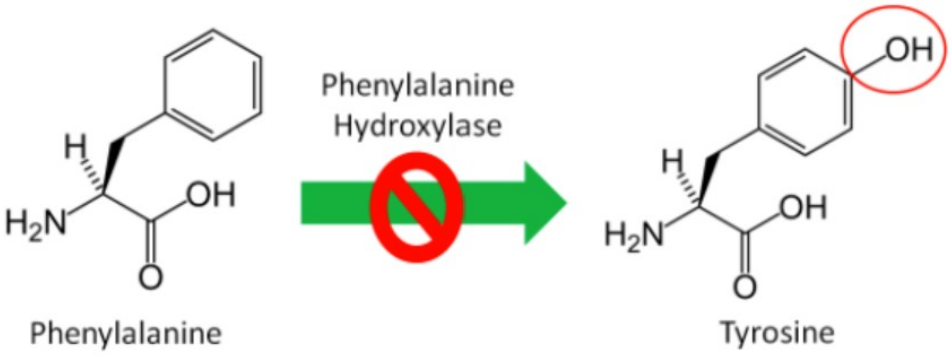


Figure **15.3.2**: Phenylketonuria (PKU) results from a mutation in the enzyme phenylalanine hydroxylase

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.



Figure **15.3.3** 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 **15.3.2** 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 **15.3.3** 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 **15.3.4**) *Complementary proteins are kind of like puzzle pieces.*

Two examples of complementary proteins are shown below.



Figure **15.3.5**) *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 **15.3.4** 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.

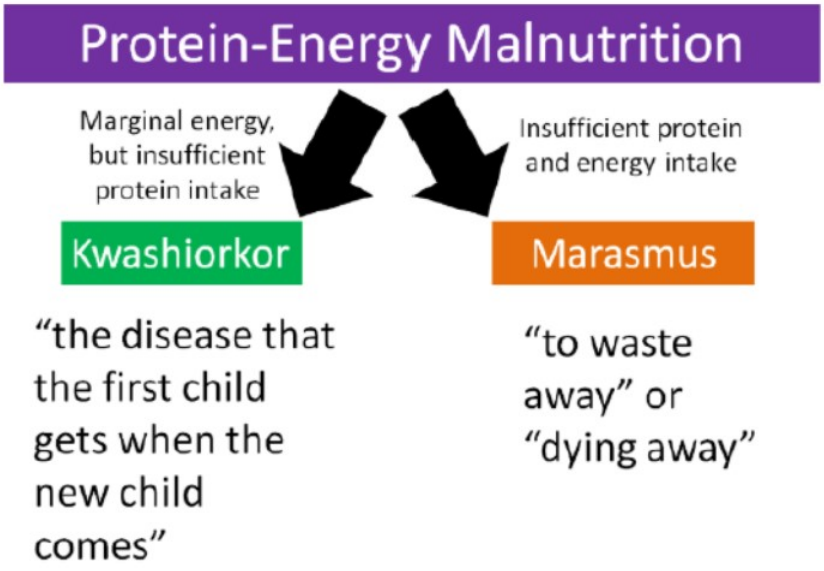


Figure **15.3.6** The two types of protein-energy malnutrition.

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 **15.3.7**: 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 **15.3.8** 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

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15.4: 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 **15.4.1**) 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.

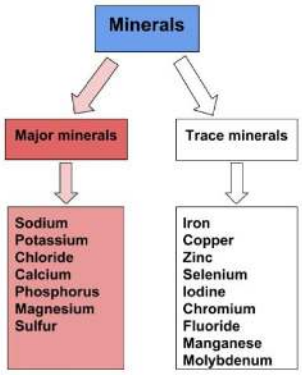


Figure **15.4.1** The major and trace minerals. Image by Allison Calabrese / CC BY 4.0.

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 **15.4.1** and **15.4.2** provide a summary of minerals and their function in the body.

***Table* 15.4.1** *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* 15.4.2** *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
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

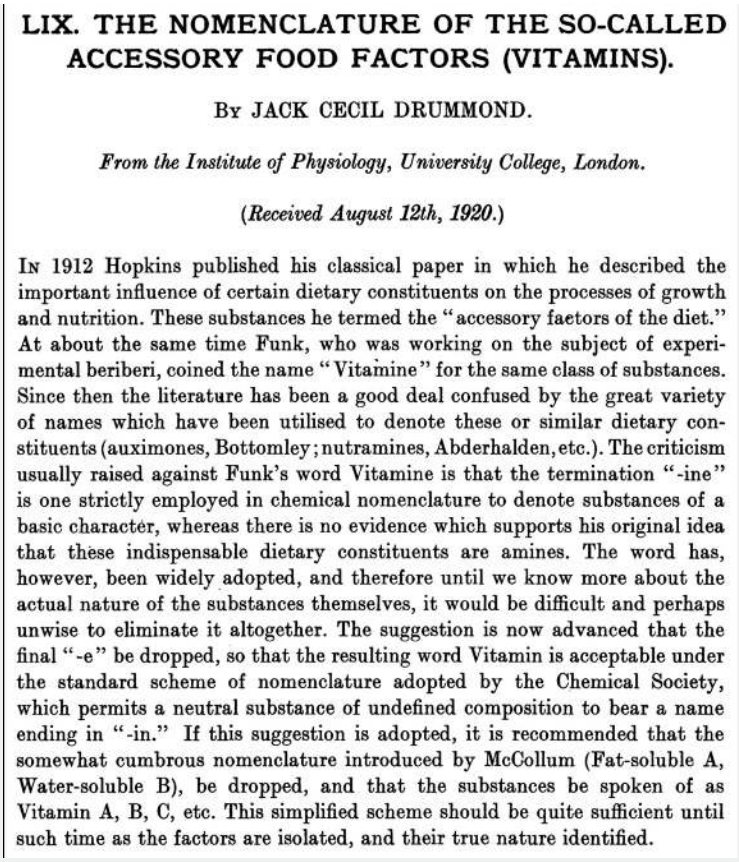
In 1747, the Scottish surgeon James Lind discovered that citrus foods helped prevent scurvy, a particularly deadly disease in which collagen is not properly formed, causing poor wound healing, bleeding of the gums, severe pain, and death. In 1753, Lind published his *Treatise on the Scurvy*, which recommended 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 **15.4.2** *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 **15.4.3** and **15.4.4**)

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.

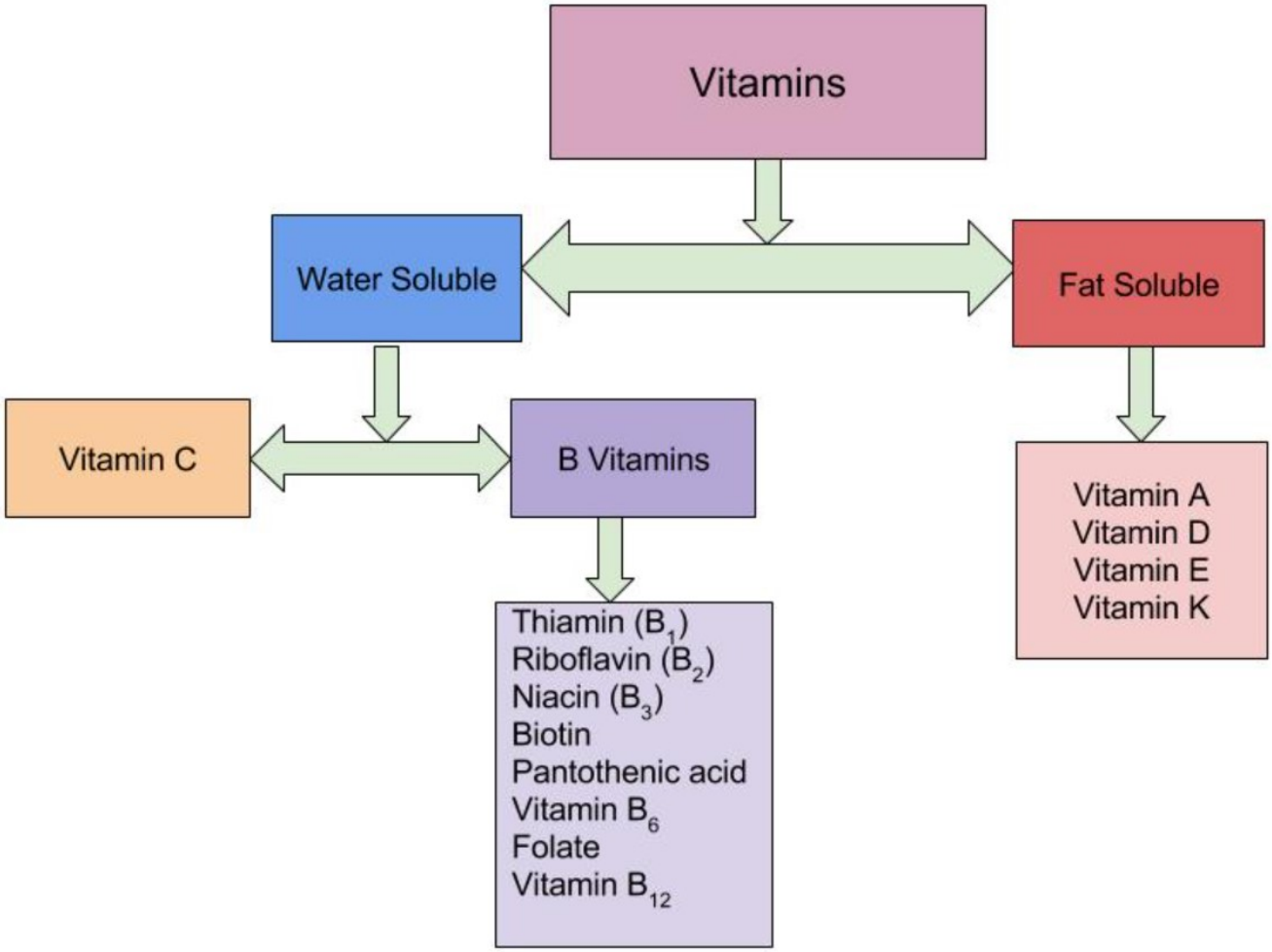


Figure 15.4.3: The Vitamins. *Image by Allison Calabrese / CC BY 4.0.*

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.

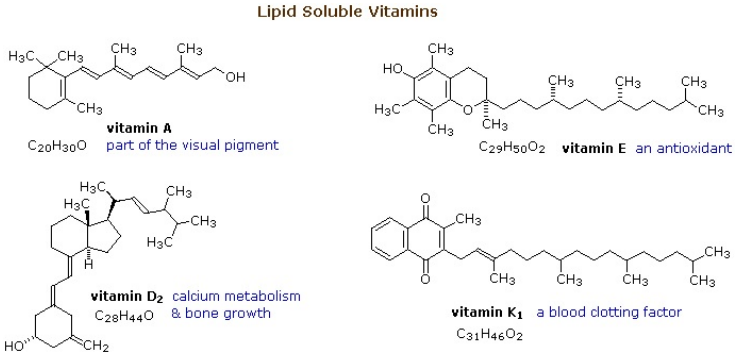


Table 15.4.3 lists the different fat soluble vitamins and its function.

Table **15.4.3** *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 **15.4.4**) 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 **15.4.4** *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
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

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 15.4.5. A simplified diagram on the role of antioxidants is shown in Figure 15.4.4.

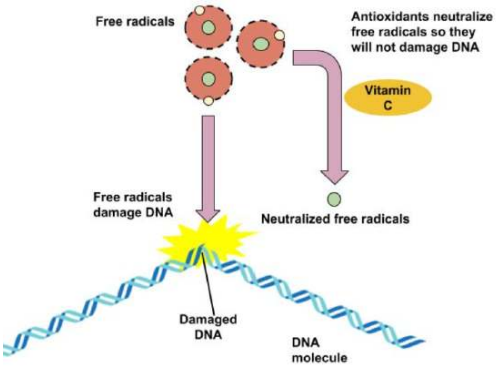


Figure 15.4.4 Antioxidants Role. Image: Allison Calabrese / CC BY 4.0

***Table* 15.4.5** *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 15.4.6 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* 15.4.6** *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 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 **15.4.7**) 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 15.4.7 *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 **15.4.8**.

***Table* 15.4.8** *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
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 **15.4.9**.

***Table* 15.4.9** *Total Dietary Fiber , Total Nonfermentable Fiber, and Total Fermentable Fiber (as percent of sample weight) in Five Different Foods.*

Food	Total Dietary Fiber	Total Insoluble (Nonfermentable)	Total Soluble (Fermentable)
Cereal, all bran	30.1	28.0	2.1
Blueberries, fresh	2.7	2.4	0.3
Br	3.	3.1	0.4

occoli, fresh, cooked	5		
Pork and beans, canned	4.4	3.0	1.4
Almonds, with hs	8.8	8.6	0.2

k i n			

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* 15.4.10** *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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15.5: 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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15.6: 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 **15.6.1**).



Figure **15.6.1** *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 **15.6.2**). 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 **15.6.2** *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 **15.6.1** list the three principal types of flavorings that are used in foods, under definitions agreed in the EU and Australia.

***Table* 15.6.1** *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 15.6.2 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 **15.6.3**) 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.

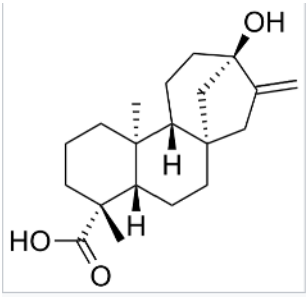


Figure **15.6.3** *Steviol, the basic building block of stevia's sweet glycosides.*

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* 15.6.3** *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 **15.6.4**) 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.

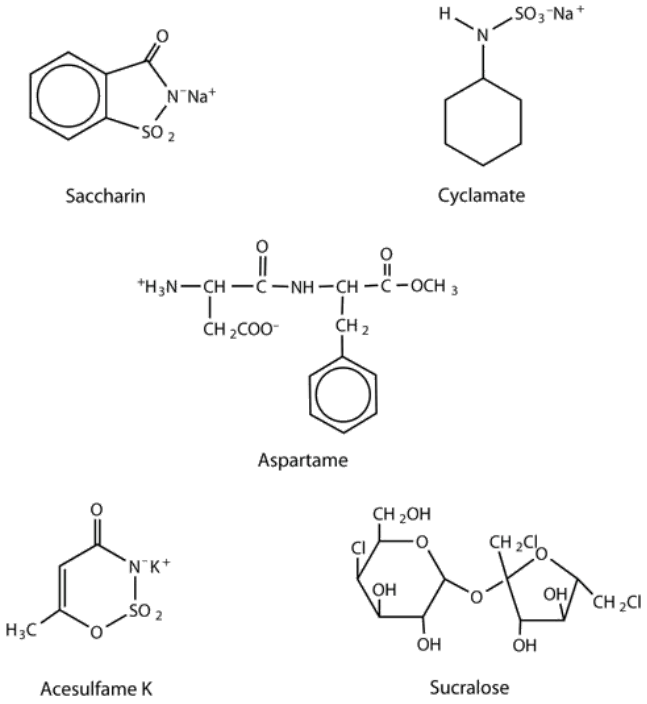


Figure **15.6.4** Different Artificial Sweeteners.

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 **15.6.3**.

***Table* 15.6.4** *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 **15.6.5** 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.

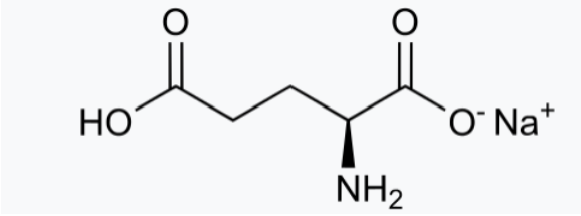


***Figure* 15.6.5** *Monosodium glutamate.*

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

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- US Food and Drug Administration (US FDA)
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15.7: 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.

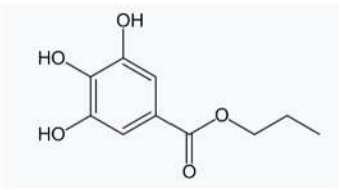
Types of Ingredients	What They Do	Examples of Uses	Names Found on Product Labels
Preservatives	Prevent food spoilage from bacteria, molds, fungi, or yeast (antimicrobials); slow or prevent changes in color, flavor, or texture and delay rancidity (antioxidants); maintain freshness	Fruit sauces and jellies, 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,

Types of Ingredients	What They Do	Examples of Uses	Names Found on Product Labels
			Vitamin D, amino acids (L-tryptophan, L-lysine, L-leucine, L-methionine)
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

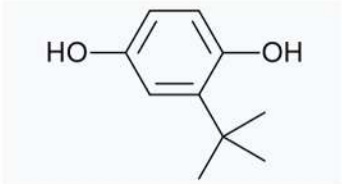
Antioxidants: BHA and BHT

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%

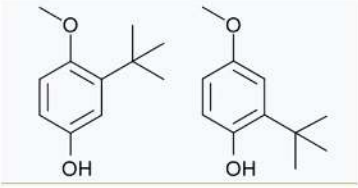
oxygen atmosphere. Antioxidants are an especially important class of preservatives as, unlike bacterial or fungal spoilage, oxidation reactions still occur relatively rapidly in frozen or refrigerated food. These preservatives include natural antioxidants such as ascorbic acid (AA) and tocopherols , as well as synthetic antioxidants such as propyl gallate, tertiary butylhydroquinone (TBHQ), butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT).



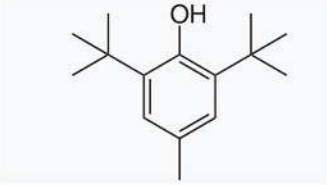
Propyl gallate



tert-Butylhydroquinone (TBHQ)



Butylated hydroxyanisole (BHA)



Butylated hydroxytoluene (BHT)

Figure **15.7.1** 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)

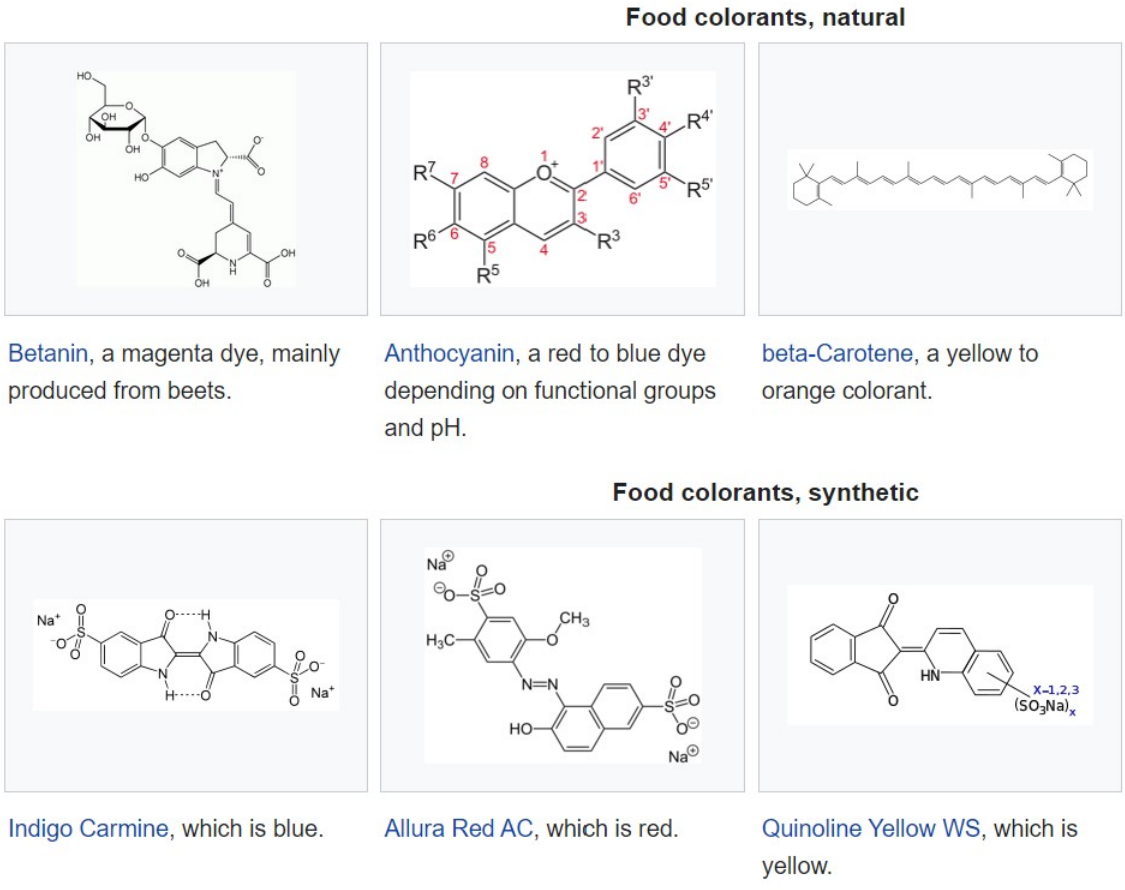


Figure **15.7.2** Chemical Structures of representative colorants. Source: Wikipedia.

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 **15.7.3** *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
- Marisa Alviar-Agnew (Sacramento City College)

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15.8: 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 **15.8.1** *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 **15.8.2** *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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